Title

DERIVATION OF KINETIC EQUATIONS FOR MIXTURES

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MECH ENG

FUNDAMENTAL CONCEPTS CONCERNING THE DERIVATION OF KINETIC EQUATIONS FOR MIXTURES

by

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ABSTRACT

The present thesis discusses some of the important fundamental problems related to the derivation of kinetic equations for simple fluids and mixtures from the Hamilton equations governing the motion of the individual particles. After deriving the Liouville equation for the full N point particle probability distribution, and the B.B.G.K.Y. hierarchy for the reduced S < N particle distribution, the study initiates an extensive nondimensionalization designed to highlight the average magnitude of the various terms of these equations, over a given volume in phase space, in terms of a set of dimensionless parameters. Using the latter as classification indices and expansion parameters, "non-dense", "weakly coupled" and "Brownian" systems are considered. Each of these systems is first treated, for the simple spatially uniform case, using a straightforward initial value expansion which, as first noted by Bogoliubov, renders divergent solutions for the single particle distribution. A natural extension of this simple approach, however, involving the integration of the B.B.G.K.Y. hierarchy over a time interval sufficiently short to prevent divergence, yet adequately long to impose suitable boundary conditions, is shown to yield, for the spatially uniform case, familiar kinetic equations such as those of Boltzmann and Uhlenbeck-Choh for the non-dense system and of Fokker-Planck for the Brownian system. Finally this simple method of "reinitialization" is applied to more complex non-uniform mixtures interacting with an external field.

SOMMAIRE

Cette thèse se propose d'étudier certains problèmes fondamentaux touchant à la dérivation d'équations cinétiques pour des fluides simples et des mélanges à partir des équations d'Hamilton qui indiquent l'évolution d'un ensemble classique de particules. Suivant, une dérivation des équations de Liouville et B.B.G.K.Y. pour les distribution de probabilité respectives de N et S < N particules, on entreprend une étude dimensionnelle afin d'établir, pour un certain volume dans l'espace de phase, l'ordre de grandeur moyen des divers termes de ces equations en fonction d'un ensemble de paramètres sans dimensions. Ceux-ci sont par la suite utilisés comme indices de classification et paramètres d'expansion dans le but d'étudier les systèmes dilués, faiblement couplés et ceux de Brown. Comme point de départ, on traite d'abord le système homogène se servant d'une expansion simple, avec conditions initiales, qui aboutit à une solution, pour la distribution de probabilité d'une seule particule, exposant une divergence temporelle telle que prévue par Bogoliubov. Par suite, on démontre q'une simple modification de cette méthode, qui intègre l'équation B.B.G.K.Y. sur une durée assez courte afin de réduire les erreurs d'expansion mais, néamoins, suffisamment longue afin d'imposer des conditions frontières raisonnables, aboutit aux equations populaires de Boltzmann et de Uhlenbeck-Choh pour un système non-dense et à l'équation de Fokker-Planck pour le système de Brown.

Enfin on démontre que cette nouvelle méthode de "réinitialisation" s'appliquer à l'étude de mélanges non-homogènes de plusieurs espèces de particules sous l'influence d'une force externe.

PREFACE

The present thesis discusses some of the main mathematical and physical concepts pertaining to the derivation of kinetic equations for a system of particles. Due to the nature of the subject, it is difficult to truly appreciate the physical aspects involved without introducing a fair degree of mathematics. Furthermore, since this study has been generalized to include mixtures of various species of particles, the equations which emerge often display a complex array of mathematical symbols, subscripts, superscripts and so forth which do not make the reading of this thesis a trivial task. For these reasons I would like to offer a few casual suggestions which may help you, the reader, to discover, or assess, as the case may be, the scientific implications of the present study.

This thesis is presented in the form of five main chapters preceded and followed by an introduction and conclusion. Each main chapter ends with a "summary and conclusion" section which outlines, with a minimum of mathematics, its main objectives and results. As a first reading I would therefore suggest the introductory chapter I, the summaries of chapters II - VI and the concluding chapter VII. This will essentially give you the "gist" of the thesis and, hence,

allow you to decide for yourself, according to your background and interest, those chapters which you wish to explore in greater detail. Hopefully, by proceeding in this manner, the flow of information will proceed along its merry path of least resistance.

STATEMENT OF ORIGINALITY

AND

CONTRIBUTIONS TO KNOWLEDGE

The author claims originality for the following contributions to the field of nonequilibrium statistical mechanics:

1. the presentation of an extensive and systematic nondimensionalization of the Hamilton, Liouville and B.B.G.K.Y. equation for a mixture of point particles designed to highlight the average relative importance, over a restricted volume in phase space, of the various terms in these equations;
2. the development of a new simple perturbation scheme which consists of integrating the expanded B.B.G.K.Y. hierarchy over a time interval sufficiently short to prevent the breakdown of the resulting solutions, yet sufficiently long to impose reasonable boundary conditions. This method is similar in spirit yet much more flexible and simpler in form than the Lewis and Harris time expansion method. It also clarifies many of the assumptions and limitations in the functional expansion of Bogoliubov and the multiple time scale technique of Frieman.

3. The application of this concise "reinitialization" expansion to alternate derivations of:

   a) the Boltzmann and Uhlenbeck-Choh equations for simple spatially uniform non-dense gases;

   b) the spatially uniform Fokker Planck equation for a single heavy Brownian particle in a bath of light bath particles;

   c) a set of M coupled Boltzmann equations for a spatially non-uniform and non-dense mixture of M species of particles interacting with a weak external field;

   d) a "generalized Liouville" equation for a non-uniform mixture of Brownian particles interacting with a weak external field and coexisting with a mixture of light bath particles.

4. The presentation of new scaling arguments, based on the aforementioned nondimensionalization of the B.B.G.K.Y. hierarchy, which suggest, near equilibrium, inconsistencies in previous derivations, by Bogoliubov, Sandri and others, of kinetic equations for uniform weakly coupled systems.

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LIST OF SYMBOLS

LATIN SYMBOLS

${}^{I}a^{\alpha\beta}, {}^{II}a^{\alpha\beta}$	Characteristic energies used in the nondimensionalization of ${}^{I}\phi^{\alpha\beta}$ and ${}^{II}\phi^{\alpha\beta}$ respectively; (III-C-12), 65 and (III-C-14), 66.
A^{α}	Dimensionless parameter; (III-C-21), 68.
b	Radial component in cylindrical coordinate system; (IV-B-20), 128.
b^{α}	Characteristic energy used in the nondimensionalization of u^{α} ; (III-C-16), 66.
$\bar{\bar{b}}$	Defined on page 146.
$\bar{\bar{b}}^{i\alpha, i'\alpha'}$	Defined on page 236.
$\bar{\bar{B}}$	Defined on page 145.
C_N	Volume in Γ_N used in the nondimensionalization of F_N ; (III-C-22), 69.
$C_{1s\}}$	Volume in $\Gamma_{1s\}}$ used in the nondimensionalization of $F_{1s\}}$; (III-C-38), 74.
D	Bogoliubov functional derivative; (V-A-6), 154.
$\{e\}$	Basic energy set used in the nondimensionalization of the governing equations, 63.
f_1	Single particle distribution function; (IV-B-19), 128.
F_N	N particle distribution function; 38.
F_s	s particle distribution function (S<N)
$F_{1s\}}$	Distribution function for a subgroup of particles $\{1s\}$; 42.

$F_{\{N,\alpha\}_{eq}}$	Equilibrium distribution function associated with H_N^I ; (IV-B-56), 142.
$F_{\{1,\beta\}_{eq}}$	Equilibrium distribution function associated with H_1 ; (IV-B-63), 144.
$F_{\{N_b\}_{eq}}$	Equilibrium distribution function associated with $H_{\{N_b\}}$; (VI-B-24), 229.
$F_{\{1,\beta\}_{eq}}$	Equilibrium distribution function associated with $H_{\{1,\beta\}}$; (VI-B-30), 230.
$\tilde{F}_s$	S particle distribution function; 175.
$\vec{\mathcal{F}}$	Force acting on a Brownian particle; (IV-B-60), 143.
$\vec{\mathcal{F}}(-t)$	Force acting on a Brownian particle at an earlier time; 143.
$\vec{\mathcal{F}}^{i\omega}$	Force acting on particle $\{i,\alpha\}$; (III-C-30), 72 and (VI-B-36), 231.
$\vec{\mathcal{F}}^{i\omega}(-t)$	Force acting on a Brownian particle $\{i,\alpha\}$ at an earlier time: (VI-B-41), 233.
g_s	S particle correlation function; 175.
$\vec{q}_{ij}$	Relative velocity between particles i and j; 128.
H	N particle Hamiltonian; (II-A-1), 31.
H_N^I	Hamiltonian for N_b bath particles in the presence of a fixed Brownian particle; (IV-B-56), 142.
H_1	Single particle Hamiltonian; (IV-B-63), 144.
$H^I_{\{N_b\}}$	Hamiltonian for N_b bath particles in the presence of a mixture of fixed Brownian particles; (VI-B-25), 229.
$H^I_{\{1,\beta\}}$	Hamiltonian for a single bath particle of specie β in the presence of a mixture of fixed Brownian particles; (VI-B-31), 230.

$\mathcal{H}_N$	N particle Hamiltonian operator; (II-A-6), 36.
$\mathcal{H}_S$	S particle Hamiltonian operator (S<N)
$\mathcal{H}_{\{S\}}$	Hamiltonian for a subgroup of particles $\{S\}$; 49.
$\mathcal{H}^I_{\{S\}}, \mathcal{H}^{II}_{\{S\}}$	Hamiltonian operators used for non-dense mixtures; (VI-A-8&9), 216.
$\mathcal{H}^I_{\{N,1\}}, \mathcal{H}^{II}_{\{N,1\}}$	Hamiltonian operators used for Brownian motion; (IV-B-47), 139.
$\mathcal{H}^I_{\{N\}}, \mathcal{H}^{II}_{\{N\}}, \mathcal{H}^{III}_{\{N\}}$ $\mathcal{H}^{A}_{\{N\}}, \mathcal{H}^{B}_{\{N\}}$	Hamiltonian operators used for Brownian mixtures; (VI-B-12 to 16), 226&227.
I_S	S particle interaction operator; (IV-B-38), 135.
J_B	Boltzmann collision term for simple gas; (IV-B-20), 128.
J_B^{β}	Boltzmann collision term for mixture; (VI-A-31), 222.
$J_{F.P.}$	Fokker-Planck operator; 146.
K_S	S particle momentum convection term; (IV-B-38), 135.
K^{α}	Dimensionless parameter; (III-C-21), 68.
$K^{\alpha}_{\{S\}}$	Dimensionless parameter; (III-D-1), 79.
$\{\ell\}$	Basic length set used in the nondimensionalization of the governing equations; (III-C-6), 63.
$\{\ell_s\}$	Subset of $\{\ell\}$; (III-C-6), 63.
L^{α}	Range of external field U^{α}, 62.
$\mathcal{L}^{\alpha\beta}_{\Delta\nu}$	Mixing operator; (II-C-12), 46.
$\mathcal{L}$	Mixing operator; (III-E-8), 109.
$\mathcal{L}_{\{N\beta\}}$	Mixing operator; (VI-B-17), 227.
$\tilde{\mathcal{L}}_S$	Mixing operator; 175.

$\{m\}$	Basic mass set used in the nondimensionalization of the governing equations; 62.
m_α	Mass of particle of specie α ; 31.
M	Number of species in mixture; 30.
m	Average particle number density; 53.
m_α	Average particle number density of specie α ; 75.
N	Total number of particles in system; 31.
N_β	Total number of particles of specie β in system; 30.
$\mathcal{N}$	Number of systems in ensemble; 29.
$\vec{P}_i^\alpha$	Momentum of particle $\{i,\alpha\}$; 30.
P_N	N particle conditional distribution function; (III-C-27), 71.
$P_{\{s\}}$	Conditional distribution function for a subgroup of particles $\{s\}$; (III-C-45), 76.
$P^\circ_{\{s\}}$	$P_{\{s\}}$ at time=0; (III-C-47), 76.
$\vec{R}_i(t)$	Transformed momentum of i^{th} particle; (IV-B-12), 122.
$\vec{P}_i^*(t)$	Transformed momentum of i^{th} particle; (V-A-11), 157.
$\vec{P}_i^{\alpha*}(t)$	Transformed momentum of particle $\{i,\alpha\}$; (V-A-20), 219.
$\vec{q}_i^\alpha$	Position of particle $\{i,\alpha\}$; 30.
Q_N	Momentum integrated N particle distribution function; (III-C-32), 73.
$\vec{Q}_i^\alpha(t)$	Transformed position of particle $\{i,\alpha\}$; (VI-A-22) 219.
$\vec{r}_{ij}^{\alpha\beta}$	Separation vector between particles $\{i,\alpha\}$ and $\{j,\beta\}$; 46.

$^{x}r^{\alpha\phi}, {}^{II}r^{\alpha\beta}$	Range of strong and weak interaction potentials $^{x}\phi_{ij}^{\alpha\beta}$ and $^{II}\phi_{ij}^{\alpha\beta}$ respectively; 62.
$\bar{r}$	Mean range of interaction potentials $^{x}\Phi_{ij}^{\alpha\beta}$ and $^{II}\phi_{ij}^{\alpha\beta}$; (III-D-3), 81; (III-D-34), 93.
r_o	Typical range of interaction potential Φ_{ij} for a simple system; 52.
r_c	Radius of physical volume $V_c = 4/3\ \pi\ r_c^3$ over which the governing equations are nondimensionalized; 64.
r_+	Range of the two particle correlation function; 124.
R	Characteristic length used in the nondimensionalization of time; 67.
$^{x}\mathcal{R}^{\alpha\beta}, {}^{II}\mathcal{R}^{\alpha\beta}$	Dimensionless parameters; (III-C-21), 68.
$\mathcal{R}^{\alpha}, \mathcal{R}^{\alpha}_{iss}$	Characteristic lengths used in the nondimensionalization of $\tilde{q}_i^{\alpha}$ in governing equations; (III-C-8), 63; (III-C-46), 76.
$^{x}SR_{iss}^{\alpha\beta}, {}^{II}\overline{SR}^{\alpha\beta}$	Characteristic lengths; (III-C-51), 77.
$\vec{R}_{ij}(t)$	Transformed particle separation vector; (IV-B-12), 122.
t	Time.
$t_1, t_2 \quad t_i$	Time scales in Multiple Time Scale expansion. (V-A-18), 166.
T_o	Temperature.
u^{α}	External field exerted on particle of specie α ; 31.
$\bar{u}^{\alpha}$	Average strength of external field u^{α} ; (III-C-5), 62.
v_o	Mean particle speed.

V — Physical volume.

V_c — Physical volume over which the governing equations are nondimensionalized; 64.

V_N — Volume in Γ_N over which the Liouville equation is nondimensionalized; (III-C-24), 70.

V_{1s} — Volume in Γ_{1s} over which the B.B.G.K.Y. hierarchy is nondimensionalized; (III-C-41), 75.

V^+_{1s} — Sub-volume in V_{1s}; 186.

W_N — Probability that $\vec{X}_N \in V_N$; (III-C-27), 71.

$\vec{X}_i$ — Phase vector of particle i ; 175.

$\vec{X}_{(i,\alpha)}$ — Phase vector of particle (i,α); 219.

$\vec{X}_N$ — Phase vector in Γ_N ; 31.

$\vec{X}_{1s}$ — Phase vector in Γ_{1s} ; 42.

$\vec{X}_s$ — S particle phase vector; 122.

β — Axial component in cylindrical coordinate system; 128.

Z_N — Partition function associated with H_N ; (III-C-1), 61.

Z^I_N — Partition function associated with H^I_N ; (IV-B-56), 142.

$Z^I_{(N_b)}$ — Partition function associated with $H^I_{(N_b)}$; (VI-B-25), 229.

Z^I_1 — Partition function associated with H_1 ; (IV-B-63), 144.

$Z^I_{(1,\beta)}$ — Partition function associated with $H_{(1,\beta)}$; (VI-B-31), 230.

GREEK SYMBOLS

α — Defined in (V-A-39), 176.

β	Defined in (V-A-40), 176.
γ	Defined in (V-A-41), 176.
γ^{α}	Root-mass-ratio; (III-C-21); 68.
Γ_N	N particle phase space; 32.
$\Gamma_{\{s\}}$	Phase space for a subgroup of particles $\{s\}$.
$\delta(x-x_0)$	Dirac delta function; 39.
ε	Expansion parameter (general).
$\{\varepsilon\}$	Set of intrinsic dimensionless parameters; 79.
$\varepsilon_1^{\alpha\beta}$	Dimensionless interaction parameter; (III-D-1), 80.
$^{I}\varepsilon_{2\,\{s\}}^{\alpha\beta}$, $^{II}\varepsilon_{2\,\{s\}}^{\alpha\beta}$	Dimensionless density parameters; (III-D-1), 80.
$\theta_{i,j}$	Two particle interaction operator; 176.
K	Boltzmann constant.
λ	Mean free path.
$\mu_{\alpha\eta}$	Probability defined on page 71.
ρ_N	Density of phase points in Γ_N ; 33.
ρ_m^{α}	Mass density of specie α ; 40.
$\rho_{\vec{p}}^{\alpha}$	Momentum density of specie α ; 40.
$\rho_{\mathcal{E}}^{\alpha}$	Energy density of specie α ; 41.
τ	Characteristic time (general).
τ_0	Typical duration of interaction between two particles; 124.
τ_1	Typical time interval between collisions; 152.
$\tau^{(0)}$	Characteristic time in Bogoliubov's boundary condition; 162.
τ_b	Relaxation time of bath particles; 193.

τ_B Relaxation time of Brownian particle; 197.

τ_+ Typical correlation duration between two particles; 124.

ϕ Angular component in cylindrical coordinate system tem; 128.

$\phi_{ij}^{\alpha\beta}$ Interaction potential between particles $\{i,\alpha\}$ and $\{j,\beta\}$; 31.

ϕ_0 Typical strength of interaction potential $\phi_{ij}^{\alpha\alpha}$; 52.

$^{I}\phi_{ij}^{\alpha\beta}$, $^{II}\phi_{ij}^{\alpha\beta}$ Strong and weak components of interaction potential $\phi_{ij}^{\alpha\beta}$; (III-C-2), 61.

$^{I}\overline{\phi}^{\alpha\beta}$, $^{II}\overline{\phi}^{\alpha\beta}$ Average strength of strong and weak interaction potentials $^{I}\phi_{ij}^{\alpha\beta}$ and $^{II}\phi_{ij}^{\alpha\beta}$; (III-C-3&4), 62.

χ^{α} Dimensionless parameter; (III-C-21), 68.

MISCELLANEOUS SYMBOLS

$\langle\ \rangle$ Ensemble average of enclosed quantity

$\sim o[\ ]$ Of the same order of magnitude as enclosed quantity

$\gtrsim$ Larger than and of the same order of magnitude as...

$\lesssim$ Smaller than and of the same order of magnitude as...

$\in$ Enclosed in...

$\in$ Element of...

$\forall$ For all...

TABLE OF CONTENTS

APPENDICES

CHAPTER I

INTRODUCTION

A. THE EARLY DAYS OF BOLTZMANN AND GIBBS[1]

The intense controversy confronting the supporters of the caloric nature of heat and promoters of the molecular theory during the late nineteenth century undoubtably represents one of the most productive disputes in the history of physical sciences. During these years of active debate, Ludwig Boltzmann was attempting to explain the macroscopically observed second law of thermodynamics from a purely molecular and statistical point of view. Amongst Boltzmann's prolific research, one may acknowledge, as outstanding contributions, his discovery of the now well known Boltzmann kinetic equation for dilute gases and his H theorem of irreversibility. Boltzmann's equation represented a balance equation in the six dimensional "μ" space,[2] for point particles, accounting for the appearance and escape of phase points in every cell of that space. The equation included the gain and loss of

1 Much of the account of Boltzmann's and Gibb's ideas presented herein is based on the fine reviews by Martin Klein,[1] Paul and Tatiana Ehrenfest[2] and George Uhlenbeck and George W. Ford.[3]

2 This space contains one axis for each component of the coordinate and momentum of a particle. Consequently, the state of a molecule is represented by a point in "μ" space and the state of a system of N particles is depicted by a set of N points in the space.

phase points resulting from:

1) the change in position of each molecule with finite velocity;
2) the change of momentum of each molecule due to the presence of an external field; and
3) the change of momentum of the molecules due to their mutual binary collisions.

In his evaluation of the third contribution, Boltzmann introduced what is now known as the "Stosszahlansatz" assumption which asserted that the collision frequency between molecules with momenta $\vec{p}_1$ and $\vec{p}_1$ at a location $\vec{q}$ could be assumed proportional to the product $f(q,\vec{p}_1,t)f(q,\vec{p}_1,t)$ where $f(\vec{q},\vec{p},t)$ represents the local density of phase points in the "μ" space. As a direct consequence of this hypothesis,[1] Boltzmann could then show that the H function:

$$H \equiv \iint f(\vec{q},\vec{p};t)\ln f(\vec{q},\vec{p},t)\,d\vec{q}\,d\vec{p} \qquad \text{(I-A-1)}$$

would monotonically decrease to a limiting value which would be attained when the system reached a state of equilibrium at which time, $f(\vec{q},\vec{p})$ would obey the Maxwell-Boltzmann distribution. Soon after deriving these results, Boltzmann encountered, on one hand, a natural skepticism from the caloric theorists and, on the other hand, stiff criticism from other kinetic theorists, such as Loschmidt who, in 1876,

1 It should perhaps be noted here that when Boltzmann first derived his kinetic equation, he gave no indication that this was indeed an assumption. [1]

raised serious doubts on the feasibility of rigorously extracting irreversible behavior from mechanical laws displaying complete time reversibility. Further criticism emerged from Zermelo who, in 1896, noted that mechanical systems were not only reversible in time but exhibited quasiperiodic motion as shown by Poincaré in 1890. Though Zermelo's comments seemingly excluded any possibility of an everlasting equilibrium state, Boltzmann quite easily dismissed his criticism on the grounds that, for large systems (containing, for example, 10^{18} molecules), Poincaré's cycles were much too long to be of any practical significance or importance. Loschmidt's remarks, on the other hand, which, in essence, implied that any entropy increasing system could be transformed into an entropy decreasing one by reversing the momenta of all the molecules, could not be dispensed with using purely mechanistic arguments. In fact, Boltzmann could only reinforce his own views by indicating that the second law of thermodynamics should never be construed as an exact law emerging from the laws of mechanics but should be regarded as a probabilistic law indicating the most probable direction in time of a large system of molecules. Consequently, though some systems, such as those proposed by

Loschmidt, may indeed adopt an entropy decreasing path, the occurrence of such systems may well be sufficiently rare to be of little practical interest. Boltzmann further expanded this idea by also noting that any system which momentarily suffered an entropy decrease could be expected to quickly readopt an entropy increasing behavior and eventually reach a state of equilibrium where it would thereafter spend the great majority of its time. The "Stosszahlansatz" along with the resulting Boltzmann equation and H theorem thus seemingly represented in Boltzmann's mind, valid statements for the great majority of systems at any given time or for any given system most of the time. Unfortunately, Boltzmann could not rigorously prove these intuitive arguments and hence never convincingly refuted Loschmidt's criticism. He did, nevertheless, display tremendous insight on a dilemma which, as will be shown later, lingers to this very day.

In spite of Boltzmann's continual reference to the probabilistic behavior of a system, he never clearly indicated how a probability distribution $F_N(\vec{X}_N, t)$ could be constructed to suitably represent the probability of finding a system in a given microstate $\vec{X}_N$.[1] A precise definition of $F_N(\vec{X}_N, t)$ was finally proposed by W. Gibbs in 1902, who showed that a

1 $\vec{X}_N$ represents a vector in a $6N$ dimensional Γ_N space with one axis for each component of the coordinate and momentum of each molecule. $\vec{X}_N$ thus completely describes the microstate of a system of point particles.

probability distribution function could be constructed by introducing an "ensemble" of $\mathcal{N}$ systems which initially varied in their microstate $\vec{X}_N$ but were macroscopically identical.[1] The state of the ensemble $\{\vec{X}'_N, \ldots, X'_N, \ldots, X^{\mathcal{N}}_N\}$ could then be represented by a set, or "cloud" of phase points located at the tips of the individual state vectors $\vec{X}_N$ $(i = 1 \ldots \mathcal{N})$. Each of these phase points would naturally travel in time according to the mechanical laws governing the motion of the molecules. Choosing $\mathcal{N}$ large, one could then obtain a probability measure by normalizing the local density of phase points $\rho_N(\vec{X}_N, t)$ over $\mathcal{N}$ so as to define:

$$F_N(\vec{X}_N, t) \equiv \rho_N(\vec{X}_N, t)/\mathcal{N} \qquad \text{(I-A-2)}$$

Using a theorem of Liouville, Gibbs then concluded that, for a conservative system, the phase cloud would flow in phase space as an incompressible fluid and derived a linear partial differential equation for $F_N(\vec{X}_N, t)$ which is generally referred to as the Liouville equation. Unfortunately, the transient solution to this time reversible equation required a parallel solution of the complete set of Hamiltonian equations. Since the task of deriving such a solution was generally unfeasible for systems containing a large number of molecules, Gibbs introduced some fundamental hypotheses concerning the behavior of $F_N(\vec{X}_N, t)$. His first assumption was one of "equi-a priori",

1 These systems were also microscopically identical in the sense that they contained the same number and type of molecules.

which simply stated that, for an isolated system at equilibrium, every microstate within the accessible volume of the Γ_N space should be equally probable. He then further suggested that any phase cloud that did not initially occupy this phase volume uniformly would eventually do so through a diffusion process in this space. Furthermore, since such a diffusion process was not completely compatible with the incompressibility of the phase cloud (as dictated by the Liouville equation) Gibbs further suggested that the latter would spread into fine filaments throughout the accessible phase space such that its average density would eventually be the same for all cells of finite size within the accessible volume. Gibbs further expanded this idea by introducing a coarse grain density $\bar{F}_N^i$, where i denotes the i^{th} cell of the Γ_N space, and defining a new H function.

$$\bar{H} \equiv \sum \bar{F}_N^i \ln \bar{F}_N^i \qquad \text{(I-A-3)}$$

By finally showing that $\bar{H}$ would reach a minimum as time approached infinity and that this minimum would correspond to a uniform distribution for $\bar{F}_N^i$, he was able to draw a somewhat intuitive link between the reversible mechanical laws and the second law of thermodynamics.

Reviewing the ideas of Boltzmann and Gibbs, it soon becomes apparent that a degree of coarse-graining in phase space ("μ" or "Γ_N") played an important role in their concepts of irreversibility. Indeed, as a coarse-graining in "μ" space was necessary for Boltzmann's derivation of his

irreversible kinetic equation, similarly a coarse-graining in Γ_N space was crucial in Gibb's equi-a-priori and diffusion assumptions. With any such coarse-graining in phase space, one must, of course, associate some coarse-graining (or averaging) in time since any phase point (in μ or Γ_N space) will require a finite time to traverse a finite size cell. In view of Boltzmann's and Gibb's ideas, one is thus tempted to dismiss Loschmidt's criticism on the grounds that any macroscopic measurement implies some physical space coarse-graining and time averaging which, in turn, is responsible for the apparent macroscopically irreversible trend of the system. This was indeed the view of George Uhlenbeck[3] who suggested that the conflict between microscopic reversibility and macroscopic irreversibility could be resolved if one acknowledged "the different levels of observation and description" used on the microscopic and macroscopic scales. Unfortunately, such a view, though certainly rich in content, does not tell the whole story and somewhat belittles the depth of Loschmidt's criticism and of Boltzmann's reply. Clearly, any system, which to a macroscopic observer is apparently irreversible in one direction, may be transformed to seem irreversible in the opposite direction by reversing the momenta of all the molecules within the system. Naturally, since this reversal cannot be accomplished by the macroscopic observer, the key question thus becomes - Can the system, on its own, reverse the direction of motion of all its mole-

cules? - or, more precisely, - What is the probability that a system will suddenly suffer a reversal in momenta of all its molecules? The answer to this question would not only shed light on the Boltzmann-Loschmidt debate but would play, as will be shown later, an important role in later developments of the nonequilibrium statistical mechanical theory of matter.

Before closing this section on Boltzmann's and Gibb's ideas, a few words should perhaps be added concerning the role of the space-time resolution of the observer in the quest of physical laws for classical many-body systems. One may acknowledge for such systems the possible existence of two extreme observers: one fine-grain observer (such as an astronomer observing planetary motion, or a "Maxwell demon" monitoring molecular motion) which can detect the instantaneous change of position and momenta of the individual bodies, and, on the other hand, the coarse-grain macroscopic observer (such as a human observing the flow of a gas or liquid) which can only react to the global time-smoothed thermodynamic properties, such as density, pressure, temperature, and so on. While the fine-grain observer is generally contented to use the set of deterministic Hamiltonian equations to describe the system, the macroscopic examiner will quite often resort to the deterministic macroscopic equations such as the equations of Navier-Stokes, for example, to describe what he sees and feels. In addition to the above two extreme

cases, there may exist, however, many other observers with a space-time resolution sufficiently fine to observe the internal erratic fluctuations of the system, yet not fine enough to detect the exact origin of such chaotic behavior. Such observers will thus witness random motions and, consequently, turn to stochastic equations to relate their observations. From such equations these observers can, by taking appropriate averages, not only describe the system as seen by the macroscopic observer, but also derive the statistical properties of the fluctuations. Such observers do, indeed, exist and may be found in the form of an individual monitoring the fluctuations of electric current with the use of a sensitive galvanometer or one observing Brownian motion through a microscope.

B. BROWNIAN MOTION AND THE CONFIRMATION OF THE MOLECULAR HYPOTHESIS

The contributions of Boltzmann and Gibbs to the understanding of the probabilistic mechanical theory of irreversible processes, customarily referred to as "Non-equilibrium Statistical Mechanics", are indeed astonishing, if one considers that they were formulated and presented at a time when many still frowned on the possible existence of molecules too small to be seen. Those who demanded to see to believe were finally satisfied in 1908, when Albert Einstein's [4] theories on Brownian motion, developed between 1905 and 1908, were verified by Jean Baptiste Perrin.

Einstein, as Carbonelle and Gouy before him, believed that the irregular motion of small particles bathing in a fluid, as first observed through a microscope by Brown in 1828, could only be explained by the chaotic collisions between the "Brownian" particle and the neighboring fluid molecules. He then proceeded to study the motion of such particles by considering a set of identical and independent particles initially located at the same point in space. According to the molecular hypothesis, these particles should behave like molecules of a dissolved solute, and hence, be subjected to an osmotic force resulting from the presence of spacial gradients in their concentration. Balancing this force with the viscous drag, Einstein evaluated the flux of particles which he, in turn, equated to the diffusion flux as given by the macroscopic Ficks law. This allowed him to evaluate the diffusion coefficient and the mean square displacement of each Brownian particle in terms of the temperature of the bath T, the drag coefficient β, and Boltzmann's constant k. In spite of Perrin's verification of Einstein's result:

$$\langle x^2 \rangle = 2Dt = 2 (kT/\beta)t \qquad \text{(I-B-1)}$$

for the mean square displacement $\langle x^2 \rangle$, it should be noted that Einstein used a rather macroscopic model to describe the irratic motions of a microscopic particle. In fact, Einstein's theory had a major loophole in that it could not explain why a <u>single</u> Brownian particle, free of osmotic forces, should exhibit a mean square displacement given by

equation (I-B-1). This difficulty was removed when Langevin[5], Uhlenbeck and Ornstein[6] investigated Brownian motion on a finer time scale by assuming the force exerted on the Brownian particle as consisting of an average drag force and a rapidly fluctuating stochastic force both resulting from interactions with the bath molecules. By taking appropriate averages of the resulting stochastic momentum equation and using the law of equipartition of energy at equilibrium, they were thus able to reproduce Einstein's result for a single Brownian particle. A yet finer grain description was later presented by Résibois, Davis, Lebowitz and Rubin[7],[8],[9] who reconsidered Brownian motion in terms of the Liouville equation for the complete system of bath molecules and a single Brownian particle. One should note, however, that though these latter theories were far superior in rigor to Einstein's original theory, they in no way belittled the important role played by the combined work of Einstein and Perrin towards a general acceptance of statistical mechanics.

C. YEARS LEADING TO BOGOLIUBOV

After Perrin's experiments, the ideas of Boltzmann were further developed and two important contributions emerged. One notable work was Paul and Tatiana Ehrenfest's "Conceptual Foundations of the Statistical Approach in Mechanics"[2] written in 1911 which must be considered as an important contribution to the understanding of both

Boltzmann's and Gibb's ideas. This work not only presented a clear review of the structure of statistical mechanics but presented a critique of the Boltzmann-Loschmidt controversy with such depth that many of the ideas presented therein were to play a key role in later debates on thermodynamic irreversibility. A second major contribution emerged from the research of Chapman[10] and Enskog[11] who, in 1911-12, independently derived the Navier-Stokes equations and calculated the transport coefficients by taking moments of the Boltzmann kinetic equation and obtaining successive approximate solutions for the one particle distribution.

After the work of Ehrenfest, Chapman and Enskog, one encounters a certain stagnant period in the development of nonequilibrium statistical mechanics which may be explained by the internal structure and motivation of that field at that time. During the days of Boltzmann and Gibbs, the main objective of statistical mechanics consisted of explaining the well known macroscopic continuum laws (such as the second law of thermodynamics) from a discrete molecular probabilistic-mechanistic approach. Such a motivation was certainly valid, at least in the academic sense, as it led to a better understanding of these laws. Through the years, however, the statistical mechanical approach had developed from within sufficient confidence to seek a more ambitious and utilitarian goal of deriving new macroscopic laws not easily derived from a continuum approach. The possibility of a predictive power

of statistical mechanics in the relatively underdeveloped fields of plasma flow, phase transition, turbulent flow, and transport processes in colloids, for example, represented a new and exciting objective for the statistical mechanical approach. Such an endeavor naturally would necessitate some generalization of Boltzmann's work to include dense systems with long range and, in some cases, attractive potentials. More precisely, one would need either a generalization of Boltzmann's kinetic equation or a new set of kinetic equations valid for various special classes of systems. Unfortunately, Boltzmann's highly intuitive approach did not seem to shed much light on how such equations could be systematically extracted from the mechanical laws governing the motion of molecules. It soon became evident, in fact, that important gaps were plaguing the fundamental structure linking these mechanical laws to the macroscopic continuum laws.

Following the results of Chapman and Enskog, the general structure of nonequilibrium statistical mechanics could be divided into two basic sections. On one side, one found the time reversible equations of Hamilton and Liouville which were, in the classical sense, completely general, while on the other side, there existed the irreversible kinetic and transport equations derived by Boltzmann and Chapman - Enskog respectively for dilute gases.

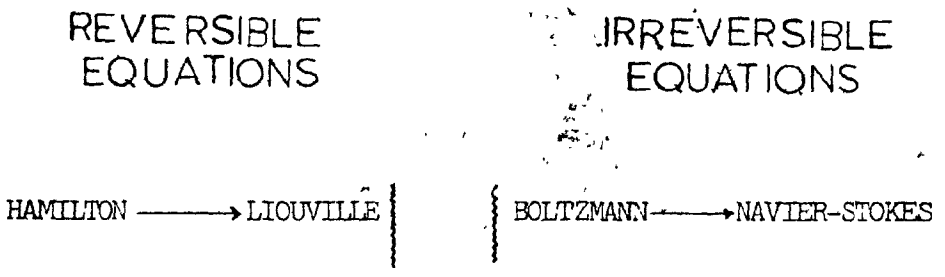


Figure I-1

An important link was thus missing between the reversible Liouville equation for the N particle distribution and the irreversible Boltzmann equation for the one particle distribution. Clearly, if the statistical mechanical approach was to yield new macroscopic laws, this link would eventually need to be constructed.

The important gap, mentioned above, was finally partially filled by Bogoliubov,[12] Born-Green,[13] Kirkwood[14] and Yvon[15] who independently derived an equation governing the probability distribution $F_s(\vec{x}_s,t)$ for a subgroup of s particles by integrating the Liouville equation over the coordinates and momenta of the remaining $(N-S)$ molecules. This equation, now referred to as the B.B.G.K.Y. hierarchy, had the form of a Liouville equation for S particles with an added "mixing" term which included the higher order distribution function $F_{s+1}(\vec{x}_{s+1},t)$ and described the interactions between the subgroup S and the remaining $(N-s)$ particles. Since this hierarchy was also time reversible, one could then draw the following revised structure:

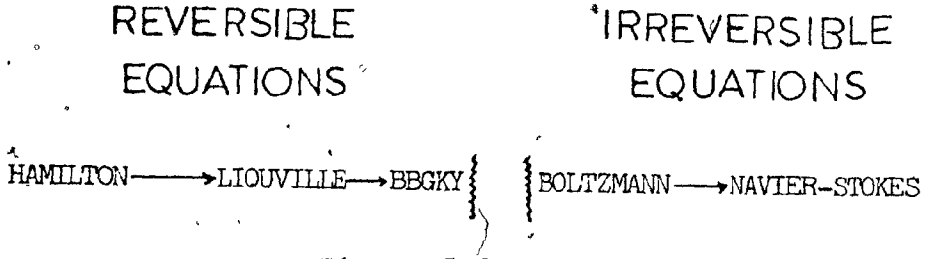


Figure I-2

Because of the presence of the higher order distribution F_{s+1} in the B.B.G.K.Y. equation for F_s, this equation had an open form and hence could not be solved without introducing some approximation or assumption to close or "truncate" it. The closure of the hierarchy, regardless of the mathematical technique used, was to represent a key physical link in the general structure joining reversible mechanics to irreversible thermodynamics.

D. THE LAST LINK

In 1946, N. N. Bogoliubov[12] showed that special kinetic equations could be obtained by considering special cases where some of the terms of the hierarchy, including the mixing term which was responsible for its open form, could be neglected as a zeroth order approximation. One approach in such cases consisted of solving the resulting approximate closed equations via some initial conditions so as to obtain a zeroth order solution. Substituting the latter back into the terms of the hierarchy originally neglected, one could then derive a first order solution which, in turn, could be resubstituted to obtain more accurate

solutions for F_s . Naturally, if such a simple method of successive approximations converged, one could circumvent tricky solutions of cumbersome differential-integral kinetic equations, such as Boltzmann's kinetic equation. Unfortunately, as first revealed by Bogoliubov, this simple initial value perturbation technique yielded results that were divergent or secular in time. More precisely, one found that the higher order correction terms were "secular" in that they rapidly grew with time to eventually dominate the lower order solutions. In order to eliminate these divergences or "secularities", Bogoliubov proposed an alternate perturbation scheme which would seek approximate solutions for $F_s(\vec{x}_s,t)$ of the form $F_s(\vec{x}_s \mid F_1(\vec{q}_1,\vec{p}_1,t))$ with a time dependence only implicit through a functional dependence on $F_1(\vec{q}_1,\vec{p}_1,t)$. Clearly, by obtaining such a solution, one could derive approximate closed kinetic equations for the one particle distribution $F_1(\vec{q}_1,\vec{p}_1,t)$.

Bogoliubov's derivation of kinetic equations could be described in four important steps. The first step consisted of considering special classes of systems and ordering the various terms of the hierarchy in terms of their relative importance. This ordering could be carried out by finding some dimensionless parameters constructed from quantities which were characteristic of the system (such as the average density and the range of the interaction potential, for example) and which dictated the order of magnitude of the

various terms in the hierarchy. The second stage in the analysis consisted of assuming F_s, ($s \gg 2$), as a functional of $F_1(\vec{q}_1, \vec{p}_1, t)$, as previously mentioned, so as to replace all time derivatives $\frac{\partial F_s}{\partial t}$ $s \gg 2$ by functional derivatives $\mathcal{D} F_s \equiv \left\{ \frac{\delta F_s}{\delta F_1} ; \frac{\partial F_1}{\partial t} \right\}$. The third step involved an expansion of F_s and the functional derivative $\mathcal{D}$ in powers of a characteristic dimensionless parameter much smaller than unity so as to systematically perform the perturbation scheme previously described. Finally, the last step consisted of introducing appropriate boundary conditions so as to hopefully obtain increasingly accurate functional solutions for $F_s(X, | F_1)$ $s \gg 2$ and kinetic equations for F_1. The boundary conditions which Bogoliubov imposed stated that any group of particles streamed back in the infinite past under their mutual interaction (for strong repulsive potentials) or under no interaction (for very weak potentials) would be sufficiently separated from each other to be assumed uncorrelated. This particular boundary condition, as will be seen later, was to play a key role in the time direction (or irreversibility) of the kinetic equations derived.

Using the method described in four steps above and summarized schematically below, Bogoliubov was able to derive Boltzmann's kinetic equation for dilute gases with strong short range interactions and Landau's equation for gases with weak interactions between the particles.

Summary of Bogoliubov Scheme

1. Evaluation of order of magnitude of the various terms of the B.B.G.K.Y. hierarchy for special classes of systems (construction of characteristic dimensionless parameters.)
2. Functional assumption.
3. Expansion in small parameter
4. Statement of boundary conditions.

⇒ Kinetic equations

Figure 1-3

As Bogoliubov was developing his functional perturbation scheme, John G. Kirkwood was devising his own method of deriving kinetic equations from the B.B.G.K.V. hierarchy. Kirkwood[14] rederived in 1946 the Boltzmann equation for dilute gases using a structure similar to that utilized by Bogoliubov. He replaced Bogoliubov's second step (i.e., functional assumption) by introducing a time averaged one particle distribution function:

$$\bar{F}_1(\vec{q}_1, \vec{p}_1, t) = \frac{1}{\tau} \int_0^{\tau} F_1(\vec{q}_1, \vec{p}_1, t+\lambda)\, d\lambda \qquad \text{(I-D-1)}$$

which was averaged over a time interval larger than the mean collision duration yet much shorter than the Poincaré period.[1]

1 In fact, τ would have to be chosen much shorter than the kinetic relaxation time of the system.

Furthermore, he substituted for Bogoliubov's boundary condition, in step four, the assumption that the system was sufficiently near equilibrium for the one particle distributions $F_i(\vec{q}_i, \vec{p}_i, t)$ and $F_j(\vec{q}_j, \vec{p}_j, t)$ to be uncorrelated in time: i.e.,

$$\overline{F_i(\vec{q}_i, \vec{p}_i, t) F_j(\vec{q}_j, \vec{p}_j, t)} = \overline{F_i}(\vec{q}_i, \vec{p}_i, t)\, \overline{F_j}(\vec{q}_j, \vec{p}_j, t) \qquad \text{(I-D-2)}$$

The success of Bogoliubov's and Kirkwood's perturbation scheme was deeply rooted in the wise choice of steps two and four, which allowed the derivation of non-secular kinetic equations through the use of a boundary value perturbation scheme as opposed to a simple "secular" initial value expansion. It should also be noted that the irreversibility emerging from these two methods stemmed, in part, from the coarse-graining in time which they injected. While Kirkwood performed this coarse-graining explicitly by defining time averaged distributions, Bogoliubov did so implicitly through his functional assumption and his boundary conditions.[1] The coarse-graining introduced in both expansion schemes were, in this respect, reminiscent of Boltzmann's and Gibb's coarse-graining in phase space which, as previously

1 One may recall here that in order to justify his functional assumption, Bogoliubov suggested the existence of three time scales governing the evolution of a molecular system: a fast "dynamic" time during which the initial correlations were remembered and the time dependence of $F_s(\vec{x}_s, t)$ $(s \gg 1)$ was explicit, a slower "kinetic" time scale during which initial correlations were forgotten and the time dependence of $F_s(X_s | F_1)_{s \gg 1}$ was implicit through $F_1(\vec{q}_i, \vec{p}_i, t)$ and finally, a "hydrodynamic" time scale during which the time dependence of F_1 was implicit through the macroscopic moments.

noted, directly implied a simultaneous coarse-graining in time.

After the results of Kirkwood and Bogoliubov, the general structure of nonequilibrium statistical mechanics seemed to be in a relatively healthier state. Indeed, the structure now possessed seemingly logical links between the reversible mechanical equations and the macroscopic irreversible laws. Furthermore, the expansion techniques used by Bogoliubov and Kirkwood seemed to indicate a path for finding more general and accurate kinetic equations. Finally, one could envisage the possibility of using such generalized kinetic equations to derive, using Chapman's and Enskog's ideas, new macroscopic laws. With this hope in mind, S. T. Choh [16] extended Bogoliubov's perturbation in density for dilute gases to one higher order so as to obtain a new kinetic equation accounting for three body collisions. Choh then used Chapman's and Enskog's method to derive the usual Navier-Stokes equations and obtained new expressions for transport properties in dense gases. Another important and encouraging contribution came in the early 1960's from Lebowitz-Rubin, Résibois and Davis who, as previously mentioned, derived from the Liouville equation a Fokker-Planck equation governing the probability distribution for a heavy Brownian particle in a bath of light molecules.[1]

1 Kirkwood [14] had also presented earlier a molecular theory of Brownian motion using the time averaging technique previously described.

These derivations, based on a root-mass-ratio expansion, represented the first clear molecular theories of Brownian motion.

During the early years of the 1960's, the research in the derivation of kinetic equations from the B.B.G.K.Y. hierarchy was, to say the least, intense as new kinetic equations were being derived using new expansion schemes. Much of the productivity of this period was certainly due, in part, to George Uhlenbeck who not only introduced Bogoliubov's work to the western world, but also did much to clarify some of Bogoliubov's fundamental concepts. In particular, one recalls Uhlenbeck's clear explanation of the distinct time scales, or relaxation rates, needed to extract from the Liouville equation, governing equations for "contracted" variables such as the one particle distribution and the macroscopic variables.[17] [18] One should also give due credit here to E. G. D. Cohen, who, on one hand clearly showed the similarities and equivalence between the various derivations of kinetic equations for dilute and moderately dense gases[19] and, on the other hand, studied in detail the breakdown of such derivations at higher orders.[20] [21] [22] Finally, as will be discussed shortly, Cohen (and Berlin) revealed the important role played by the boundary conditions in the irreversibility of the kinetic equations derived via a perturbation approach.[23] In conclusion, it is probably fair to say that Uhlenbeck and Cohen did for Bogoliubov's work what Paul and Tatiana Ehrenfest had done for Boltzmann.

In spite of the apparent continual success of the perturbation approach in the derivation of kinetic equations, many new difficulties were rapidly brewing. In 1962, G. Sandri, using a new expansion technique developed by E. Frieman[24], rederived Bogoliubov's results for dilute and weakly coupled systems. Frieman's method consisted of replacing Bogoliubov's step two by extending the time domain into successively slower time scales: t_0 , t_1 , t_2 ...(with $t_0 = t$, $t_1 = \varepsilon t$, $t_2 = \varepsilon^2 t$ ... where ε is the expansion parameter) so as to replace $F_s(\vec{X}_s, t)$ by $F_s(\vec{X}_s, t_1, t_2, t_3 \cdots)$ and write the time derivatives in the expanded form:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2} + \cdots$$

By imposing in step four of Bogoliubov's structure the boundary condition that all divergent terms in the fast time scale solutions vanish as $t_0 \to \infty$, one could then obtain kinetic equations on the slower time scales t_1, t_2 ... Using this method of "multiple time scales" Sandri[25] and Frieman[26][27] reconsidered the dilute and weakly coupled case and showed that local divergences and singularities existed in both expansions at higher orders. These divergences were confirmed and studied by others[20][28][29] as they created serious difficulties not only at the kinetic level but also in the evaluation of the macroscopic transport coefficients thus greatly hampering the predictive goal of the statistical mechanical approach.

Another embarassing blow to the perturbation methods was rendered by E. G. D. Cohen and T. H. Berlin in 1960, who noted that the direction of time (or irreversibility) was not totally inherent in the coarse-graining in time introduced, but was, in fact, injected through the particular choice of boundary conditions imposed in step four. They further demonstrated that seemingly equally plausible boundary conditions in the reverse direction of Bogoliubov's boundary conditions and in which particles would become uncorrelated when streamed forward in the distant future, would lead to a so-called "anti-Boltzmann" equation and a monotonically increasing H function. Finally, they showed that Kirkwood's formulation could also render an anti-Boltzmann equation by time averaging over previous times in the boundary conditions (I-D-2).[1] The authors then reasoned that the Boltzmann equation was founded on the assumption that all particles were uncorrelated before collision and became correlated immediately after colliding, while the anti-Boltzmann equation implied the hopefully less probable occurrence that correlations would exist before collision

1 This possibility of deriving time irreversible equations going the wrong way was also noted by C. H. Su, E. Frieman and M. D. Kruskal [30] who indicated that an anti-Fokker Planck equation for the weakly coupled case could be derived using the multiple time scale technique by imposing that all secular terms on the fast time scale vanish as $t \to -\infty$

and be washed away immediately after encounter.[1] An interesting reply to this argument, however, is that any gas obeying Bogoliubov's boundary conditions and evolving according to the Boltzmann equation can be transformed into one obeying the Cohen-Berlin reversed boundary conditions by reversing the momenta of all the molecules in the system. In such a case, all correlations carried during the forward collisions would be destroyed in the reverse collisions and the new system would evolve according to the anti-Boltzmann equation for at least as long as the original system obeyed Boltzmann's equation. The Cohen-Berlin reverse boundary conditions thus represented a haunting return of Loschmidt's criticism of Boltzmann's ideas. It is also interesting, if not ironic, to note that their arguments relating to the probability of occurrences of these reverse boundary conditions were highly reminiscent of Boltzmann's (and Ehrenfest's) reply to Loschmidt.

E. AIM OF PRESENT THESIS

In the above historical expose we have discussed the underlying mathematical structure and physical arguments which have allowed previous authors to derive, via a perturbation

1 It should perhaps be noted that if one interprets Bogoliubov's boundary conditions literally, this argument should not be expected to hold since steaming the particle forward in the infinite future would give the particles an infinite separation in which case one would not expect them to be correlated. The appropriate interpretation of Bogoliubov's boundary condition will be investigated in a later chapter.

approach, irreversible kinetic equations from the reversible mechanical laws governing the motion of individual particles. We have also highlighted some of the difficulties encountered in properly interpreting the boundary conditions and the numerous time scales involved in the thermodynamic relaxation process and of avoiding divergent terms at the higher orders of the expansions. In response to such difficulties there exists essentially two basic approaches which one may envisage. On one hand one may seek slight modifications of the existing perturbation schemes, such as those of Bogoliubov and Frieman which, for example, would strive to eliminate higher order secularities in particular expansions. Indeed research in this direction, for dilute and weakly coupled systems, has been discussed in considerable detail by Cohen [22] and Su et al [30] respectively. Another approach, however, would consist of re-evaluating the basic structure from its roots and seeking mathematical simplifications and physical clarifications which could result in a sharper general picture of the essential conceptual links between the Liouville equation and the kinetic equations. One of many factors favouring such an approach rests on the numerous kinetic equations which have been derived in the past using a multitude of expansion schemes. The sheer number of such expansion techniques has, to say the least, made it extremely difficult for a student in this field of research to grasp their underlying common structure.

Furthermore, as will be shown in the present thesis, many of these techniques bear a mathematical structure far more complex than what is in fact needed to derive the desired kinetic equations. This complexity, which is often introduced either in the form of abstract operators or auxiliary time scales has obscured many of the fundamental conceptual problems involved in deriving irreversible kinetic equations from reversible mechanical laws. For these reasons the present thesis hopes to outline and reevaluate the essential ingredients necessary to recover kinetic equations via a perturbation approach.

The starting point in our analysis will consist of the Hamilton equations, for a mixture of M species of point particles, from which we shall derive the corresponding Liouville and B.B.G.K.Y. hierarchy. We shall then consider the mathematical and physical arguments which justify a particular expansion for a given system. Since the initial work by Bogoliubov, the conventional approach in the literature has consisted on non-dimensionalizing the B.B.G.K.Y. hierarchy with respect to a set of seemingly reasonable characteristic quantities (such as the typical interaction potential range r_0 and strength $\langle\phi\rangle$) and using the resulting dimensionless parameters (such as $\varepsilon_1 = \frac{\langle\phi\rangle}{kT}$ and $\varepsilon_2 = n r_0^3$) to classify molecular systems and to indicate possible expansions of the hierarchy for particular systems. For example,

in a dilute system where $\varepsilon_2 \ll 1$, one would perform an expansion of F_3 in powers of ε_2 so as to obtain a kinetic equation(s) for F_1. This simple approach inherently assumes that the relative weight of the various terms in the resulting dimensionless B.B.G.K.Y. hierarchy is completely dictated by the magnitude of these dimensionless parameters thus implying that the variable terms which they accompany are all of the same order of magnitude. The validity of such an assumption naturally depends, partly on the characteristic quantities chosen in the nondimensionalization. Clearly if these are not very carefully chosen one may find that the resulting dimensionless parameters represent very poorly the relative importance of the various terms in the hierarchy. Furthermore, since individual terms in the latter may vary in order of magnitude and relative importance over the full range of the independent variables, it is not at all clear that it is in fact feasible to obtain a set of dimensionless parameters which dictate the relative importance of various terms over the entire phase space. Hence any expansion performed without these particular problems in mind becomes somewhat hazardous. For this reason one objective of this thesis consists of developing a systematic nondimensionalization of the Hamilton, Liouville and B.B.G.K.Y. equations in which the dimensionless parameters should reveal the average relative magnitude of the various terms over a restricted volume in their respective phase space. We shall then consider the

simple initial value perturbation scheme, which was first discarded by Bogoliubov due to the divergences occurring even at the lower order of the expansion, and show that a simple extension of this approach, which does not rely on the introduction of auxiliary time scales, leads to a simple method of deriving kinetic equations. This method, which, briefly stated, consists of integrating the B.B.G.K.Y. hierarchy over a time interval adequately short to maintain a reasonable accuracy in the expansion, yet sufficiently long to impose suitable boundary conditions will then be applied to a wide variety of systems from the spatially uniform[1] dilute gas to a non-uniform mixture of Brownian particles interacting with an external field and coexisting with a mixture of light bath particles. Hopefully the systematic nondimensionalization of the governing equations and the development of a simple alternate perturbation scheme will not only clarify some of the previously described difficulties in the proper interpretation of time scales and boundary conditions and the elimination of divergent terms occurring at the higher order of various expansions, but will also eventually lead to a greater accessibility of kinetic equations, and their derivation, to the general scientific community.

1 Also referred to by other authors as spatially homogeneous.

CHAPTER II

GENERAL FORMULATION

The general formulation of classical nonequilibrium statistical mechanics for a conservative system of particles is founded on the deterministic set of Hamiltonian equations governing the motion of the individual particles. Since the number of such coupled equations for a macroscopic system (containing, for example, 10^{23} particles) is exceedingly large so as to prohibit, practically speaking, any solution, and that the exact initial positions and momenta of the individual particles are generally unknown to a macroscopic observer with a coarse-grain space-time resolution, one usually prefers substituting this set of equations for a single probabilistic equation governing the system. Such an equation may be derived by considering an ensemble of identical systems containing the same number and type of molecules. The state of the ensemble can then be represented by a set of η points in Γ_N space located at the tips of the micro-state vectors ($\vec{X}_N^1$, ... $\vec{X}_N^i$ ... $\vec{X}_N^\eta$) of the individual systems. If one takes η large, so as to obtain a continuum of points, and acknowledges the conservation of phase points, one can then derive from the Hamilton equations a Liouville equation governing the evolution of the cloud density $\rho_N(\vec{X}_N,t)$ and the probability distribution $F_N(\vec{X}_N,t) \equiv \frac{\rho_N(\vec{X}_N,t)}{\eta}$. The Liouville equation, because of the large number of independent variables

which it contains, is in no way simpler to solve for large systems than the complete set of Hamilton equations for a single system. Fortunately, since most observers are generally insensitive to the fine-grain detailed information which it contains, one is generally contented in seeking an equation for the less informative reduced probability distribution $F_{\{s\}}(\vec{X}_{\{s\}}, t)$ $s \ll N$ from which most observable quantities may be derived. Such an equation, known as the B.B.G.K.Y. hierarchy, may be derived from the Liouville equation by integrating the latter over the coordinates and momenta of all $N - s$ particles outside the group $\{s\}$. As the Hamilton, Liouville and B.B.G.K.Y. equations represent the foundations of the classical statistical mechanical formulation, this chapter will be devoted in presenting the mathematical form and the physical consequences of such equations for a mixture of point particles.[1]

A. HAMILTON AND LIOUVILLE EQUATIONS

Consider a mixture of M species of point particles with each specie α containing N_α particles. Let $\vec{q}_i$ and $\vec{p}_i$ represent the coordinate and momentum vectors for the i th

[1] The mathematical derivations of the Liouville equation and B.B.G.K.Y. hierarchy for a mixture of M species, presented in this chapter, follow closely the derivations of similar equations for a single specie system presented by J. H. S. Lee in his lecture notes on "The Fundamental Structure of Classical Statistical Mechanics"[31] written and presented at l'Université de Provence, France.

particle of the α^{th} specie. Defining:

m_α ≡ mass of a particle of specie α

$U^\alpha(\vec{q}_i^\alpha)$ ≡ external energy potential acting on an α particle

$\phi_{i,j}^{\alpha\beta}(|\vec{q}_i^\alpha - \vec{q}_j^\beta|)$ ≡ interaction energy potential between the i^{th} α particle and the j^{th} β particle,

we may write the Hamiltonian of the system as:

$$H = \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left\{ \frac{\vec{p}_i^\alpha \cdot \vec{p}_i^\alpha}{2 m_\alpha} + U^\alpha(\vec{q}_i^\alpha) + \frac{1}{2} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \phi_{i,j}^{\alpha\beta}(|\vec{q}_i^\alpha - \vec{q}_j^\beta|) \right\} \qquad \text{(II-A-1)}$$

where the condition $\phi_{ii}^{\alpha\alpha} = 0$ is necessarily imposed.

The Hamilton equations for the system may then be written as:

$$\dot{\vec{q}}_i^\alpha = \frac{\partial H}{\partial \vec{p}_i^\alpha} \quad , \quad \dot{\vec{p}}_i^\alpha = -\frac{\partial H}{\partial \vec{q}_i^\alpha} \qquad \text{(II-A-2a)}$$

or as:

$$\dot{\vec{q}}_i^\alpha = \frac{\vec{p}_i^\alpha}{m_\alpha}$$

$$\dot{\vec{p}}_i^\alpha = -\left[\left(\sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{i,j}^{\alpha\beta}}{\partial \vec{q}_i^\alpha} \right) + \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha} \right] \qquad \text{(II-A-2b)}$$

The "state" of this mixture of N particles where,

$$N = \sum_{\alpha=1}^{M} N_\alpha \qquad \text{(II-A-3)}$$

may be represented by a 6N dimensional vector:

$$\vec{X}_N \triangleq \vec{X}_{\{N_1, N_2 \cdots N_M\}} = \{ \vec{q}_1^1, \vec{p}_1^1, \ldots, \vec{q}_i^\alpha \vec{p}_i^\alpha, \ldots, \vec{q}_{N_M}^M \vec{p}_{N_M}^M \}$$

located in a $6N$ dimensional Γ_N space.

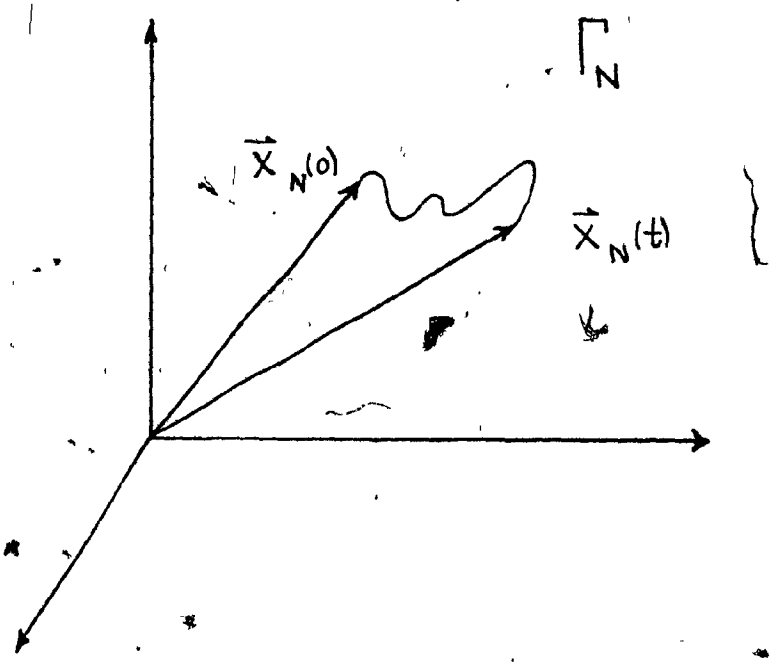


Figure II-1

This vector, as shown in Figure II-1, traces out a trajectory in time which is completely prescribed by the solution of the Hamilton equations subject to some initial condition, $\vec{X}_N(0)$. Since, for large systems it is not feasible to determine $\vec{X}_N(0)$ precisely, a conceptual ensemble of $\mathcal{N}$ identical systems with initial conditions $\left\{ \vec{X}_N^1(0), \ldots, \vec{X}_N^i(0), \ldots, \vec{X}_N^{\mathcal{N}}(0) \right\}$ is constructed, as illustrated in Figure II-2, to account for such inevitable uncertainties in the initial "state" of the particular system under study.

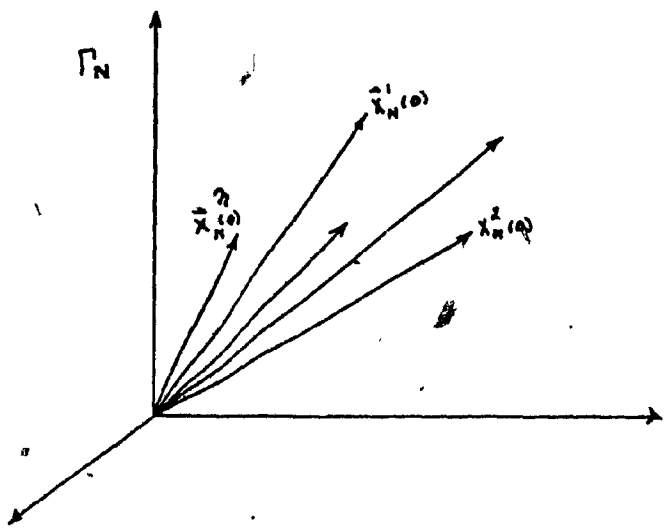


Figure II-2

Taking η to be large, with every system evolving independently of each other, it is clear that the tips of the sequence of vectors $\{\vec{X}_N^1 \quad \ldots \quad \vec{X}_N^\eta\}$ will form a cloud of phase points which flows in the Γ_N space. This cloud will have a density $\rho_N(X_N,t)$ where:

$$\rho_N(\vec{X}_N,t) \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^\alpha \, d\vec{p}_i^\alpha$$

is the number of phase points found in the volume $\prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^\alpha \, d\vec{p}_i^\alpha$ [1] centered at $\vec{X}_N$ at time t.

1 Hereon, the differential $d\vec{q}$ will be used to indicate a differential volume:

$$d\vec{q} \equiv dq_x \, dq_y \, dq_z$$

in configuration space. Similarly, $d\vec{p}$ will represent a differential volume in momentum space:

$$d\vec{p} \equiv dp_x \, dp_y \, dp_z$$

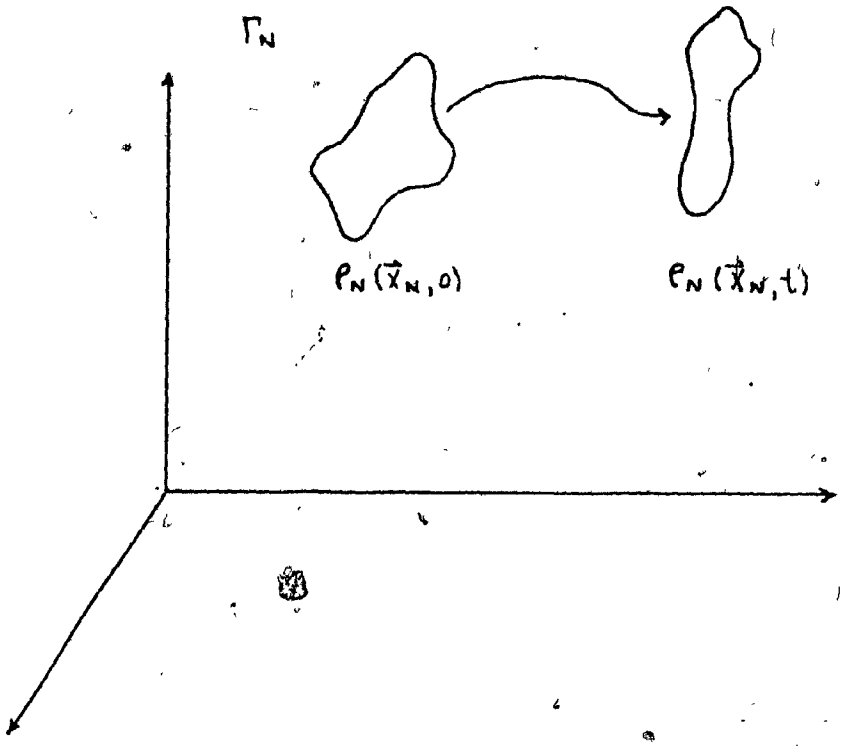


Figure II-3

Since the number of systems in the ensemble is constant, phase points cannot be created or destroyed. Consequently, for any control volume V_N in the Γ_N space:

$$\int\cdots\int_{V_N} \frac{\partial \rho_N}{\partial t}(\vec{X}_N, t) \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\,\alpha}\, d\vec{p}_i^{\,\alpha} = -\int\cdots\int_{A_N} \rho_N(\vec{X}_N, t)\, \vec{v}_N \cdot d\vec{A}_N$$

where $\vec{v}_N$ is the velocity of a phase point in Γ_N space, and A_N is the surface area of the control volume. Using Gauss's theorem, the above may be written as:

$$\int\int\int_{V_N} \left\{ \frac{\partial \rho_N}{\partial t} + \vec{\nabla}_N \cdot \vec{v}_N\, \rho_N \right\} \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\,\alpha}\, d\vec{p}_i^{\,\alpha} = 0$$

Since V_N is arbitrary, we have:

$$\frac{\partial \rho_N}{\partial t} + \vec{\nabla}_N \cdot \vec{v}_N \rho_N = 0 \qquad \text{(II-A-4)}$$

The second term of the above equation may be written as:

$$\begin{aligned}\vec{\nabla}_N \cdot \vec{v}_N \rho_N &= \vec{v}_N \cdot \vec{\nabla}_N \rho_N + \rho_N \vec{\nabla}_N \cdot \vec{v}_N \\ &= \vec{v}_N \cdot \vec{\nabla}_N \rho_N + \rho_N \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left[\frac{\partial}{\partial \vec{q}_i^\alpha} \cdot \dot{\vec{q}}_i^\alpha + \frac{\partial}{\partial \vec{p}_i^\alpha} \cdot \dot{\vec{p}}_i^\alpha \right] \\ &= \vec{v}_N \cdot \vec{\nabla}_N \rho_N + \rho_N \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left[\frac{\partial^2 H}{\partial \vec{q}_i^\alpha \cdot \partial \vec{p}_i^\alpha} - \frac{\partial^2 H}{\partial \vec{p}_i^\alpha \cdot \partial \vec{q}_i^\alpha} \right] \\ &= \vec{v}_N \cdot \vec{\nabla}_N \rho_N\end{aligned}$$

Hence, (II-A-4) reduces to:

$$\frac{\partial \rho_N}{\partial t} + \vec{v}_N \cdot \vec{\nabla}_N \rho_N = 0 \qquad \text{(II-A-5a)}$$

or:

$$\frac{\partial \rho_N}{\partial t} + \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left[\dot{\vec{q}}_i^\alpha \cdot \frac{\partial \rho_N}{\partial \vec{q}_i^\alpha} + \frac{\dot{\vec{p}}_i^\alpha}{m_\alpha} \cdot \frac{\partial \rho_N}{\partial \vec{p}_i^\alpha} \right] = 0 \qquad \text{(II-A-5b)}$$

or:

$$\frac{\partial \rho_N}{\partial t} + \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left[\frac{\partial H}{\partial \vec{p}_i^\alpha} \cdot \frac{\partial \rho_N}{\partial \vec{q}_i^\alpha} - \frac{\partial H}{\partial \vec{q}_i^\alpha} \cdot \frac{\partial \rho_N}{\partial \vec{p}_i^\alpha} \right] \qquad \text{(II-A-5c)}$$

or, finally:

$$\frac{\partial \rho_N}{\partial t} + \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left[\frac{\vec{p}_i^\alpha}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^\alpha} - \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha} \cdot \frac{\partial}{\partial \vec{p}_i^\alpha} - \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha} \cdot \frac{\partial}{\partial \vec{p}_i^\alpha} \right] \rho_N = 0 \qquad \text{(II-A-5d)}$$

This last equation, which is the Liouville equation, for the mixture, can also be given the compact form:

$$\frac{\partial \rho_N}{\partial t} + \mathcal{H}_N \rho_N = 0 \qquad \text{(II-A-5d)}$$

where:

$$\mathcal{H}_N = \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left(\frac{\vec{p}_i^{\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha}} - \frac{\partial \mathcal{U}^{\alpha}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha}} - \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha}} \right) \qquad \text{(II-A-6)}$$

is referred to as the Hamiltonian operator.

B. SOLUTION TO THE LIOUVILLE EQUATION

A solution to (II-A-5d) may be sought by operating both sides by $e^{\mathcal{H}_N t}$.

Doing so, we obtain:

$$\frac{\partial e^{\mathcal{H}_N t} \rho_N}{\partial t} = 0$$

Upon integration of this equation, we conclude that:

$$\rho_N(\vec{X}_N, t) = e^{-\mathcal{H}_N t} \rho_N(\vec{X}_N, 0) \qquad \text{(II-B-1)}$$

The role of the operator, $e^{\mathcal{H}_N t}$ and $e^{-\mathcal{H}_N t}$ is quite clear, if we also note that the Hamilton equations may be written as:

$$\dot{\vec{q}}_i^{\alpha} = \mathcal{H}_N \vec{q}_i^{\alpha} \quad ; \quad \dot{\vec{p}}_i^{\alpha} = \mathcal{H}_N \vec{p}_i^{\alpha} . \qquad \text{(II-B-2)}$$

Operating both sides of these equations by $e^{\mathcal{H}_N t}$ and integrating, we have the solution:

$$\vec{q}_i^{\alpha}(t) = e^{\mathcal{H}_N t} \vec{q}_i^{\alpha}(0) ; \quad \vec{p}_i^{\alpha}(t) = e^{\mathcal{H}_N t} \vec{p}_i^{\alpha}(0) \qquad \text{(II-B-3)}$$

Hence, the operator, $e^{\mathcal{H}_N t}$, streams the coordinates and momenta of the particles forward in time from their initial values to their values at time t.

For this reason, it is referred to as a "forward streaming operator", which is sometimes written as:

$$e^{\mathcal{H}_N t} \equiv S_t^N$$

Similarly, by operating both sides of (II-B-3) by $e^{-\mathcal{H}_N t}$, we may write:

$$\vec{q}_i^{\alpha}(0) = e^{-\mathcal{H}_N t}\, \vec{q}_i^{\alpha}(t) \quad , \quad \vec{p}_i^{\alpha}(0) = e^{-\mathcal{H}_N t}\, \vec{p}_i^{\alpha}(t)$$

and conclude that the operator, $e^{-\mathcal{H}_N t}$, streams the coordinates and momenta of the particles back in time from their values at time t to their initial values. This operator is a "backward streaming operator" and is often written as:

$$e^{-\mathcal{H}_N t} = S^N_{-t}$$

The properties of the operator S^N_t for all real values of have been discussed by E.G.D. Cohen[32]; they include

$$S^N_{t_1}\, S^N_{t_2} = S^N_{(t_1+t_2)}$$

$$\frac{\partial S^N_t}{\partial t} = \mathcal{H}_N\, S^N_t = S^N_t\, \mathcal{H}_N$$

Returning to the solution of the Liouville equation, (II-B-1), it is now clear that the backward streaming operator, $e^{-\mathcal{H}_N t}$, operates on the state vector, $\vec{X}_N$. Hence, (II-B-1) may be written as:

$$\rho_N(\vec{X}_N, t) = \rho_N(S^N_{-t}\, \vec{X}_N, 0) = \rho_N(\vec{X}^{\circ}_N, 0) \qquad \text{(II-B-1)}$$

where $\vec{X}^{\circ}_N$ indicates the location of the state vector at time $t = 0$, given that it is at $\vec{X}_N$ at time t. The above solution thus states that the density, ρ_N, around any phase point at time t is equal to the density around the same phase point at $t = 0$. The phase cloud thus flows, in a Lagrangian frame of reference, as an incompressible fluid. This fact is confirmed by recalling the Liouville equation, (II-A-5a):

$$\frac{\partial \rho_N}{\partial t} + \vec{v}_N \cdot \vec{\nabla}_N \rho_N = 0$$

and rewriting it as:

$$\frac{D\rho_N}{Dt} = 0 \qquad \text{(II-B-4)}$$

where:

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \vec{v}_N \cdot \vec{\nabla}_N \qquad \text{(II-B-5)}$$

is the time derivative in a Lagrangian frame of reference.

Since, practically speaking, one deals with a single system, it is conceptually advantageous to seek for the probability of finding a particular system in a certain state. This probability can be evaluated by normalizing the point density as follows:

$$F_N = \frac{\rho_N}{\eta}$$

Doing so, we obtain the distribution $F_N(\vec{X}_N, t)$ where $F_N \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\alpha} \, d\vec{p}_i^{\alpha}$ now represents the probability of finding a system's phase point in the volume $\prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\alpha} \, d\vec{p}_i^{\alpha}$ centered around $\vec{X}_N$. This distribution also obeys the Liouville equation:

$$\frac{\partial F_N}{\partial t} + \mathcal{H}_N F_N = 0 \qquad \text{(II-B-6)}$$

with the solution given by:

$$F_N(\vec{X}_N, t) = F_N(S_{-t}^N \vec{X}_N, 0)$$
$$= F_N(\vec{X}_N^0, 0) \qquad \text{(II-B-7)}$$

It should be noted here that in order to evaluate S_{-t}^N or $\vec{X}_N^0$, one must solve the complete set of Hamilton equations. Hence, solving the Liouville equation also implies solving the Hamilton equations. This is, of course, not surprising since the Liouville equation is simply a probabilistic equation for a Hamiltonian system with uncertain initial conditions.

Indeed, if there are no uncertainties as to the coordinates and momenta of all the particles in the system, the distribution $F_N(\vec{x}_N,t)$ takes on the form:

$$F_N(\vec{x}_N,t) = \prod_{\alpha=1}^{M}\prod_{i=1}^{N_\alpha} \delta(\vec{q}_i^{\,\alpha} - \vec{q}_i^{\,\alpha}(t))\,\delta(\vec{p}_i^{\,\alpha} - \vec{p}_i^{\,\alpha}(t)) \qquad \text{(II-B-8)}$$

where $\delta(x-x(t))$ is the Dirac delta function. We can now show that for this deterministic case, the Liouville equation is simply an alternate form of the Hamilton equations. To prove this, we simply substitute (II-B-8) into (II-A-5c), multiply by $\vec{q}_i^{\,\alpha}$ and integrate over the coordinates and momenta of all the particles to find that:

$$\frac{\partial}{\partial t}\int\cdots\int \vec{q}_i^{\,\alpha}\prod_{\alpha=1}^{M}\prod_{i=1}^{N_\alpha}\delta(\vec{q}_i^{\,\alpha} - \vec{q}_i^{\,\alpha}(t))\,\delta(\vec{p}_i^{\,\alpha} - \vec{p}_i^{\,\alpha}(t))\prod_{\beta=1}^{M}\prod_{j=1}^{N_\beta} d\vec{q}_j^{\,\beta}\,d\vec{p}_j^{\,\beta}$$

$$+\int\cdots\int \vec{q}_i^{\,\alpha}\,\frac{\partial H}{\partial \vec{p}_i^{\,\alpha}}\cdot\frac{\partial}{\partial \vec{q}_i^{\,\alpha}}\prod_{\alpha=1}^{M}\prod_{i=1}^{N_\alpha}\delta(\vec{q}_i^{\,\alpha} - \vec{q}_i^{\,\alpha}(t))\,\delta(\vec{p}_i^{\,\alpha} - \vec{p}_i^{\,\alpha}(t))\prod_{\beta=1}^{M}\prod_{j=1}^{N_\beta} d\vec{q}_j^{\,\beta}\,d\vec{p}_j^{\,\beta}$$

$$-\int\cdots\int \vec{q}_i^{\,\alpha}\,\frac{\partial H}{\partial \vec{q}_i^{\,\alpha}}\cdot\frac{\partial}{\partial \vec{p}_i^{\,\alpha}}\prod_{\alpha=1}^{M}\prod_{i=1}^{N_\alpha}\delta(\vec{q}_i^{\,\alpha} - \vec{q}_i^{\,\alpha}(t))\,\delta(\vec{p}_i^{\,\alpha} - \vec{p}_i^{\,\alpha}(t))\prod_{\beta=1}^{M}\prod_{j=1}^{N_\beta} d\vec{q}_j^{\,\beta}\,d\vec{p}_j^{\,\beta}$$

$$= 0$$

Using the following properties of the δ function:

$$\int_{-\infty}^{\infty}\delta(x-x_0)\,dx = 1$$

$$\int_{-\infty}^{\infty}\phi(x)\,\delta(x-x_0)\,dx = \phi(x_0)$$

$$\int_{-\infty}^{\infty}\phi(x)\,\frac{d\delta(x-x_0)}{dx}\,dx = -\int_{-\infty}^{\infty}\frac{d\phi(x)}{dx}\,\delta(x-x_0)\,dx$$

the above Liouville equation reduces to:

$$\dot{\vec{q}}_i^{\,\alpha}(t) = \frac{\partial H}{\partial \vec{p}_i^{\,\alpha}}$$

Similarly, substituting (II-B-8) into (II-A-5c), multiplying by $\vec{p}_i^{\alpha}$ and integrating over the coordinates and momenta of all the particles we easily obtain:

$$\dot{\vec{p}}_i^{\alpha} = -\frac{\partial H}{\partial \vec{q}_i^{\alpha}} \qquad 1$$

The Liouville equation and the Hamilton equations thus contain identical and complete information concerning the detailed dynamics of the system. For small systems containing only a few particles, one could solve either the deterministic Hamilton equations or the probabilistic Liouville equation. On the other hand, for macroscopic systems containing a very large number of particles (e.g., 10^{23} particles), it is clearly unfeasible to evaluate the streaming operators. For such systems, one can neither predict the trajectory of the phase point or the time evolution of the phase cloud in Γ_N space. Fortunately, for large systems, one is not at all interested in the complete and cumbersome microscopic information which the solution of the Liouville equation would offer. Indeed, one is usually much more concerned with the macroscopic properties, such as:

$$\rho_m^{\alpha} \equiv N m \int F_1^{\alpha}(\vec{q}, \vec{p}, t)\, d\vec{p}$$

$\equiv$ mass density of specie α

$$\rho_{\vec{p}}^{\alpha} \equiv N \int \vec{p}\, F_1(\vec{q}, \vec{p}, t)\, d\vec{p}$$

$\equiv$ momentum density of specie α

1 The technique used here to rederive the Hamiltonian equations from the Liouville equations is essentially Carlo Cercignani's[33] method of obtaining the Liouville equation applied in reverse.

$$\rho_{\alpha}^{\alpha}(\vec{q},t) \equiv N \int \frac{|\vec{p}|^2}{2m} F_1^{\alpha}(\vec{q},\vec{p},t)\, d\vec{p}$$

≡ kinetic energy density of specie α

where:

$$F_1^{\alpha}(\vec{q},\vec{p},t) = \int\cdots\int F_N(\vec{X}_N,t) \prod_{\substack{\gamma=1 \\ (\beta,\gamma)\neq(1,\alpha)}}^{M} \prod_{R=1}^{N_\gamma} d\vec{q}_R^{\gamma}\, d\vec{p}_R^{\gamma}$$

These quantities represent contracted variables for the system containing much lower grade information than the microscopic state vector $\vec{X}_N(t)$ or the complete joint probability distribution F_N. The task of obtaining such important thermodynamic variables from the Liouville equation represents one of the major aims of the nonequilibrium statistical approach.

C. THE B.B.G.K.Y. HIERARCHY

Since most of the macroscopic variables are derivable from the lower level, one particle distributions $F_1(\vec{q}_i^{\alpha},\vec{p}_i^{\alpha},t)$, it is of great interest to derive "kinetic equations" which govern the time evolution of these distributions. The first step in extracting such equations from the Liouville equation consists of focusing our attention on a subgroup of particles $\{S\}$ which contain:

- S_1 type 1 particle
- S_α type α particles
- ⋮
- S_M type M particles.

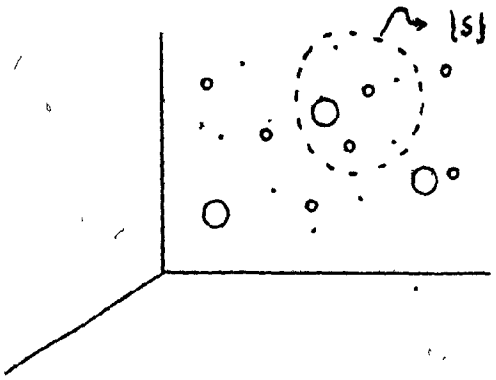


Figure II-4

Let us now seek some equation which dictates the evolution of the reduced probability distribution $F_{\{s\}}(\vec{X}_{\{s\}},t)$. In order to obtain such an equation, we merely integrate the Liouville equation over the coordinates and momenta of all the particles outside of $\{s\}$. Before performing such an integration, however, let us introduce the following notation:

a) let $\mathcal{H}_{\{s\}}$ represent the Hamiltonian operator for an isolated subgroup of particles $\{s\}$;

b) let $F_{\{s,j,\beta\}}(\vec{X}_{\{s\}},\vec{q}_j^{\,\beta},\vec{p}_j^{\,\beta},t)$ represent the joint probability distribution for all the particles inside $\{s\}$ and the j^{th} β particle with $\{j,\beta\}\notin\{s\}$.

Proceeding with the forementioned integration, we write:

$$\int\cdots\int\left\{\frac{\partial F_N}{\partial t}+\mathcal{H}_N F_N\right\}\prod_{\gamma=1}^{M}\prod_{k=s_\gamma+1}^{N_\gamma} d\vec{q}_k^{\,\gamma}\,d\vec{p}_k^{\,\gamma}=0 \qquad \text{(II-C-1)}$$

or:

$$\int\cdots\int\left\{\frac{\partial F_N}{\partial t}+\sum_{\alpha=1}^{M}\sum_{i=1}^{N_\alpha}\left[\frac{\vec{p}_i^{\,\alpha}}{m_\alpha}\cdot\frac{\partial F_N}{\partial\vec{q}_i^{\,\alpha}}-\frac{\partial U^\alpha}{\partial\vec{q}_i^{\,\alpha}}\cdot\frac{\partial F_N}{\partial\vec{p}_i^{\,\alpha}}\right]\right.$$
$$\left.-\sum_{\alpha=1}^{M}\sum_{i=1}^{N_\alpha}\sum_{\beta=1}^{M}\sum_{j=1}^{N_\beta}\frac{\partial\phi_{ij}^{\alpha\beta}}{\partial\vec{q}_i^{\,\alpha}}\cdot\frac{\partial F_N}{\partial\vec{p}_i^{\,\alpha}}\right\}\prod_{\gamma=1}^{M}\prod_{k=s_\gamma+1}^{N_\gamma} d\vec{q}_k^{\,\gamma}\,d\vec{p}_k^{\,\gamma}=0 \qquad \text{(II-C-2)}$$

We note that:

$$\int\cdots\int \frac{\partial F_N}{\partial t} \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma} = \frac{\partial}{\partial t} \int\cdots\int F_N \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma}$$

$$= \frac{\partial F_{(s)}}{\partial t} \qquad \text{(II-C-3)}$$

and:

$$\int\cdots\int \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial F_N}{\partial \vec{q}_{0_i}^{\,\alpha}} \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma}$$

$$= \int\cdots\int \sum_{\alpha=1}^{M} \left[\sum_{i=1}^{S_\alpha} + \sum_{i=S_\alpha+1}^{N_\alpha} \left(\frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial F_N}{\partial \vec{q}_i^{\,\alpha}} \right) \right] \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma}$$

$$= \sum_{\alpha=1}^{M} \sum_{i=1}^{S_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial F_{(s)}}{\partial \vec{q}_i^{\,\alpha}}$$

$$+ \sum_{\alpha=1}^{M} \sum_{i=S_\alpha+1}^{N_\alpha} \int\int \left[\frac{\partial F_N}{\partial \vec{q}_i^{\,\alpha}}\, d\vec{q}_i^{\,\alpha} \right] \cdot \frac{\vec{p}_i^{\,\alpha}}{m_\alpha}\, d\vec{p}_i^{\,\alpha} \prod_{\substack{\gamma=1 \\ \{R,\gamma\} \neq \{i,\alpha\}}}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma}$$

Since:

$$\lim_{|q_i^\alpha| \to \infty} F_N = 0 \qquad \text{(II-C-4)}$$

the second term vanishes and we retain:

$$\int\cdots\int \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial F_N}{\partial \vec{q}_i^{\,\alpha}} \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma} =$$

$$\sum_{\alpha=1}^{M} \sum_{i=1}^{S_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial F_{(s)}}{\partial \vec{q}_i^{\,\alpha}} \qquad \text{(II-C-5)}$$

Similarly:

$$\int\cdots\int \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial F_N}{\partial \vec{p}_i^{\,\alpha}} \prod_{\gamma=1}^{M} \prod_{R=S_{\gamma+1}}^{N_\gamma} d\vec{q}_R^{\,\gamma}\, d\vec{p}_R^{\,\gamma} =$$

$$\int\cdots\int \sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_N}{\partial \vec{p}_i^\alpha} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma$$

$$+\int\cdots\int \sum_{\alpha=1}^{M}\sum_{i=S_\alpha+1}^{N_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_N}{\partial \vec{p}_i^\alpha} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma$$

$$= \sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_{1s}}{\partial \vec{p}_i^\alpha}$$

$$+\sum_{\alpha=1}^{M}\sum_{i=S_\alpha+1}^{N_\alpha}\int\cdots\int\left[\int \frac{\partial F_N}{\partial \vec{p}_i^\alpha}\, d\vec{p}_i^\alpha\right]\cdot\frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\, d\vec{q}_i^\alpha \prod_{\substack{\gamma=1\\ \{k,\gamma\}\neq\{i,\alpha\}}}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma$$

Since F_N is normalized (i.e., $\int\cdots\int F_N(X_N,t)\,d\vec{\Gamma}_N = 1$) we must have

$$\lim_{|\vec{p}_i^\alpha|\to\infty} F_N(X_N,t) = 0 \qquad \text{(II-C-6)}$$

in which case the second term vanishes and:

$$\int\cdots\int \sum_{\alpha=1}^{M}\sum_{i=1}^{N_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_N}{\partial \vec{p}_i^\alpha} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma =$$

$$\sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha} \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_{1s}}{\partial \vec{p}_i^\alpha} \qquad \text{(II-C-7)}$$

Finally:

$$\int\cdots\int \sum_{\alpha=1}^{M}\sum_{i=1}^{N_\alpha}\sum_{\beta=1}^{M}\sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_N}{\partial \vec{p}_i^\alpha} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma$$

$$= \int\cdots\int \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\left[\sum_{i=1}^{S_\alpha}\left(\sum_{j=1}^{S_\beta}+\sum_{j=S_\beta+1}^{N_\beta}\right)+\sum_{i=S_\alpha+1}^{N_\alpha}\sum_{j=1}^{N_\beta}\right]$$

$$\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_N}{\partial \vec{p}_i^\alpha} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^\gamma\, d\vec{p}_k^\gamma$$

$$= \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{S_\alpha}\sum_{j=1}^{S_\beta}\left(\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha}\cdot\frac{\partial F_{1s}}{\partial \vec{p}_i^\alpha}\right) +$$

$$\sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{L_\alpha}\sum_{j=S_\beta+1}^{N_\beta}\int\cdots\int \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s;j_\beta\}}}{\partial \vec{p}_i^{\alpha}} \, d\vec{q}_j^{\beta}\, d\vec{p}_j^{\beta}$$

$$+\sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int\cdots\int\left[\int \frac{\partial F_N}{\partial \vec{p}_i^{\alpha}}\, d\vec{p}_i^{\alpha}\right] \cdot \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}}\, d\vec{q}_i^{\alpha} \prod_{\substack{\gamma=1 \\ \{k,\gamma\}\neq\{i,\alpha\}}}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^{\gamma}\, d\vec{p}_k^{\gamma}$$

Making further use of (II-C-6), the above reduces to:

$$\int\cdots\int\sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_N}{\partial \vec{p}_i^{\alpha}} \prod_{\gamma=1}^{M}\prod_{k=S_\gamma+1}^{N_\gamma} d\vec{q}_k^{\gamma}\, d\vec{p}_k^{\gamma} =$$

$$\sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{S_\alpha}\sum_{j=1}^{S_\beta}\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s\}}}{\partial \vec{p}_i^{\alpha}} +$$

$$\sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{S_\alpha}\sum_{j=S_\beta+1}^{N_\beta}\int\int\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s,j_\beta\}}}{\partial \vec{p}_i^{\alpha}}\, d\vec{q}_j^{\beta}\, d\vec{p}_j^{\beta} \qquad \text{(II-C-8)}$$

Combining (II-C-2), (II-C-3), (II-C-5), (II-C-7) and (II-C-8), we have:

$$\frac{\partial F_{\{s\}}}{\partial t} + \mathcal{H}_{\{s\}} F_{\{s\}} = \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{i=1}^{S_\alpha}\sum_{j=S_\beta+1}^{N_\beta}\int\int\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s;j_\beta\}}}{\partial \vec{p}_i^{\alpha}}\, d\vec{q}_j^{\beta}\, d\vec{p}_j^{\beta} \qquad \text{(II-C-9)}$$

Since there exists no special need of distinguishing, a priori, between molecules of the same specie, we may assume that the distribution $F_{\{s\}}$ possesses a symmetry for all particles of the same type and that consequently:

$$F_{\{s,j,\beta\}} = F_{\{s,k,\beta\}} = F_{\{s;s_\beta+1\}}$$

where $F_{\{s;s_\beta+1\}}$ represents the joint distribution for the particles of $\{s\}$ and the $(s_\beta+1)^{th}$ β particle.

We may thus rewrite (II-C-9) as:

$$\frac{\partial F_{\{s\}}}{\partial t} + \mathcal{H}_{\{s\}} F_{\{s\}} = \sum_{\beta=1}^{M}(N_\beta - s_\beta)\sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha}\int\int\frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s,s_\beta+1\}}}{\partial \vec{p}_i^{\alpha}}\, d\vec{q}_{s_\beta+1}^{\beta}\, d\vec{p}_{s_\beta+1}^{\beta} \qquad \text{(II-C-10)}$$

or, more compactly as:

$$\frac{\partial F_{\{s\}}}{\partial t} + \mathcal{H}_{\{s\}} F_{\{s\}} = \sum_{\beta=1}^{m} (N_\beta - s_\beta) \sum_{\alpha=1}^{m} \mathcal{L}^{\alpha\beta}_{s_\alpha} F_{\{s; s_{\beta+1}\}} \qquad \text{(II-C-11)}$$

[1]

where:

$$\mathcal{L}^{\alpha\beta}_{s_\alpha} = \sum_{i=1}^{s_\alpha} \int\!\!\int \frac{\partial \phi^{\alpha\beta}_{i,s_{\beta+1}}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \, d\vec{q}^{\,\beta}_{s_{\beta+1}} \, d\vec{p}^{\,\beta}_{s_{\beta+1}} \qquad \text{(II-C-12a)}$$

is a "phase mixing" operator which may be rewritten as:

$$\mathcal{L}^{\alpha\beta}_{s_\alpha} = \sum_{i=1}^{s_\alpha} \int\!\!\int \frac{\partial \phi^{\alpha\beta}_{i,s_{\beta+1}}(|\vec{r}^{\,\alpha\beta}_{i,s_{\beta+1}}|)}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \, d\vec{r}^{\,\alpha\beta}_{i,s_{\beta+1}} \, d\vec{p}^{\,\beta}_{s_{\beta+1}} \qquad \text{(II-C-12b)}$$

by defining the separation vector:

$$\vec{r}^{\,\alpha\beta}_{ij} \equiv \vec{q}^{\,\beta}_j - \vec{q}^{\,\alpha}_i$$

SCHEMATIC REPRESENTATION OF

PHASE MIXING OPERATOR

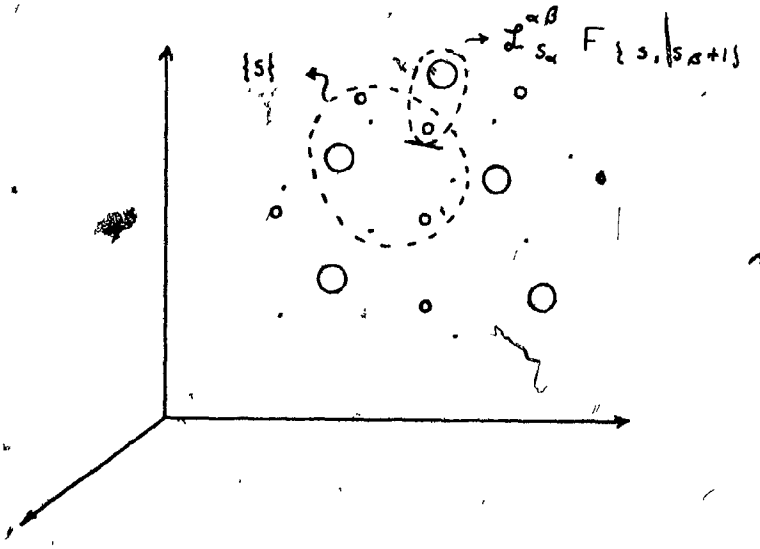


Figure II-5

[1] When the mixture only contains two species, this equation reduces to the B.B.G.K.Y. hierarchy derived by Brown Flores and García-Colín.[34]

Equation (II-C-11) is generally referred to as the B.B.G.K.Y. hierarchy as it relates the lower level distribution $F_{\{s\}}$ to the higher level distribution $F_{\{s,s_{\beta+1}\}}$. The term $\mathcal{H}_{\{s\}}$ on the left hand side of the hierarchy is representative of the interactions occurring within $\{s\}$ while the mixing term on the right hand side, as illustrated by Figure II-5 expresses the influence of the particles outside of $\{s\}$ on those within $\{s\}$. This latter term imposes an open form on the hierarchy thus making any exact solution for $F_{\{s\}}$ impossible if the higher level distribution $F_{\{s,s_{\beta+1}\}}$ is unknown. Such a state of affairs was, of course, to be expected, since interactions across the boundary of $\{s\}$ do, indeed, exist and it would have been rather naive to expect that a pure mathematical manipulation of the Liouville equation might erase such interactions.

D. SUMMARY

The results of this chapter may briefly be summarized as follows:

1) The evolution of a single system of interacting particles (described by the trajectory of a state vector $\vec{X}_N(t)$ in a $6N$ dimensional Γ_N space) is governed by the set of Hamilton equations which may be written as:

$$\left.\begin{aligned} \dot{\vec{q}}_i^{\alpha} &= \frac{\vec{p}_i^{\alpha}}{m_{\alpha}} \\ \dot{\vec{p}}_i^{\alpha} &= -\left[\sum_{\beta=1}^{M}\sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}}\right] - \frac{\partial \mathcal{U}^{\alpha}}{\partial \vec{q}_i^{\alpha}} \end{aligned}\right\} \qquad \text{(II-A-2b)}$$

or equivalently as:

$$\dot{\vec{q}}_i^{\alpha} = \mathcal{H}_N \vec{q}_i^{\alpha}$$

$$\dot{\vec{p}}_i^{\alpha} = \mathcal{H}_N \vec{p}_i^{\alpha} \qquad \text{(II-B-2)}$$

where:

$$\mathcal{H}_N = \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \left\{ \frac{\vec{p}_i^{\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha}} - \frac{\partial u^{\alpha}}{\partial \vec{q}_i^{\alpha}} \right.$$

$$\left. - \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha}} \right\} \qquad \text{(II-A-6)}$$

The solution to these equations is given by:

$$\vec{q}_i^{\alpha}(t) = e^{\mathcal{H}_N t} \vec{q}_i^{\alpha}(0) = S_t^N \vec{q}_i^{\alpha}(0)$$

$$\vec{p}_i^{\alpha}(t) = e^{\mathcal{H}_N t} \vec{p}_i^{\alpha}(0) = S_t^N \vec{p}_i^{\alpha}(0)$$

2) The evolution of an ensemble of $\mathcal{N}$ identical systems with $\mathcal{N}$ large is described by a density distribution $\rho_N(\vec{X}_N, t)$ in Γ_N space or an N particle probability distribution $F_N(\vec{X}_N, t)$ and is governed by the Liouville equation:

$$\frac{\partial F_N}{\partial t} + \mathcal{H}_N F_N = 0 \qquad \text{(II-B-6)}$$

which has the solution:

$$F_N(\vec{X}_N, t) = e^{-\mathcal{H}_N t} F_N(\vec{X}_N, 0) = F_N(S_{-t}^N \vec{X}_N, 0) \qquad \text{(II-B-7)}$$

If all the systems of the ensemble are initially in the same known microstate $\vec{X}_N(0)$, the Liouville equation then reduces to the Hamilton equations.

3) The evolution of the reduced probability distribution $F_{\{s\}}(\vec{X}_{\{s\}},t)$ is governed by the open B.B.G.K.Y. hierarchy:

$$\frac{\partial F_{\{s\}}}{\partial t} + \mathcal{H}_{\{s\}} F_{\{s\}} = \sum_{\beta=1}^{M} (N_\beta - s_\beta) \sum_{\alpha=1}^{M} \mathcal{L}^{\alpha\beta}_{s_\alpha} F_{\{s;s_\beta+1\}} \qquad \text{(II-C-11)}$$

where

$$\mathcal{H}_{\{s\}} \equiv \sum_{\alpha=1}^{M} \sum_{i=1}^{s_\alpha} \left\{ \frac{\vec{p}_i^{\,\alpha}}{m^\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha}} - \frac{\partial U^\alpha}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} - \sum_{\beta=1}^{M} \sum_{j=1}^{s_\beta} \frac{\partial \psi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \right\}$$

$$\mathcal{L}^{\alpha\beta}_{s_\alpha} \equiv \sum_{i=1}^{s_\alpha} \int\int \frac{\partial \phi^{\alpha\beta}_{i,s_\beta+1}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \, d\vec{q}^{\,\beta}_{s_\beta+1} \, d\vec{p}^{\,\beta}_{s_\beta+1}$$

$$= \sum_{i=1}^{s_\alpha} \int\int \frac{\partial \phi^{\alpha\beta}_{i,s_\beta+1}(|\vec{r}^{\alpha\beta}_{ij}|)}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \, d\vec{r}^{\,\alpha\beta}_{i,s_\beta+1} \, d\vec{p}^{\,\beta}_{s_\beta+1}$$

The Hamilton, Liouville and B.B.G.K.Y. equations, as previously noted, represent the foundations of the statistical mechanical formulation and will be referred to hereon as the "governing equations" for classical molecular systems.

CHAPTER III

NONDIMENSIONALIZATION OF THE GOVERNING EQUATIONS

The B.B.G.K.Y. hierarchy (II-C-11), derived in the previous chapter for a mixture of classical point particles, represents, on one hand, a key governing equation, and on the other hand, a major obstacle in the statistical mechanical study of molecular systems. Indeed, one would like to derive from such an equation general analytical expressions for the one particle distribution $F_1^{\alpha}(\vec{q},\vec{p},t)$ from which the relevant macroscopic properties of the system could eventually be extracted. Unfortunately, it is abundantly clear from the open form of the hierarchy that such a general task is impossible without some knowledge of the higher level two particle distributions. Since these latter distributions are themselves governed by yet higher level distributions and that this interlocking chain of dependence propagates to the highest level distribution $F_N(\vec{X}_N,t)$, one then reluctantly concludes that the derivation of general and exact expressions for $F_1^{\alpha}(\vec{q},\vec{p},t)$, represents, in practical terms, an unrealistic objective. The problem at hand, therefore, consists of somehow closing or "truncating" the hierarchy so as to obtain approximate closed equations for a group of low level reduced distributions $F_{1\ldots s}(\vec{X}_{1\ldots s},t)$. This simpler task may be accomplished by seeking special

classes of mixtures for which some of the terms of the hierarchy, including the troublesome "mixing" term responsible for its open form, may be neglected as a "zeroth order" approximation. For such mixtures one may derive approximate zeroth order distributions $F_{\{s\}}$ (and $F_{\{s;j,\beta\}}$) which may then be resubstituted into the terms initially discarded so as to obtain more accurate "1rst order" equations for $F_{\{s\}}$. Repeating this process of successive approximation, one would then hopefully emerge with increasingly accurate closed equations for $F_{\{s\}}$. This method of closing the hierarchy, often referred to as a "perturbation approach", has been extensively exploited in the past to derive approximate closed kinetic equations for the one particle distributions. The viability of this method in the derivation of such equations represents, furthermore, the main concern of this thesis.

A. ESTIMATING ORDERS OF MAGNITUDE:

Before any truncation of the B.B.G.K.Y. hierarchy via a perturbation approach is pursued, one should naturally devise some method of estimating the relative importance of the various terms in this equation. One such method consists of seeking some characteristic quantities which are inherent to the system and constructing from these dimensional quantities, dimensionless intrinsic parameters which govern the relative weight of the various terms of the

hierarchy. This method, initially proposed by Bogoliubov[12] in 1946, was later exploited by Frieman[24] and Sandri[25] in 1962 and 1963 respectively. Sandri, in particular, defined the following characteristic quantities.

$r_0 \equiv$ typical range of the interaction potential.

$\phi_0 \equiv$ typical strength of the interaction potential.

$m v_{th}^2 \equiv$ "kinetic temperature"

so as to derive for a simple gas[1], in the absence of an external field, the dimensionless hierarchy.

$$\frac{\partial F_s^*}{\partial t^*} + K_s^* F_s + \varepsilon_1 I_s^* F_s^* = \varepsilon_1 \varepsilon_2 L_s^* F_s^* \qquad \text{(III-A-1)}^2$$

where:

$$K_s^* = -\sum_{i=1}^{s} \vec{p}_i^* \cdot \frac{\partial}{\partial \vec{q}_i^*}$$

$$I_s^* = \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}^*}{\partial \vec{q}_i^*} \cdot \frac{\partial}{\partial \vec{p}_i^*} \qquad \text{(III-A-2)}$$

$$L_s^* = \sum_{i=1}^{s} \int\int \frac{\partial \phi_{ij}^*}{\partial \vec{q}_i^*} \cdot \frac{\partial}{\partial \vec{p}_i^*} \, d\vec{q}_{s+1}^* \, d\vec{p}_{s+1}^*$$

[1]Hereon gases containing a single specie of particles will be referred to as "simple gases".

[2]Hereon '*' superscripts will be used to denote dimensionless quantities and operators.

$$\vec{q}_i^{\,*} \equiv \frac{\vec{q}_i}{r_0}$$

$$\vec{p}_i^{\,*} \equiv \frac{\vec{p}_i}{m v_{th}}$$

$$\phi_{ij}^{*} \equiv \frac{\phi_{ij}}{\phi_0}$$

$$F_s^{*} \equiv F_s V^{s} (m v_{th})^{3s}$$

$V \equiv$ physical volume

and where $\varepsilon_1 \equiv \frac{\phi_0}{m v_{th}^2}$, $\varepsilon_2 \equiv n r_0^3$ (with $n \equiv \lim_{\substack{V\to\infty \\ N\to\infty}} \frac{N}{V} \equiv$ average particle density) represented the dimensionless intrinsic parameters. From the definition of these parameters Sandri could then interpret ε_1 as the typical ratio of potential to kinetic energy during an interaction between two particles, and ε_2 as a measure of the typical number of neighboring particles within any particle's interaction sphere. Sandri further noted that these parameters could be used in a systematic classification of molecular systems. Consequently, using ε_1 and ε_2 as index codes, he identified the following four classes of mixtures:

1) dilute gases with $\varepsilon_1 \sim O[1]$ $\varepsilon_2 \ll 1$

2) weakly coupled gases with $\varepsilon_1 \ll 1$, $\varepsilon_2 \sim O[1]$

3) gases displaying weak long range interactions (including Coulomb interactions) with $\varepsilon_1 \ll 1$, $\varepsilon_1 \varepsilon_2 \sim O[1]$

4) weakly coupled dilute gases with $\varepsilon_1 \sim o[\varepsilon_2] \ll 1$

Since, in each of the above cases, there existed at least one parameter ε which was much smaller than unity, Sandri then reasoned that such a parameter could be utilized as a perturbation parameter in the following expansion of

$$\overset{*}{F}_s = \overset{*}{F}_s^{(0)} + \varepsilon \overset{*}{F}_s^{(1)} + \varepsilon^2 \overset{*}{F}_s^{(2)} + \cdots \qquad \text{(III-A-3)}$$

By substituting this expansion into equation (III-A-1) and collecting terms of the same order as ε^i ($i = 0, 1, 2 \ldots$) he could then systematically carry out the method of successive approximation, or perturbation, previously described. While collecting terms of the same order of magnitude, however, Sandri tacitly assumed that the relative weight of the various terms of the hierarchy was entirely dictated by the magnitude of the intrinsic parameters ε_1 and ε_2, thus implying that the variable terms $K_s^* F_s^*$, $I_s^* F_s^*$ and $L_s F_{s+1}^*$ were all of the same order of magnitude. The validity of such an assumption should naturally depend, in part, on the characteristic quantities chosen to nondimensionalize the hierarchy. Indeed, if these are not very carefully chosen, one may find that the intrinsic parameters obtained represent very poorly the relative importance of the various

terms in this equation. In the following section we shall consider the feasibility of deriving dimensionless equations in which the intrinsic parameters dictate the relative importance of the various terms for the entire range of the independent variables. These equations, which we shall refer to hereon as 'properly ordered', distinguish themselves by the fact that each term (with the exception of the time derivative) may be written as a product of a variable nondimensional term of $\sim o(1)$ and a group of dimensionless intrinsic parameters. Naturally, if such equations could be derived, the problem of extracting uniformly valid solutions from the governing equations would be greatly facilitated.

B. GENERAL REMARKS ON THE FEASIBILITY OF DERIVING PROPERLY ORDERED GOVERNING EQUATIONS

The Hamilton, Liouville and B.B.G.K.Y. equations represent equivalent forms of the governing laws of mechanics and, hence, are founded on three fundamental and independent units: length, mass and time. These equations may thus be nondimensionalized by chosing three 'basic sets' of 'characteristic quantities'. The properties of these sets may be summarized as follows;

1) the elements of any single set bear the same units;
2) the elements of each set bear units which are functions of mass, length and time only;
3) the units of the elements of any set are independent of the elements of the remaining sets;
4) the elements of each set are constant for a given mixture.

Choosing the elements of these sets remains, of course, a purely arbitrary matter if one simply wishes to derive governing equations which are free of units. On the other hand, if one seeks dimensionless equations which lend themselves easily to a "perturbation" scheme, it becomes desirable, for reasons discussed in the previous section, to find basic sets of characteristic quantities which will render "properly ordered" dimensionless governing equations. This added criteria that the governing equations be "properly ordered" greatly reduces the arbitrariness in the choice of the basic sets. In fact, one can easily verify that there generally does not exist any three basic sets which will yield dimensionless governing equations which are "properly ordered" over the entire range of the independent variables. Consider, for example, the Hamilton equations, as given by (II-A-2b):

$$\dot{\vec{q}}_i^{\alpha}(t) = \frac{\vec{p}_i^{\alpha}}{m_\alpha}$$

$$\dot{\vec{p}}_i^{\alpha} = -\sum_{\beta=1}^{M}\sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}\left(\left|\vec{q}_i^{\alpha} - \vec{q}_j^{\beta}\right|\right)}{\partial \vec{q}_i^{\alpha}} - \frac{\partial U^{\alpha}(\vec{q}_i^{\alpha})}{\partial \vec{q}_i^{\alpha}}$$

The first equation may be nondimensionalized by choosing (or constructing), from the basic sets, a characteristic

time T_o, length L_i^α and momentum $|\vec{P}_i^\alpha|$ such that the following dimensionless variables may be defined:

$$t^* \equiv \frac{t}{T_o} \quad , \quad \vec{q}_i^{\alpha *} \equiv \frac{\vec{q}_i^\alpha}{L_i^\alpha} \quad , \quad \vec{p}_i^{\alpha *} \equiv \frac{\vec{p}_i^\alpha}{|\vec{P}_i^\alpha|} \qquad \text{(III-B-1)}$$

One may then easily derive the nondimensional equation:

$$\dot{\vec{q}}_i^{\alpha *} = \xi_i^\alpha \vec{p}_i^{\alpha *}$$

where:

$$\xi_i^\alpha \equiv \frac{|\vec{P}_i^\alpha| T_o}{m_\alpha L_i^\alpha} \qquad \text{(III-B-2)}$$

This equation will be properly ordered if one can find a $|\vec{P}_i^\alpha|$ such that $\vec{p}_i^{\alpha *} \sim O[1]$ for all t^*. This $|\vec{P}_i^\alpha|$ will naturally only exist if $\vec{p}_i^\alpha(t)$ remains of the same order of magnitude for all t. Unfortunately, since particle (i,α) may be expected to suffer numerous encounters with other particles or interact with a strong external field, it would seem only reasonable to believe that the momentum of such a molecule would repeatedly vary in magnitude and occasionally suffer changes of order(s) of magnitude. Consequently, one cannot generally hope to derive a dimensionless form of (III-B-2) which is properly ordered for all time. One faces a similar problem when dealing with the second equation of (II-A-2b) which may be freed of units by choosing (or constructing) from the basic sets the characteristic energies $\bar{\phi}_{ij}^{\alpha\beta}$ and $\bar{u}_i^\alpha$ so as to define the dimensionless potentials:

$$\phi_{ij}^{*\alpha\beta} = \frac{\phi_{ij}^{\alpha\beta}}{\bar{\phi}_{ij}^{\alpha\beta}} \quad , \quad \vec{u}_i^{\alpha *} = \frac{\vec{u}_i^\alpha}{\bar{u}_i^\alpha} \qquad \text{(III-B-3)}$$

One then obtains the dimensionless equation:

$$\dot{\vec{p}}_i^{\alpha *} = \sum_{j=1}^{N} \sum_{\beta=1}^{N} \mu_{ij}^{\alpha\beta} \frac{\partial \phi_{ij}^{*\alpha\beta}}{\partial \vec{q}_i^{\alpha *}} \qquad \text{(III-B-4)}$$

$$= \chi_i^{\alpha} \frac{\partial u^{*\alpha}}{\partial \vec{q}_i^{\alpha *}}$$

where

$$\mu_{ij}^{\alpha\beta} \equiv \frac{\bar{\phi}_{ij}^{\alpha\beta} T_0}{P_i^{\alpha} L_i^{\alpha}} \qquad \text{(III-B-5)}$$

$$\chi_i^{\alpha} \equiv \frac{u_i^{\alpha} T_0}{P_i^{\alpha} L_i^{\alpha}}$$

This equation will be properly ordered if, for all t,

$$\left| \frac{\partial \phi_{ij}^{*\alpha\beta}}{\partial \vec{q}_i^{\alpha *}} \right| \sim o[1] \qquad \left| \frac{\partial u_i^{*}}{\partial \vec{q}_i^{\alpha *}} \right| \sim o[1]$$

This will, furthermore, only be the case if the forces $\left| \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \right|$ and $\left| \frac{\partial u^{\alpha}}{\partial \vec{q}_i^{\alpha}} \right|$ preserve their order of magnitude for all t. Since during a collision or an interaction with a strong external barrier (such as a vessel wall) these forces may be expected to vary in order of magnitude, one should not expect (III-B-4) to be properly ordered for very long times. It thus follows from the above arguments that a general derivation of dimensionless Hamilton equations, properly ordered for all t, cannot be regarded

as a feasible task. Using similar arguments it can also be shown that the derivation of dimensionless Liouville and B.B.G.K.Y. equations which are properly ordered for the entire range of the independent variables is equally intractible. The reason for this is that these equations, in their dimensional forms, contain terms like $\frac{\vec{p}_i^{\alpha}}{m_\alpha} \cdot \frac{\partial F_{\{s\}}}{\partial \vec{q}_i^{\alpha}}$, $\frac{\partial \Phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s\}}}{\partial \vec{p}_i^{\alpha}}$, $\frac{\partial U^{\alpha}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial F_{\{s\}}}{\partial \vec{p}_i^{\alpha}}$ .... which cannot generally be expected to preserve their order of magnitude (or relative weight) over the full range of the independent variables $\vec{q}_i^{\alpha}$, $\vec{p}_i^{\alpha}$ and t.

The implications of the above discussion are indeed serious since, as previously noted, one should usually not hope to derive uniformly valid perturbation solutions by expanding in equations which do not preserve a certain order in the relative importance of their terms over the entire range of the independent variables. Fortunately, many kinetic equations may be derived by performing expansions which are, in fact, only valid for a restricted yet significant range of the independent variables. One reason for this is that, in order to close the hierarchy for $F_{\{s\}}$, one only needs approximate solutions for $F_{\{s;j\beta\}}$ over a range of $\vec{q}_j^{\beta}$ and $\vec{p}_j^{\beta}$ which significantly contribute to the integrals of the mixing terms in (II-C-11). Furthermore, since these integrals vanish for $\vec{q}_j^{\beta}$ chosen outside the interaction spheres of the particles within $\{S\}$ and that $F_{\{s;j\beta\}}$ itself may be neglected for large values of $|\vec{p}_j^{\beta}|$, it thus follows

that, for $S \ll N$, the contributing range for $\vec{q}_j^{\beta}$ and $\vec{p}_j^{\beta}$ is, in fact, quite restricted. Consequently, one is somewhat justified in seeking dimensionless governing equations which are properly ordered, on the average, over a limited range of the independent variables. These equations, which shall be referred hereon as "quasi-ordered" equations would then contain dimensionless intrinsic parameters which dictate locally and on the average the order of magnitude of the various terms in these equations. Finally, these parameters, when much smaller than unity, would represent suitable expansion parameters in a perturbation scheme yielding approximate local expansion solutions.

Many of the dimensionless governing equations previously derived by Sandri and others in the field of statistical mechanics are, in fact, quasi-ordered equations. Unfortunately, these equations have very often been used without a clear knowledge of the range of the independent variables over which they are properly ordered. Such a casual approach has not only left a cloud of uncertainty on the range of validity of the perturbation solutions derived from such equations but has often led to local, and sometimes, global breakdown of the perturbation scheme.

C. DERIVATION OF "QUASI-ORDERED" DIMENSIONLESS EQUATIONS

This section presents a derivation of "quasi-ordered" dimensionless equations based on the following assumptions:

1) the system is near canonical equilibrium such that F_N is reasonably close to the canonical distribution:

$$F_N \sim \frac{e^{-H/kT}}{Z_N}$$

$$Z_N \equiv \int \cdots \int e^{-H/kT} \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\alpha}\, d\vec{p}_i^{\alpha} \qquad \text{(III-C-1)}$$

2) all interaction potentials are bounded (in magnitude and range) and may be written as:

$$\phi_{ij}^{\alpha\beta} = {}^{I}\phi_{ij}^{\alpha\beta} + {}^{II}\phi_{ij}^{\alpha\beta} \qquad \text{(III-C-2)}$$

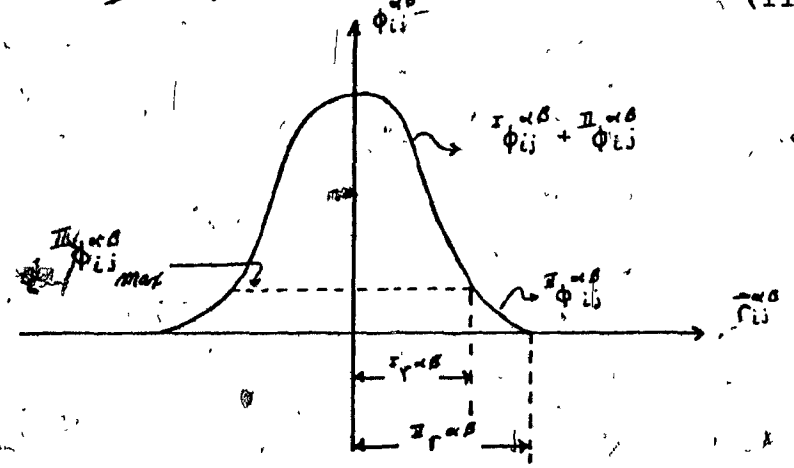


Figure III-1

where:

$$ {}^{I}\phi_{ij}^{\alpha\beta} \equiv \phi_{ij}^{\alpha\beta} - {}^{II}\phi_{ij\,max}^{\alpha\beta} \quad , |\vec{r}_{ij}^{\alpha\beta}| < {}^{I}r^{\alpha\beta} $$

$$ \equiv 0 \quad , |\vec{r}_{ij}^{\alpha\beta}| > {}^{I}r^{\alpha\beta} $$

$$ {}^{I}\bar{\phi}^{\alpha\beta} \equiv \frac{3}{({}^{I}r^{\alpha\beta})^3} \int_0^{{}^{I}r^{\alpha\beta}} (|\vec{r}_{ij}^{\alpha\beta}|)^2 \, {}^{I}\phi^{\alpha\beta}(|\vec{r}_{ij}^{\alpha\beta}|) \, d|\vec{r}_{ij}^{\alpha\beta}| $$

$$ \sim O[kT] \qquad \text{(III-C-3)} $$

$$ {}^{II}\phi_{ij}^{\alpha\beta} \equiv {}^{II}\phi_{ij\,max}^{\alpha\beta} \equiv \phi_{ij}^{\alpha\beta}({}^{I}r^{\alpha\beta}) \quad , |\vec{r}_{ij}^{\alpha\beta}| \leq {}^{I}r^{\alpha\beta} $$

$$ \equiv \phi_{ij}^{\alpha\beta} \quad , {}^{I}r^{\alpha\beta} \leq |\vec{r}_{ij}^{\alpha\beta}| \leq {}^{II}r^{\alpha,\beta} \quad ; \equiv 0 \quad , |\vec{r}_{ij}^{\alpha\beta}| > {}^{II}r^{\alpha,\beta} $$

$$ {}^{II}\bar{\phi}^{\alpha\beta} \equiv \frac{3}{({}^{II}r^{\alpha\beta})^3} \int_0^{{}^{II}r^{\alpha\beta}} (|\vec{r}_{ij}^{\alpha\beta}|)^2 \, {}^{II}\phi^{\alpha\beta}(|\vec{r}_{ij}^{\alpha\beta}|) \, d|\vec{r}_{ij}^{\alpha\beta}| \qquad \text{(III-C-4)} $$

$$ \ll kT $$

3) The external potential U^{α} is weak and has a finite range L^{α} such that:

$$ \bar{U}^{\alpha} \equiv \frac{3}{4\pi (L^{\alpha})^3} \iiint_{V=\frac{4}{3}\pi(L^{\alpha})^3} U^{\alpha}(\vec{q}_i) \, dv \qquad \text{(III-C-5)} $$

$$ \ll kT $$

The nondimensionalization will be founded on the three basic sets $\{m\}$, $\{e\}$ and $\{l\}$ bearing the units of mass, energy and length respectively and defined as follows:

$$ \{m\} \equiv \{m_1, m_2 \ldots, m_\alpha, \ldots m_M\} $$

$$\{e\} \equiv \{kT, \overline{\Pi\Phi}^{1,1}, \ldots, \overline{\Pi\Phi}^{\alpha\beta}, \ldots \overline{\Pi\Phi}^{M,M}, \bar{u}^1, \ldots, \bar{u}^\alpha, \ldots \bar{u}^M\}$$

$$\{\ell\} \equiv \{{}^{I}r^{1,1}, {}^{II}r^{1,1}, \ldots, {}^{I}r^{\alpha\beta}, {}^{II}r^{\alpha\beta}, \ldots, {}^{I}r^{M,M}, {}^{II}r^{M,M}, \ell^1, \ldots, \ell^\alpha, \ldots \ell^M, \{\ell_o\}\} \qquad \text{(III-C-6)}$$

where the subset $\{\ell_o\}$ contains a set of characteristic lengths to be defined later.

a) Hamilton Equations:

Quasi-ordered Hamilton equations may be derived by first constructing from the basic sets the characteristic momenta $(m_\alpha kT)^{1/2}$, and defining

$$\vec{p}_i^{\alpha *} \equiv \frac{\vec{p}_i^\alpha}{(m_\alpha kT)^{1/2}} \qquad \text{(III-C-7)}$$

such that for the average molecule:

$$|\vec{p}_i^{\alpha *}| \sim O[1]$$

We may then nondimensionalize the coordinate $\vec{q}_i^\alpha$ by introducing some $\mathcal{R}^\alpha \in \{\ell_o\}$, which shall be left arbitrary for the time being, and define:

$$\vec{q}_i^{\alpha *} \equiv \frac{\vec{q}_i^\alpha}{\mathcal{R}^\alpha} \qquad \text{(III-C-8)}$$

We shall now free the potentials ${}^{I}\phi_{ij}^{\alpha\beta}$, ${}^{II}\phi_{ij}^{\alpha\beta}$ of their units by defining:

$$ {}^{I}\phi_{ij}^{\alpha\beta *} \equiv {}^{I}\phi_{ij}^{\alpha\beta} / {}^{I}a^{\alpha\beta} $$

$$ {}^{II}\phi_{ij}^{\alpha\beta *} \equiv {}^{II}\phi_{ij}^{\alpha\beta} / {}^{II}a^{\alpha\beta} \qquad \text{(III-C-9)} $$

(where ${}^{I}a^{\alpha\beta}$ and ${}^{II}a^{\alpha\beta}$ are to be constructed from $\{m\}$, $\{l\}$ and $\{e\}$). We shall also impose that $\left| \frac{\partial {}^{I}\phi^{\alpha\beta *}}{\partial q_i^{\alpha *}} \right|$ and $\left| \frac{\partial {}^{II}\phi_{ij}^{\alpha\beta *}}{\partial q_i^{\alpha *}} \right|$ are typically of the order of one over some dimensionless physical volume ${}^{*\beta}V_c$, where:

$$ {}^{*\beta}V_c \equiv V_c / (\mathcal{R}^{\beta})^3 $$

and $V_c \equiv \frac{4}{3} \pi r_c^3$ is some characteristic physical volume. More precisely, we shall demand that:

$$ \frac{1}{{}^{*\beta}V_c} \iiint_{{}^{*\beta}V_c} \left| \frac{\partial {}^{I}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}} \right| d\vec{q}_j^{\beta *} \sim \phi[1] $$

$$ \frac{1}{{}^{*\beta}V_c} \iiint_{{}^{*\beta}V_c} \left| \frac{\partial {}^{II}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}} \right| d\vec{q}_j^{\beta *} \sim o[1] \qquad \text{(III-C-10)} $$

such that the gradients $\frac{\partial {}^{I}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}}$ and $\frac{\partial {}^{II}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}}$ are properly ordered over a finite range in the physical space.

The first equation in (III-C-10) may also be written as:

$$\frac{1}{V_c} \cdot \frac{R^\alpha}{{}^I a^{\alpha\beta}} \iiint_{V_c} \left| \frac{\partial {}^I\phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\,\alpha}} \right| d\vec{q}_j^{\,\beta} \sim O[1]$$

(III-C-11)

If V_c is chosen sufficiently large to enclose the spherical interaction volume $4/3\ \pi({}^I r^{\alpha\beta})^3$, we may rewrite (III-C-11) as:

$$\frac{3R^\alpha}{{}^I a^{\alpha\beta}(r_c)^3} \int_0^{{}^I r^{\alpha\beta}} r^2 \left| \frac{\partial {}^I\phi^{\alpha\beta}(r)}{\partial r} \right| dr \sim O[1]$$

Furthermore, assuming the potential to be reasonably smooth such that $\frac{\partial {}^I\phi^{\alpha\beta}}{\partial r}$ is typically of the order of $\frac{kI}{{}^I r^{\alpha\beta}}$ for $r < {}^I r^{\alpha\beta}$, we then obtain:

$$\frac{kT}{{}^I a^{\alpha\beta}} \left(\frac{R^\alpha}{{}^I r^{\alpha\beta}}\right)\left(\frac{{}^I r^{\alpha\beta}}{r_c}\right)^3 \sim O[1]$$

Consequently choosing:

$${}^I a^{\alpha\beta} \equiv kT \left(\frac{R^\alpha}{{}^I r^{\alpha\beta}}\right)\left(\frac{{}^I r^{\alpha\beta}}{r_c}\right)^3$$

$$r_c \in \{\lambda_0\}$$

(III-C-12)

we may define the dimensionless potential:

$${}^I\phi_{ij}^{*\alpha\beta} \equiv \frac{{}^I\phi_{ij}^{\alpha\beta}}{kT}\left(\frac{{}^I r^{\alpha\beta}}{R^\alpha}\right)\left(\frac{r_c}{{}^I r^{\alpha\beta}}\right)^3$$

(III-C-13)

Similarly, we obtain from the second equation in (III-C-10):

$$\frac{{}^{II}\bar{\phi}^{\alpha\beta}}{{}^{II}a^{\alpha\beta}}\left(\frac{R^\alpha}{{}^{II}r^{\alpha\beta}}\right)\left(\frac{{}^{II}r^{\alpha\beta}}{r_c}\right)^3 \sim O[1]$$

such that choosing:

$$\Pi a^{\alpha\beta} \equiv \Pi\bar{\Phi}^{\alpha\beta}\left(\frac{R^{\alpha}}{\Pi r^{\alpha\beta}}\right)\left(\frac{\Pi r^{\alpha\beta}}{r_c}\right)^3 \qquad \text{(III-C-14)}$$

we may define

$$\Pi\Phi_{ij}^{\alpha\beta *} \equiv \frac{\Pi\Phi_{ij}^{\alpha\beta}}{\Pi\bar{\Phi}_{ij}^{\alpha\beta}}\left(\frac{\Pi r^{\alpha\beta}}{R^{\alpha}}\right)\left(\frac{r_c}{\Pi r^{\alpha\beta}}\right)^3 \qquad \text{(III-C-15)}$$

In an analogous way we can define a dimensionless potential:

$$u^{\alpha *} \equiv \frac{u^{\alpha}}{b^{\alpha}} \qquad \text{(III-C-16)}$$

such that:

$$\frac{1}{V_c^{\alpha}}\iiint_{V_c^{\alpha *}} \left|\frac{\partial u^{\alpha *}}{\partial \vec{q}_i^{\alpha *}}\right| d\vec{q}_i^{\alpha *} \sim O[1]$$

We then obtain two possible definitions for b^{α}. If the characteristic volume V_c is enclosed in the volume $(L^{\alpha})^3$ (i.e., $V_c \subset (L^{\alpha})^3$) we conclude that:

$$u^{\alpha *} = \left(\frac{u^{\alpha}}{\bar{u}^{\alpha}}\right)\cdot\left(\frac{L^{\alpha}}{R^{\alpha}}\right) \qquad (V_c \subset (L^{\alpha})^3) \qquad \text{(III-C-17a)}$$

On the other hand, if $(L^{\alpha})^3 \subset V_c$, we then obtain:

$$u^{\alpha *} = \left(\frac{u^{\alpha}}{\bar{u}^{\alpha}}\right)\cdot\left(\frac{L^{\alpha}}{R^{\alpha}}\right)\left(\frac{r_c}{L^{\alpha}}\right)^3 \qquad (V_c \supset (L^{\alpha})^3) \qquad \text{(III-C-17b)}$$

Finally, we may nondimensionalize time itself by

defining some characteristic time t_o :

$$t_o \equiv R \Big/ \left(E/M\right)^{1/2}$$

where $M \in \{m\}, R \in \{\ell\}$ and $E \in \{e\}$

There exists naturally many possible choices for t_o, some of which are more physically meaningful that others. In this thesis, we shall define:

$$M \equiv m_1 \quad , \quad E \equiv kT$$

and leave R arbitrary such that:

$$t_o \equiv R \Big/ \left(\frac{kT}{m_1}\right)^{1/2} \qquad \text{(III-C-18)}$$

represents the typical time for a particle of the first specie to traverse some characteristic length R . Defining:

$$t^* \equiv \frac{t}{t_o} \equiv \left(\frac{kT}{m_1}\right)^{1/2} \frac{t}{R} \qquad \text{(III-C-19)}$$

and substituting the previously defined dimensionless quantities into (II-A-2b), we then obtain the following set of dimensionless Hamilton equations:

$$\frac{d\vec{q}_i^{\alpha *}}{dt^*} = K^{\alpha} \gamma^{\alpha} \vec{p}_i^{\alpha *}$$

$$\frac{d\vec{p}_i^{\alpha *}}{dt^*} = -\gamma^{\alpha} \sum_{\beta=1}^{M} \sum_{J=1}^{N\beta} \left\{ {}^{I}R^{\alpha\beta} \cdot \frac{\partial {}^{I}\phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha *}} \right.$$

$$\left(+ {}^{II}\mathcal{R}^{\alpha\beta}\,\varepsilon_i^{\alpha\beta}\,\frac{\partial \phi_{ij}}{\partial \vec{q}_i^{\alpha *}} \right\}$$

$$- \gamma^{\alpha}\,\mathcal{A}^{\alpha}\,\chi^{\alpha}\,\frac{\partial U^{\alpha *}}{\partial \vec{q}_i^{\alpha *}} \qquad \text{(III-C-20)}$$

where:

$$\mathcal{K}^{\alpha} \equiv \frac{R}{\mathcal{R}^{\alpha}} \quad ; \quad \gamma^{\alpha} \equiv \left(\frac{m_i}{m_{\alpha}}\right)^{1/2}$$

$${}^{I}\mathcal{R}^{\alpha\beta} \equiv \frac{R}{{}^{I}r^{\alpha\beta}}\left(\frac{{}^{I}r^{\alpha\beta}}{r_c}\right)^{3} ; \quad {}^{II}\mathcal{R}^{\alpha\beta} \equiv \frac{R}{{}^{II}r^{\alpha\beta}}\left(\frac{{}^{II}r^{\alpha\beta}}{r_c}\right)^{3}$$

$$\varepsilon_i^{\alpha\beta} \equiv \frac{{}^{II}\bar{\phi}^{\alpha\beta}}{kT} \quad ; \quad \chi^{\alpha} \equiv \frac{\bar{U}^{\alpha}}{kT}$$

$$\mathcal{A}^{\alpha} \equiv \frac{R}{L^{\alpha}} \quad ; \quad \mathcal{A}^{\alpha} \equiv \frac{R}{L^{\alpha}}\left(\frac{L^{\alpha}}{r_c}\right)^{3} ;$$

$$v_c \subset (L^{\alpha})^3 \qquad (L^{\alpha})^3 \subset v_c \qquad \text{(III-C-21)}$$

Note that in the above equations R, $\mathcal{R}^{\alpha}$ and r_c are totally arbitrary. While the choice of R in essence depends on the time scale we wish to use to describe the evolution of the system, the selection of $\mathcal{R}^{\alpha}$ hinges on the particular length scale we wish to utilize to investigate the motion of specie α. In many cases, one can choose $\mathcal{R}^{\alpha} = R$ so as

to make $K^{**} = 1$. Since the terms on the right hand side of (III-C-20) are properly ordered over a physical volume V_c we should choose the latter according to the volume in physical space which interests us at the time. Naturally, if V_c is chosen large, there may exist a large section within V_c where the equations do not find proper order. The reason for this lies in the fact that the equations are only properly ordered on the average over V_c . Choosing V_c very large may then cause some local breakdown if one seeks an approximate perturbation solution of the Hamilton equations. Finally, it must be noted that the above equations are only properly ordered if all the particles have a momentum $O[(m_\alpha \kappa T)^{1/2}]$. Naturally, if N is sufficiently large, this condition will always be violated by some particles. In such a case a few of the terms in the Hamilton equations will not be properly ordered.

b. Liouville Equation:

Using the same procedure as in the previous subsection, we may derive a quasi-ordered Liouville equation by defining a dimensionless probability distribution:

$$F_N^* \equiv C_N F_N \qquad \text{(III-C-22)}$$

such that the terms $\frac{\partial F_N^*}{\partial \vec{q}_i^{**}}$ and $\frac{\partial F_N^*}{\partial \vec{p}_i^{**}}$ are typically of the order of one over some volume V_N^* in Γ_N^* space. Using the previous nondimensionalization for $\vec{q}_i^{**}$ and $\vec{p}_i^{**}$, this volume may be written as:

$$V_N^* \equiv V_N \Big/ \prod_{\alpha=1}^{M} \left(\mathcal{R}^\alpha \sqrt{m_\alpha k T}\right)^{3N_\alpha} \qquad \text{(III-C-23)}$$

where:

$$V_N \equiv \mathcal{V}_c^N \prod_{\alpha=1}^{M} \left(m_\alpha k T\right)^{3N_\alpha/2} \qquad \text{(III-C-24)}$$

represents approximately the volume in Γ_N where $\vec{q}_i^{\alpha} \in V_c$ and $|\vec{p}_i^{\alpha}| \sim o[\sqrt{m_\alpha k T}]$, $\forall (i,\alpha)$. Consequently, we shall impose the following two conditions:

$$\left|\frac{\partial F_N^*}{\partial \vec{q}_i^{\alpha *}}\right| = \frac{1}{V_N^*} \int\cdots\int_{V_N^*} \left|\frac{\partial F_N^*}{\partial \vec{q}_i^{\alpha *}}\right| dV_N^* \sim o[1] \qquad \text{(III-C-25a)}$$

$$\left|\frac{\partial F_N^*}{\partial \vec{p}_i^{\alpha *}}\right| = \frac{1}{V_N^*} \int\cdots\int_{V_N^*} \left|\frac{\partial F_N^*}{\partial \vec{p}_i^{\alpha *}}\right| dV_N^* \sim o[1] \qquad \text{(III-C-25b)}$$

where: $dV_N^* = \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\alpha *}\, d\vec{p}_i^{\alpha *}$

Using (III-C-22) (III-C-23) and (III-C-24) and the previous nondimensionalization of $\vec{q}_i^{\alpha}$ and $\vec{p}_i^{\alpha}$, criteria (III-C-25b) may be written as:

$$\frac{C_N}{V_N} \sqrt{m_\alpha k T} \int\cdots\int_{V_N} \left|\frac{\partial F_N}{\partial \vec{p}_i^{\alpha}}\right| dV_N \sim o[1]$$

Since we have assumed that the system is near canonical equilibrium this reduces to:

$$\frac{C_N}{V_N}\frac{1}{\sqrt{m_\alpha KT}}\int\cdots\int_{V_N}|\vec{p}_i^{\,\alpha}|\,F_N\,dV_N \sim o[1] \qquad \text{(III-C-26)}$$

Now, if we define $W_N(t)$ to represent the probability that, for a system chosen at random, $\vec{X}_N \in V_N$, $F_N(X_N,t)$ may be written as the product:

$$F_N(X_N,t) = W_N(t)\,P_N(\vec{X}_N,t\,|\,\vec{X}_N \in V_N) \qquad \text{(III-C-27)}$$

where P_N denotes the conditional probability distribution for $\vec{X}_N$ given that $\vec{X}_N \in V_N$. Substituting (III-C-27) into (III-C-26), one obtains:

$$\frac{C_N}{V_N}\frac{W_N(t)}{\sqrt{m_\alpha KT}}\int\cdots\int_{V_N}|\vec{p}_i^{\,\alpha}|\,P_N\,dV_N \sim o[1] \qquad \text{(III-C-28)}$$

Since:

$$\int\cdots\int_{V_N}|\vec{p}_i^{\,\alpha}|\,P_N\,dV_N \sim o[\sqrt{m_\alpha KT}]$$

and:

$$W_N(t) \sim o\left[\left(\frac{V_c}{V}\mu_{eq}\right)^N\right]$$

where μ_{eq} denotes the probability, at equilibrium, that $|\vec{p}_i^{\,\alpha}| \sim o[\sqrt{m_\alpha KT}]$, (III-C-28) may then be written in the form:

$$\mu_{eq}^N\,\frac{C_N}{V_N}\left(\frac{V_c}{V}\right)^N \sim o[1]$$

or:

$$\frac{\mu_{eq}^N\,C_N}{V^N\prod_{\alpha=1}^{N}[m_\alpha KT]^{3N_\alpha/2}} \sim o[1]$$

Consequently, defining:

$$C_N \equiv \left(\frac{V}{\mu_{eq}}\right)^N \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3N_\alpha/2}$$

we have

$$F_N \equiv \left(\frac{V}{\mu_{eq}}\right)^N \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3N_\alpha/2} \quad F_N \qquad \text{(III-C-29)}$$

Substituting back into (III-C-25a) one has:

$$\left(\frac{V}{v_c \mu_{eq}}\right)^N \mathcal{R}^\alpha \int \cdots \int \left| \frac{\partial F_N}{\partial \vec{q}_i^\alpha} \right| dV_N \sim O[1]$$

or:

$$\mathcal{R}^\alpha \int \cdots \int \left| \frac{\partial P_N}{\partial \vec{q}_i^\alpha} \right| dV_N \sim O[1]$$

Near canonical equilibrium, this criteria may be written as:

$$\frac{\mathcal{R}^\alpha}{\kappa T} \int \cdots \int |\vec{\mathcal{F}}^{i\alpha}| \, P_{N_{eq}} \, dV_N \sim O[1] \qquad \text{(III-C-30)}$$

where:

$$\vec{\mathcal{F}}^{i\alpha} \equiv - \sum_{\beta=1}^{M} \sum_{j=1}^{N\beta} \left\{ \frac{\partial^I \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha} + \frac{\partial^{II} \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^\alpha} \right\}$$

$$= \frac{\partial U^\alpha}{\partial \vec{q}_i^\alpha}$$

(III-C-31)

represents the external force exerted on the particle by the remaining particles and the external field.

Defining:

$$Q_N \equiv \int \cdots \int_{V_N} P_N \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{p}_i^{\,\alpha} \qquad \text{(III-C-32)}$$

(III-C-30) becomes:

$$\frac{\mathcal{R}^\alpha}{kT} \langle |\delta\vec{F}^{i\alpha}| \rangle_{eq} \sim O[1] \qquad \text{(III-C-33)}$$

where:

$$\langle |\delta\vec{F}^{i\alpha}| \rangle_{eq} \equiv \int \cdots \int |\delta\vec{F}^{i\alpha}| \, Q_{N_{eq}} \prod_{\alpha=1}^{M} \prod_{i=1}^{N_\alpha} d\vec{q}_i^{\,\alpha} \qquad \text{(III-C-34)}$$

represents the average magnitude of the force $\delta\vec{F}^{i\alpha}$ at $\mathcal{R}^\alpha$ equilibrium. Since all the particles of the same specie are identical, we have:

$$\langle |\delta\vec{F}^{i\alpha}| \rangle_{eq} = \langle |\delta\vec{F}^{j\alpha}| \rangle_{eq} \equiv \langle |\delta\vec{F}^{\alpha}| \rangle_{eq} \qquad \text{(III-C-35)}$$

It now seems quite clear from (III-C-33) that $\mathcal{R}^\alpha$ may no longer be left arbitrary. Consequently, we define:

$$\mathcal{R}^\alpha \equiv \frac{kT}{\langle |\delta\vec{F}^{\alpha}| \rangle_{eq}} \qquad \text{(III-C-36)}$$

such that $\mathcal{R}^\alpha$ represents the distance over which the force $\langle |\delta\vec{F}^{\alpha}| \rangle_{eq}$ must be exerted to accelerate, from rest, a particle (i,α) to a kinetic energy kT.

With F_N^* defined by (III-C-29), along with the previously defined dimensionless quantities, one obtains the following dimensionless Liouville equation:

$$\frac{\partial F_N^*}{\partial t^*} + \mathcal{H}_N^* F_N^* = 0 \qquad \text{(III-C-37)}$$

where:

$$\mathcal{H}_N^* \equiv \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \mathcal{K}^\alpha \gamma^\alpha \vec{p}_i^{\alpha *} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha *}}$$

$$- \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \gamma^\alpha \left({}^{I}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{I}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}} + {}^{II}\mathcal{R}^{\alpha\beta} \varepsilon_i^{\alpha\beta} \frac{\partial {}^{II}\phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\alpha *}} \right) \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}}$$

$$- \sum_{\alpha=1}^{M} \sum_{i=1}^{N_\alpha} \gamma^\alpha \mathcal{A}^\alpha \chi^\alpha \frac{\partial U^{\alpha *}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}}$$

and

$$\mathcal{K}^\alpha \equiv \frac{R}{kT} \langle |\vec{F}^{i\alpha}| \rangle_{eq}$$

which is properly ordered on average over V_N^*.

c) B.B.G.K.Y. Hierarchy:

The B.B.G.K.Y. hierarchy may be nondimensionalized so as to be properly ordered, on the average, over some volume $V_{\{s\}}^*$ in the reduced phase space $\Gamma_{\{s\}}^*$ by defining:

$$F_{\{s\}}^* \equiv C_{\{s\}} F_{\{s\}} \qquad \text{(III-C-38)}$$

and imposing that:

$$\frac{1}{V^*_{\{s\}}} \int\cdots\int^{V^*_{\{s\}}} \left| \frac{\partial F^*_{\{s\}}}{\partial \vec{q}^{\alpha *}_i} \right| dV^*_{\{s\}} \sim O[1] \qquad \text{(III-C-39a)}$$

$$\frac{1}{V^*_{\{s\}}} \int\cdots\int^{V^*_{\{s\}}} \left| \frac{\partial F^*_{\{s\}}}{\partial \vec{p}^{\alpha *}_i} \right| dV^*_{\{s\}} \sim O[1] \qquad \text{(III-C-39b)}$$

$$\frac{1}{V^*_{\{s\}}} \int\cdots\int^{V^*_{\{s\}}} \left| {}^{\kappa}L^{\alpha\beta *}_{\{s\}} F^*_{\{s,s_{\beta+1}\}} \right| dV^*_{\{s\}}$$

$$\equiv \frac{1}{V^*_{\{s\}}} \int\cdots\int^{V^*_{\{s\}}} \left| \iint \frac{\partial \Phi^{\alpha\beta *}_{i s_{\beta+1}}}{\partial \vec{q}^{\alpha *}_i} \frac{\partial F^*_{\{s;\, s_{\beta+1}\}}}{\partial \vec{p}^{\alpha *}_i} d\vec{r}^{\alpha *}_{i s_{\beta+1}} d\vec{p}^{\beta *}_{s_{\beta+1}} \right| dV^*_{\{s\}}$$

$$\sim O[1] \qquad \text{(III-C-39c)}$$

where:

$$V^*_{\{s\}} \equiv V_{\{s\}} \Big/ \prod_{\alpha=1}^{M} \left(\mathcal{R}^{\alpha} \sqrt{m_\alpha \kappa T} \right)^{3 s_\alpha} \qquad \text{(III-C-40)}$$

and:

$$V_{\{s\}} \equiv V_c^S \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3 s_\alpha / 2} \qquad \text{(III-C-41)}$$

Proceeding exactly as in the previous subsection, one can satisfy (III-C-39b) by defining:

$$C_{\{s\}} \equiv \left(\frac{V}{\mu_{eq}} \right)^S \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3 s_\alpha / 2} \qquad \text{(III-C-42)}$$

such that:

$$F^*_{\{s\}} \equiv \left(\frac{V}{\mu_{eq}} \right)^S \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3 s_\alpha / 2} F_{\{s\}} \qquad \text{(III-C-43)}$$

Similarly, criteria (III-C-39a) may be shown to imply that:

$$\mathcal{R}^{\alpha} \int\cdots\int_{V_{\{s\}}} \left| \frac{\partial P_{\{s\}}}{\partial \vec{q}_i^{\alpha}} \right| \, dV_{\{s\}} \sim O[1] \tag{III-C-44}$$

where:

$$P_{\{s\}}(\vec{X}_{\{s\}}, t) \equiv \left(\frac{V_c}{V} \mu_{eq} \right)^{-s} F_{\{s\}}(\vec{X}_{\{s\}}, t) \tag{III-C-45}$$

represents a conditional probability distribution for $X_{\{s\}}$ given that $X_{\{s\}} \in V_{\{s\}}$. Since it becomes evident from (III-C-44) that $\mathcal{R}^{\alpha}$ should be chosen according to the subgroup $\{s\}$ we shall define:

$$\mathcal{R}^{\alpha}_{\{s\}} \equiv \left\{ \int\cdots\int \left| \frac{\partial P^{\circ}_{\{s\}}}{\partial \vec{q}_i^{\alpha}} \right| \, dV_{\{s\}} \right\}^{-1} \tag{III-C-46}$$

where the initial distribution:

$$P^{\circ}_{\{s\}}(\vec{X}_{\{s\}}) \equiv P_{\{s\}}(\vec{X}_{\{s\}}, 0) \tag{III-C-47}$$

has been introduced so as to make $\mathcal{R}^{\alpha}_{\{s\}}$ time independent.

Finally, defining the dimensionless separation vector:

$$k\vec{r}^{*\alpha\beta}_{ij} \equiv {}^{k}r^{\alpha\beta}_{ij} / {}^{k}\mathcal{R}^{\alpha\beta} \qquad k = 1, 2 \tag{III-C-48}$$

criteria (III-C-39c) may be written as:

$$\frac{V\sqrt{m_\alpha KT}}{\mu_{eq}}\,\frac{{}^{k}r^{\alpha\beta}}{({}^{k}\mathfrak{R}^{\alpha\beta})^{3}\,{}^{k}\phi^{\alpha\beta}}\left(\frac{r_c}{{}^{k}r^{\alpha\beta}}\right)^{3}$$

$$\times\int_{V_{\{ss\}}}\cdots\int\left|\iint\frac{\partial\,{}^{k}\phi^{\alpha\beta}_{ij}}{\partial\,\vec{q}_i^{\,\alpha}}\cdot\frac{\partial P_{\{s,s_{\beta+1}\}}}{\partial\,\vec{p}_i^{\,\alpha}}\,d\vec{r}^{\,\alpha\beta}_{i\,s_{\beta+1}}\,d\vec{p}^{\,\beta}_{s_{\beta+1}}\right|dV_{\{ss\}}$$

$$\sim O[1] \qquad \text{(III-C-49)}$$

where:

$$P_{\{s,s_{\beta+1}\}}\left(\vec{X}_{\{ss\}},\,\vec{q}^{\,\beta}_{s_{\beta+1}},\,\vec{p}^{\,\beta}_{s_{\beta+1}},\,t\;\middle|\;\vec{X}_{\{ss\}}\in V_{\{ss\}}\right)$$

$$\equiv F_{\{s,s_{\beta+1}\}}\left(\vec{X}_{\{ss\}},\,\vec{q}^{\,\beta}_{s_{\beta+1}},\,\vec{p}^{\,\beta}_{s_{\beta+1}},\,t\right)\Big/\;W_{\{ss\}}(t)$$

(III-C-50)

represents the conditional probability distribution for $\{\vec{X}_{\{ss\}},\,\vec{q}^{\,\beta}_{s_{\beta+1}},\,\vec{p}^{\,\beta}_{s_{\beta+1}}\}$ given that $\vec{X}_{\{ss\}}\in V_{\{ss\}}$. Consequently, we shall define:

$${}^{k}\mathfrak{R}^{\alpha\beta}_{\{ss\}}\equiv\left\{\frac{1}{V\sqrt{m_\alpha KT}}\,\frac{{}^{k}r^{\alpha\beta}}{\mu_{eq}\,{}^{k}\phi^{\alpha\beta}}\left(\frac{r_c}{{}^{k}r^{\alpha\beta}}\right)^{3}\right.$$

$$\left.\times\int_{V_{\{ss\}}}\cdots\int\left|\iint\frac{\partial\,{}^{k}\phi^{\alpha\beta}_{ij}}{\partial\,\vec{q}_i^{\,\alpha}}\cdot\frac{\partial P^{\circ}_{\{s,s_{\beta+1}\}}}{\partial\,\vec{p}_i^{\,\alpha}}\,d\vec{r}^{\,\alpha\beta}_{i\,s_{\beta+1}}\,d\vec{p}^{\,\beta}_{s_{\beta+1}}\right|dV_{\{ss\}}\right\}^{1/3}$$

$$k=I,II \qquad \text{(III-C-51)}$$

Substituting (III-C-43), (III-C-48) (along with previously defined dimensionless quantities) into (II-C-11), we then obtain the following dimensionless B.B.G.K.Y. hierarchy.

$$\frac{\partial F^{*}_{\{s\}}}{\partial t^{*}} + \mathcal{H}^{*}_{\{s\}} F^{*}_{\{s\}} =$$

$$\sum_{\beta=1}^{M}\sum_{\alpha=1}^{M}\sum_{R=I}^{II} {}^{R}\mathcal{L}^{\alpha\beta\,*}_{\{s\}} F^{*}_{\{s,s_{\beta+1}\}} \qquad \text{(III-C-52)}$$

where:

$$\mathcal{H}^{*}_{\{s\}} \equiv \sum_{\alpha=1}^{M} \gamma^{\alpha} \mathcal{K}^{\alpha}_{\{s\}} \sum_{i=1}^{S_\alpha} \vec{p}^{\alpha\,*}_{i} \cdot \frac{\partial}{\partial \vec{q}^{\alpha\,*}_{i}}$$

$$- \sum_{\beta=1}^{M}\sum_{j=1}^{S_\beta}\sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha} \gamma^{\alpha} \left({}^{I}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{I}\phi^{\alpha\beta\,*}_{ij}}{\partial \vec{q}^{\alpha\,*}_{i}} + \varepsilon_1^{\alpha\beta}\, {}^{II}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{II}\phi^{\alpha\beta\,*}_{ij}}{\partial \vec{q}^{\alpha\,*}_{i}} \right) \cdot \frac{\partial}{\partial \vec{p}^{\alpha\,*}_{i}}$$

$$- \sum\sum \gamma^{\alpha} \mathcal{A}^{\alpha} \chi^{\alpha} \frac{\partial U^{\alpha\,*}}{\partial \vec{q}^{\alpha\,*}_{i}} \cdot \frac{\partial}{\partial \vec{p}^{\alpha\,*}_{i}} \qquad \text{(III-C-53)}$$

$${}^{I}\mathcal{L}^{\alpha\beta\,*}_{\{s\}} \equiv {}^{I}\varepsilon_2^{\alpha\beta}\, {}^{I}\mathcal{R}^{\alpha\beta}\, \gamma^{\alpha}\, \mu_{eq}$$

$$\sum_{i=1}^{S_\alpha} \int\int \frac{\partial {}^{I}\phi^{*\alpha\beta}_{ij}}{\partial \vec{q}^{\alpha\,*}_{i}} \cdot \frac{\partial}{\partial \vec{p}^{\alpha\,*}_{i}} \, d{}^{I}\vec{r}^{\alpha\beta\,*}_{i\,s_{\beta+1}} \, d\vec{p}^{\beta\,*}_{s_{\beta+1}}$$

$${}^{II}\mathcal{L}^{\alpha\beta\,*}_{\{s\}} \equiv {}^{II}\varepsilon_2^{\alpha\beta}\, \varepsilon_1^{\alpha\beta}\, {}^{II}\mathcal{R}^{\alpha\beta}\, \gamma^{\alpha}\, \mu_{eq}$$

$$\sum_{i=1}^{S_\alpha} \int\int \frac{\partial {}^{II}\phi^{\alpha\beta\,*}}{\partial \vec{q}^{\alpha\,*}_{i}} \cdot \frac{\partial}{\partial \vec{p}^{\alpha\,*}_{i}} \, d{}^{II}\vec{r}^{\alpha\beta\,*}_{i\,s_{\beta+1}} \, d\vec{p}^{\beta\,*}_{s_{\beta+1}}$$

and $$\mathcal{K}^{\alpha}_{\{s\}} \equiv \mathcal{R} / \mathcal{R}^{\alpha}_{\{s\}} \qquad \text{(III-C-54)}$$

$$ {}^{k}\mathcal{E}_{2\,|s|}^{\alpha\beta} \equiv \frac{(N_\beta - s_\beta)}{V} \left({}^{k}\delta\mathcal{R}_{|s|}^{\alpha\beta} \right)^3 \qquad \text{(III-C-55)} $$

Taking the so called "thermodynamic limit",

$$ \lim_{\substack{N_\beta \to \infty \\ V \to \infty}} \frac{N_\beta}{V} = \rho_\beta $$

the last parameter, ${}^{k}\mathcal{E}_{2\,|s|}^{\alpha\beta}$, may be written as:

$$ {}^{k}\mathcal{E}_{2\,|s|}^{\alpha\beta} \equiv \rho_\beta \left({}^{k}\delta\mathcal{R}_{|ss|}^{\alpha\beta} \right)^3 \qquad \text{(III-C-56)} $$

It should once again be emphasized that equation (III-C-52) is properly ordered on the average only over a phase volume $V_{|s|}^{*}$ for $F_{|s|}^{*}$ reasonably close to equilibrium.

D. CLASSIFICATION OF MIXTURES:

The dimensionless B.B.G.K.Y. hierarchy contains the following set of intrinsic parameters:

$$ \{\mathcal{E}\} = \left\{ \gamma^{\alpha}, \mathcal{K}_{|ss|}^{\alpha}, {}^{k}\mathcal{R}^{\alpha\beta}, \mathcal{E}_{1}^{\alpha\beta}, \chi^{\alpha}, \mathcal{A}^{\alpha}, {}^{k}\mathcal{E}_{2\,|s|}^{\alpha\beta} \right\} $$

$$ \alpha = 1, \cdots M \; ; \; \beta = 1, \cdots M \; ; \; k = I, II $$

where in summary:

$$ \gamma^{\alpha} \equiv \sqrt{\frac{m_1}{m_\alpha}} $$

$$ \mathcal{K}_{|ss|}^{\alpha} \equiv \frac{R}{\mathcal{R}_{|s|}^{\alpha}} $$

$$ {}^{k}\mathcal{R}^{\alpha\beta} \equiv \frac{R}{{}^{k}r^{\alpha\beta}} \left(\frac{{}^{k}r^{\alpha\beta}}{r_c} \right)^3 $$

$$
\left.
\begin{aligned}
\varepsilon_1^{\alpha\beta} &\equiv \frac{{}^{\Pi}\bar{\Phi}^{\alpha\beta}}{kT} \\
\chi^{\alpha} &\equiv \frac{\bar{U}^{\alpha}}{kT} \\
A^{\alpha} &\equiv \frac{R}{L^{\alpha}} \quad , \; V_c < (L^{\alpha})^3 \\
A^{\alpha} &\equiv \frac{R}{L^{\alpha}} \left(\frac{L^{\alpha}}{r_c}\right)^{3} , \; (L^{\alpha})^3 < V_c \\
{}^{k}\varepsilon_{\ell\{S\}}^{\alpha\beta} &\equiv n_{\beta} \left({}^{k}R_{\{S\}}^{\alpha\beta}\right)^3 \quad , \; k = I, II
\end{aligned}
\right\} \qquad \text{(III-D-1)}
$$

These parameters, provided R and V_c are first defined, may be used as index codes in a classification of mixtures. Naturally, since two of these intrinsic parameters are dependent on the subgroup $\{S\}$ where the number of elements in $\{S\}$ varies from 1 to N, it follows that the number of elements in the "index set" $\{\varepsilon\}$ may become awkwardly large for systems containing many particles. Indeed, if the thermodynamic limit is imposed, $\{\varepsilon\}$ will, in fact, possess an infinite number of elements. This thesis, therefore, will not attempt to present a complete and general classification of mixtures on the basis of $\{\varepsilon\}$ but rather will consider very special classes of molecular systems which are

compatible with a truncation of the hierarchy via a perturbation approach. More precisely, we shall restrict our attention to those systems, of physical interest, which contain in their index set $\{\varepsilon\}$, some intrinsic parameter(s) which is (are) sufficiently smaller than one to qualify as an expansion parameter. These parameters, furthermore, will usually reside in the right hand side of the B.B.G.K.Y. hierarchy so as to allow the omission of the "mixing term" of the hierarchy as a zeroth order approximation. In particular, three classes of mixtures will be studied: non dense, weakly coupled, and so-called "Brownian" mixtures.

a) Non-Dense Mixtures:

Non-dense mixtures distinguish themselves by the low percentage of molecules which are interacting at any given time.[1] Our analysis of such mixtures will be based on the following assumptions:

1) the strong interaction potential ${}^{I}\bar{\Phi}_{ij}^{\alpha\beta}$ is repulsive and its range is roughly the same for all pairs of molecules;

i.e. $${}^{I}r^{\alpha\beta} \sim O[\bar{r}] \qquad \text{for all } \alpha,\beta, \qquad \text{(III-D-2)}$$

where:

$$\bar{r} \equiv \sum_{\beta=1}^{M}\sum_{\alpha=1}^{M} \frac{n_\beta n_\alpha \, {}^{I}r^{\alpha\beta}}{n^2} \qquad \text{(III-D-3)}$$

and:

$$n \equiv \sum_{\alpha=1}^{M} n_\alpha \qquad \text{(III-D-4)}$$

[1] If there is only a single specie present, such systems are usually referred to as "dilute gases". However, since the word "dilute" is also commonly used to indicate the low concentration of one or more species in a mixture, we shall avoid using it in this thesis.

2) all the molecules have similar masses:

i.e. $\gamma^{\alpha} \sim O[1]$ (III-D-5)

3) the particle density is roughly the same for each specie:

i.e. $n^{\alpha} \sim O[n/N]$ (III-D-6)

4) the weak interaction potential $^{II}\bar{\phi}_{ij}^{\alpha\beta}$ may be neglected:

i.e. $\varepsilon_1^{\alpha\beta} \rightarrow 0$ (III-D-7)

with $^{II}\gamma^{\alpha\beta}$ finite

5) the external field is weak:

i.e. $\chi^{\alpha} << 1$ (III-D-8)

and long range such that:

$L^{\alpha} > r_c$ (III-D-9)

6) the average number of particles in each particle's interaction sphere is very small:

i.e.

$$n_\beta \, (^{2}\gamma^{\alpha\beta})^{3} \sim O\left[n_\beta \, \bar{r}^{3}\right] << 1 \qquad \text{(III-D-10)}$$

Let us now consider, in the light of the above assumptions, the magnitude of the various intrinsic parameters in $\{\varepsilon\}$ by restricting ourselves to subgroups $\{S\}$ containing a small number of particles (i.e. $S \sim O[1]$). In order to evaluate these parameters, the characteristic lengths R and r_c must first be defined. Let us prescribe:

$$R \equiv \bar{r} \qquad \text{(III-D-11)}$$

such that the characteristic time:

$$t_o = \bar{r} \sqrt{\frac{m_i}{KT}} \qquad \text{(III-D-12)}$$

represents the typical interaction time between molecules and choose r_c as follow:

$$\bar{r} \overset{\circ}{<} r_c << n^{-1/3} \qquad \text{(III-D-13)}^{1}$$

such that the hierarchy becomes properly ordered over a physical volume larger than the size of a molecule's interaction sphere but much smaller than the molecular "specific volume" n^{-1}. With these selections for R and r_c, one then obtains from (III-D-1):

$$\mathcal{R}^{\alpha\beta} \equiv \frac{\bar{r}}{r^{\alpha\beta}} \left(\frac{r^{\alpha\beta}}{r_c} \right)^3 \qquad \text{(III-D-14)}$$

The remaining intrinsic parameters $\mathcal{K}^{\alpha}_{\{s\}}$ and $\mathcal{E}^{\alpha\beta}_{2\{s\}}$ may also be evaluated by estimating the magnitudes of the characteristic lengths $\mathcal{R}^{\alpha}_{\{s\}}$ and $\mathcal{R}^{\alpha\beta}_{\{s\}}$. The former length

$$\mathcal{R}^{\alpha} = \left\{ \int_{V_{\{s\}}} \left| \frac{\partial P^{\circ}_{\{s\}}}{\partial \bar{q}^{\alpha}_{i}} \right| d V_{\{s\}} \right\}^{-1}$$

shall be considered for two special cases: $S > 1$ and $S = 1$. In the first instance, we shall assume that the magnitude of the gradient $\frac{\partial P^{\circ}_{\{s\}}}{\partial \bar{q}^{\alpha}_{i}}$ is mostly governed by the correlations between the molecules within $\{S\}$ which, in turn, will be assumed to be dictated by the strength of the interaction potential. Consequently, it would seem reasonable to approximate $P^{\circ}_{\{s\}}$ as the canonical distribution for a group $\{s\}$ and hence assume that:

1. Hereon the symbol $\overset{\circ}{<}$ in $x \overset{\circ}{<} y$ denotes that x is smaller than and of the same order of magnitude as y.

$$P^{\circ}_{\{s\}} \sim o\Big[Z^{-1}_{\{s\}} e^{-\frac{1}{2\kappa T}\left\{\sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha}\left[\left(\sum_{\beta=1}^{M}\sum_{j=1}^{S_\beta}\phi^{\alpha\beta}_{ij}\right) + \vec{p}^{\alpha}_{i}\cdot\vec{p}^{\alpha}_{i}/m_\alpha\right]\right\}}\Big]$$

where:

$$Z_{\{s\}} = \int\!\!\int_{V_{\{s\}}} e^{-\frac{1}{2\kappa T}\left\{\sum_{\alpha=1}^{M}\sum_{i=1}^{S_\alpha}\left[\left(\sum_{\beta=1}^{M}\sum_{j=1}^{S_\beta}\Phi^{\alpha\beta}_{ij}\right) + \vec{p}^{\alpha}_{i}\cdot\vec{p}^{\alpha}_{i}/m_\alpha\right]\right\}} dV_{\{s\}}$$

(III-D-15)

such that:

$$\left|\frac{\partial P^{\circ}_{\{s\}}}{\partial \vec{q}^{\alpha}_{i}}\right| \sim o\Big[\left|\sum_{\beta=1}^{M}\sum_{j=1}^{S_\beta}\frac{\partial {}^{I}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}^{\alpha}_{i}}\right| \frac{P^{\circ}_{\{s\}}}{\kappa T}\Big]$$

(III-D-16)

Substituting the above into (III-C-46), we then have:

$$\mathcal{R}^{\alpha}_{\{s\}} \sim o\Big[\frac{1}{\kappa T}\int\!\!\int_{V_{\{s\}}}\left|\sum_{\beta=1}^{M}\sum_{j=1}^{S_\beta}\frac{\partial {}^{s}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}^{\alpha}_{i}}\right| P^{\circ}_{\{s\}}\, dV_{\{s\}}\Big]^{-1}$$

(III-D-17)

Finally, since within V_c one has, on the average:

$$\frac{\partial {}^{I}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}^{\alpha}_{i}} \sim o\Big[\left(\frac{\kappa T}{{}^{I}r^{\alpha\beta}}\right)\left(\frac{{}^{I}r^{\alpha\beta}}{r_c}\right)^{3}\Big]$$

$$\sim o\Big[\frac{\kappa T}{\bar{r}}\left(\frac{\bar{r}}{r_c}\right)^{3}\Big]$$

(III-D-18)

and $s \sim O[1]$, we may write

$$\mathcal{R}^{\alpha}_{\{s\}} \sim O\left[\frac{1}{\bar{r}} \left(\frac{\bar{r}}{r_c} \right)^3 \int\!\!\cdots\!\!\int^{V_{\{s\}}} P^{\circ}_{\{s\}} \, dV_{\{s\}} \right]^{-1} \qquad \text{(III-D-19)}$$

or:

$$\mathcal{R}^{\alpha}_{\{s\}} \sim O\left[\bar{r} \left(\frac{r_c}{\bar{r}} \right)^3 \right] \qquad \begin{matrix} s>1 \\ \sim O[1] \end{matrix} \qquad \text{(III-D-20)}$$

For the special case $s=1$, we shall only consider moderate spatial gradients so as to assume:

$$\int\!\!\int^{V_{\{i\}}} \left| \frac{\partial P^{\circ}_{\{i\}}}{\partial \hat{q}^{\alpha}_i} \right| dV_{\{i\}} < \left[\frac{1}{r_c} \right]$$

and obtain:

$$\mathcal{R}^{\alpha}_{\{i\}} > r_c \qquad \text{(III-D-21)}$$

Substituting (III-D-20) and (III-D-21) into (III-D-1), we then conclude that:

$$\mathcal{K}^{\alpha}_{\{s\}} \sim O\left[\frac{\bar{r}}{r_c} \right]^3 \qquad s>1 \qquad \text{(III-D-22)}$$

which, from (III-D-13), implies:

$$1 \overset{\circ}{>} \mathcal{K}^{\alpha}_{\{s\}} \gg m \bar{r}^3 \qquad \text{(III-D-23)}$$

Similarly, for $s=1$, one obtains from (III-D-1) and (III-D-21):

$$\mathcal{K}^{\alpha}_{\{1\}} < \frac{\bar{r}}{r_c} < 1 \qquad \text{(III-D-24)}$$

We shall now estimate the order of magnitude of:

$$ {}^{I}\mathcal{JR}^{\alpha\beta}_{|s|} \equiv \left\{ \frac{V \sqrt{m_\alpha}\ {}^{I}r^{\alpha\beta}}{\mu_{eq}\sqrt{KT}} \left(\frac{r_c}{{}^{I}r^{\alpha\beta}} \right)^3 \right. $$

$$ \left. \times \int\cdots\int_{V_{|s|}} \left| \iiint \frac{\partial\, {}^{I}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha}} \cdot \frac{\partial P^{\circ}_{|s,\, s_{\beta+1}|}}{\partial \vec{p}_i^{\alpha}}\, d\vec{r}^{\alpha\beta}_{i,s_{\beta+1}}\, d\vec{p}^{\beta}_{s_{\beta+1}} \right| dV_{|s|} \right\}^{1/3} $$

by noting, on one hand, that:

$$ {}^{I}\mathcal{JR}^{\alpha\beta} \leq \left\{ \frac{V \sqrt{m_\alpha}\ {}^{I}r^{\alpha\beta}}{\mu_{eq}\sqrt{KT}} \left(\frac{r_c}{{}^{I}r^{\alpha\beta}} \right)^3 \right. $$

$$ \left. \times \int\cdots\int_{V_{|s|}} \iiint \left| \frac{\partial^2 \phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha}} \right| \left| \frac{\partial P^{\circ}_{|s,\, s_{\beta+1}|}}{\partial \vec{p}_i^{\alpha}} \right| d\vec{r}^{\alpha\beta}_{i,s_{\beta+1}}\, d\vec{p}^{\beta}_{s_{\beta+1}}\, dV_{|s|} \right\}^{1/3} $$

and, on the other hand, that the integration over $d\vec{r}_{i\,s_{\beta+1}}$ is performed over the entire physical volume, where on the average:

$$ \left| \frac{\partial^2 {}^{I}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha}} \right| \sim o\left[\frac{KT}{{}^{I}r^{\alpha\beta}} \quad \frac{({}^{I}r^{\alpha\beta})^3}{V} \right] $$

$$ \sim o\left[\frac{KT}{V} \frac{1}{r^2} \right] $$

Assuming that $P^{\circ}_{|s,s_{\beta+1}|}$ is sufficiently near equilibrium to write:

$$\frac{\partial P^{\circ}_{|s,s_{\beta+1}|}}{\partial \vec{p}^{\alpha}_{c}} \sim o\left[\frac{\vec{p}^{\alpha}_{c}}{m_{\alpha} KT} P^{\circ}_{|s,s_{\beta+1}|}\right]$$

we then have, approximately:

$$\begin{aligned} {}^{I}\delta R^{\alpha\beta}_{|s|} &\lesssim o\left[\left\{\frac{V\sqrt{m_{\alpha}}}{\mu_{\alpha q}\sqrt{KT}} {}^{I}\Gamma^{\alpha\beta}\left(\frac{r_c}{{}^{I}\Gamma^{\alpha\beta}}\right)^{3}\right.\right. \\ &\times \int_{V_{|s|}}\left.\left.\int\int \frac{KT\,\bar{r}^{2}}{V}\frac{|\vec{p}^{\alpha}_{c}|}{m_{\alpha}KT} P^{\circ}_{|s,s_{\beta+1}|}\, d\vec{r}^{\alpha\beta}_{ij}\, d\vec{p}^{\beta}_{s_{\beta+1}}\, dV_{|s|}\right\}^{1/3}\right] \\ &\lesssim o\left[r_c/\sqrt[3]{\mu_{\alpha q}}\right] \end{aligned}$$

Since ${}^{\circ}\mu_{\alpha q} \sim o[1]$, the above result reduces to:

$${}^{I}\delta R^{\alpha\beta}_{|s|} \lesssim o[r_c] \qquad \text{(III-D-25)}$$

such that:

$$\begin{aligned} {}^{I}\varepsilon^{\alpha\beta}_{2_{|s|}} &\equiv n_{\beta}\left({}^{I}\delta R^{\alpha\beta}_{|s|}\right)^{3} \\ &\lesssim o\left[n_{\beta} r_c^{3}\right] \\ &\lesssim o\left[n_{\beta}\bar{r}^{3}\right] \\ &\ll 1 \end{aligned}$$

(III-D-26)

Listing of Intrinsic Parameters

For Non-Dense Mixtures

$\mathcal{K}^{\alpha}_{\substack{\{s\} \\ s>1}}$	$\equiv \dfrac{R}{\mathcal{R}^{\alpha}_{\{s\}}}$	$\sim$	$O\left[\dfrac{\bar{r}}{r_c}\right]^3$	$\gg n\bar{r}^3$ $\lesssim 1$
$\mathcal{K}^{\alpha}_{\{1\}}$	$\equiv \dfrac{R}{\mathcal{R}^{\alpha}_{\{1\}}}$	$<$	$\left[\dfrac{\bar{r}}{r_c}\right]$	< 1
γ^{α}	$\equiv \sqrt{\dfrac{m_1}{m_\alpha}}$	$\sim$	$O[1]$	$\sim O[1]$
${}^{I}\mathcal{R}^{\alpha\beta}$	$\equiv \dfrac{R}{{}^{I}r^{\alpha\beta}}\left[\dfrac{{}^{I}r^{\alpha\beta}}{r_c}\right]^3$	$\sim$	$O\left[\dfrac{\bar{r}}{r_c}\right]^3$	$\gg n\bar{r}^3$ $\lesssim 1$
$\varepsilon_1^{\alpha\beta}$	$\equiv \dfrac{{}^{II}\bar{\phi}^{\alpha\beta}}{KT}$	$\to$	0	$\to 0$
χ^{α}	$\equiv \dfrac{U^{\alpha}}{KT}$	$\ll$	1	$\ll 1$
$\mathcal{A}^{\alpha}$	$\equiv \dfrac{R}{L^{\alpha}}$	$\lesssim$	$O\left[\dfrac{\bar{r}}{r_c}\right]$	$\lesssim O[1]$
${}^{I}\varepsilon^{\alpha\beta}_{2_{\{s\}}}$	$\equiv m_\beta\left({}^{I}\delta R^{\alpha\beta}_{\{s\}}\right)^3$	$\lesssim$	$O\left[m_\beta\bar{r}^3\right]$	$\ll 1$

Table III-1

The above results are summarized in Table III-1 where the first column denotes the intrinsic parameters, the second column gives the precise definition of these parameters, the third column lists their order of magnitude in terms of $\bar{r}$, n_β and r_c, and the last column tabulates the orders of magnitudes when r_c is chosen according to (III-D-13).

Let us now consider some of the implications of the dimensionless B.B.G.K.Y. hierarchy (III-C-52) and Table III-1 for non-dense mixtures by comparing these results with the analysis of Sandri previously described. Sandri restricted his nondimensionalization to simple (single specie) systems in the absence of an external field so as to obtain the dimensionless B.B.G.K.Y. hierarchy:

$$\frac{\partial F_s^*}{\partial t^*} + K_s^* F_s^* - \varepsilon_1 I_s^* F_s^* = \varepsilon_1 \varepsilon_2 L_s^* F_{s+1}^* \qquad \text{(III-A-1)}$$

where K_s^*, I_s^* and L_s^* were defined in equation (III-A-2). For non-dense systems, Sandri reasoned that:

$$\varepsilon_1 \sim O[1] \qquad \varepsilon_2 \ll 1$$

such that $L_s F_{s+1}^*$ could be assumed very small and would be neglected at the zeroth order of an expansion in ε_2. For the same physical system, and using similar notation, the B.B.G.K.Y. hierarchy (III-C-52) of the present thesis may be shown to reduce to:

$$\frac{\partial F_s^*}{\partial t^*} + \partial K_s \; K_s^* F_s^* - {}^{I}\partial R \; I_s^* F_s^* = {}^{I}\varepsilon_{2_{(s)}} {}^{I}\partial R \, \mu_{sq} L_s^* F_{s+1}^* \qquad \text{(III-D-27)}^1$$

Now, choosing r_c according to (III-D-13) one sees from the last column of Table III-1 that ${}^{I}\varepsilon_2(\ll 1)$ represents the predominantly small parameter. Furthermore, it is clearly evident that any perturbation of (III-D-27) in terms of ${}^{I}\varepsilon_2$ is equivalent to a similar perturbation of (III-A-1) in terms of ε_2. It would, therefore, seem that the above nondimensionalization of the B.B.G.K.Y. hierarchy for non-dense systems is completely consistent with Sandri's ideas.

In spite of the apparent mutual agreement between the above analysis and Sandri's nondimensionalization, one important dissimilarity must be noted. We recall that the dimensionless B.B.G.K.Y. hierarchy as given by (III-C-52) is only properly ordered over a characteristic volume:

$$V_{(s)} = V_c^s \prod_{\alpha=1}^{M} (m_\alpha \kappa T)^{3s_\alpha/2}$$

such that any expansion performed on this equation should be restricted to thermal molecules (i.e. molecules with momenta $o[\sqrt{m_\alpha \kappa T}]$ sharing the same volume V_c). This

[1] The definition for K_s^*, I_s^* and L_s^* are as given by (III-A-2) with the exception that $\vec{q}_i^*$, $\vec{p}_i^*$, Φ_{ij}^*, F_s^* are defined differently.

latter volume may be regarded as a "floating" volume which may be chosen anywhere within the physical space and could, in fact, travel to follow a given particle if so desired. Once chosen, however, it may not vary in size and must remain more or less spherical.[1] Clearly, if one wishes to enlarge the range of validity of any expansion performed on (III-C-52) or (III-D-27) one must initially choose a larger volume V_c . Unfortunately, any attempt to inflate this volume will provoke two undesirable effects. On one hand, since the B.B.G.K.Y. hierarchy is properly ordered on the average over $V_{|s|}$, any enlargement of this volume through an inflation of V_c may eventually create large local regions within $V_{|s|}$ over which the hierarchy is not at all properly ordered. Furthermore, as can be seen from the third column in Table III-1, any enlargement of V_c to the size $O[m^{-1}]$ will increase the magnitude of ${}^{I}\varepsilon_2$ in (III-D-27) from ${}^{I}\varepsilon_2 \ll 1$ to ${}^{I}\varepsilon_2 \leq O[1]$. Furthermore, one notes from the same column that this choice of V_c will yield for ${}^{I}\mathcal{R}$ and $\mathcal{K}_s$ (in III-D-27) magnitudes which are much smaller than unity. For such a choice of V_c it would, therefore, seem more reasonable to expand in ${}^{I}\mathcal{R}$ and $\mathcal{K}_s$ than in ${}^{I}\varepsilon_2$. If one, in fact, performed such an expansion one would then

[1] The reason for this is that in evaluating the typical order of magnitude of $\left|\frac{\partial \phi_{ij}}{\partial q_i}\right|$ over V_c , a spherical volume was assumed. Clearly, if this volume is drastically distorted in shape, these estimates may no longer hold.

naturally find that all the terms in (III-D-27) (with the exception of the time derivative) would be neglected at the zeroth order. Finally, one may easily note from the third column in III-1 that though ${}^{I}_{e}\mathcal{R}^{\alpha\beta}$ decreases rapidly in order of magnitude with an increase in ℓ_c, the product ${}^{I}_{e}\mathcal{R}^{\alpha\beta}\,{}^{I}\mathcal{E}^{\alpha\beta}_{i}{}_{|s|}$ generally remains insensitive to such an enlargement of V_c. Consequently, one may conclude from (III-D-27) that an inflation of V_c will generally have the effect of decreasing the magnitude of $\mathcal{H}^{*}_{\alpha\beta}\Gamma^{*}_{i|s|}$ while leaving the mixing terms more or less unchanged in their order of magnitude. Hence, any attempt of overenlarging through an increase of V_c will generally intensify the relative importance of the troublesome mixing terms.

We may conclude from the above arguments that the expansion parameters chosen in a perturbation analysis greatly depend on the volume $V_{|s|}$ over which the proposed expansion will be performed. Furthermore, any attempt to increase $V_{|s|}$ will, on one hand, create local regions in $V_{|s|}$ in which the expansion is not at all valid and on the other hand, increase the relative importance of the troublesome mixing terms. These conclusions, which were not at all evident from previous nondimensionalizations of the hierarchy (such as Sandri's) will bear heavily on the expansions to be performed in later chapters of this thesis for non-dense mixtures.

b) Weakly Coupled Mixtures:

We shall now evaluate the intrinsic parameters for a mixture which displays extremely short range strong interactions and moderately long range weak interactions such that:

$$n_\beta ({}^{I}r^{\alpha\beta})^3 \longrightarrow 0 \qquad \text{(III-D-28)}$$

$$n_\beta ({}^{II}r^{\alpha\beta})^3 \sim o[1] \qquad \text{(III-D-29)}$$

and:

$$\varepsilon_1^{\alpha\beta} \equiv \frac{\bar{\Phi}^{\alpha\beta}}{kT} \ll 1 \qquad \text{(III-D-30)}$$

The analysis will rest on the following assumptions:

1) All particles have roughly the same mass:

i.e. $\gamma^\alpha \sim o[1]$ (III-D-31)

2) All species have similar particle densities:

i.e.

$$n_\beta \sim o[n_\alpha] \sim o\left[\frac{n}{M}\right] \qquad \text{(III-D-32)}$$

as a result of equation (III-D-29) this assumption also implies:

$${}^{II}r^{\alpha\beta} \sim o[{}^{II}r^{\gamma\delta}]$$

$$\sim o[\bar{r}] \qquad \text{(III-D-33)}$$

where, in this subsection, $\bar{r}$ is defined by:

$$\frac{1}{\bar{r}} = \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M} \frac{n_\alpha n_\beta}{n^2} {}^{II}r^{\alpha\beta} \qquad \text{(III-D-34)}$$

3) The external field is very weak and long range:

i.e. $\chi^\alpha \ll 1$ (III-D-35)

$L^\alpha \gg r_c$ (III-D-36)

For the weakly coupled case, we shall prescribe:

$$R \equiv \bar{r} \qquad \text{(III-D-37)}$$

such that the characteristic time:

$$t_o = R \Big/ \sqrt{\frac{kT}{m_1}} = \bar{r} \Big/ \sqrt{\frac{kT}{m_1}}$$

represents the typical duration of a weak interaction. Furthermore, we shall choose r_c slightly larger but of the same order of magnitude as $\bar{r}$:

i.e. $$r_c \gtrsim \bar{r} \qquad \text{(III-D-38)}$$

As in the non-dense case, the characteristic length $\mathcal{R}^{\alpha}_{\{s\}}$ will be estimated for two cases. On one hand, we consider $\mathcal{R}^{\alpha}_{\{s\}}$ $(s > 1)$ for a mixture with weak nonuniformities. For such mixtures, the gradients $\frac{\partial P_{\{s\}}}{\partial \vec{q}_i^{\alpha}}$ are essentially governed by the correlations resulting from the strong and weak interactions between the molecules. Consequently, for such mixtures, we shall estimate $\mathcal{R}^{\alpha}_{\{s\}}$ $(s>1)$ by assuming that initially $P_{\{s\}}$ is not too distant from the canonical distribution for a subgroup $\{s\}$. Hence, $P^{o}_{\{s\}}$ will be approximated by:

$$P^{o}_{\{s\}} \sim o\left[Z^{-1}_{\{s\}} \; e^{-\frac{1}{2kT}\left\{\sum_{\alpha=1}^{M}\sum_{i=1}^{s_\alpha}\left[\sum_{\beta=1}^{M}\sum_{j=1}^{s_\beta}\left({}^{I}\phi^{\alpha\beta}_{ij} + {}^{II}\phi^{\alpha\beta}_{ij}\right) + |\vec{p}_i^{\alpha}|^2/m_\alpha\right]\right\}}\right]$$

$$Z_{\{s\}} \equiv \int\cdots\int_{V_{\{s\}}} e^{-\frac{1}{2kT}\left\{\sum_{\alpha=1}^{M}\sum_{i=1}^{s_\alpha}\left[\sum_{\beta=1}^{M}\sum_{j=1}^{s_\beta}\left({}^{I}\phi^{\alpha\beta}_{ij} + {}^{II}\phi^{\alpha\beta}_{ij}\right) + |\vec{p}_i^{\alpha}|^2/m_\alpha\right]\right\}} dV_{\{s\}}$$

such that:

$$\frac{\partial P_{\{s\}}}{\partial \vec{q}_i^{\alpha}} \sim o\left[\left|\sum_{\beta=1}^{M}\sum_{j=1}^{s_\beta}\left(\frac{\partial\, {}^{I}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha}} + \frac{\partial\, {}^{II}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha}}\right)\right| \frac{P^{o}_{\{s\}}}{kT}\right]$$

and

$$\mathcal{R}_{[s]} \sim O\left[\frac{1}{\kappa T} \iint^{V_{[s]}} \left| \sum_{\alpha=1}^{M} \sum_{j=1}^{S_\alpha} \left(\frac{\partial {}^{I}\phi_{ij}^{\alpha\beta}}{\partial \bar{q}_i^{\alpha}} + \frac{\partial {}^{II}\phi_{ij}^{\alpha\beta}}{\partial \bar{q}_i^{\alpha}} \right) \right| P^{\circ}_{[s]} \, dV_{[s]} \right]^{-1}$$

Now, within V_c, we note that:

$$\frac{\partial {}^{I}\phi_{ij}^{\alpha\beta}}{\partial \bar{q}_i^{\alpha}} \sim O\left[\frac{\kappa T}{{}^{I}r^{\alpha\beta}} \left(\frac{{}^{I}r^{\alpha\beta}}{r_c} \right)^3 \right]$$

and:

$$\frac{\partial {}^{II}\phi_{ij}^{\alpha\beta}}{\partial \bar{q}_i^{\alpha}} \sim O\left[\frac{{}^{II}\bar{\phi}^{\alpha\beta}}{{}^{II}r^{\alpha\beta}} \left(\frac{{}^{II}r^{\alpha\beta}}{r_c} \right)^3 \right]$$

Furthermore since:

$$n \left({}^{I}r^{\alpha\beta} \right)^3 \to 0$$

and

$$r_c \sim O[\bar{r}] \sim O[n^{-1/3}]$$

we then have

$$\left(\frac{{}^{I}r^{\alpha\beta}}{r_c} \right)^3 \to 0 \qquad \text{(III-D-39)}$$

Consequently, for $S \sim O[1]$, we conclude that:

$$\mathcal{R}^{\alpha}_{[s]} \sim O\left[\frac{{}^{II}\bar{\phi}^{\alpha\beta}}{\kappa T} \cdot \frac{1}{{}^{II}r^{\alpha\beta}} \left(\frac{{}^{II}r^{\alpha\beta}}{r_c} \right)^3 \iint^{V_{[s]}} P^{\circ}_{[s]} \, V_{[s]} \right]^{-1}$$

or:

$$\mathcal{R}^{\alpha}_{[s]} \sim O\left[\frac{\bar{r}}{\varepsilon_1^{\alpha\beta}} \left(\frac{r_c}{\bar{r}} \right)^3 \right] \qquad \text{(III-D-40)}$$

and therefore:

$$\mathcal{K}^{\alpha}_{\{s\}} = \frac{R}{\mathcal{R}^{\alpha}_{\{s\}}} \sim o\left[\left(\frac{\bar{r}}{r_c}\right)^3 \cdot \varepsilon_i^{\alpha\beta}\right]$$

$$\sim o\left[\varepsilon_i^{\alpha\beta}\right]$$

$$\ll 1 \qquad \text{(III-D-41)}$$

We shall now consider, as the second case, a mixture in which the gradients $\frac{\partial P_{\{s\}}}{\partial q_i^{\alpha}}$ are mostly due to the spatial nonuniformities within the system rather than to the correlations. For such mixtures, it is preferable to choose for $P^{\circ}_{\{s\}}$

$$P^{\circ}_{\{s\}} \sim o\left[\prod_{\alpha=1}^{M}\prod_{i=1}^{S_\alpha} P_{\{i,\alpha\}}(\vec{q}_i^{\alpha}, \vec{p}_i^{\alpha}, o)\right]$$

such that:

$$\mathcal{R}^{\alpha}_{\{s\}} \sim o\left[\int\int_{V_{\{s\}}} \left|\frac{\partial P^{\circ}_{\{i,\alpha\}}(\vec{q}_i^{\alpha}\vec{p}_i^{\alpha})}{\partial \vec{q}_i^{\alpha}}\right| \left|\prod_{\substack{\beta=1\\ \{\beta,s\}\neq\{j,\beta\}}}^{M} P_{\{j,\beta\}}(\vec{q}_j^{\beta}\vec{p}_j^{\beta})\, dV_{\{s\}}\right]^{-1}$$

$$\sim o\left[\int\int_{V_{\{i,\alpha\}}} \left|\frac{\partial P^{\circ}_{\{i,\alpha\}}(\vec{q}_i^{\alpha}\vec{p}_i^{\alpha})}{\partial \vec{q}_i^{\alpha}}\right| dV_{\{i,\alpha\}}\right]^{-1}$$

Assuming that for all α, the gradiemts due to spatial nonuniformities are moderate such that:

$$\int\int_{V_{\{i,\alpha\}}} \left|\frac{\partial P^{\circ}_{\{i,\alpha\}}}{\partial \vec{q}_i^{\alpha}}\right|(\vec{q}_i^{\alpha}, \vec{p}_i^{\alpha})\, dV_{\{i,\alpha\}} < o\left[\frac{1}{r_c}\right]$$

we then obtain:

$$\mathcal{R}^{\alpha}_{ijj} \rangle o[r_c]$$

and hence

$$\mathcal{K}^{\alpha}_{ijj} < o[\frac{\bar{r}}{r_c}] < o[1] \qquad \text{(III-D-42)}$$

Finally, the characteristic length ${}^{k}\mathcal{SR}^{\alpha\beta}_{ijj}$ $(k = I, II)$ may be evaluated exactly as in the non dense case to yield

$${}^{k}\mathcal{SR}^{\alpha\beta}_{ijj} \leqslant o[r_c] \qquad k = I, II$$

such that:

$${}^{k}\mathcal{E}^{\alpha\beta}_{2\,ijj} \leqslant o[n r_c^3] \leqslant o[n \bar{r}^3] \leqslant o[1] \qquad \text{(III-D-43)}$$

The above results may be summarized, as in the previous section, by Table III-2, where the third column indicates the orders of magnitude of the intrinsic parameters when r_c is arbitrary and the last column lists the respective orders of magnitude when $r_c \sim o[\bar{r}]$

Let us now consider the implications of these results in terms of Sandri's analysis of simple weakly coupled gases in the absence of any external field.

Listing of Intrinsic Parameters For Weakly Coupled Mixtures

$\mathcal{K}^{\alpha}_{\substack{[ss]\\ s>1}}$ [1]	$\equiv \dfrac{R}{\mathcal{R}^{\alpha}_{[ss]}}$	$\sim O\left[\dfrac{\bar{r}}{r_c}\right]^3 \varepsilon_1^{\alpha\beta}$	$\sim O[\varepsilon_1^{\alpha\beta}] \ll 1$
$\mathcal{K}^{\alpha}_{\substack{[ss]\\ s>1}}$ [2]	$\equiv \dfrac{R}{\mathcal{R}^{\alpha}_{[ss]}}$	$< O\left[\dfrac{\bar{r}}{r_c}\right]$	$< O[1]$
γ^{α}	$\equiv \sqrt{\dfrac{m_1}{m_\alpha}}$	$\sim O[1]$	$\sim O[1]$
${}^{I}\mathcal{R}^{\alpha\beta}$	$\equiv \dfrac{R}{{}^{I}r^{\alpha\beta}}\left(\dfrac{{}^{I}r^{\alpha\beta}}{r_c}\right)^3$		$\to 0$
${}^{II}\mathcal{R}^{\alpha\beta}$	$\equiv \dfrac{R}{{}^{II}r^{\alpha\beta}}\left(\dfrac{{}^{II}r^{\alpha\beta}}{r_c}\right)^3$	$\sim O\left[\dfrac{\bar{r}}{r_c}\right]^3$	$\sim O[1]$
$\varepsilon_1^{\alpha\beta}$	$\equiv \dfrac{{}^{II}\bar{\phi}^{\alpha\beta}}{\kappa T}$	$\ll 1$	$\ll 1$
χ^{α}	$\equiv \dfrac{u^{\alpha}}{\kappa T}$	$\ll 1$	$\ll 1$
$\mathcal{A}^{\alpha}$	$\equiv \dfrac{R}{L^{\alpha}}$	$\lesssim O\left[\dfrac{\bar{r}}{r_c}\right]$	$\lesssim O[1]$
${}^{k}\varepsilon 2^{\alpha\beta}_{[ss]}$	$\equiv m_\beta ({}^{k}\mathcal{R}^{\alpha\beta}_{[ss]})^3$	$\lesssim O[m_\beta r_c^3]$	$\lesssim O[1]$

Table III-2

1 Weak spatial nonuniformities
2 Moderate spatial nonuniformities

Using a notation similar to Sandri's, the B.B.G.K.Y. hierarchy (III-C-52) may be written for this simple system as:

$$\frac{\partial F_s^*}{\partial t^*} + \mathcal{K}_s \; K_s^* F_s^* - {}^{II}\mathcal{R}\, \varepsilon_1 I_s^* F_s^* = \varepsilon_1 \varepsilon_2 {}^{II}\mathcal{R}\, \mu_{eq} L_s^* F_{s+1}^* \qquad \text{(III-D-44)}$$

If one now considers the case where the spatial nonuniformities are moderate and one chooses $r_c \sim o(\bar{r})$, one can then conclude from the last column in Table III-2 that $\varepsilon_1 << 1$ represents the predominantly small parameter in (III-D-44). Furthermore, it is evident that any expansion of F_s^* in powers of ε_1, in (III-D-44) is equivalent to a similar expansion in Sandri's ε_1 in (III-A-1). Hence, for this particular case of moderate nonuniformities, the above analysis is apparently consistent with Sandri's ideas. On the other hand, if one considers the particular case of weak spatial nonuniformities , it becomes apparent from the last column in (III-2) that, along with ε_1, a second parameter $\mathcal{K}_s$, of the same order of magnitude as ε_1, emerges. Furthermore, it is evident that any simultaneous expansion of F_s^* in powers of ε_1 and $\mathcal{K}_s$ will result in the neglect of all the terms of (III-D-44) (with the exception of the time derivative) at the zeroth order. This result, which is in direct conflict with the analyses of Sandri and others for uniform weakly coupled gases stems from the fact that, near

equilibrium, if one neglects the interactions contained in $I_s^* F_s^*$ one must similarly discard the correlations created by these interactions in $K_s^* F_s^*$. This point, seemingly overlooked by Sandri and many others will have grave consequences when a truncation of the B.B.G.K.Y. hierarchy for uniform weakly coupled gases is attempted in later chapters of the present thesis.

Before concluding the present discussion, one should perhaps note that many of the remarks presented previously for non-dense mixtures apply equally to weakly coupled systems. In particular, it should be emphasized that any attempt to increase the range of validity of an expansion by inflating $V_{\{s\}}$ through an enlargement of V_c will have the undesirable effect of creating on one hand local regions within $V_{\{s\}}$ where the dimensionless hierarchy is not properly ordered and intensifying, on the other hand, the relative importance of the troublesome mixing terms.

c) Brownian Mixtures:

As a final special class of mixtures, let us now consider systems which consist of a group of heavy particles coexisting in a bath of light molecules. Identifying species $\alpha = M_0 \cdots M$ as the heavy "Brownian" particles and species $\alpha = 1 \cdots (M_0-1)$ as the "bath" molecules, we shall investigate such "Brownian" mixtures under the following assumptions:

1) All the Brownian particles are roughly of the same mass:

i.e. $m_\alpha \sim o[m_1]$ for $M_0 \leq \alpha \leq M$

2) All the bath particles are roughly of the same mass:
i.e. $m_\alpha \sim O[m_1]$ for $\alpha < M_0$

3) The Brownian particles are much heavier than the bath particles:
i.e.

$$\gamma^\alpha \equiv \sqrt{\frac{m_1}{m_\alpha}} \ll 1 \qquad \text{(III-D-45)}$$

for $\alpha \geq M_0$

4) The external field exerted on the system is weak:
i.e. $\chi^\alpha \ll 1$ (III-D-46)
for all α

With these assumptions, we immediately obtain two intrinsic parameters χ^α and $\gamma^\alpha (\alpha \geq M_0)$ which, because of their very small order of magnitude, may be used as expansion parameters in any of the dimensionless governing equations, provided, of course, that they, in fact, dictate the order of magnitude of the various terms in these equations. Strictly speaking, this will only be the case if the remaining parameters are $\sim O[1]$, on the average over some range of the independent variables. On the other hand, if one does not propose to pursue the expansion to high orders of $(\gamma^\alpha, \alpha \geq M_0, \chi^\alpha)$, we simply demand that the remaining intrinsic parameters be within the range:

$$\max.[\gamma^\alpha (\alpha \geq M_0), \chi^\alpha] \ll \varepsilon_0 \ll \min.[1/\gamma^\alpha (\alpha \geq M_0), 1/\chi^\alpha] \qquad \text{(III-D-47)}$$

(for all $\varepsilon_0 \in \{\varepsilon\}$, $\varepsilon_0 \neq \gamma^\alpha (\alpha \geq M_0), \chi^\alpha$)

In order to verify (III-D-47) one should, of course, proceed as in the previous sections and define some characteristic lengths $\bar{R}$, r_c and introduce some reasonable initial conditions $\bar{P}^{\circ}_{[s]}$ to estimate the orders of magnitude of all the intrinsic parameters. Unfortunately, for the general case of Brownian mixtures, it becomes impossible to choose reasonable initial conditions for $\bar{P}_{[s]}$ without resorting to very special cases (such as non-dense or weakly coupled systems). For this reason, it will be assumed in the present thesis that (III-D-47) is, in fact, valid for some choice of r_c and $\bar{R}$ and hence, some range of the independent variables. Such an assumption, though rarely acknowledged, is, in fact, implied in all previous perturbational analyses of Brownian motion, including those of Lebowitz-Rubin,[8] Résibois-Davis,[7] Lebowitz-Résibois,[9] Cuckier and Deutch,[35] Deutch and Oppenheim[36] and R. Mazo.[37] It is, indeed, regrettable that this hypothesis be needed, since it leaves us somewhat in the dark as to the range of validity of the expansions. Suffice it to say, therefore, that the truncation of the B.B.G.K.Y. hierarchy presented in the following chapters of this thesis via an expansion in $\{\gamma^{(\alpha)}(\kappa,\kappa_0), \chi^{\alpha}\}$ will be presented with some reservations.

E. Summary and Conclusions

The present chapter has developed a systematic method of nondimensionalizing the governing equations, for systems

not too distant from equilibrium, such that on the average, over a restricted domain in phase space, the various terms of these equations, excepting the time derivatives, may be written as the product of non dimensional terms $\sim O[1]$ and dimensionless parameters which dictate the relative weight of each term in the respective equations. This method differs considerably from the more casual approach adopted by others[12],[25] which consists of non dimensionalizing the governing equations with respect to a set of seemingly physically reasonable quantities and assuming that the relative weight of the various terms are in fact solely dictated by the estimated magnitude of resulting dimensionless parameters such as $\varepsilon_1 = \frac{\phi_0}{m v_{th}^2}$, $\varepsilon_2 = n r_0^3$ where ϕ_0 and r_0 represent the characteristic particle interaction potential energy and range while n and ϕ_0 denote mean particle density and kinetic temperature respectively. This latter method though considerably simpler, unfortunately becomes extremely risky when such parameters are later used as expansion coefficients to truncate the B.B.G.K.Y. hierarchy since throughout the expansion, one remains uncertain of the range of validity in phase space, if any, of the resulting perturbation solutions. In such a bold approach one is then obliged to pursue the expansion until divergent terms appear at higher orders and assume (i.e., hope) that the convergence of the lower order solutions will also imply their validity.

Having derived dimensionless governing equations which

are "well ordered" over a restricted volume in phase space we may then, through estimates of the various dimensionless parameters, undertake a classification of molecular systems and seek for particular systems for which some of the terms in these equations may be neglected as a zeroth order approximation. In the present thesis three such systems have been considered: "non-dense" systems in which the percentage of molecules interacting at a given time is very low, "weakly coupled" systems characterized by the negligible effect of strong interactions and a moderate percentage of weakly interacting particles and finally "Brownian" systems distinguishing themselves by the presence of heavy "Brownian" particles coexisting with a bath of light particles.

For the particular case of non-dense systems, the dimensional arguments in the present chapter suggest that the relative weight of the various terms in the B.B.G.K.Y. may be expressed as follows

$$\frac{\partial F_s}{\partial t} + \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i} - \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s'}{\partial \vec{p}_i} = \mathcal{L}_s F_{s+1}$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$1 \qquad\qquad 1 \qquad\qquad [\varepsilon_s \leq \alpha(m\sigma^3)] \ll 1$$

(III-E-1)

where $\vec{X}_{1s1}$ is chosen within the phase volume V_{1s1} in which $|\vec{p}_i| \sim O[\sqrt{mkT}]$ and $\vec{q}_i$, $i = 1 \ldots s$, $s \ll N$ may be enclosed in in a spherical volume V_1 , where $\frac{4}{3}\pi r_0^3 \overset{\bullet}{<} V_1 \ll n^{-1}$.[1] Consequently, over the small phase volume V_{1s1} (and physical volume V_1), one may follow Bogoliubov [12] , Sandri [25] and others by assuming that the momentum convection term $\sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i}$ and the interaction term $\sum_{j=1}^{s}\sum_{i=1}^{s} \frac{\partial \Phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s}{\partial \vec{p}_i}$ dominate over the mixing term $\mathcal{L}_s F_{s+1}$. Hence, whithin this small volume, a perturbation scheme which neglects the mixing term as a zeroth order approximation would seem reasonable. However, over a larger volume $V_2 \sim O[n^{-1}]\lambda^3$ where λ denotes the mean free path, the nondimensionalization executed in this chapter suggests the following scaling of terms for uniform (or quasi-uniform) systems.

$$\underset{\downarrow}{\frac{\partial F_s}{\partial t}} + \sum_{i=1}^{s} \underset{\downarrow\; n r_0^3}{\frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i}} - \sum_{j=1}^{s}\sum_{i=1}^{s} \underset{\downarrow\; n r_0^3}{\frac{\partial \Phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s}{\partial \vec{p}_i}} = \underset{\downarrow\; \frac{1}{5} n r_0^3}{\mathcal{L}_s F_{s+1}}$$

(III-E-2)

Consequently, over this larger physical volume (and hence larger phase volume) the momentum convection and interaction terms do not necessarily dominate over the remaining mixing term.

1 The symbol $\overset{\bullet}{<}$ in $x \overset{\bullet}{<} y$ denotes that x is smaller than and of the same order of magnitude as y .

The reason for this rests on the fact that within such a volume the mean distance between s particles, where $s \sim O[1]$, is much larger than the range of strong interaction between particles. Furthermore, the resulting weak average interaction between the molecules implies near equilibrium a correspondingly weak average correlation and consequently, for a uniform (or quasi uniform system) a small spacial gradient $\frac{\partial F_s}{\partial \vec{q}_i}$. Fortunately the derivation of a closed equation for the single particle distribution only requires an approximate solution for $F_2(\vec{x}_i, \vec{x}_j, t)$ only when $|\vec{q}_i - \vec{q}_j| < r_0$. Hence one may pursue on the basis of the ordering of terms indicated by equation (III-E-1) provided of course that the limited range of validity of the solution for F_2 is taken into account when boundary conditions are imposed.

The dimensional analysis presented in this chapter for weakly coupled systems have resulted in a somewhat disconcerting observation. For the case of moderate nonuniformities one may follow Bogoliubov, Sandri and others and express the ordering of terms as follows

$$\frac{\partial F_s}{\partial t} + \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i} - \sum_{j=1}^{s} \sum_{i=1} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s}{\partial \vec{p}_i} = \mathcal{L}_s F_{s+1}$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$1 \qquad\qquad \varepsilon_1 = \frac{\Phi_0}{KT} \ll 1 \qquad\qquad \varepsilon_1$$

(III-E-3)

when X_{1s} is chosen in the volume V_{1s} where $|\vec{p}_i| \sim O[\sqrt{mkT}]$ and $\vec{q}_i, i=1 \ldots s$ are found in the physical volume $V_c \sim O[r_0^3]$. However, in the uniform (or weakly non-uniform) case one finds that within the same phase volume V_{1s} the ordering of terms becomes

$$\frac{\partial F_s}{\partial t} + \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i} - \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \frac{\partial F_s}{\partial \vec{p}_i} = \mathcal{L}_s F_{s+1}$$

$$\varepsilon_1 = \frac{\phi_0}{kT} \ll 1 \qquad \varepsilon_1 \qquad \varepsilon_1$$

(III-E-4)

Indeed in this case contrary to the views of Bogoliubov and others, the momentum convection term no longer dominates over the mutual interaction and mixing terms since the average weak interactions occuring within V_c will, near equilibrium, result in similarly weak correlations and consequently small gradients $\frac{\partial F_s}{\partial \vec{q}_i}$. Naturally, when all the terms become equally small, the truncation of the B.B.G.K.Y. hierarcy via a perturbation approach represents a most difficult, if not impossible task.

The particular case of a Brownian system also presents its own hardships as it seems rather difficult to estimate the magnitudes of the relevant dimensionless parameters without seeking further specialization such as low density or weak coupling. The approach adopted in the thesis has therefore consisted of assuming that the dimensionless parameter $\gamma = \sqrt{\frac{m_b}{m_B}}$ emerging from the nondimen-

sionalization dictates the relative weight of the various terms in the dimensionless Liouville and B.B.G.K.Y. hierarchy. Consequently, for a single Brownian particle (B) in a bath of indentical light particles (b) one would have in the spacially uniform case the following ordering of terms in the dimensional Liouville equation (for the N bath particles and single Brownian particle) and B.B.G.K.Y. equation (for the single Brownian particle) respectively:

$$\frac{\partial F_{(N,1)}}{\partial t} + \mathcal{H}^{I}_{(N,1)} F_{(N,1)} + \mathcal{H}^{II}_{(N,1)} F_{(N,1)} = 0$$

$\mathcal{H}^{I}_{(N,1)} \downarrow$ 1 ; $\mathcal{H}^{II}_{(N,1)} \downarrow$ $\gamma = \sqrt{\frac{m_b}{m_B}} \ll 1$

$$\frac{\partial F_{(0,1)}}{\partial t} = \mathcal{L} F_{(1,1)} \qquad \text{(III-E-5)}$$

$\mathcal{L} \downarrow$ γ

where

$$\mathcal{H}^{II}_{(N,1)} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,b}}{m_b} \cdot \frac{\partial}{\partial \vec{q}_i^{\,b}} - \sum_{i=1}^{N} \left[\left(\sum_{j=1}^{N} \frac{\partial \phi_{ij}^{bb}}{\partial \vec{q}_i^{\,b}} \right) + \frac{\partial \phi_{i1}^{bB}}{\partial \vec{q}_i^{\,b}} \right] \cdot \frac{\partial}{\partial \vec{p}_i^{\,b}} \qquad \text{(III-E-6)}$$

represents the Hamiltonian operator for the N bath particle interacting with themselves and the Brownian particle

$$\mathcal{H}^{II}_{(N,1)} = \frac{\vec{p}^{B}}{m_B} \cdot \frac{\partial}{\partial \vec{q}^{B}} - \sum_{j=1}^{N} \frac{\partial \phi_{1,j}^{Bb}}{\partial q^{B}} \cdot \frac{\partial}{\partial \vec{p}^{B}}$$

(III-E-7)

denotes the Hamiltonian operator for the Brownian particle interacting with all the bath particles and finally

$$\mathcal{L} = N \int \cdots \int \frac{\partial \phi_{1,1}^{Bb}}{\partial \vec{q}^{B}} \cdot \frac{\partial}{\partial \vec{p}^{B}} \, d\vec{r}_{1,1}^{Bb} \, d\vec{p}^{B}$$

(III-E-8)

represents the mixing term in the B.B.G.K.Y. hiemarchy indicating the interactions between the Brownian particle and the N bath particles. Hence all terms associated with the slow motion of the heavy Brownian particle are assumed much smaller than those related to the fast movement of the light bath particles. Although this casual approach is also inherent in previous studies by Lebowitz-Resibois[9] and others[8][9] we must acknowledge that the range of validity in phase space of any expansion solution based on the above ordering must remain somewhat in doubt.

CHAPTER IV

THE INITIAL VALUE PERTURBATION SCHEME

The preceding chapter, devoted to the nondimensionalization of the governing equations for classical mixtures, has been presented to set the scene, and to establish the mathematical foundations for a subsequent perturbational study of these equations. As a first phase in such a study, this chapter will consider the initial value perturbation scheme, which undoubtably represents one of the simplest methods of truncating the B.B.G.K.Y. hierarchy. In general terms, the initial value perturbation (IVP) scheme involves an expansion of the dependent variable of a governing equation in powers of a small intrinsic parameter and a subsequent solution of the resulting simplified equation through the introduction of some known (or assumed) initial condition(s). The first attempt of applying this scheme to the truncation of the hierarchy was made by Bogoliubov,[12] in 1946, who expediently abandoned it on the grounds that it could only lead to approximate solutions which rapidly diverged in time. Since the (IVP) scheme could not produce well behaved solutions, which adequately described the approach of a given molecular system to an equilibrium state, Bogoliubov subsequently developed an alternate "functional" perturbation method which could

yield, at the lower orders of the expansion, useful kinetic equations governing the single particle distribution $F_1(\vec{q}_1, \vec{p}_1, t)$. As a direct result of the evident inadequacies of the (IVP) scheme, and of Bogoliubov's search for alternate expansion methods, few investigators have reconsidered this method, preferring to devote their effort in developing their own alternate perturbation schemes. This hasty rejection of the (IVP) scheme seems somewhat unfortunate for two very important reasons. On one hand, the lack of a true appreciation of this perturbation method has led to the devisal of alternate schemes containing often unnecessary assumptions and usually displaying a mathematical structure which is far more complex than what is, in fact, needed to suitably truncate the hierarchy. Furthermore, because of these superfluous ingredients, it has become exceedingly difficult to pin-point the exact origin of the divergences plaguing most of these alternate perturbation schemes at the higher orders of the expansions. For these reasons, the present chapter will be completely devoted to a detailed study of the relevant and important features of the very simple (IVP) scheme.

In spite of the very lean research on the use of the (IVP) scheme in the truncation of the B.B.G.K.Y. hierarchy, significant contributions in this area may, nevertheless, be found in the work of Montgomery[38] and Sandri,[25] who have discussed the application of this perturbation method

to uniform "non-dense" and "weakly coupled" systems respectively. The studies presented by these investigators, however, tend to be rather brief and extremely restrictive in their choice of initial conditions. Furthermore, as noted in the previous chapter, Sandri's ordering of terms in the B.B.G.K.Y. hierarchy for weakly coupled gases seems somewhat questionable. Consequently, this chapter proposes to investigate, in much greater detail and scope, the main features of the (IVP) scheme when applied to "non-dense", "weakly coupled" and also "Brownian" systems. Such a comprehensive review of this perturbation method will justify itself in the following chapter of this thesis by the valuable insight it will cast on the development of a simple and concise alternate method of truncating the hierarchy.

A. SIMPLE MATHEMATICAL EXAMPLES

The initial value perturbation scheme represents, generally speaking, one of many methods of extracting approximate solutions from ordinary or partial differential (and integral) equations. Since this method may be applied to equations which bear a much simpler form than the complex B.B.G.K.Y. hierarchy, it would seem advisable to seek extremely simple and illustrative examples which can highlight some of its main features.

As a first example, let us consider the trivial equation:

$$\frac{dx}{dt} = -\varepsilon x \qquad \text{(IV-A-1)}$$

which has also been considered by Su, Frieman and Kruskal[30]. If we assume that $x \ll o[1]$ and $\varepsilon \ll o[1]$, it then follows that the right hand side of this equation remains very small in magnitude. Consequently, one may seek approximate solutions to (IV-A-1) by expanding x in powers of the small parameter ε

i.e., $$x = x^{(0)} + \varepsilon x^{(1)} + \varepsilon^2 x^{(2)} + \cdots \qquad \text{(IV-A-2)}$$

such that by substituting (IV-A-2) into (IV-A-1), one obtains:

$$[\dot{x}^{(0)} + \varepsilon \dot{x}^{(1)} + \varepsilon^2 \dot{x}^{(2)} + \ldots] = -\varepsilon [x^{(0)} + \varepsilon x^{(1)} + \varepsilon^2 x^{(2)} + \ldots]$$

If we now assume that $x^{(i)}$ and $\dot{x}^{(i)}$ are typically of the same order of magnitude for all i

i.e. $$\dot{x}^{(i)} \sim o[\dot{x}^{(k)}] \sim o[x^{(i)}] \sim o[x^{(k)}] \qquad \text{(IV-A-3)}$$

for all $i \neq k$

we may isolate terms of the same order of magnitude by simply collecting terms with the same powers of ε. Doing so, we obtain the equations:

$$\begin{aligned} \dot{x}^{(0)} &= 0 \\ \dot{x}^{(1)} &= -x^{(0)} \\ &\vdots \\ \dot{x}^{(i)} &= -x^{(i-1)} \end{aligned} \qquad \text{(IV-A-4)}$$

The (IVP) scheme consists of solving the above equations in terms of some initial conditions. Imposing that the zeroth order solution $x^{(0)}$ is initially exact,

i.e. $$\begin{aligned} x^{(0)}(0) &= x(0) \equiv x_0 \\ x^{(i)}(0) &= 0 \quad \text{, for } i \geq 1 \end{aligned} \qquad \text{(IV-A-5)}$$

equations (IV-A-4) may be trivially solved to yield

$$X^{(0)}(t) = X_0$$
$$X^{(1)}(t) = -X_0 t$$
$$\vdots$$
$$X^{(i)}(t) = (-1)^i X_0 t^i / i! \qquad \text{(IV-A-6)}$$

such that, substituting back into (IV-A-2), one obtains

$$X(t) \sim X_0 (1 - \varepsilon t + \varepsilon^2 t^2 - \ldots + (-1)^i \frac{\varepsilon^i t^i}{i!} + \ldots) \qquad \text{(IV-A-7)}$$

From equation (IV-A-6), we may easily note that the higher order connections, $\varepsilon^i X^{(i)} (i > 1)$ rapidly diverge in time and eventually dominate the lowest order solution $X^{(0)}$ so as to discredit the earlier assumption (IV-A-3). This behaviour of the (IVP) solutions, which is usually referred to as "secular", clearly prevents one from obtaining, with a finite number of contributing terms, approximate solutions which are well behaved for large values of the independent variable . Nevertheless, for the problem at hand, one may obtain a solution for $X(t)$ by noting that the infinite sum in (IV-A-7) converges for all values of t and simply represents the Maclaurin series expansion for $X = X_0 e^{-\varepsilon t}$ which, naturally, expresses the exact solution to equation (IV-A-1). Unfortunately, the infinite series obtained from a simple (IVP) expansion may not always uniformly converge. For example, consider the following simple equation:

$$\frac{dX}{dt} = -\varepsilon X^2 \qquad \text{(IV-A-8)}$$

One can show without great difficulty, that following the same steps as in the previous example, the (IVP) scheme will yield the infinite series solution

$$x(t) \sim x_0 \sum (-1)^i (x_0 \varepsilon t)^i \qquad \text{(IV-A-9)}$$

which diverges when $t > 1/x_0\varepsilon$. In fact, the only means we have of extracting useful asymptotic information from (IV-A-9) is by noticing that the infinite sum in fact represents the Maclaurin series expansion for

$$x(t) = x_0 / \{1 + x_0 \varepsilon t\}$$

which, once again, expresses the exact solution to the problem at hand. We note, however, that such an identification of an (IVP) series with that of a well known and well behaved function remains, for more complex equations, an extremely difficult and often impossible task.[1] Consider, as a final example, the following "time delay" equation

$$\frac{dx}{dt} = -\varepsilon x(t-\tau) \qquad \text{(IV-A-10)}$$

which has an exact solution, provided that the past history of $x(t)$ is known for $\tau < t < 0$. Expanding (IV-A-10) in the power series (IV-A-2) and collecting, as in the previous examples, powers of ε, we obtain the following set of equations:

1 This view has also been expressed by Su, Frieman and and Kruskal [30].

$$\dot{X}^{(0)} = 0$$

$$\dot{X}^{(1)} = -X^{(0)}(t-\tau)$$

$$\dot{X}^{(2)} = -X^{(1)}(t-\tau)$$

$$\vdots$$

$$\dot{X}^{(k)} = -X^{(k-1)}(t-\tau)$$

(IV-A-11)

which, as usual, shall be solved by requiring the zeroth order solution to be initially exact:

i.e.

$$X^{(0)}(0) = X(0) = X_0$$

$$X^{(k)}(0) = 0 \qquad k \geq 1$$

Successively solving equations (IV-A-11) with the above initial conditions, we then obtain for $X^{(k)}(t)$, $k=1,\ldots 4$ the following expressions:

$$X^{(0)} = X_0$$

$$X^{(1)} = -X_0 t$$

$$X^{(2)} = X_0 t\left(\frac{t}{2} - \tau\right)$$

$$X^{(3)} = -\frac{X_0 t}{2}\left(\frac{t^2}{3} - 2\tau t + 3\tau^2\right)$$

$$X^{(4)} = \frac{X_0 t}{6}\left(\frac{t^3}{4} - 3\tau t^2 + 12\tau^2 t - 16\tau^3\right)$$

such that, to the fourth order of ε, one obtains for $x(t)$:

$$X(t) = x_0 \left[1 - \varepsilon t \left(1 + \varepsilon\tau + \frac{3}{2}\varepsilon^2\tau^2 + \frac{8}{3}\varepsilon^3\tau^3 \right) + \frac{\varepsilon^2 t^2}{2}\left(1 + 2\varepsilon\tau + 4\varepsilon^2\tau^2 \right) - \frac{\varepsilon^3 t^3}{6}\left(1 + 3\varepsilon\tau \right) + \frac{\varepsilon^4 t^4}{24} \right]$$

The above expression once again illustrates the secular nature of the (IVP) perturbation solutions. Furthermore, we note, from the progressive complexity of the higher order solutions, the extreme difficulty (and perhaps impossibility) of identifying the infinite series emerging from such an expression with that of a well behaved and well known function.

The foregoing simple mathematical examples have illustrated some of the main features and downfalls of the (IVP) scheme. In particular, the frequent secular behavior of this type of expansion, which prohibits well behaved approximate solutions to be extracted using a finite number of terms, should be kept in mind. Furthermore, the difficulty of identifying the infinite series resulting from such an expansion in complex equations should be emphasized since this burden will become a natural handicap in the truncation of the relatively complex B.B.G.K.Y. hierarchy.

B. APPLICATION OF THE (IVP) SCHEME TO THE TRUNCATION OF THE B.B.G.K.Y. HIERARCHY

The present section will investigate the implications of the above discussions on the truncation of the B.B.G.K.Y. hierarchy via an initial value perturbation approach. To avoid sacrificing conceptual clarity for mathematical generality (and complexity), we shall restrict our considerations to very simple physical systems. These will include:

a) a simple uniform non-dense gas,

b) a simple uniform weakly coupled gas, and

c) a system consisting of a single large Brownian particle in a uniform bath of light bath particles.

a) Simple Uniform Non-Dense Gas

A non-dense gas, we recall, characterizes itself by the very low percentage of particles interacting at any given time. A simple uniform system, furthermore, distinguishes itself by the presence of a single type of particle and the independence of the one particle distribution F_1 on the coordinate $\bar{q}_i$. For such a system one may easily reduce the B.B.G.K.Y. hierarchy (III-C-52), with the help of the assumptions and results in the subsection (III-D-a) to the simpler equation

$$\frac{\partial F_s^*}{\partial t^*} + \mathcal{H}_s^* F_s^* = {}^*\varepsilon_2 \mathcal{L}_s^* F_{s+1}^* \qquad \text{(IV-B-1)}$$

where,(in this subsection):

$$\mathcal{H}_s^* \equiv {}^{\mathcal{I}}\mathcal{K}_s \sum_{i=1}^{s} \vec{p}_i^{\,*} \cdot \frac{\partial}{\partial \vec{q}_i^{\,*}} - {}^{\mathcal{I}}\mathcal{R} \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial {}^{\mathcal{I}}\phi_{ij}^{*}}{\partial \vec{q}_i^{\,*}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,*}}$$

$$\mathcal{L}_s^* \equiv {}^{\mathcal{I}}\mathcal{R}\, \mu_{eq} \sum_{i=1}^{s} \int\int \frac{\partial {}^{\mathcal{I}}\phi_{i,s+1}^{*}}{\partial \vec{q}_i^{\,*}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,*}} \, d\,{}^{\mathcal{I}}\vec{r}_{i,s+1}^{\,*} \, d\,\vec{p}_{s+1}^{\,*} \qquad \text{(IV-B-2)}^{1}$$

and:

$$\mathcal{K}_s \;\begin{cases} \gg O[m\bar{r}^9] \\ \ll O[1] \end{cases}$$

$${}^{\mathcal{I}}\mathcal{R} \;\begin{cases} \gg O[m\bar{r}^3] \\ \ll O[1] \end{cases}$$

$${}^{\mathcal{I}}\mathcal{E}_2 \;\ll O[1]$$

Equation (IV-B-1), we recall, is properly ordered on the average over the phase space volume

$$V_s^* \equiv V_s / (\mathcal{R}_s \sqrt{mkT})^{3s}$$

where

$$V_s \equiv V_c^s (mkT)^{3s/2}, \quad \mathcal{R}_s \sim O\left[\frac{1}{\bar{r}}\left(\frac{\bar{r}}{r_c}\right)^9\right] \text{ FOR } s>1, \quad \gg O[r_c] \text{ FOR } s=1$$

and $V_c \equiv \frac{4}{3}\pi r_c^9 \ll O[m^{-1}]$

Consequently, one may attempt, within this volume, to truncate this hierarchy by expanding F_s^* in powers of the small intrinsic parameter ${}^{\mathcal{I}}\mathcal{E}_2$.

[1] No external field term has been included in $\mathcal{H}_s$ since it would forcibly create spatial nonuniformities within the system. This omission of an external force will also prevail in the remaining examples of this chapter.

i.e.

$$F_s^* = F_s^{(0)*} + {}^{I}\varepsilon_2 F_s^{(1)*} + ({}^{I}\varepsilon_2)^2 F_s^{(2)*} + \cdots \qquad \text{(IV-B-3)}$$

Before doing so, however, it would seem desirable, for the sake of mathematical convenience, to rewrite (IV-B-1) in the following dimensional form:

$$\frac{\partial F_s}{\partial t} + \mathcal{H}_s F_s = \varepsilon \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-4)}$$

where

$$\mathcal{H}_s \equiv \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} - \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}$$

$$\mathcal{L}_s \equiv (N-s) \sum_{i=1}^{s} \int\int \frac{\partial \phi_{i,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \, d\vec{r}_{i,s+1} \, d\vec{p}_{s+1} \qquad \text{(IV-B-5)}$$

and where $\varepsilon (\equiv 1)$ is simply a label parameter denoting the small term which will be neglected at the zeroth order of the expansion. One easily notes that the expansion (IV-B-3) of F_s^* within (IV-B-1) is equivalent to the following expansion of F_s

$$F_s = F_s^{(0)} + \varepsilon F_s^{(1)} + \varepsilon^2 F_s^{(2)} + \cdots \qquad \text{(IV-B-6)}$$

within (IV-B-4), provided one collects powers of ε when substituting (IV-B-6) into (IV-B-4). Proceeding as such, one then obtains, after collection of terms, the following set of equations:

$$\frac{\partial F_s^{(0)}}{\partial t} + \mathcal{H}_s F_s^{(0)} = 0$$

$$\frac{\partial F_s^{(1)}}{\partial t} + \mathcal{H}_s F_s^{(1)} = \mathcal{L}_s F_{s+1}^{(0)}$$

$$\vdots$$

$$\frac{\partial F_s^{(k)}}{\partial t} + \mathcal{H}_s F_s^{(k)} = \mathcal{L}_s F_{s+1}^{(k-1)}$$

(IV-B-7)

We shall now seek solutions to the above equations by imposing an initial exactness on the zeroth order solution; i.e.

$$F_s^{(0)}(\vec{X}_s, 0) = F_s(\vec{X}_s, 0)$$

$$F_s^{(k)}(\vec{X}_s, 0) = 0 \qquad k \geq 1 \qquad \text{(IV-B-8)}$$

Noting that for a spatially uniform gas

$$\mathcal{H}_1 F_1 = 0$$

we may easily integrate equations (IV-B-7), for $s = 1$, and obtain:

$$F_1^{(0)}(\vec{p}_1, t) = F_1^{(0)}(\vec{p}_1, 0)$$

$$F_1^{(1)}(\vec{p}_1, t) = \int_0^t \mathcal{L}_1 F_2^{(0)}(\vec{X}_2, t')\, dt'$$

$$\vdots$$

$$F_1^{(k)}(\vec{p}_1, t) = \int_0^t \mathcal{L}_1 F_2^{(k-1)}(\vec{X}_2, t')\, dt'$$

(IV-B-9)

Solutions for $F_s^{(k)}(X_s, t)$ $(s \geq 2)$ may also be derived by integrating equations (IV-B-7) after operating both sides by the forward streaming operator $e^{\mathcal{H}_s t}$, and recalling from

Chapter II that:

$$\ell^{\mathcal{H}_s t}\,\mathcal{H}_s = \frac{\partial}{\partial t}\,\ell^{\mathcal{H}_s t}$$

After integration, we then obtain the solutions

$$F_s^{(0)}(\vec{x}_s, t) = \ell^{-\mathcal{H}_s t}\, F_s(x_s, 0)$$

$$F_s^{(1)}(\vec{x}_s t) = \int_0^t \ell^{-\mathcal{H}_s(t-t')}\,\mathcal{L}_s\, F_{s+1}^{(0)}(\vec{x}_{s+1}, 0)\, dt'$$

$$\vdots$$

$$F_s^{(k)}(\vec{x}_s t) = \int_0^t \ell^{-\mathcal{H}_s(t-t')}\,\mathcal{L}_s\, F_{s+1}^{(k-1)}(\vec{x}_{s+1}, 0)\, dt' \qquad \text{(IV-B-10)}$$

Let us now investigate the asymptotic behavior of the above solutions when $s=1$. The first time dependent solution is:

$$F_1^{(1)}(\vec{p}_i, t) = \int_0^t \mathcal{L}_1 F_2^{(0)}(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j, 0)\, dt'$$

which, using (IV-B-5) and (IV-B-10), may also be written as:

$$F_1^{(1)}(\vec{p}_i, t) = \int_0^t \iint \frac{\partial \phi_{ij}(|\vec{r}_{ij}|)}{\partial \vec{q}_i}\, F_2^{(0)}(\vec{R}_{ij}(t'), \vec{P}_i(t'), \vec{P}_j(t'), 0)\, d\vec{r}_{ij}\, d\vec{p}_j\, dt' \qquad \text{(IV-B-11)}$$

where:

$$\vec{R}_{ij}(t) \equiv \ell^{-\mathcal{H}_2(i,j)t}\,\vec{r}_{ij}$$

and

$$\vec{P}_i(t) \equiv \ell^{-\mathcal{H}_2(i,j)t}\,\vec{p}_i$$

$$\vec{P}_j(t) \equiv \ell^{-\mathcal{H}_2(i,j)t}\,\vec{p}_j \qquad \text{(IV-B-12)}$$

represent, as illustrated in Figure IV-1, the separation and momenta of molecules i and j after these have been streamed

back, in time t , under their mutual interaction.[1]

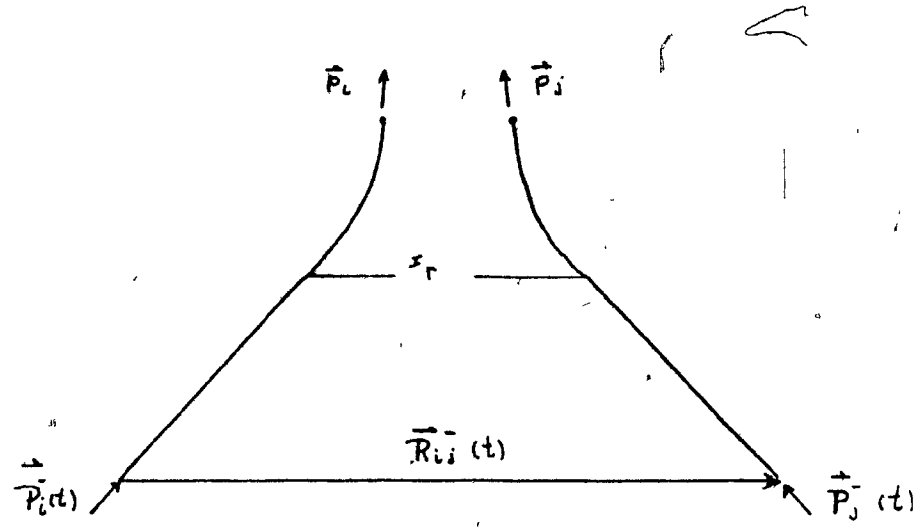


Figure IV-1

We note that the only contribution to the integration over $\vec{r}_{ij}$ in (IV-B-11), lies within the region where $|\vec{r}_{ij}|$ is smaller than the interaction radius r_r . Now, if we maintain the assumption of the previous chapter that the interaction potential is purely repulsive:

i.e. $\frac{\partial \phi_{ij}}{\partial |\vec{r}_{ij}|} < 0$ for $0 < r_{ij} \leq r_r$

and if we further assume that $\left|\frac{\partial \phi_{ij}}{\partial |\vec{r}_{ij}|}\right|$ [2] has a finite magnitude for $0 < r_{ij} \leq r_r$, it then follows that for all $|\vec{r}_{ij}|$

[1] Expressed otherwise, $\vec{R}_{ij}(t)$, $\vec{P}_i(t)$ and $\vec{P}_j(t)$ represent the initial separation and momenta of particles i and j which will lead to, after a transit time t , a separation $\vec{r}_{ij}$ and momenta $\vec{P}_i$ and $\vec{P}_j$.

[2] Since these assumptions imply that $\left|\frac{\partial \phi_{ij}}{\partial \vec{q}_i}\right|$ is undefined when $\vec{r}_{ij} = 0$, we shall omit this singular point in the integration over $\vec{r}_{ij}$ in (IV-B-11).

within this domain, and for all possible values of $\vec{p}_i$ and $\vec{p}_j$, there exists a finite time $\tau_o(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$ such that

$$\vec{R}_{ij}(t) > {}^{I}r \qquad \text{for} \quad t > \tau_o(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$$

Since the particles conserve their individual momentum when they are outside each other's interaction range; we then conclude that:

$$\vec{p}_i^{-}(t) = \vec{p}_i(\infty)$$
$$\vec{p}_j^{-}(t) = \vec{p}_j(\infty) \qquad \text{(IV-B-13)}$$

for $t > \tau_o(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$. Consequently, the solution for $F_1^{(1)}(\vec{p}_i, t)$, as given by (IV-B-13), may also be written for t larger than the maximum value of $\tau_o(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$, as:[1]

$$F_1^{(1)}(\vec{p}_i, t) = (N-1)\iint \frac{\partial \phi_{ij}}{\partial \vec{q}_i}\left[\int_o^{\tau_o} \frac{\partial F_2^{(\infty)}(R_{ij}(t'), p_i(t'), p_j(t'), 0)}{\partial \vec{p}_i}\, dt' + \int_{\tau_o}^{t} \frac{\partial F_2(R_{ij}(t'), p_i(\infty), p_j(\infty), 0)}{\partial \vec{p}_i}\, dt'\right] d\vec{r}_{ij}\, d\vec{p}_j$$

$$t > \max \tau_o(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j) \qquad \text{(V-B-14)}$$

Furthermore, assuming all initial statistical correlations to have a finite range r_+, with $r_+ > {}^{I}r$, we may also define a time $\tau_+(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$ such that, as illustrated in Figure III-2:

$$|\vec{R}_{ij}(t)| > r_+ > {}^{I}r$$

[1] This maximization is to be performed over the range $o < |\vec{r}_{ij}| < {}^{I}r$ and over all possible values of $\vec{p}_i$ and $\vec{p}_j$.

for $t > \tau_+(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$

and $|\vec{r}_{ij}| < {}^{I}r$

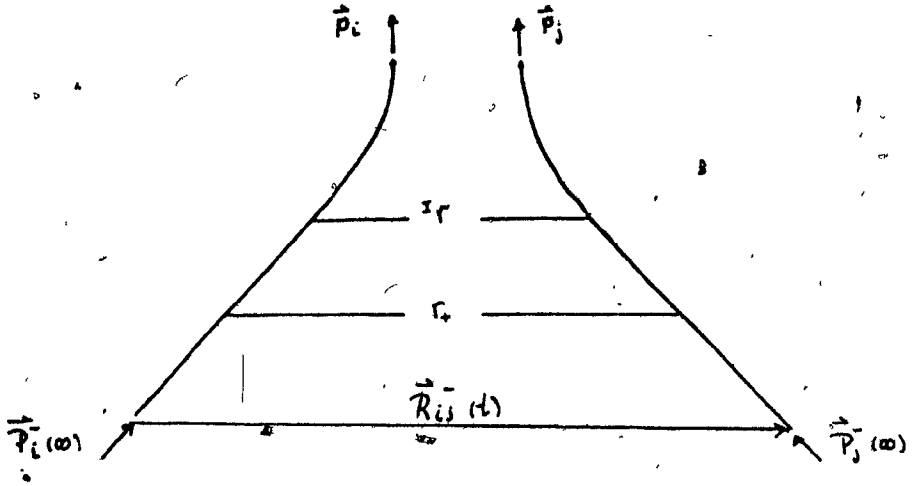


Figure III-2

Consequently for $|\vec{r}_{ij}| < {}^{I}r$

and $t > \tau_+(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j)$

we have

$$F_2(\vec{R}_{ij}(t), \vec{p}_i(\infty), \vec{p}_j(\infty)) = F_1(\vec{p}_i(\infty), 0)\, F_1(\vec{p}_j(\infty), 0) \qquad \text{(IV-B-15)}$$

such that, for $t > \max \tau_+$, we may rewrite equation (IV-B-14) as:

$$F_1^{(1)}(\vec{p}_i, t) = (N-1)\int\int \frac{\partial^{I}\phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \left[\int_0^{\tau_0} F_2(\vec{R}_{ij}(t'), \vec{p}_i(t'), \vec{p}_j(t'), 0)\, dt' \right.$$

$$+ \int_{\tau_0}^{\tau_+} F_2\left(R_{ij}(t'), \vec{P}_i(\infty), \vec{P}_j(\infty), 0\right) dt'$$

$$+ (t-\tau_+)\; F_2(\vec{P}_i(\infty), 0)\, F_1(\vec{P}_j(\infty), 0)\, 0 \Big]\, d\vec{r}_{ij}\, d\vec{p}_j$$

It becomes evident from the above expression that for $t > \max \tau_+$ the solution for $F_1^{(1)}(\vec{p}_i, t)$ will diverge at a constant rate such that, for $t \gg \max \tau_+$

$$F_1^{(1)}(\vec{p}_i, t) \sim (N-1)t \int\int \frac{\partial^2 \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} F_1(\vec{P}_i(\infty), 0)\, F_1(\vec{P}_j(\infty), 0)\, d\vec{r}_{ij}\, d\vec{p}_j$$

(IV-B-16)[1]

Consequently, it also follows that this solution will eventually dominate the lower order solution $F_1^{(0)}(\vec{p}_i, t)$, given by (III-B-9) thus establishing the "secular" behavior of the IVP expansion.

The above results, which are consistent with the simple examples of the previous section, seem also to agree with previous intuitive arguments given by Bogoliubov[12] and a simple analysis given by Montgomery[38] using the very specialized initial conditions.

$$F_2(\vec{q}_i, \vec{p}_i, \vec{q}_j, \vec{p}_j, 0) = F_1(\vec{p}_i, 0)\, F_1(\vec{p}_j, 0)$$

[1] One may easily verify that this result would also emerge if one assumed the initial correlation range r_+ to be smaller than r.

The present and previous analyses, indeed, seem to establish the limited value of the (IVP) scheme in producing well behaved solutions for the one particle distribution $F_1(\vec{p}_1,t)$ This is clearly the case if the expansion is carried out to a finite order ε^m of the expansion parameter ε. Furthermore, because of the progressive complexity of the higher order solutions in (IV-B-10), one can readily dismiss any attempt of obtaining an infinite sequence which can be easily identified. For these reasons, most researchers have completely disregarded the (IVP) scheme to seek alternate expansion approaches, which could divulge some information on the approach of a uniform non-dense system to an equilibrium state. Such a hasty dismissal of the (IVP) scheme seems indeed regrettable since this method, in spite of its obvious downfalls, can offer much insight on the development of a simple alternate scheme. Consider, for example, equation (IV-B-16) which describes the asymptotic behavior of the first order (IVP) solution for $F_1^{(1)}(\vec{p}_1,t)$. From this expression we conclude that for $t \gg \max \tau_+$

$$\frac{\partial F_1^{(1)}}{\partial t} = (N-1) \int\int \frac{\partial \phi_{1j}}{\partial \vec{q}_1} \cdot \frac{\partial F_1(\vec{p}_1(\infty),0)\, F_1(\vec{p}_j(\infty),0)}{\partial \vec{p}_1}\, d\vec{r}_{1j}\, d\vec{p}_j \qquad \text{(IV-B-17)}$$

Now, after some mathematical manipulation, this equation may be reduced to the following form:[1]

[1] See Appendix I for details.

$$\frac{\partial f_1}{\partial t}\bigg|_{coll} = J_B\left(f_1(\vec{P}_1, 0)\right) \qquad \text{(IV-B-18)}$$

where $f_1(\vec{P}_1, t) = N F_1(\vec{P}_1, t)$ (IV-B-19)

$$J_B\left(f_1(P_1, 0)\right) \equiv \int_0^{2\pi}\int_0^{\infty} b\,|\vec{g}_{12}|\left[f_2(\vec{P}_1', 0)\, f_1(\vec{P}_2', 0) - f_1(\vec{P}_1, 0)\, f_1(\vec{P}_2, 0)\right] db\, d\phi\, d\vec{P}_2 \qquad \text{(IV-B-20)}$$

and where $\vec{P}_1'$, $\vec{P}_2'$ represent the momenta of particles 1 and 2 after colliding with a relative approach velocity $\vec{g}_{12} \equiv \frac{\vec{P}_1 - \vec{P}_2}{m}$; the variables b and ϕ, as illustrated in Figure IV-3, simply denote (along with a third variable, z) cylindrical coordinates describing the relative position of the two molecules.

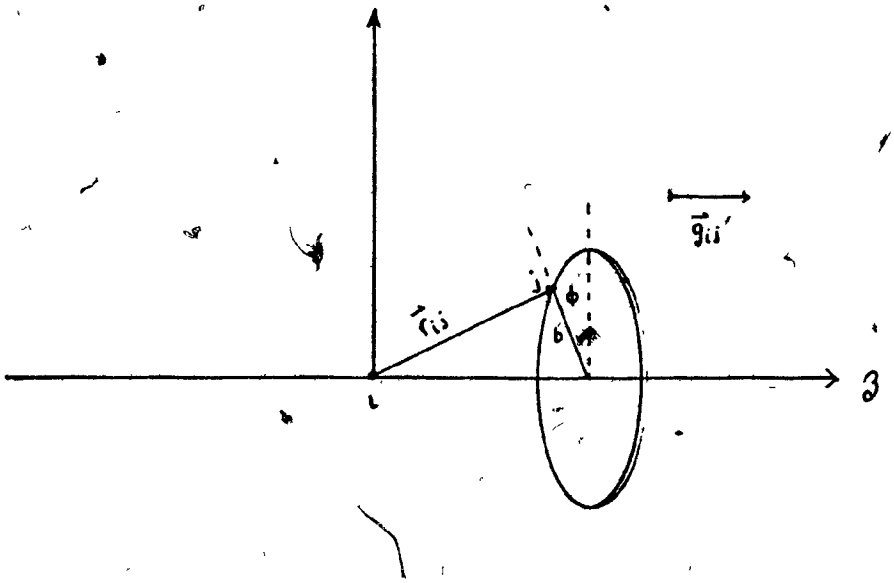


Figure IV-3

Combining (IV-B-18) and (IV-B-19) with the zeroth order solution in (IV-B-9) and the expansion (IV-B-6), one then obtains the approximate equation

$$\frac{\partial f_1}{\partial t} \simeq N \left[\frac{\partial F_1^{(0)}}{\partial t} + \varepsilon \frac{\partial F_1^{(1)}}{\partial t} \right] \simeq J_B \left(f_1(\vec{p}_1, 0) \right) \qquad \text{(IV-B-21)}$$

This result seems highly reminiscent of the well known, and highly useful, kinetic equation:

$$\frac{\partial f_1}{\partial t} = J_B \left(f_1(\vec{p}_1, t) \right) \qquad \text{(IV-B-22)}$$

derived by Boltzmann, using intuitive arguments, during the late nineteenth century, and rederived by many others using various perturbation schemes. Evidently, the only difference between equations (IV-B-21) and (IV-B-22) lies in the time dependence of $J_B(f_1(\vec{p}_1, t))$ in the latter and the time independence of $J_B(f_1(\vec{p}_1, 0))$ in the former. This minute, yet crucial, difference which distinguishes the secular behavior of the solution of (IV-B-21) from the well behaved solutions of Boltzmann's equation seems to pinpoint exactly the dominant feature and the ultimate deficiency of the initial value perturbation scheme when applied to the truncation of the B.B.G.K.Y. hierarchy for a non-dense gas. In fact, this seemingly "uncanny" resemblance between equations (IV-B-21) and (IV-B-22) will play an important role in the forthcoming development of a simple alternate perturbation scheme.

b) Simple Uniform Weakly Coupled SYSTEM

The (IVP) scheme, used in the above subsection to truncate the hierarchy for a non-dense gas, may also be applied, without considerable modifications, to a simple uniform weakly coupled system. The latter, we recall, distinguishes itself by the infinitesimal range of its strong interaction potential ${}^{I}\phi_{ij}$, and the moderate range of its weak potential ${}^{II}\phi_{ij}$. Proceeding as in the previous subsection, we may, for this system of molecules, reduce the dimensionless hierarchy (III-C-52) to the less cumbersome form:

$$\frac{\partial F_s^*}{\partial t^*} + {}^{II}\varepsilon_1 \, \mathcal{H}_s^* F_s^* = {}^{II}\varepsilon_1 \, \mathcal{L}_s^* F_{s+1}^* \qquad \text{(IV-B-23)}$$

where, in this subsection,

$$\mathcal{H}_s^* \equiv -\frac{\mathcal{K}_s}{{}^{II}\varepsilon_1} \sum_{i=1}^{s} \vec{p}_i^{\,*} \cdot \frac{\partial}{\partial \vec{q}_i^{\,*}} - {}^{II}\mathcal{R} \sum_{i=1}^{s} \sum_{j=1}^{s} \frac{\partial {}^{II}\phi_{ij}^*}{\partial \vec{q}_i^{\,*}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,*}}$$

$$\mathcal{L}_s^* \equiv {}^{I}\varepsilon_2 \, {}^{II}\mathcal{R} \, \mu_{eq} \sum_{i=1}^{s} \iint \frac{\partial {}^{II}\phi_{i\,s+1}^*}{\partial \vec{q}_i^{\,*}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,*}} \, d{}^{II}\vec{r}_{i\,s+1}^{\,*} \, d\vec{p}_{s+1}^{\,*} \qquad \text{(IV-B-24)}$$

and

$${}^{II}\varepsilon_1 \ll 1$$

$$\mathcal{K}_s \sim O\left[{}^{II}\varepsilon_1\right]$$

$$\mathcal{R} \sim o[1]$$

Since equation (IV-B-23) is properly ordered over the phase volume $V_s^* = V_s \Big/ (\sqrt{mKT}\ \mathcal{R}_s)^{3s}$

where $V_s = V_c^s\ (mKT)^{3s/2}$

$$V_c \sim o[\pi r^3]$$

$$\mathcal{R}_i \sim o\left[\frac{\pi r}{\varepsilon_i}\right]$$

we may attempt, within this volume, to truncate the hierarchy by expanding ε_i in powers of the small intrinsic parameter

i.e. $$F_s^* = F_s^{(0)*} + \varepsilon_1 F_s^{(1)} + \varepsilon_1^2 F_s^{(2)} + \ldots \qquad \text{(IV-B-25)}$$

As in the non-dense case, we shall find it convenient to first rewrite the hierarchy in the dimensional form:

$$\frac{\partial F_s}{\partial t} + \varepsilon \mathcal{H}_s F_s = \varepsilon \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-26)}$$

where

$$\mathcal{H}_s \equiv \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} - \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}$$

$$\mathcal{L}_s \equiv (N-s) \sum_{i=1}^{s} \iint \frac{\partial^{II} \phi_{i\,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}\, d\vec{r}_{i\,s+1}\, d\vec{p}_{s+1} \qquad \text{(IV-B-27)}$$

and where ($\varepsilon \equiv 1$) , once again, is the label parameter. We shall now proceed with the expansion

$$F_s = F_s^{(0)} + \varepsilon F_s^{(1)} + \varepsilon^2 F_s^{(2)} + \ldots$$

(IV-B-28)

in (IV-B-26), which, we recall, is equivalent to the expansion (IV-B-25) in (IV-B-23), provided we collect powers of ε in (IV-B-26). Proceeding as in the non-dense case, we obtain, after collection of terms, the following equations:

$$\frac{\partial F_s^{(0)}}{\partial t} = 0$$

$$\frac{\partial F_s^{(1)}}{\partial t} = -\mathcal{H}_s F_s^{(0)} + \mathcal{L}_s F_{s+1}^{(0)}$$

$$\frac{\partial F_s^{(k)}}{\partial t} = -\mathcal{H}_s F_s^{(k-1)} + \mathcal{L}_s F_{s+1}^{(k-1)}$$

(IV-B-29)

Imposing, as usual, the initial conditions

$$F_s^{(0)}(\vec{X}_s, 0) = F_s(\vec{x}_s, 0)$$

$$F_s^{(k)}(\vec{X}_s, 0) = 0 \qquad k \geq 1$$

(IV-B-30)

we may then easily integrate equations (IV-B-29), so as to obtain the following solutions:

$$F_s^{(0)}(\vec{X}_s, t) = F_s(X_s, 0)$$

$$F_s^{(1)}(\vec{X}_s, t) = \int_0^t \left[-\mathcal{H}_s F_s^{(0)}(\vec{x}_s, t') + \mathcal{L}_s F_{s+1}^{(0)}(\vec{X}_{s+1}, t') \right] dt'$$

$$\vdots$$

$$F_s^{(k)}(\vec{x}_s, t) = \int_0^t \left[-\mathcal{H}_s F_s^{(k-1)}(x_s t') + \mathcal{L}_s F_{s+1}^{(k-1)}(\vec{x}_{s+1}, t') \right] dt'$$

(IV-B-31)

Let us now investigate the nature of these solutions when $\delta = 1$. For this special case we obtain, at the zeroth order, the time independent solution:

$$F_1^{(0)}(\vec{p}_i, t) = F_1(\vec{p}_i, 0) \qquad \text{(IV-B-32)}$$

Furthermore, since

$$\mathcal{H}_1 F_1(\vec{p}_i, t) = 0$$

the first order solution reduces to:

$$\left.\begin{aligned} F_1^{(1)}(\vec{p}_i, t) &= \int_0^t \mathcal{L}_1 F_2^{(0)}(\vec{x}_2, t')\, dt' \\ &= \mathcal{L}_1 F_2(\vec{x}_2, 0)\, t \end{aligned}\right\} \qquad \text{(IV-B-33)}$$

Consequently, if

$$\mathcal{L}_2 F_2(\vec{x}_2, 0) \equiv (N-2) \iint \frac{\partial^2 \phi_{ij}}{\partial \vec{q}_i \cdot \partial \vec{p}_i} \cdot \frac{\partial F_2(\vec{r}_{ij}, \vec{p}_i, \vec{p}_j, 0)}{\partial \vec{p}_i}\, d\vec{r}_{ij}\, d\vec{p}_j$$

does not vanish, the first order solution diverges at a constant rate and will eventually dominate the zeroth order solution, thus introducing a secular behavior to the expansion. If, on the other hand, $\mathcal{L}_2 F_2(\vec{x}_2, 0)$ vanishes, which, for example is the case if the particles are initially free of statistical correlations,

i.e. $$F_s(\vec{x}_s, 0) = \prod_{i=1}^{s} F_1(\vec{p}_i, 0) \qquad \text{(IV-B-34)}$$

we then obtain the trivial solution

$$F_1(\vec{p}_i, t) = 0$$

One may show, however, from the second equation in (IV-B-31) (and from the definition of $\mathcal{H}_s$ and $\mathcal{L}_s$) that, for such an initially correlation free gas, the solution for $F_2^{(1)}(\vec{x}_2, t)$

will itself diverge at the following rate:

$$F_2^{(1)}(\vec{X}_2,t) = \frac{\partial \phi_{ij}}{\partial \vec{q}_i}\cdot\left[F_1(\vec{p}_i,0)\frac{\partial F_1(\vec{p}_j,0)}{\partial \vec{p}_j} + F_1(\vec{p}_j,0)\frac{\partial F_1(\vec{p}_i,0)}{\partial \vec{p}_i}\right] t$$

The above results seem to reinforce, once more, the views of the previous investigators on the inadequacy of the (IVP) scheme in yielding useful approximate solutions to the B.B.G.K.Y. hierarchy. We hasten to add, however, that the above analysis of the uniform weakly coupled gas, diverges considerably from a previous (IVP) investigation of a similar system by G. Sandri. Sandri, as mentioned in the previous chapter of this thesis, has considered the problem at hand from a completely different approach by using the following dimensionless equation as a starting point:

$$\frac{\partial F_s^*}{\partial t^*} + K_s^* F_s^* + \varepsilon_1 I_s^* F_s^* = \varepsilon_1\varepsilon_2 L_s^* F_{s+1}^* \qquad \text{(IV-B-35)}$$

where

$$K_s^* = \sum_{i=1}^{s} \vec{p}_i^{\,*}\cdot\frac{\partial}{\partial \vec{q}_i^{\,*}}$$

$$I_s^* = -\sum_{j=1}^{s}\sum_{i=1}^{s}\frac{\partial \phi_{ij}^*}{\partial \vec{q}_i^{\,*}}\cdot\frac{\partial}{\partial \vec{p}_i^{\,*}}$$

$$L_s^* = \sum_{i=1}^{s}\iint \frac{\partial \phi_{i,s+1}^*}{\partial \vec{q}_i^{\,*}}\cdot\frac{\partial}{\partial \vec{p}_i^{\,*}}\, d\vec{q}_{s+1}^{\,*}\, d\vec{p}_{s+1}^{\,*} \qquad \text{(IV-B-36)}$$

and by expanding F_s^* in powers of the small coupling parameter ε_1. Such an approach, which is equivalent to expanding F_s

in powers of the label parameter ε in the following dimensional form of the hierarchy:

$$\frac{\partial F_s}{\partial t} + K_s F_s + \varepsilon I_s F_s = \varepsilon L_s F_{s+1} \qquad \text{(IV-B-37)}$$

where

$$K_s = \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i}$$

$$I_s = \sum_{j=1}^{s} \sum_{i=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}$$

$$L_s = (N-s) \sum_{i=1}^{s} \int\int \frac{\partial \phi_{i\,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \, d\vec{r}_{i\,s+1} \, d\vec{p}_{s+1} \qquad \text{(IV-B-38)}$$

differs from our own analysis based on equation (IV-B-26) by the assignment of a much smaller magnitude to the interaction term $I_s F_s$ than to the momentum streaming term $K_s F_s$. This peculiar ordering of terms in the hierarchy, which emerges as a direct consequence of the different set of characteristic quantities chosen by Sandri in his nondimensionalization of the hierarchy, must naturally result in perturbation solutions which differ drastically from those derived in the present study. Furthermore, in light of the detailed arguments given in the previous chapter with regard to the dimensional analysis of Sandri for a uniform weakly coupled gas, one may justifiably question his ordering of terms on the grounds that, when such a gas approaches a state of equilibrium, the weak potential ϕ_{ij} in the interaction

term $I_s F_s$ of the dimensional equation (IV-B-37) will eventually cause correspondingly weak correlations in F_s which, in turn, will result in small gradients $\frac{\partial F_s}{\partial \vec{q}_i}$ for $s \gg 1$. Hence, following the analysis of the previous chapter, one should have in (IV-B-36)

$$K_s F_s \equiv \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i} \sim O\left[\sum_{i=1}^{s} \sum_{j=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s}{\partial \vec{p}_i} \right] = O\left[I_s F_s \right]$$

Consequently, the expansion parameter ϵ should, on the left hand side of (III-B-37), accompany not only $I_s F_s$, as suggested by Sandri, but should also reside with $K_s F_s$. Sandri's initial value perturbation solutions furthermore seem even less plausible due to his choice of the very special initial conditions

$$F_s(\vec{X}_s, 0) = \prod_{i=1}^{s} F_1(\vec{p}_i, 0)$$

which, we recall, presume that the particles are initially completely uncorrelated. Clearly, if one substitutes these initial conditions into (IV-B-37), one immediately notes in the spatially uniform case the vanishing of the momentum and mixing terms $K_s F_s$ and $L_s F_{s+1}$. Since $I_s F_s$ will not generally vanish with these initial conditions it then follows that the latter are completely inconsistent with Sandri's assumption that $K_s F_s$ is much larger in magnitude than $I_s F_s$.

Before closing the present discussion, it would seem worthwhile to note that many of the inconsistencies, which

emerge from Sandri's analysis of the weakly coupled system (and which have been emphasized here because of their relevance to future discussions concerning this system), stem from his somewhat casual approach of nondimensionalizing the hierarchy with a set of apparently physically plausible characteristic quantities, and expanding F_s^* within the resulting dimensionless equations in powers of whatever small intrinsic parameters that emerge. Proceeding in this manner, without verifying, a priori or a posteriori, that these parameters in fact dictate the relative magnitude of the various terms in these equations, represents, as emphasized in the previous chapter of the present thesis, a very risky approach.

c) Brownian Mixture

As a final example of the application of the (IVP) scheme to the truncation of the B.B.G.K.Y. hierarchy, this section will consider a very simple Brownian mixture consisting of a single heavy Brownian particle in a uniform bath of identical light bath particles. We shall further restrict ourselves, for the sake of mathematical simplicity, to the special case where the Brownian particles' probability distribution is uniform in physical space. Denoting as $F_{(s,1)}$ the joint probability distribution for the s bath particle and the single Brownian particle, and employing the superscript B to denote the Brownian particle and superscript b to identify a bath particle, we may write the B.B.G.K.Y.

hierarchy (III-C-52) for $F_{\{o,l\}}(\vec{p}_i^{\,\beta}, t)$ and the Liouville equiation (III-C-37) for $F_{\{N,l\}}(\vec{X}_{\{N,l\}}, t)$ in the following form:

$$\frac{\partial F^*_{\{o,l\}}}{\partial t^*}(\vec{p}_i^{\,\beta *}, t^*) = \gamma \, \mathcal{L}^*_{\{o,l\}} F^*_{\{l,l\}} \qquad \text{(IV-B-39)}$$

where:

$$\mathcal{L}^*_{\{o,l\}} = \sum_{K=I}^{II} {}^{K}\mathcal{E}_2^{\beta b} \, {}^{K}\mathcal{R}^{\beta b} \mu_{eq} \iint \frac{\partial {}^{K}\phi^{\beta b *}}{\partial \vec{q}^{\,\beta *}} \cdot \frac{\partial}{\partial \vec{p}^{\,\beta *}} \, d\vec{r}^{\,K\,\beta b *}_{i,l} \, d\vec{p}_i^{\,b *} \qquad \text{(IV-B-40)}$$

and:

$$\frac{\partial F^*_{\{N,l\}}}{\partial t^*} + \left\{ \mathcal{H}^{I *}_{\{N,l\}} + \gamma \mathcal{H}^{II *}_{\{N,l\}} \right\} F^*_{\{N,l\}} = 0 \qquad \text{(IV-B-41)}$$

where:

$$\mathcal{H}^{I *}_{\{N,l\}} = \mathcal{K}^{b}_{\{N,l\}} \sum_{i=1}^{N} \vec{p}_i^{\,b *} \cdot \frac{\partial}{\partial \vec{q}_i^{\,b *}}$$

$$- \sum_{j=1}^{N} \sum_{i=1}^{N} \left\{ {}^{I}\mathcal{R}^{bb} \frac{\partial {}^{I}\phi^{bb *}}{\partial \vec{q}_i^{\,b *}} + {}^{II}\mathcal{R}^{bb} \mathcal{E}_i^{bb} \frac{\partial {}^{II}\phi^{bb *}_{ij}}{\partial \vec{q}_i^{\,b *}} \right\} \cdot \frac{\partial}{\partial \vec{p}_i^{\,b *}}$$

$$- \sum_{i=1}^{N} \left\{ {}^{I}\mathcal{R}^{b\beta} \frac{\partial {}^{I}\phi^{b\beta *}_{ii}}{\partial \vec{q}_i^{\,b *}} + {}^{II}\mathcal{R}^{b\beta} \mathcal{E}_i^{b\beta} \frac{\partial {}^{II}\phi^{b\beta *}_{ii}}{\partial \vec{q}_i^{\,b}} \right\} \cdot \frac{\partial}{\partial \vec{p}_i^{\,b *}} \qquad \text{(IV-B-42)}$$

$$\mathcal{H}^{II *}_{\{N,l\}} = \mathcal{K}^{\beta} \gamma \vec{p}^{\,\beta *} \cdot \frac{\partial}{\partial \vec{q}^{\,\beta *}}$$

$$- \sum_{j=1}^{N} \left\{ {}^{I}\mathcal{R}^{\beta b} \cdot \frac{\partial {}^{I}\phi^{\beta b *}_{ij}}{\partial \vec{q}^{\,\beta *}} + {}^{II}\mathcal{R}^{\beta b} \mathcal{E}_i^{\beta b} \frac{\partial {}^{II}\phi^{\beta b *}}{\partial q^{\beta *}} \right\} \cdot \frac{\partial}{\partial \vec{p}_\beta^{\,*}} \qquad \text{(IV-B-43)}$$

We may now attempt to truncate (IV-B-39) by expanding both $F^{*}_{\{0,1\}}$ and $F^{*}_{\{N,1\}}$ in powers of the root—mass ratio parameter γ. Before doing so, however, we shall, as in the previous cases, rewrite the above equations in the more convenient dimensional form

$$\frac{\partial F_{\{0,1\}}}{\partial t} = \varepsilon \mathcal{L} F_{\{1,1\}} \qquad \text{(IV-B-44)}$$

$$\frac{\partial F_{\{N,1\}}}{\partial t} + \left\{ \mathcal{H}^{I}_{\{N,1\}} + \varepsilon \mathcal{H}^{II}_{\{N,1\}} \right\} F_{\{N,1\}} = 0 \qquad \text{(IV-B-45)}$$

where, in this subsection,

$$\mathcal{L}^{*} \equiv N \int\int \frac{\partial \phi_{1,1}}{\partial \vec{q}^{\beta}}^{\beta b} \cdot \frac{\partial}{\partial \vec{p}^{\beta}} \, d\vec{r}_{11}^{\beta b} \, d\vec{p}_{1}^{b} \qquad \text{(IV-B-46)}$$

$$\mathcal{H}^{I}_{\{N,1\}} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,b}}{m_b} \cdot \frac{\partial}{\partial \vec{q}_i^{\,b}} - \sum_{i=1}^{N} \left\{ \left[\sum_{j=1}^{N} \frac{\partial \phi_{ij}^{bb}}{\partial \vec{q}_i^{\,b}} \right] + \frac{\partial \phi_{11}^{b\beta}}{\partial \vec{q}_i^{\,b}} \right\} \cdot \frac{\partial}{\partial \vec{p}_i^{\,b}}$$

$$\mathcal{H}^{II}_{\{N,1\}} = \frac{\vec{p}^{\,\beta}}{m_\beta} \cdot \frac{\partial}{\partial \vec{q}^{\beta}} - \sum_{j=1}^{N} \frac{\partial \phi_{1,j}}{\partial \vec{q}^{\beta}}^{\beta b} \cdot \frac{\partial}{\partial \vec{p}^{\beta}} \qquad \text{(IV-B-47)}$$

Expanding $F_{\{0,1\}}$, $F_{\{1,1\}}$ and $F_{\{N,1\}}$ in powers of the label parameter ε

i.e.

$$\begin{aligned} F_{\{0,1\}} &= F^{(0)}_{\{0,1\}} + \varepsilon F^{(1)}_{\{0,1\}} + \varepsilon^2 F^{(2)}_{\{0,1\}} \\ F_{\{1,1\}} &= F^{(0)}_{\{1,1\}} + \varepsilon F^{(1)}_{\{1,1\}} + \varepsilon^2 F^{(2)}_{\{1,1\}} \\ F_{\{N,1\}} &= F^{(0)}_{\{N,1\}} + \varepsilon F^{(1)}_{\{N,1\}} + \varepsilon^2 F^{(2)}_{\{N,1\}} \end{aligned} \qquad \text{(IV-B-48)}$$

and collecting powers of ϵ in (IV-B-44) and (IV-B-45), we then obtain the following set of equations:

$$\frac{\partial F^{(0)}_{\{0,1\}}}{\partial t} = 0$$

$$\frac{\partial F^{(1)}_{\{0,1\}}}{\partial t} = \mathcal{L}_{\{0,1\}} F^{(0)}_{\{1,1\}}$$

$$\vdots$$

$$\frac{\partial F^{(R)}_{\{0,1\}}}{\partial t} = \mathcal{L}_{\{0,1\}} F^{(R-1)}_{\{0,1\}}$$

(IV-B-49)

$$\frac{\partial F^{(0)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(0)}_{\{N,1\}} = 0$$

$$\frac{\partial F^{(1)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(1)}_{\{N,1\}} = -\mathcal{H}^{II}_{\{N,1\}} F^{(0)}_{\{N,1\}}$$

$$\vdots$$

$$\frac{\partial F^{(R)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(R)}_{\{N,1\}} = -\mathcal{H}^{II}_{\{N,1\}} F^{(R-1)}_{\{N,1\}}$$

(IV-B-50)

Imposing the initial conditions,

$$F^{(0)}_{\{S,1\}}(\vec{X}_{\{S,1\}}, 0) = F_{\{S,1\}}(\vec{X}_{\{S,1\}}, 0)$$

$$F^{(R)}_{\{S,1\}}(\vec{X}_{\{S,1\}}, 0) = 0 \qquad S > 1 \qquad \text{(IV-B-51)}$$

we may integrate equations (IV-B-50) so as to obtain the following solutions:

$$F^{(0)}_{\{0,1\}}(\vec{p}^{\,B},t) = F_{\{0,1\}}(\vec{p}_B,0)$$

$$F^{(1)}_{\{0,1\}}(\vec{p}^{\,B},t) = \int_0^t \mathcal{L}_{\{0,1\}} F^{(0)}_{\{1,1\}}(\vec{X}_{\{1,1\}},t')\,dt'$$

$$\vdots$$

$$F^{(k)}_{\{0,1\}}(\vec{p}^{\,B},t) = \int_0^t \mathcal{L}_{\{0,1\}} F^{(k-1)}_{\{1,1\}}(\vec{X}_{\{1,1\}},t')\,dt' \qquad \text{(IV-B-52)}$$

These solutions may be evaluated explicitly by first evaluating $F^{(k)}_{\{1,1\}}$, which may be expressed in terms of $F^{(k)}_{\{N,1\}}$ by integrating the latter over the coordinates and momenta of every bath particle except the first: i.e.

$$F^{(k)}_{\{1,1\}}(\vec{r}^{\,Bb}_{1,1},\vec{p}^{\,B},\vec{p}^{\,b}_1) = \int\cdots\int F^{(k)}_{\{N,1\}}(X_{\{N,1\}},t)\prod_{j=2}^{N} d\vec{q}^{\,b}_j\, d\vec{p}^{\,b}_j \qquad \text{(IV-B-53)}$$

Solutions for $F^{(k)}_{\{N,1\}}$, on the other hand, may be derived by operating both sides of the equations (IV-B-50) by the forward streaming operator $e^{\mathcal{H}^{I}_{\{N,1\}}t}$ and integrating over t. Proceeding as such, one easily obtains the following solutions:

$$F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = e^{-\mathcal{H}^{I}_{\{N,1\}}t} F_{\{N,1\}}(X_{\{N,1\}},0)$$

$$F^{(1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = -\int_0^t e^{-\mathcal{H}^{I}_{\{N,1\}}(t-t')}\mathcal{H}^{II}_{\{N,1\}} F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t')\,dt'$$

$$\vdots$$

$$F^{(k)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = -\int_0^t e^{-\mathcal{H}^{I}_{\{N,1\}}(t-t')}\mathcal{H}^{II}_{\{N,1\}} F^{(k-1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t')\,dt' \qquad \text{(IV-B-54)}$$

Now, we easily note from (IV-B-47) that $\mathcal{H}^{I}_{\{N,1\}}$ simply represents the Hamiltonian operator for a system of N bath particles in the presence of a fixed Brownian particle. Consequently, $e^{-\mathcal{H}_{\{N,1\}}t}$ simply streams these bath particles under their mutual interaction and their interaction with the single Brownian particle, without affecting in any way the coordinate and momentum of the latter. Naturally, because of the large number of bath particles, one cannot, in most cases, explicitly evaluate the zeroth order solution in (IV-B-54). However, if we restrict ourselves to the very special case where the bath particles are initially in equilibrium with themselves and with the single Brownian particle:

i.e. $$F_{\{N,1\}}(\{\vec{X}_{\{N,1\}}, 0) = F_{\{N,0\}eq}\, F_{\{0,1\}}(\vec{P}_1^{\,1}, 0) \qquad \text{(IV-B-55)}^1$$

where

$$F_{\{N,0\}_{eq}} \equiv (Z_N^I)^{-1} e^{-H_N^I/kT}$$

$$H_N^I \equiv \sum_{i=1}^{N} \left\{ \frac{|\vec{p}_i^{\,b}|^2}{2m_b} + \Phi_{oi}^{bB} + \frac{1}{2}\sum_{j=1}^{N} \Phi_{ij}^{bb} \right\}$$

$$Z_N^I \equiv \int\int e^{-H_N^I/kT} \prod_{k=1}^{N} d\vec{q}_k^{\,b}\, d\vec{p}_k^{\,b}$$

(IV-B-56),

[1] Note this restriction does not require the Brownian particle to be initially in equilibrium with the bath molecules.

we may then note that:

$$e^{-\mathcal{H}_N^I t} F_{\{N,0\}eq} = F_{\{N,0\}eq} \qquad \text{(IV-B-57)}$$

and hence write the first two equations in (IV-B-54) as:

$$F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = F_{\{N,0\}eq} F_{\{0,1\}}(\vec{p}^{\beta},0)$$

$$F^{(1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = -\int_0^t e^{-\mathcal{H}^I_{\{N,1\}}(t-t')} \mathcal{H}^{II}_{\{N,1\}} F_{\{N,0\}eq} F_{\{0,1\}}(\vec{p}^{\beta},0)\,dt' \qquad \text{(IV-B-58)}$$

Now, from the definition of $\mathcal{H}^{II}_{\{N,1\}}$, we have

$$\mathcal{H}^{II}_{\{N,1\}} F_{\{N,0\}eq} F_{\{0,1\}}(\vec{p}^{\beta},0) = \left\{ \frac{\vec{p}^{\beta}}{m_\beta} \cdot \frac{\partial}{\partial \vec{q}_\beta} - \sum_{j=1}^{N} \frac{\partial \phi^{\beta b}_{1,j}}{\partial \vec{q}^{\beta}} \cdot \frac{\partial}{\partial \vec{p}^{\beta}} \right\} F_{\{N,0\}eq} F_{\{0,1\}}(\vec{p}^{\beta},0) \qquad \text{(IV-B-59)}$$

Furthermore, defining:

$$\vec{\mathcal{F}} \equiv -\sum_{j=1}^{N} \frac{\partial \phi^{Bb}_{0,j}}{\partial \vec{q}^{B}} \equiv \sum_{j=1}^{N} \vec{\mathcal{F}}_j \qquad \text{(IV-B-60)}$$

as the total force exerted on the Brownian particle by the bath molecules, and substituting (IV-B-55) into (IV-B-59), we then obtain from (IV-B-58) the following expressions for $F^{(1)}_{\{N,1\}}$.

$$F^{(1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = -\int_0^t \vec{\mathcal{F}}(-t')\,dt' \left\{ \frac{\vec{p}^{\beta}}{m_\beta kT} + \frac{\partial}{\partial \vec{p}^{\beta}} \right\} F_{\{N,0\}eq} F_{\{0,1\}}(\vec{p}^{\beta},0) \qquad \text{(IV-B-61)}$$

where $\vec{\mathcal{F}}(-t') = e^{-\mathcal{H}^I_{\{N,1\}} t'} \vec{\mathcal{F}}$ represents the force acting

on the Brownian particle when the bath particles are streamed back in time by the operator $e^{-\mathcal{H}_{(N,1)}t'}$. Using (IV-B-61) along with the first equation in (IV-B-58), we may, with the help of (IV-B-53), obtain the following expressions for $F^{(0)}_{(1,1)}$ and $F^{(1)}_{(1,1)}$:

$$F^{(0)}_{(1,1)} = F_{(0,1)}(\vec{p}^B, 0)\, F_{(1,0)eq}$$

$$F^{(1)}_{(1,1)} = -\int_0^t \iint \mathcal{SF}(-t')\, F_{(N,0)eq} \prod_{k=2}^{N} d\vec{q}^b_k\, d\vec{p}^b_k\, dt'$$

$$\cdot \left[\frac{\vec{p}^B}{m_B KT} + \frac{\partial}{\partial \vec{p}^B} \right] F_{(0,1)}(\vec{p}^B, 0) \qquad \text{(IV-B-62)}$$

where:

$$F_{(1,0)eq} = Z_1^{-1} e^{-H_1/KT}$$

$$H_1 = \frac{|p^b_1|^2}{2m_b} + \phi^{bB}_{1,1}$$

$$Z_1 = \iint e^{-H_1/KT}\, d\vec{p}^b_1\, d\vec{q}^b_1 \qquad \text{(IV-B-63)}$$

Finally, substituting (IV-B-63) into (IV-B-52) and noting that:

$$\mathcal{L}_{(0,1)} F_{(0,1)}(\vec{p}^B, 0)\, F_{(1,0)eq} = 0$$

we can then obtain the following solutions for $F^{(k)}_{(1,1)}$ $k = 0, 1, 2$

$$F^{(0)}_{\{0,1\}}(\vec{p}^{\,B},t) = F^{(0)}(\vec{p}^{\,B},0)$$

$$F^{(1)}_{\{0,1\}}(\vec{p}^{\,B},t) = 0$$

$$F^{(2)}_{\{0,1\}}(\vec{p}^{\,B},t) =$$

$$-\int_0^t \mathcal{L}_{\{0,1\}} \int_0^{t'} \iint \vec{\mathcal{F}}(-t'')\, F_{\{N,0\}_{eq}} \prod_{k=2}^{N} d\vec{q}_k^{\,b}\, d\vec{p}_k^{\,b}\, dt''$$

$$\cdot \left[\frac{\vec{p}^{\,B}}{m_B K T} + \frac{\partial}{\partial \vec{p}^{\,B}} \right] F_{\{0,1\}}(\vec{p}^{\,B},0)\, dt'$$

Using the definition of $\mathcal{L}_{\{0,1\}}$ as given by (IV-B-46), one may transform, after some manipulation, the second order solution $F^{(2)}_{\{0,1\}}(\vec{p}^{\,B},t)$ to the following form:

$$F^{(2)}_{\{0,1\}} = \int_0^t \bar{\bar{B}}(t')dt' : \frac{\partial}{\partial \vec{p}^{\,B}} \left[\frac{\vec{p}^{\,B}}{m_B K T} + \frac{\partial}{\partial \vec{p}^{\,B}} \right] F_{\{0,1\}}(\vec{p}^{\,B},0)$$

where:

$$\bar{\bar{B}}(t) \equiv \int_0^t \langle \vec{\mathcal{F}}\, \vec{\mathcal{F}}(-t') \rangle_{eq}\, dt'$$

and where:

$$\langle \vec{\mathcal{F}}\, \vec{\mathcal{F}}(-t) \rangle_{eq} \equiv \int\int \vec{\mathcal{F}}\, \vec{\mathcal{F}}(-t)\, F_{\{N,0\}_{eq}} \prod_{k=1}^{N} d\vec{q}_k^{\,b}\, d\vec{p}_k^{\,b}$$

represents a measure of the autocorrelation of the force exerted on the Brownian particle by the neighboring bath particles. Since this autocorrelation may be expected to decay rapidly with time, it would seem only reasonable to

assume that there exists some time τ_b such that, for $t > \tau_b$

$$\langle \vec{\delta F}\ \vec{\delta F}(t) \rangle_{eq} = 0$$

Consequently, we conclude that for

$$F^{(2)}_{\{0,1\}}(\vec{p}^B, t) = \left[\int_0^{\tau_b} \bar{\bar{B}}(t')\,dt' + (t-\tau_b)\,\bar{\bar{b}} \right] \cdot \frac{\partial}{\partial \vec{p}^B} \left[\frac{\vec{p}^B}{m_B KT} + \frac{\partial}{\partial \vec{p}^B} \right] F_{\{0,1\}}(\vec{p}^B, 0)$$

where: $\bar{\bar{b}} = \bar{\bar{B}}(\infty)$

This solution, naturally, diverges at a constant rate thus causing, as in the previous cases, a secular behavior of the (IVP) expansion. We note, however, that for $t \gg \tau_b$ that the rate equation for $F^{(2)}_{\{0,1\}}$ may be written as:

$$\frac{\partial F^{(2)}_{\{0,1\}}}{\partial t} = J_{F.P.}\left(F^{(0)}_{\{0,1\}}(\vec{p}^B, 0) \right)$$

where

$$J_{F.P.} \equiv \bar{\bar{b}} : \frac{\partial}{\partial \vec{p}^B} \left[\frac{\vec{p}^B}{m_B KT} + \frac{\partial}{\partial \vec{p}^B} \right]$$

Combining this last equation with the constant first and zeroth order solutions, we may then write the following approximate equation for $F_{\{0,1\}}(\vec{p}^B, t)$

$$\frac{\partial F_{\{0,1\}}}{\partial t} = J_{F.P.}\left(F_{\{0,1\}}(\vec{p}^B, 0) \right)$$

This equation is highly reminiscent of the equation

$$\frac{\partial F_{\{0,1\}}}{\partial t} = J_{F.P.}\left(F_{\{0,1\}}(\vec{p}^B, t) \right)$$

known as the Fokker-Planck equation which has been used with great success by many investigators to describe the evolution of the probability distribution of a single Brownian particle in a bath. As in the non-dense case, the characteristic distinguishing the secular equation from the well behaved equation lies in the absence of a time dependence in the right hand side.

C. Summary and conclusions

As previously stated, one of the simplest methods of extracting approximate solutions from the complex B.B.G.K.Y. hierarchy, for a particular system, would involve a straightforward expansion of the s particle distribution F_s in powers of a relevant small dimensionless parameter, derived from the nondimensionalization of the previous chapter, and a solution of the resulting set of simplified perturbed equations with respect to a set of given or assumed initial conditions. In general, the feasibility of using such an initial value perturbation (IVP) scheme to obtain approximate solutions to any differential (or differential-integral) equation varies considerably from one particular equation to another. In the more fortunate cases one may either obtain well behaved solutions at every order of the expansion or an infinite sum of divergent terms which converges to an easily recognizable function representing the exact solution to the original equation. Unfortunately, as noted by Bogoliubov, the B.B.G.K.Y. hierarchy does not so easily lend itself to an IVP scheme since, as illustrated in the present chapter for spatially uniform "non dense", "weakly coupled" and "Brownian" systems, this simple scheme when applied, renders an infinite sum of divergent terms so complex that one could neither hope to identify it with any well known function or, even establish its convergence. In spite of

this major breakdown of the IVP scheme some interesting results nevertheless emerge from such a simple approach. In particular the first order equations for the single particle distribution for spatially uniform non-dense, and Brownian systems, may be written in the simple form

$$\frac{\partial f_1(\vec{p}_i,t)}{\partial t} = J(f_1(\vec{p}_i,0)) \qquad \text{(IV-C-1)}$$

where

$$J(f_1(\vec{p}_i,0)) = \int_{-\infty}^{\infty}\int_{0}^{2\pi}\int_{0}^{\infty} b\,|\vec{q}_{ij}|\,[f_1(\vec{p}_i',0)\,f_1(\vec{p}_j',0) - f_1(\vec{p}_i,0)\,f_1(\vec{p}_j,0)]\,db\,d\phi\,d\vec{p}_j = J_B(f_1(\vec{p}_i,0)) \qquad \text{(IV-C-2)}$$

and

$$J(f_1(\vec{p}_i,0)) = \bar{\bar{b}} : \frac{\partial}{\partial \vec{p}_i}\left\{\frac{\vec{p}_i}{mKT} + \frac{\partial}{\partial \vec{p}_i}\right\} f_1(\vec{p}_i,0) = J_{FP}(f_1(\vec{p}_i,0)) \qquad \text{(IV-C-3)}$$

for the former and latter systems respectively. In equations (IV-C-2) b, ϕ and z represent cylindrical coordinates with the z-axis chosen in the direction of the relative velocity $\vec{q}_{ij}$ and in (IV-C-3), $\bar{\bar{b}} = \int_0^\infty \langle \vec{\mathcal{F}}\vec{\mathcal{F}}(t') \rangle_{eq}\, dt'$, where $\vec{\mathcal{F}}$ denotes the force exerted by the bath particles on the Brownian particle and $\langle\ \rangle_{eq}$. indicates an equilibrium ensemble average. Now, these equations bear a form very similar to the familiar Boltzmann and Fokker-Planck equations, of the form

$$\frac{\partial f_1(\vec{p}_i,t)}{\partial t} = J(f_1(\vec{p}_i,t)) \qquad \text{(IV-C-4)}$$

often used to describe the evolution of these systems. Indeed the only difference between equations (IV-C-1) and (IV-C-4) lies in the time dependence and independence of the right hand side of the latter and former. Consequently the solution of (IV-C-1) diverges while that of (IV-C-4) evolves towards the well known Maxwell-Boltzmann distribution law. In the case of a uniform non dense system, for example, the IVP solution for f_1 diverges at such a rate that the scaling of terms assumed in (III-E-1) prior to the expansion breaksdown after a time $\sim o[\lambda/\nu_0]$ characteristic of the time interval between collisions. The elimination of such divergences and the derivation of useful kinetic equations such as those of Boltzmann and Fokker-Planck represents therefore the major concern of the following chapter.

CHAPTER V

DERIVATION OF KINETIC EQUATIONS FOR SIMPLE UNIFORM SYSTEMS

The foregoing discussions on the Initial Value Perturbation scheme have essentially set the groundwork for the development of a simple alternate method of truncating the B.B.G.K.Y. hierarchy. Indeed, as will be shown shortly, the (IVP) approach requires only minor modifications to render useful, non secular, kinetic equations. Before disclosing the 'gist' of these alterations, however, it would only seem reasonable, for the sake of completeness, to establish suitable points of reference by considering some of the alternate methods previously used by numerous investigators to close the hierarchy. For this reason, the present chapter, which is devoted to the derivation of kinetic equations for spatially uniform systems, will dedicate its first section to some of those who, through their own alternate perturbation techniques, have significantly contributed to the formulation of this thesis.

A. THE FORERUNNERS

The last four decades have witnessed the unfolding of numerous perturbation schemes, designed for, or applied to, the derivation of kinetic equations. While many of these expansion methods remain buried in the vast literature, a few techniques, such as Bogoliubov's functional expansion, Frieman's multiple time scale perturbation and Zwanzig's projection operator approach, have succeeded in drawing a substantial audience.

The aim of the present section consists of highlighting, amidst a formidable inventory of available expansion schemes, a select few which, from this author's experience, may best illustrate the fundamental structures common to most perturbational derivations of kinetic equations. These representative selections, which have been chosen for their pedagogical value rather than their mathematical elegance or their current popularity, include the distinct methods of Bogoliubov,[12] Frieman [24] and Harris-Lewis.[39]

a) Bogoliubov's Functional Expansion

In 1946, I. Bogoliubov briefly stated the inadequacies of the (IVP) scheme and proposed another perturbation approach which he and Krylov [40] had earlier devised to analyze the motion of various non-linear oscillators. This alternate technique basically consisted of replacing

the explicit time dependence of a given time sensitive variable by a functional dependence on a less sensitive "contracted" variable. Applied to a non-linear oscillator, the method involved substituting the explicit time dependence of the position variable $X(t)$ by a functional dependence on the slowly varying amplitude $A(t)$ and frequency $\omega(t)$. In an analogous manner, Bogoliubov suggested that one could, in principle, perform a fruitful expansion of the hierarchy by choosing some suitable contracted variable(s) which would describe, on a "slow" time scale, the evolution of a molecular system. He further expanded this idea by pointing to the plausible existence of two characteristic time scales associated with the natural molecular relaxation process. The first "dynamic" or "fast" time scale consisted of a brief regime during which the initial correlations between molecules remained important and joint probability distributions $F_s(\vec{x}_s, t)$ $(s \geq 1)$ depended on time explicitly. This initial phase would only last, however, for the typical duration, τ_0, of an interaction between two molecules so as to give way to a longer "kinetic" or "slow" regime, during which the initial correlations would be forgotten and F_s $(s>1)$ would only bear an implicit time dependence through a functional dependence on F_1. For a non-dense system, this latter regime would persist for a period, τ_1, comparable to the time interval between col-

isions (i.e. $\tau_1 \sim o[\lambda/v_o]$) with λ = mean free path and $v_o \equiv$ average molecular speed). With these important time scales in mind, Bogoliubov concluded that kinetic equations could be derived for $t \gg \tau_o$ by simply seeking solutions for F_s bearing a time dependence only through a functional dependence on F_1 which thus became the desired "contracted" variable.

In order to illustrate the application of Bogoliubov's ideas let us reconsider the simple non-dense system and recall the B.B.G.K.Y. hierarchy in the form given by (IV-B-4)

$$\frac{\partial F_s}{\partial t} + \mathcal{H}_s F_s = \varepsilon \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-4)}$$

$$\mathcal{H}_s \equiv \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} - \sum_{i=1}^{s}\sum_{j=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \qquad \text{(IV-B-5)}$$

$$\mathcal{L}_s \equiv \sum_{i=1}^{s} \iint \frac{\partial \phi_{i,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \, d\vec{r}_{i,s+1} \, d\vec{p}_{s+1}$$

The initial, and crucial step in Bogoliubov's approach consists of seeking approximate solutions for F_s which carry a functional dependence on the one particle distributions $F_1(p_i, t)$ $(\forall i \in S)$

i.e. $$F_s \equiv F_s(\vec{X}_s ; F_1(\vec{p}_i, t)) \qquad \text{(V-A-1)}$$

In mathematical terms, this assumption implies that the time derivative in (IV-B-4) may be expressed in terms of appropriate functional derivative. Consequently one may

write

$$\frac{\partial F_s}{\partial t} = \left\{ \frac{\delta}{\delta F_1(\vec{p}_1,t)} \; ; \; \frac{\partial F_1}{\partial t} \right\} \qquad \text{(V-A-2)}$$

where the functional derivative $\frac{\delta}{\delta F_1(\vec{p}_1,t)}$ must be taken over all $F_1(p_1 t)$ $\iota \in S$

The second step of the scheme now involves the usual expansion of $F_s(\vec{X}_s,t)$, for $s>1$, in powers of the label parameter ε

i.e. $$F_s(\vec{X}_s,F_1) = F_s^{(0)}(\vec{X}_s,F_1) + \varepsilon F_s^{(1)}(\vec{X}_s,F_1) + \varepsilon^2 F_s^{(2)}(\vec{X}_s,F_1) + \qquad s>1 \qquad \text{(V-A-3)}$$

Substitution of this expansion into the hierarchy will then render, for a spatially uniform gas, the following kinetic equation

$$\frac{\partial F_1}{\partial t} = \sum_{k=1}^{\infty} \varepsilon^k \mathcal{L}_1 F_2^{(k-1)}(\vec{X}_2 ; F_1). \qquad \text{(V-A-4).}$$

Furthermore substituting (V-A-3) and (V-A-4) into (V-A-2), we may write the time derivative $\frac{\partial F_1}{\partial t}$ in the following expanded form

$$\frac{\partial F_s}{\partial t} = \sum_{k=1}^{\infty} \varepsilon^k \mathcal{D}^{(k)} \sum_{l=0}^{\infty} \varepsilon^l F_s^{(l)} \qquad \text{(V-A-5)}$$

where $$\mathcal{D}^{(k)} \equiv \left\{ \frac{\delta}{\delta F_1} , \mathcal{L}_1 F_2^{(k-1)} \right\} \qquad \text{(V-A-6)}$$

such that further substitution of (V-A-3) and (V-A-5) into (IV-B-4) and collection of orders of ε renders the following set of hierarchy equations

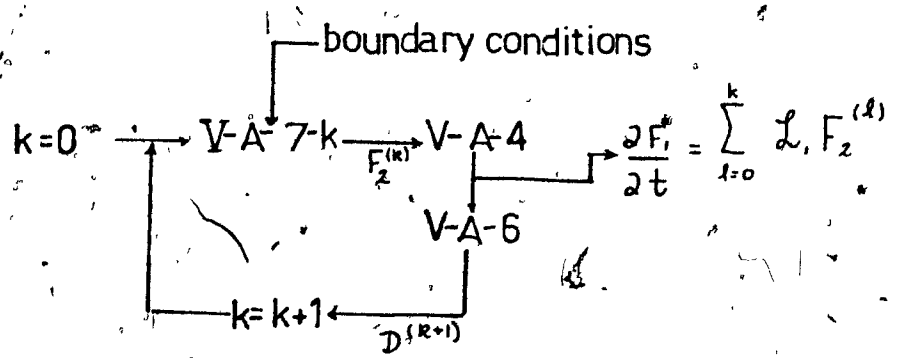
$$\mathcal{H}_s F_s^{(0)} = 0 \qquad \text{(V-A-7-0)}$$

$$\mathcal{H}_s F_s^{(1)} = \mathcal{L}_s F_{s+1}^{(0)} - \mathcal{D}^{(1)} F_s^{(0)} \qquad \text{(V-A-7-1)}$$

$$\vdots$$

$$\mathcal{H}_s F_s^{(k)} = \mathcal{L}_s F_s^{(k)} - \sum_{l=1}^{k} \mathcal{D}^{(l)} F_s^{(k-l)} \qquad \text{(V-A-7-k)}$$

Equations (V-A-4) to (V-A-7) essentially form the structure of Bogoliubov's perturbation scheme. The remaining work simply involves the solution of equations (V-A-7), subject to some plausible boundary conditions, and the substitution of these particular solutions for $F_2^{(k)}(\vec{X}_2; F_1)$ into (V-A-4) and (V-A-6) so as to obtain a k^{th} order kinetic equation for F_1 and an expression for the higher order functional derivative $\mathcal{D}^{(k+1)}$. Hence, schematically, Bogoliubov's scheme may be summarized as follows



Bogoliubov scheme

Fig. V-1

Let us now initiate this procedure by solving equation (V-A-7-0); this may be accomplished by operating both sides of the equation by $e^{\mathcal{H}_s \tau}$ and recalling,

from chapter II, the following identity

$$\ell^{\mathcal{H}_s\tau}\cdot\mathcal{H}_s = \mathcal{H}_s\,\ell^{\mathcal{H}_s\tau} = \frac{\partial}{\partial\tau}\,\ell^{\mathcal{H}_s\tau}$$

Doing so, we then obtain the following equation

$$\frac{\partial\,\ell^{\mathcal{H}_s\tau}F_s^{(o)}(F_1,t)}{\partial\tau} = 0 \qquad \text{(V-A-8)}$$

for which one may write the solution either as

$$F_s^{(o)}(\vec{X}_s;F_1(\vec{p}_i,t)) = \ell^{-\mathcal{H}_s\tau}F_s^{(o)}(\vec{X}_s;F_1(\vec{p}_i,t)) \qquad \text{(V-A-9-a)}$$

or as

$$F_s^{(o)}(\vec{X}_s;F_1(\vec{p}_i,t)) = \ell^{\mathcal{H}_s\tau}F_s^{(o)}(\vec{X}_s;F_1(\vec{p}_i,t)) \qquad \text{(V-A-9-b)}$$

Clearly neither of these equations, in their present form, seem to be of great value since they merely relate $F_s^{(o)}$ to itself. Indeed before explicit solutions may be found, in terms of F_1, some suitable boundary conditions must first be imposed. Let us therefore assume, as was done in the (B.V.P.) expansion, that all statistical correlations in F_s are finite in range such that, in the limit $\tau\to\infty$, the streaming operators $\ell^{-\mathcal{H}_s\tau}$ and $\ell^{\mathcal{H}_s\tau}$ due to the repulsive potentials ϕ_{ij} in $\mathcal{H}_s$, will ultimately displace the particles in $\{s\}$ outside their mutual correlation range. In this limit we could then impose either one of the following boundary conditions.

$$\lim_{\tau\to\infty} \ell^{-\mathcal{H}_s\tau} F_s(\vec{X}_s; F_1) = \lim_{\tau\to\infty} \ell^{-\mathcal{H}_s\tau} \prod_{i=1}^{s} F_i(\vec{P}_i, t) \qquad \text{(V-A-10-a)}$$

$$= \prod_{i=1}^{s} F_i(\vec{P}_i^-(\infty), t)$$

$$\lim_{\tau\to\infty} \ell^{\mathcal{H}_s\tau} F_s(\vec{X}_s; F_1) = \lim_{\tau\to\infty} \ell^{\mathcal{H}_s\tau} \prod_{i=1}^{s} F_i(\vec{P}_i, t) \qquad \text{(V-A-10-b)}$$

$$= \prod F_i(\vec{P}_i^+(\infty), t)$$

where

$$\vec{P}_i^-(\tau) = \ell^{-\mathcal{H}_s\tau} \vec{P}_i \qquad \text{(V-A-11)}$$

$$\vec{P}_i^+(\tau) = \ell^{\mathcal{H}_s\tau} \vec{P}_i$$

Upon substitution of the expansion (V-A-3), these boundary conditions may also be written as

$$\lim_{\tau\to\infty} \ell^{-\mathcal{H}_s\tau} F_s^{(0)}(\vec{X}_s, F_1) = \prod_{i=1}^{s} F_i(\vec{P}_i^-(\infty), t)$$

$$\lim_{\tau\to\infty} \ell^{-\mathcal{H}_s\tau} F_s^{(k)}(\vec{X}_s; F_1) = 0, \quad k \geq 1 \qquad \text{(V-A-12-a)}$$

$$\lim_{\tau\to\infty} \ell^{\mathcal{H}_s\tau} F_s^{(0)}(\vec{X}_s; F_1) = \prod_{i=1}^{s} F_i(\vec{P}_i^+(\infty), t)$$

$$\lim_{\tau\to\infty} \ell^{\mathcal{H}_s\tau} F_s^{(k)}(\vec{X}_s; F_1) = 0, \quad k \geq 1 \qquad \text{(V-A-12-b)}$$

Now since the left hand sides of (V-A-9a & b) are independent of τ, we may choose the latter at our own convenience. Considering the boundary conditions which we have just imposed, it would seem natural to choose the limiting case $\tau\to\infty$ for which we have the following two possible solutions.

$$F_s^{(0)}(\vec{X}_s; F_1) = \prod_{i=1}^{s} F_1(\vec{P}_i^-(\infty), t) \qquad \text{(V-A-13-a)}$$

$$F_s^{(0)}(\vec{X}_s; F_1) = \prod_{i=1}^{s} F_1(\vec{P}_i^+(\infty), t) \qquad \text{(V-A-13-b)}$$

Clearly, these two solutions are not equivalent since $\vec{P}_i^-(\infty)$ and $\vec{P}_i^+(\infty)$ will not generally coincide if one or more interactions occur during the backward or forward streaming of the s particles. Consequently any kinetic equations derived from such solutions should also be distinct. Following the general plan in figure V-1, let us now substitute (V-A-13-a & b) into (V-A-4) so as to obtain the following two possible first order kinetic equations.

$$\frac{\partial F_1}{\partial t} = \varepsilon \mathcal{L}_1 F_1(\vec{P}_i^-(\infty), t) F_1(\vec{P}_j^-(\infty), t) + o_1[\varepsilon^2] \qquad \text{(V-A-14a)}$$

$$\frac{\partial F_1}{\partial t} = \varepsilon \mathcal{L}_1 F_1(\vec{P}_i^+(\infty), t) F_1(\vec{P}_j^+(\infty), t) + o[\varepsilon^2] \qquad \text{(V-A-14b)}$$

The first of these equations bears a strong similarity with equation (IV-B-17) previously derived using the (IVP) scheme. In fact, with arguments similar to those presented in appendix I , we may easily show that (V-A-14-a) reduces to the familiar Boltzmann equation

$$\frac{\partial f_1}{\partial t}(\vec{p}_1, t) = J_B(f_1(\vec{p}_1, t)) \qquad \text{(IV-B-22)}$$

where we recall

$$J_{ij}[f_i(\vec{p}_i,t)] = \int_{-\infty}^{\infty}\int_{0}^{2\pi}\int_{0}^{\infty} \frac{|\vec{p}_j - \vec{p}_i|}{m} \left[f_i(p_i',t) f_j(p_j',t) - f_i(\vec{p}_i,t) f_j(\vec{p}_j,t) \right] b\,db\,d\phi\,d\vec{p}_j$$

Boltzmann, who derived this equation in the late 19th century, using rather intuitive arguments, also established some of its important properties such as the existence of a Maxwellian stationary solution and the intrinsic irreversibility of its transient solutions which must evolve in the direction of increasing entropy or decreasing H where

$$H \equiv \int f_i(\vec{p}_i,t) \ln f_i(\vec{p}_i,t)\, d\vec{p}_i$$

Since its derivation, the Boltzmann equation has been successfully applied to a wide variety of physical problems. The non-uniform version of this equation has, in particular, proved highly valuable in the calculation of transport coefficients for non-dense gases.

Bogoliubov's perturbational derivation of the Boltzmann equation undoubtedly represents a foremost contribution of the statistical mechanical approach as it draws an important link between the reversible mechanics and the familiar irreversible thermodynamics.

The exact origin of the irreversibility induced by the expansion becomes furthermore an interesting and enlightening point for discussion. Certainly as pointed

out by Uhlenbeck[3], the coarse-graining in time promoted, and implied, by Bogoliubov's functional assumption does play an important role. The fact that functional form of $F_s(\vec{X}_s, F_1(\rho,t))$ cannot resolve the short time scales of the dymamic regime does indeed imply a coarse-graining in time which is highly reminiscent to that evoked by Boltzmann through his partitioning of the μ space and his "Stosszahlansatz" assumption. Furthermore coarse-graining in Γ_N space which must accompany any loss of resolution in time also brings together Bogoliubov's time scale arguments and Gibbs discretization of the phase space. The coarse-graining in time and phase space does therefore unite Bogoliubov, Boltzmann and Gibbs in their effort to give a molecular interpretation of the second law of thermodynamics. However there does seem to exist in Bogoliubov's expansion approach a certain ambiguity as to the direction of the irreversibility which he induces. Indeed, as first noted by Cohen and Berlin,[23] Bogoliubov's derivation of Boltzmann's equation is founded on one possible solution for $F_2(\vec{X}_2, F_1)$ (that is V-A-13-a) which emerges as a consequence of the particular backward boundary condition (V-A-10-a) which he uses. Alternatively however, one could choose the forward boundary condition (V-A-10-b) with the solution (V-A-13-b) so as to emerge with the kinetic equation (V-A-14-b) which, in turn, may

be shown to imply the following equation for $f_1(\vec{p}_1, t)$

$$\frac{\partial f_1}{\partial t} = - J_3(f_1) \qquad \text{(V-A-15)}$$

This equation because of its sign, displays the interesting property of admitting only solutions which evolve in the direction of increasing H, or decreasing entropy. For this reason it has, at times, been referred to as the "anti-Boltzmann" equation. The possibility of deriving, via a Bogoliubov expansion, a kinetic equation with a time arrow seemingly pointing the wrong way remains, of course, a disturbing enigma. Cohen and Berlin have shed some light on the problem by suggesting that the backward boundary condition and, hence, the Boltzmann equation, are founded on the plausible assumption that two particles are generally statistically independent before mutually colliding and inherit a mutual correlation after collision. The forward boundary condition, and the anti-Boltzmann equation, on the other hand; would call for an intuitively less plausible case, in which two approaching particles would be peculiarly correlated before collision such that this correlation would find itself anihilated after the two particles interact. This argument, however, implies a very special physical interpretation of the mathematical limit $T \to \infty$ in both boundary conditions (V-A-10-a&b). Clearly, in this limit, any streaming operator $\mathcal{L}^{-H,T}$ or

$\ell^{\mathcal{H}_s \tau}$ which brings two particles into a collision will also subsequently separate these particles such that they ultimately become infinitely distant from one another. Now, because of the actual presence of numerous other particles, it would seem quite implausible that two particles, infinitely distant from each other, would remain correlated as the result of a remotely possible collision in the distant past. Consequently, one soon realizes that Cohen and Berlin's reasoning in favor of the backward boundary condition (V-Â-10-a) may only find proper justification if the limit $\tau \to \infty$ is not interpreted literally but, in fact, replaced, as illustrated in figure V-2, by an alternate limit $\tau \to \tau^{\circledcirc}$ where $\tau^{\circledcirc}$ is chosen within the range $\tau_0 \ll \tau^{\circledcirc} \ll \tau_1$.

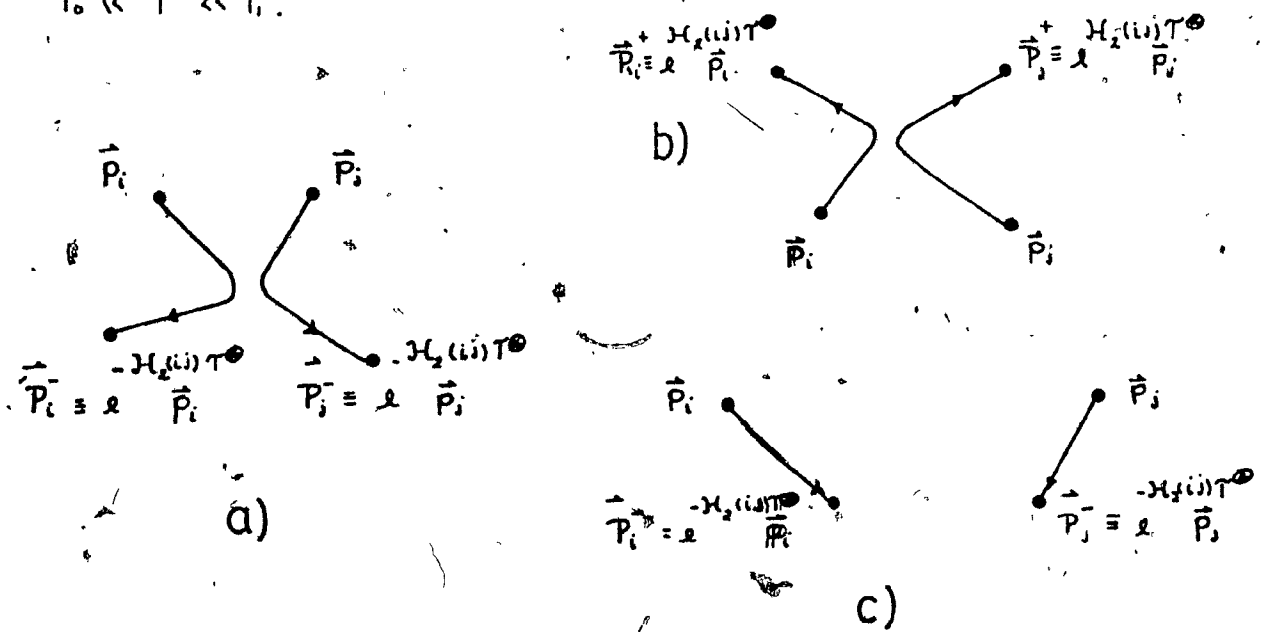


Fig. V-2

In this new limit, with $\tau^{\circledast}$ chosen much longer than the mean interaction time and yet much shorter than the mean time between collisions, one may reasonably argue that while the backward streaming operator $\ell^{-H_2(i,j)\tau^{\circledast}}$ will stream particles i and j of figure (a) into a precollisional uncorrelated state, the forward streaming operator $\ell^{H_2(i,j)\tau^{\circledast}}$ in figure (b) will displace these particles into a post-collisional correlated status. However, if one so wishes to tamper with Bogoliubov's original boundary conditions one must also face the consequence that the above restrictions on $\tau^{\circledast}$ also imply a parasitic limitation on the validity of the backward boundary condition in momentum and physical space. Indeed the modified boundary condition

$$\ell^{-H_2(i,j)\tau^{\circledast}} F_2(x_i, x_j, t) = F_1(\vec{\underset{\sim}{P}}_i, t) F_1(\vec{\underset{\sim}{P}}_j, t) \qquad \text{(V-A-16)}$$

with $\vec{\underset{\sim}{P}}_i = \ell^{-H_2(i,j)\tau^{\circledast}} \vec{p}_i$

which we suggest, cannot be expected to hold if $\vec{r}_{ij}$, $\vec{p}_i$, and $\vec{p}_j$ are so chosen that the operator $\ell^{-H_2(i,j)\tau^{\circledast}}$ streams particles i and j back in time towards or into, but not through, a binary collision (as illustrated in figure c of fig. V-2). In fact, the restrictions imposed on $\tau^{\circledast}$ would imply that Bogoliubov's solutions for $F_2^{(0)}$ should only be used for $|\vec{r}_{ij}| \ll \lambda$. Naturally since the derivation of the first order kinetic equation only requires the

knowledge of $F_s^{(0)}$ for $r_{ij} < r$ this limitation should have no bearing on the validity of the Boltzmann equation. Furthermore, recalling the dimensional arguments of chapter III, one notes that the relative weight assigned to the various terms of the hierarchy for non-dense systems no longer apply when $|\vec{r}_{ij}|$ is chosen of the same order as, or larger than, the mean particle separation. Hence the very expansion which Bogoliubov performs remains valid only when $|\vec{r}_{ij}| \ll n^{-1/3} \ll \lambda$. In fact if the perturbed equations were valid for all $|\vec{r}_{ij}|$ one could avoid Bogoliubov's boundary conditions completely, and simply recall the condition (II-C-4) imposed at $|\vec{q}_i| \to \infty$ as in the original derivation of the B.B.G.K.Y. hierarchy. Furthermore, if only the latter boundary conditions in physical space were used one could easily show that the Bogoliubov scheme would render trivial kinetic equations at all orders of the expansion.[1] This fact further confirms the limited validity, in physical space, of the expanded hierarchy (V-A-7) used by Bogoliubov.

The above discussions have suggested a modified set of boundary conditions, in the limit $T \to T^{\oplus}$, which would conform with some of the arguments presented by Cohen and Berlin. Unfortunately we have, as yet, not given much

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1 See appendix II for proof.

insight as to the exact reason for which the original forward boundary condition cannot be used in the limit $\tau \to \infty$. Certainly the very fact that this physically plausible boundary condition renders a kinetic equation which we intuitively dispute cannot seriously be accepted as suitable grounds for rejection. Indeed the possibility of deriving a questionable result from a seemingly plausible assumption simply suggests an inherent flaw, or at least ambiguity, in the perturbation scheme itself. There clearly exists, within the Bogoliubov approach, numerous subtleties which become extremely difficult to assess without considering alternate approaches to the problem. The arbitrariness of the auxiliary time variable τ introduced in the Bogoliubov approach represents only one quandary which will require future attention. The functional assumption, itself, represents a limitation which one would enjoy removing. Fortunately, alternate perturbation approaches, such as the Multiple Time Scale expansion have shed some light on these difficulties.

b Multiple Time Scale Expansion.

In 1962, E. Frieman proposed a new expansion scheme which could truncate the B.B.G.K.Y. hierarchy by explicitly introducing a discrete set of time scales and systematically eliminating secularities as they appeared. This method, which has since been referred to as the Multiple Time Scale (MTS) scheme, may be illustrated by considering, once more, the non-dense uniform system and, hence, recalling the B.B.G.K.Y. hierarchy as expressed by equation (IV-B-4).

$$\frac{\partial F_s}{\partial t} + \mathcal{H}_s F_s = \varepsilon \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-4)}$$

The (MTS) approach consists of rewriting the time dependence of F_s in terms of a discrete set of independent time scales $t_0, t_1, t_2 \ldots$

i.e. $$F_s(x_s, t) = F_s(x_s, t_0, t_1, t_2 \ldots) \qquad \text{(V-A-17)}$$

where t_i relates to the real time t as follows

$$\frac{dt_i}{dt} = \varepsilon^i \qquad \text{(V-A-18)}$$

Let us, as usual, expand F_s in powers of the label parameter

$$F_s = F_s^{(0)} + \varepsilon F_s^{(1)} + \varepsilon^2 F_s^{(2)} + \ldots \qquad \text{(V-A-19)}$$

and further note that, due to equation (V-A-18), the

derivative in (IV-B-4) may also be rewritten in the expanded form

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2} + \cdots \qquad \text{(V-A-20)}$$

Substituting (V-A-19) and (V-A-20) into (IV-B-4) we then obtain the following expanded form for the B.B.G.K.Y. hierarchy

$$\frac{\partial F_s^{(0)}}{\partial t_0} + \mathcal{H}_s F_s^{(0)} = 0 \qquad \text{(V-A-21-0)}$$

$$\frac{\partial F_s^{(1)}}{\partial t_0} + \mathcal{H}_s F_s^{(1)} = \mathcal{L}_s F_{s+1}^{(0)} - \frac{\partial F_s^{(0)}}{\partial t_1} \qquad \text{(V-A-21-1)}$$

$$\frac{\partial F_s^{(k)}}{\partial t_k} + \mathcal{H}_s F_s^{(k)} = \mathcal{L}_s F_{s+1}^{(k-1)} - \sum_{l=1}^{k} \frac{\partial F_s^{(k-l)}}{\partial t_l} \qquad \text{(V-A-21-k)}$$

Proceeding, as in the (IVP) scheme, we shall now seek solutions for $F_s^{(k)}$ on the t_0 time scale in terms of the initial conditions at $t_0 = 0$. Considering, firstly, the zeroth order single particle distribution, we note from (V-A-21-0) that

$$\frac{\partial F_1^{(0)}}{\partial t_0}\left(\vec{p}_1, t_0, t_1, t_2 \right) = 0 \qquad \text{(V-A-22)}$$

or

$$F_1^{(0)}\left(\vec{p}_1, t_0, t_1, t_2 \ldots\right) = F_1^{(0)}\left(\vec{p}_1, 0, t_1, t_2\right) \qquad \text{(V-A-23)}$$

which simply establishes the independence of $F_1^{(0)}$ on the fast time scale t_0. On the other hand, for $s>1$, equation (V-A-21-0) may be integrated in the usual manner to yield the following solution

$$F_s^{(0)}(\vec{X}_s, t_0, t_1, t_2) = e^{-\mathcal{H}_s t_0} F_s^{(0)}(\vec{X}_s, 0, t_1, t_2) \quad \text{(V-A-24)}$$

Similarily, one may move along to the next order of the expansion by substituting the above solution, for $F_2^{(0)}$ into (V-A-21-1) so as to obtain the following rate equation for $F_1^{(1)}$ on the t_0 time scale.

$$\frac{\partial F_1^{(1)}}{\partial t_0} = -\frac{\partial F_1^{(0)}}{\partial t_1} + \mathcal{L}_1 e^{-\mathcal{H}_2 t_0} F_2^{(0)}(\vec{X}_2, 0, t_1, t_2) \quad \text{(V-A-25)}$$

which, using the notation of (IV-B-12), may also be written as

$$\frac{\partial F_1^{(1)}}{\partial t_0} = -\frac{\partial F_1^{(0)}}{\partial t_1} + \mathcal{L}_1 F_2^{(0)}(\vec{R}_{ij}(t_0)\, \vec{P}_i(t_0)\, \vec{P}_j(t_0), 0, t_1, t_2) \quad \text{(V-A-26)}$$

Upon integration over t_0

$$\text{i.e.} \quad F_1^{(1)}(\vec{P}_i, t_0, t_1, t_2 \ldots) = F_1^{(1)}(\vec{P}_i, 0, t_1, t_2 \ldots)$$

$$- t_0 \frac{\partial F_1^{(0)}}{\partial t_1}(\vec{P}_i, 0, t_1, t_2 \ldots) + \int_0^{t_0} \mathcal{L}_1 F_2^{(0)}(\vec{R}_{ij}(t_0'), \vec{P}_i(t_0'), \vec{P}_j(t_0'), 0, t_1, t_2)\, dt_0' \quad \text{(V-A-27)}$$

we may now note the similarity between the above solution for $F_1^{(1)}$ and the corresponding solution (IV-B-11) previously derived using the (IVP) scheme. Indeed using arguments similar as those presented then, we may show that, for t_o larger than the maximum time τ_+, required for two interacting particles to be streamed outside each other's correlation range by $e^{-H_2(1)t_o}$, one has

$$F_2(\vec{R}_{ij}(t_o), \vec{P}_i(t_o), \vec{P}_j(t_o), o, t_1, t_2, \dots) =$$

$$F_1(\vec{P}_i(\infty), o, t_1, t_2 \dots) F_1(\vec{P}_j(\infty), o, t_1, t_2 \dots) \quad t_o > \tau_+$$

(V-A-28)

Consequently for t_o sufficiently long, both terms on the right hand side of (V-A-27) diverge at a constant rate, thus giving the solution for $F_1^{(1)}$ a secular character. However, due to the added flexibility alloted by the existence of numerous distinct time scales, one may, in the (MTS) approach eliminate the secular terms by simply imposing that, in the limit $t_o \to \infty$,

$$\frac{\partial F_1^{(0)}}{\partial t_1}(p_1, t_1, t_2 \dots) = \mathcal{L}_1 \; F_1^{(0)}(\vec{P}_i(\infty), t_1, t_2 \dots) F_1^{(0)}(\vec{P}_j(\infty), t_1, t_2 \dots)$$

which also implies that

$$\frac{\partial F_1^{(1)}}{\partial t_0}(\vec{p}_1, t_0, t_1, t_2 \ldots) = \mathcal{L}_1 \{ F_2^{(0)}(\vec{R}_{12}(t_0), \vec{p}_1(t_0), \vec{p}_2(t_0), 0, t_1, t_2, \ldots) + F_1^{(0)}(\vec{p}_1(\infty), t_1, t_2) F_1^{(0)}(\vec{p}_2(\infty), t_1, t_2 \ldots) \}$$

(V-A-30)

By thus eliminating the secular terms as they appear one then obtains a kinetic equation for $F_1^{(0)}$ on the t_1, time scale which bears a strong resemblance with equation (V-A-14-a) previously derived using the Bogoliubov scheme. Indeed, using arguments similar to those presented in appendix I and combining equations (V-B-22), (V-A-29) and (V-A-30) one may easily show, in the limit $t_0 \to \infty$, that the distribution $f_1 = n F_1$ obeys, to the first order in ε, the familiar Boltzmann equation

$$\frac{\partial f_1}{\partial t} = J_B(f_1(\vec{p}_1, t)) + O[\varepsilon^2]$$

The above expansion may be carried out to a higher order of ε by integrating the first order equation (V-A-21-1) for $s>1$, on the t_0 time scale, and substituting the solution for $F_s^{(1)}$ into the higher order equation (V-A-21-2) for $s=1$. Integration of this latter equation over t_0 and elimination of secular terms will then result in a second order kinetic equation on the t_1, time scale. In summary, the (MTS) expansion for the non-dense gas proceeds, therefore, as follows

MTS Expansion Scheme

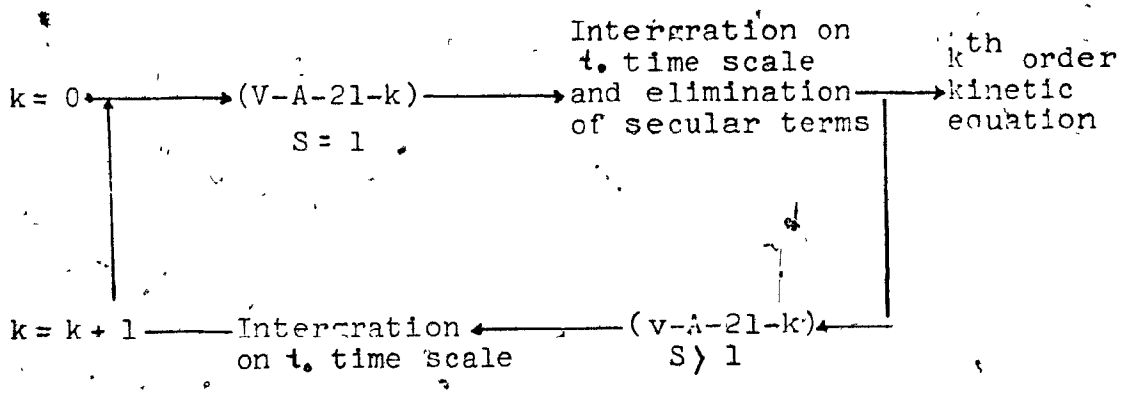

Fig. V-3

The (MTS) approach, which derives kinetic equations on one time scale by eliminating secular solutions on another time scale, represents a systematic method of circumventing the usual secularities encountered in the (IVP) scheme. The mathematical and physical significance of the discrete set of time scales, which this approach introduces, remains, however, an important point for discussion. Mathematically some investigators [25] have opted to treat the variables $t_0, t_1, \ldots$ as independent variables in the strict sense, thus allowing them to impose such limits as $t_0 \to \infty$ without implying any similar limit on the other time scales. Clearly, considering equation (V-A-18) which relates these time scales to the real time

t , one cannot accept such a premise once the constants of integration of this equation have been chosen. Indeed if one sets these constants to zero, for example, the following relationship between the time scales must be observed

$$t_0 = t_1/\varepsilon = t_2/\varepsilon^2 = \ldots = t_i/\varepsilon^i = \ldots = t \qquad \text{(V-A-31)}$$

Consequently some authors [25] have adopted the more reasonable point of view of treating the independence of the various time scales as an approximation which becomes reasonable provided one remains as close as possible to the "physical line" defined by (V-A-31). Naturally, as in the Bogoliubov expansion, this outlook requires some physical interpretation of the time scales involved, particularly when limits such as $t_0 \to \infty$ are imposed. The general physical arguments, found in the literature, describe t_0 as a "fast" or fine time scale and depict $t_1, t_2 \ldots t_i$ as progressively "slower" or coarser time bases. The reasoning behind this point of view becomes quite evident if one reconsiders the expansion parameter ε and the time variable t in their dimensionless forms $\varepsilon_2 = n r_0^3$ and $t^* = t/t_0$, where $t_0 = r_0/v_0$. Using equation (V-A-31) one may then write the multiple time scales $t_0 \ldots t_i$ in their dimensionless form

$$t_0^* = t^* = t/\tau_0$$
$$t_1^* = \varepsilon t/\tau_0$$
$$\vdots$$
$$t_i^* = \varepsilon^i t/\tau_0 \qquad \text{(V-A-32)}$$

One then notes that while t_0 is scaled on a time unit τ_0, comparable to the typical duration of a binary collision, and t_1 paces itself on a much longer characteristic time τ_1

$$\tau_1 = \tau_0/\varepsilon \sim o[\nu_0^{-1} m r_0^4] \sim o[\lambda/v_0]$$

(which is typical of the time interval between collisions) the remaining time scales $t_2^*, t_3^* \cdots t_i^*$ become normalized with respect to progressively longer characteristic time measures. Consequently t_0 and t_1 respectively follow the fast "dynamic" and slow "kinetic" regimes of the Bogoliùbov scheme. Furthermore, if one assumes that the range of correlation is such that τ_4, in boundary condition (V-A-28), may be chosen much shorter than τ_1, one may then interpret the limit $t_1 \to \infty$, in the above (MTS) expansion, as a limit $t_0 \to \tau^*$ such that t_0 plays the same role as the auxiliary time variable τ in the Bogoliubov expansion.

In spite of the numerous similarities shared by the Bogoliubov and (MTS) schemes, the latter method does offer the distinct advantage of by-passing the functional assumption required by the former. Indeed the functional form of the (MTS) solution for $F_2^{(0)}$ only emerges when

$t > \tau_+$ as a result of the boundary condition (V-A-28) which is in fact equivalent to the modified Bogoliubov boundary condition previously discussed. The (MTS) scheme on the other hand suffers a great handicap in that one must know the exact form of the secular terms in the corresponding (IVP) scheme. In the uniform case, naturally, we have previously shown that secular terms grow as powers of time. Unfortunately in non-uniform systems the exact nature of the secularities become extremely difficult to determine. For this very reason the use of the (MTS) approach has generally been restricted to uniform or quasi-uniform systems, where non-uniformities in space of F_1 may be completely neglected in the zeroth order of the expansion. Evidently both of these expansion schemes find themselves hampered by distinct and important restrictions. These limitations furthermore emerge as a result of unnecessarily complex mathematical approaches to the problem at hand. Indeed, as will be shown shortly, a clearer understanding of the time scales involved will guide us to a simple transparent method of deriving kinetic equations without resorting to restrictive functional assumptions or artificial expansions in a multitude of time scales.

c) Time Expansion of Harris and Lewis

In 1964, S.Harris and M.B. Lewis proposed an alternate technique of deriving kinetic equations, for non-dense systems, which avoided some of the previously described limitations of the Bogoliubov and (MTS) method. This scheme starts off by rewriting the hierarchy in terms of the correlation functions $g_s(\vec{x}_1 \ldots \vec{x}_s, t)$, which, for $s \geq 2, 3, 4$, may be expressed as follow: [1]

$$g_2(\vec{x}_1, \vec{x}_2, t) = F_2(\vec{x}_1, \vec{x}_2, t) - \tilde{F}_1(\vec{x}_1, t) F_1(\vec{x}_2, t) \qquad \text{(V-A-33)}$$

$$g_3(\vec{x}_1, \vec{x}_2, \vec{x}_3, t) = \tilde{F}_3(\vec{x}_1, \vec{x}_2, \vec{x}_3, t) - \prod_{k=1}^{3} F_1(\vec{x}_k, t) - \sum_{P(1,2,3)} \tilde{F}_1(\vec{x}_i, t)\, g_2(\vec{x}_j, \vec{x}_k, t) \qquad \text{(V-A-34)}$$

$$g_4(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4, t) = \tilde{F}_4(\vec{x}_1, \vec{x}_2, \vec{x}_3, \vec{x}_4, t) - \prod_{k=1}^{4} F_1(\vec{x}_k, t) - \sum_{P(1,2,3,4)} \left[\tilde{F}_1(\vec{x}_i, t)\, \tilde{F}_1(\vec{x}_j, t)\, g_2(\vec{x}_k, \vec{x}_l, t) + g_2(\vec{x}_i, \vec{x}_j, t)\, g_2(\vec{x}_k, \vec{x}_l, t) - \tilde{F}_1(\vec{x}_i, t)\, g_3(\vec{x}_j, \vec{x}_k, \vec{x}_l, t) \right] \qquad \text{(V-A-35)}$$

where $\sum_{P(1,2,3,4)}$ denotes a sum of all permutations of the indices i, j, k, l over the values $1, 2, 3, 4$.

Substituting the above expressions into the B.B.G.K.Y. hierarchy (IV-B-4), one may then obtain, after some manipulation, the following set of open equations for $\tilde{F}_1(\vec{x}, t)$, $g_2(\vec{x}_1, \vec{x}_2, t)$ and $g_3(\vec{x}_1, \vec{x}_2, \vec{x}_3, t)$

1 In this sub-section we shall use $\tilde{F}_s = V^s F_s$ and $\tilde{\mathcal{L}}_s = n \sum_{i=1}^{s} \int\int \frac{\partial \phi_{i,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial \tilde{F}_{s+1}}{\partial \vec{p}_i}\, d\vec{q}_{s+1}\, d\vec{p}_{s+1}$ with $n = \lim_{\substack{N \to \infty \\ V \to \infty}} \frac{N}{V}$

$$\frac{\partial \tilde{F}_1}{\partial t}(\vec{x}_1,t) = \varepsilon \tilde{\mathcal{L}}_1 g_2(\vec{x}_1,\vec{x}_2,t) \qquad \text{(V-A-36)}$$

$$\frac{\partial g_2}{\partial t}(\vec{x}_1,\vec{x}_2;t) + \mathcal{H}_2(1,2)\, g_2(\vec{x}_1,\vec{x}_2,t)$$
$$= \Theta_{1,2} \tilde{F}_1(\vec{x}_1,t)\tilde{F}(\vec{x}_2,t) + \varepsilon \alpha(\vec{x}_1,\vec{x}_2,t) \qquad \text{(V-A-37)}$$

$$\frac{\partial g_3(\vec{x}_1,\vec{x}_2,\vec{x}_3,t)}{\partial t} + \mathcal{H}_3(1,2,3)\, g_3(\vec{x}_1,\vec{x}_2,\vec{x}_3,t)$$
$$= \beta(\vec{x}_1,\vec{x}_2,x_3,t) + \varepsilon \gamma(\vec{x}_1,x_2,x_3,t) \qquad \text{(V-A-38)}$$

where:

$$\alpha = m \int [\Theta_{1,3} \tilde{F}_1(\vec{x}_1,t)\, g_2(\vec{x}_2,\vec{x}_3,t)$$
$$+ \Theta_{2,3} \tilde{F}_1(\vec{x}_2,t)\, g_2(\vec{x}_1,\vec{x}_3,t]\, d\vec{x}_3 + \tilde{\mathcal{L}}_2 g_3(x_1,x_2,x_3,t) \qquad \text{(V-A-39)}$$

$$\beta \equiv (\Theta_{1,2} + \Theta_{1,3})\, \tilde{F}_1(\vec{x}_1,t)\, g_2(\vec{x}_2,\vec{x}_3,t)$$
$$+ (\Theta_{1,2} + \Theta_{2,3})\, \tilde{F}_1(\vec{x}_2,t)\, g_2(\vec{x}_1,\vec{x}_3,t)$$
$$+ (\Theta_{1,3} + \Theta_{2,3})\, \tilde{F}_1(x_3,t)\, g_2(\vec{x}_1,\vec{x}_2,t) \qquad \text{(V-A-40)}$$

$$\gamma = m \int \sum_{p(1,2,3)} [\Theta_{1,4} \tilde{F}_1(\vec{x}_1,t)\, g_3(\vec{x}_2,\vec{x}_3,\vec{x}_4,t)$$
$$+ (\Theta_{1,4} + \Theta_{2,4})\, g_2(\vec{x}_1,\vec{x}_2,t)\, g_2(\vec{x}_3,\vec{x}_4,t)\, d\vec{x}_4 + \tilde{\mathcal{L}}_3 g_4(\vec{x}_1,x_2,x_3,x_4,t) \qquad \text{(V-A-41)}$$

$$\Theta_{ij} = \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \phi_{ij}}{\partial \vec{q}_j} \cdot \frac{\partial}{\partial \vec{p}_j}$$

These rather complex and cumbersome equations may now be integrated, in the usual fashion, for $s = 2,3$ over the full time interval $[0,t]$ so as to yield the follow-

ing equations.

$$g_2(\vec{x}_1,\vec{x}_2,t) = e^{-\mathcal{H}_2(1,2)t}\, g_2(\vec{x}_1,\vec{x}_2,0) + \int_0^t e^{-\mathcal{H}_2(1,2)t'}\, \Theta_{1,2}\, \tilde{F}_1(\vec{x}_1,t-t')\, \tilde{F}_1(\vec{x}_2,t-t')\, dt' + \int_0^t e^{-\mathcal{H}_2(1,2)t'}\, \varepsilon\, \alpha(\vec{x}_1,\vec{x}_2,t-t')\, dt' \qquad \text{(V-A-42)}$$

$$g_3(\vec{x}_1,\vec{x}_2,\vec{x}_3,t) = e^{-\mathcal{H}_3(1,2,3)t}\, g_3(\vec{x}_1,\vec{x}_2,\vec{x}_3,0) + \int_0^t e^{-\mathcal{H}_3(1,2,3)t'}\, [\beta(\vec{x}_1,\vec{x}_2,\vec{x}_3,t-t') + \varepsilon\, \tilde{\gamma}(\vec{x}_1,\vec{x}_2,\vec{x}_3,t-t')] \qquad \text{(V-A-43)}$$

Lewis and Harris, at this point, simplify the analysis by assuming all correlations to vanish at $t=0$ so as to eliminate the first term in the above two equations. If one then expands g_s in powers of ε

i.e. $$g_s = g_s^{(0)} + \varepsilon\, g_s^{(1)} + \varepsilon^2 g_s^{(2)} + \cdots \qquad \text{(V-A-44)}$$

and substitutes into (V-A-42) and (V-A-43), while collecting orders of ε, one then emerges with the following expressions for $g_2^{(0)}$, $g_2^{(1)}$ and $g_3^{(0)}$ which are those required to derive first and second order kinetic equations

$$g_2^{(0)} = \int_0^t e^{-\mathcal{H}_2(1,2)t'} \Theta_{1,2}\, \tilde{F}_1(\vec{x}_1, t-t')\, \tilde{F}_1(\vec{x}_2, t-t')\, dt' \qquad \text{(V-A-45)}$$

$$g_2^{(1)} = \int_0^t e^{-\mathcal{H}_2(1,2)t'} \alpha\left(F_1(t-t'), g_2^{(0)}(t-t'), g_3^{(0)}(t-t')\right) dt' \qquad \text{(V-A-46)}$$

$$g_3^{(0)} = \int_0^t e^{-\mathcal{H}_3(1,2,3)t'} \beta\left(F_1(t-t'), g_2^{(0)}(t-t')\right) dt' \qquad \text{(V-A-47)}$$

The above expansion, thus far, differs from the usual (IVP) scheme only in the initial conditions which have been assumed and the use of the correlation functions $g_s^{(k)}$. Furthermore one easily notes that the zeroth order solution bears on, one hand, an explicit time dependence (which for $|r_{1,2}| < r$ last only for a period of the order of $\tau_0 \sim [r/v_0]$) and an implicit dependence, via a functional dependence on $F_1(\vec{x}_1, t)$, which prevents the appearance of secular terms when (V-A-45) is substituted back into the rate equation (V-A-36). Now, since for $|\vec{r}_{1,2}| < r$ the integrand in equation (V-A-45) vanishes when t' is larger than the time $\tau(\vec{r}, x_2) \sim o[\tau_0]$ required for $e^{-\mathcal{H}_2(1,2)t'}$ to stream particles 1 and 2 outside the range of the interaction potentiar $\phi_{1,2}$ in $\Theta_{1,2}$ it would seem reasonable to attempt to express $F_1(\vec{x}_1, t-t')$ in terms of $F_1(\vec{x}_1, t)$ by performing some expansion in time about $t'=0$. By so doing one could

obtain a closed, markovian, kinetic equation for F_1. In order to accomplish this feat we need only to integrate equation (V-A-36) over the interval $[t-t', t]$ so as to arrive at

$$\tilde{F}_1(\vec{p}_1, t-t') = \tilde{F}_1(\vec{p}_1, t) + \varepsilon \int_0^{\Delta t} \tilde{\mathcal{L}}_1 g_2(\vec{x}_1, \vec{x}_2, t-t')\, dt' \qquad \text{(V-A-48)}$$

Furthermore, in order to formulate this expansion in time and distinguish it from the perturbation in ε one introduces a second label parameter ε_0 and rewrites (V-A-48) as

$$\tilde{F}_1(\vec{p}_1, t-t') = \tilde{F}_1(\vec{p}_1, t) + \varepsilon\varepsilon^* \int_0^{\Delta t} \tilde{\mathcal{L}}_1 g_2(\vec{x}_1, \vec{x}_2, t-t') \qquad \text{(V-A-49)}$$

or as

$$\tilde{F}_1(\vec{p}_1, t-t') = \tilde{F}_1(\vec{p}_1, t) + \varepsilon\varepsilon^* \int_0^{\Delta t} \tilde{\mathcal{L}}_1 \left\{ g_2^{(0)} + \varepsilon g_2^{(1)} + \varepsilon^2 g_2^{(2)} + \cdots \right\} dt' \qquad \text{(V-A-50)}$$

Now since $g_2^{(k)}$ are themselves functionals of $\tilde{F}_1(\vec{p}_1, t-t')$ Harris and Lewis pursue a secondary expansion of these correlation functions

$$g_3^{(k)} = g_3^{(k,0)} + \varepsilon\varepsilon_0\, g_3^{(k,1)} + (\varepsilon\varepsilon_0)^2 g_3^{(k,2)} \qquad \text{(V-A-51)}$$

Substituting (V-A-51), (V-A-49) into (V-A-45) and collecting orders of $\varepsilon\varepsilon_0$ one then obtains at the very lowest order the following solution

$$g_2^{(0,0)} = \int_0^t e^{-\mathcal{H}_2(1,2)t'} \Theta_{1,2}\, \tilde{F}_1(\vec{x}_1,t)\,\tilde{F}_1(\vec{x}_2,t)\,dt' \qquad \text{(V-A-52)}$$

which may also be written as

$$g_2^{(0,0)} = -\int_0^t e^{-\mathcal{H}_2(1,2)t'} \mathcal{H}_2(1,2)\,\tilde{F}_1(\vec{x}_1,t)\,\tilde{F}_1(\vec{x}_2,t)\,dt'$$
$$= \left[e^{-\mathcal{H}_2(1,2)t} - 1 \right] \tilde{F}_1(\vec{x}_1,t)\,\tilde{F}_1(\vec{x}_2,t) \qquad \text{(V-A-53)}$$

Consequently the lowest order kinetic equation becomes

$$\frac{\partial \tilde{F}_1(\vec{p}_1,t)}{\partial t} = \varepsilon \tilde{\mathcal{L}}_1\, e^{-\mathcal{H}_2(1,2)t}\, \tilde{F}_1(\vec{x}_1,t)\,\tilde{F}_1(\vec{x}_2,t) \qquad \text{(V-A-54)}$$

which for $t \gg \tau_0$ may also be written as

$$\frac{\partial \tilde{F}_1(\vec{p}_1,t)}{\partial t} = \tilde{\mathcal{L}}_1\, \tilde{F}_1(P_1^-(\infty),t)\,\tilde{F}_1(P_2^-(\infty),t) \qquad \text{(V-A-55)}$$

such that, using arguments similar to those in appendix I, one recovers the usual Boltzmann equation;

$$\frac{\partial f_1}{\partial t} = J_B(f_1,\,)$$

The Harris and Lewis expansion, due to its use of correlation functions and double expansions, certainly does not represent one of the simplest methods of

truncating the hierarchy. Consequently one must undertake formidable calculations to pursue the expansion to higher orders. Furthermore, because of the extremely complex form of the higher level correlation functions g_s with s large, the scheme must generally restrict itself to expansions in which only the low level correlation functions contribute to the lower order kinetic equations. For this reason this approach would not seem very well suited to the study of Brownian motion where the full N particle interactions play a role in the kinetic equations. Finally the assumption of an initially correlation free gas would seem unnecessarily restrictive. Nevertheless, in spite of these limitations, the Lewis and Harris approach does avoid Bogoliubov's functional assumption and, unlike the (MTS) perturbation, can be used for non-uniform systems. Furthermore some of the techniques used to avoid secular solutions merit special notice. These include, on one hand, the introduction of correlation functions, and on the other hand the integration of (V-A-36) over the short time interval $[t-t', t]$ with $t' \sim o[\tau_0]$, as opposed to the full range $[o,t]$ used in the (IVP) scheme. This latter procedure, which allows one to express $F_1(p_1,t)$ in terms of the nearby $F_1(\vec{p}_1,t-t')$ rather than a time independent $F_1(\vec{p}_1,o)$ represents a very clear and useful approach which will be fully exploited in the following section devoted to the development of a simple alternate expansion scheme.

B. A REINITIALIZATION PERTURBATION APPROACH

A straightforward perturbational derivation of kinetic equations may be formulated if one briefly reconsiders some of the main features of the (IVP) scheme described in the previous chapter. Let us, for instance, recall the simple illustrative time delay equation

$$\frac{dx}{dt} = -\varepsilon x(t-\tau) \qquad \text{(IV-A-10)}$$

where

$$x(t) = x_0 \quad \text{for } t>0$$

$$\tau = \text{constant}$$

$$\varepsilon \ll 1$$

Now, we recall that the simple (IVP) expansion of (IV-A-10) renders secular solutions which cause a complete breakdown of the expansion when $t \gtrsim \tau^{\Delta}$, $\tau^{\Delta} \sim o[1/\varepsilon]$. One obvious way around this obstacle consists of applying this expansion scheme only over a time interval $\Delta t \ll \tau^{\Delta}$. Indeed, let us reinstate the power expansion (IV-A-2)

$$x(t) = x^{(0)} + \varepsilon x^{(1)} + \varepsilon^2 x^{(2)} + \ldots$$

and the resulting expansion equations (IV-A-11)

$$\frac{dx^{(0)}}{dt} = 0 \qquad \text{(IV-A-11-0)}$$

$$\frac{dx^{(1)}}{dt} = -x^{(0)}(t-\tau) \qquad \text{(IV-A-11-1)}$$

$$\frac{dx^{(k)}}{dt} = -x^{(k-1)}(t-\tau) \qquad \text{(IV-A-11-k)}$$

Now integrating (IV-A-11-0) over the interval $[t-\Delta t, t]$ such that

$$x^{(0)}(t) = x^{(0)}(t-\Delta t) \quad , \Delta t \ll \tau^{A} \qquad \text{(V-B-1)}$$

and further assuming that $\tau \ll \tau^{A}$ we may then write (V-A-11-1) as

$$\frac{dx^{(1)}}{dt} = -x^{(0)}(t)$$

Consequently combining (V-B-1) and (IV-A-11-0) one thus obtains, to the first order of ε, the following, non secular rate equation for $x(t)$

$$\frac{dx}{dt} = -\varepsilon x + o[\varepsilon^2] \qquad \text{(V-B-2)}$$

Furthermore, one may pursue this type of expansion to higher orders by rewriting the second order equation as

$$\frac{dx^{(2)}}{dt} = -x^{(1)}(t-\tau)$$

$$= -\left\{ x^{(1)}(t) + \int_{t-\tau}^{t} x^{(0)}(t')\,dt' \right\}$$

$$= -[x^{(1)}(t) + \tau x^{(0)}(t)]$$

such that combining this equation with the lower order

expressions one obtains

$$\frac{dx}{dt} = -\varepsilon\,[1+\varepsilon\tau]\,x(t) + o[\varepsilon^3] \qquad \text{(V-B-4)}$$

The above perturbation scheme distinguishes itself from the (IVP) expansion only by the fact that solutions for $X^{(k)}(t)$ are expressed in terms of $X^{(k)}(t-\Delta t)$, $\Delta t \ll \tau^*$ rather than $X(0)$; in this way the scheme reinitializes itself so as to prevent the appearance of secular terms. This of course does not at all imply that the solutions extracted from this scheme will, in fact, converge to the exact solution. Indeed, since the latter requires the previous history $x(t)$, $-\tau < t < 0$, while the solutions of the expansion equations (V-B-2) and (V-B-4) may be obtained from $x(0)$ alone, it is clear that, for this simple example, the above perturbation can, at best, lead to approximate solutions for $x(t)$.

a) <u>The Simple Uniform Non-Dense System</u>.

The above reinitialization perturbation approach may now be applied to the truncation of the B.B.G.K.Y. hierarchy for particular molecular systems. Let us for example, reconsider the simple uniform non-dense gas by recalling the hierarchy in the following form

$$\frac{\partial F_s}{\partial t} + \mathcal{H}_s F_s = \varepsilon\, \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-4)}$$

and expanding F_s in powers of ε

i.e. $F_s = F_s^{(0)} + \varepsilon F_s^{(1)} + \varepsilon^2 F_s^{(2)}$

such that, collecting orders of ε one retains

$$\frac{\partial F_s^{(0)}}{\partial t} + \mathcal{H}_s F_s = 0 \qquad \text{(IV-B-7-0)}$$

$$\frac{\partial F_s^{(1)}}{\partial t} + \mathcal{H}_s F_s^{(1)} = \mathcal{L}_s F_{s+1}^{(0)} \qquad \text{(IV-B-7-1)}$$

$$\frac{\partial F_s^{(k)}}{\partial t} + \mathcal{H}_s F_s^{(k)} = \mathcal{L}_s F_{s+1}^{(k-1)} \qquad \text{(IV-B-7-k)}$$

The main feature of the reinitialization approach consists of integrating the above equations over a time interval Δt sufficiently short to preserve the validity of the expansion. Now since the (IVP) scheme completely breaks down when $t^* > o[1/\varepsilon_1]$, or, in dimensional terms, when $t > o[\tau_1] \sim o[\lambda/v_0]$, one should therefore restrict Δt to values much smaller than the time interval τ_1 between collisions. With this constraint in mind, let us integrate the zeroth order equation (IV-B-7-0) over the interval $[t-\Delta t, t]$ so as to obtain the following solution for $F_s^{(0)}$

$$F_s^{(0)}(x_s, t) = e^{-\mathcal{H}_s \Delta t} F_s^{(0)}(x_s, t-\Delta t) \qquad \Delta t \ll \tau_1 \qquad \text{(V-B-5)}$$

Now assuming that for a given $\tau_{\{s\}} \ll \tau_1$, there exists a

volume $V^{+}_{\{s\}} \subset V_{\{s\}}$ in $\Gamma_{\{s\}}$ space for which the backward streaming operator $\mathcal{L}^{-\mathcal{H}_s \Delta t}$ (with $\Delta t > \tau_{\{s\}}$) will stream the s particles permanently outside their mutual range of interaction and correlation, one may then impose the following modified Bogoliubov boundary conditions

$$\mathcal{L}^{-\mathcal{H}_s \Delta t} F_s(x_s, t) = \prod_{i=1}^{s} F_1(\vec{P}_i^{-}(\infty), t) \qquad \text{(V-B-6)}$$

$$\Delta t > \tau_{\{s\}}$$
$$X_{\{s\}} \in V^{+}_{\{s\}}$$

Substituting the expansion of F_s into the above equation and collecting orders of ε we may then write the following particular boundary conditions required to derive first and second order kinetic equations.

$$\mathcal{L}^{-\mathcal{H}_2(i,j)\Delta t} F_2^{(0)}(\vec{x}_i, \vec{x}_j, t) = F_1(\vec{P}_i^{-}(\infty), t)\, F_1(\vec{P}_j^{-}(\infty), t) \qquad \text{(V-B-7)}$$

$$\vec{X}_2 \in V^{+}_{\{2\}}$$
$$\Delta t > \tau_{\{2\}}$$

$$\mathcal{L}^{-\mathcal{H}_3(i,j,k)\Delta t} F_3^{(0)}(\vec{x}_i, \vec{x}_j, x_k) = \lim_{\tau \to \infty} \mathcal{L}^{-\mathcal{H}_3(i,j,k)\tau} F_1(\vec{P}_i, t)\, F_1(\vec{P}_j, t)\, F_1(\vec{P}_k, t) \qquad \text{(V-B-8)}$$

$$\vec{X}_3 \in V^{+}_{\{3\}}$$
$$\Delta t > \tau_{\{3\}}$$

$$\mathcal{L}^{-\mathcal{H}_2(i,j)\Delta t} F_2^{(1)}(\vec{x}_i, \vec{x}_j, t) = \left[F_1^{(0)}(\vec{P}_i^{-}(\infty), t)\, F_1^{(1)}(\vec{P}_j^{-}(\infty), t) + F_1^{(0)}(\vec{P}_j^{-}(\infty), t)\, F_1^{(1)}(\vec{P}_i^{-}(\infty), t) \right] \qquad \text{(V-B-9)}$$

$$\vec{X}_2 \in V^{+}_{\{2\}}$$
$$\Delta t > \tau_{\{2\}}$$

With these boundary conditions, and equation (V-B-5), at hand one may then write the following zeroth order solutions which should hold for $\vec{X}_s \in V^+_{(s)}$, and chosen such that $\tau_{(s)} \ll \tau_1$

$$F_1^{(0)}(\vec{p}_i, t) = F_1^{(0)}(\vec{p}_i, t - \Delta t) \qquad \Delta t \ll \tau_1 \qquad \text{(V-B-10)}$$

$$F_2^{(0)}(\vec{X}_i, \vec{X}_j, t) = F_1^{(0)}(\vec{P}_i^-(\infty), t) F_1^{(0)}(\vec{P}_j^-(\infty), t) \qquad \text{(V-B-11)}$$
$$X_{(2)} \in V^+_{(2)}$$
$$\tau_{(2)} \ll \tau_1$$

$$F_3^{(0)}(\vec{X}_i, \vec{X}_j, \vec{X}_k, t) = \lim_{\tau \to \infty} e^{-\mathcal{H}_3(i,j,k)\tau} F_1(\vec{p}_i, t) F_1(\vec{p}_j, t) F_1(\vec{p}_k, t) \qquad \text{(V-B-12)}$$
$$X_{(3)} \in V^+_{(3)}$$
$$\tau_{(3)} \ll \tau_1$$

Now since one may derive a first order kinetic equation with the knowledge of $F_2(x_i, x_j, t)$ for $|\vec{r}_{ij}| < r_0$ and that, for such a restricted domain, $\tau_{(2)} \sim O[\tau_0] \sim O[r_0/v_0] \ll \tau_1$ one may then use the solution (V-B-11) and substitute it into (IV-B-7-1), for $s=1$, so as to obtain the following first order equation for F_1 ,

$$\frac{\partial F_1^{(1)}}{\partial t} = \mathcal{L}_1 F_1^{(0)}(\vec{P}_i^-(\infty), t) F_1^{(0)}(\vec{P}_j^-(\infty), t) \qquad \text{(V-B-13)}$$

Furthermore, combining (V-B-13) and (IV-B-7-1) for $s=1$, and resorting to arguments similar to those of appendix

I , one then retains the familiar Boltzmann equation for f_1:

$$\frac{\partial f_1}{\partial t} = J_B(f_1)$$

as a first order kinetic equation.

The above expansion may be pursued to a higher order by first integrating (V-B-13) over a time interval $[t-\Delta t, t]$, $\Delta t \ll \tau_1$, so as to obtain a suitable expression of $F_1^{(1)}(t-\Delta t)$ in terms of $F_1^{(1)}(t)$ and $F_1^{(0)}(t)$. One can then integrate the first order equation (V-B-7-1) for $s=2$, also over the time interval $[t-\Delta t, t]$ so as to derive with the help of boundary condition (V-B-9) a suitable solution for $F_2^{(1)}$ which may then be utilized to derive the second order Uhlenbeck and Choh [41] kinetic equation. [1] In summary, therefore the reinitialization scheme may be described schematically as follow.

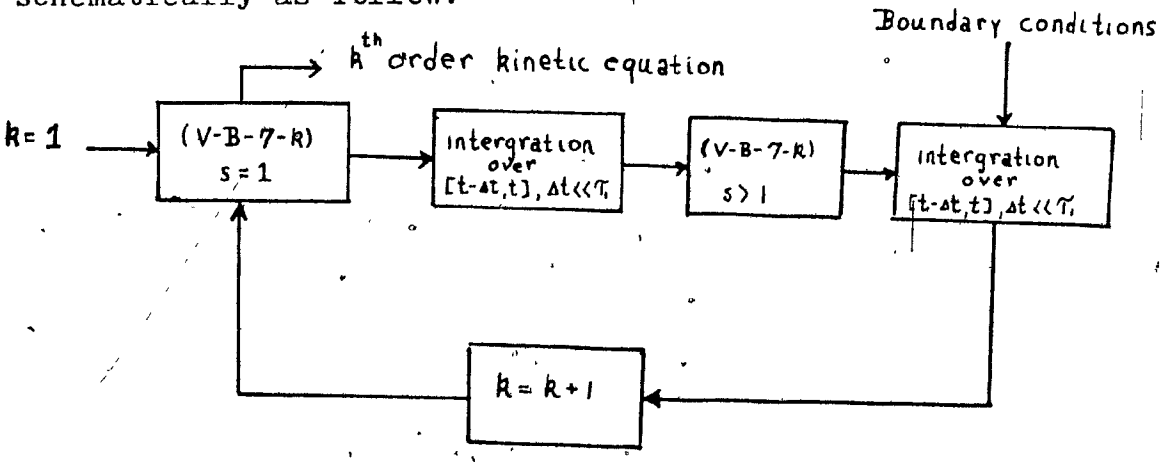

Fig. V-5

1 See appendix III for details

The reinitialization perturbation scheme described above, simply involves the integration of the perturbed rate equations over a time interval Δt reasonably short to preserve the validity of the expansion yet sufficiently long to impose reasonable boundary conditions. This simple approach offers the advantage of avoiding Bogoliubov's restrictive functional assumption and the previously described limitations of Harris and Lewis' complex double expansion of correlation functions. Finally, as will be shown in chapter VI , one may apply this scheme to non-uniform simple gases or mixtures which do not lend themselves to an (MTS) expansion.

b) Simple Uniform Weakly Coupled System

Let us now consider the feasibility of applying the reinitiatization expansion to a simple uniform weakly coupled system by recalling the B.B.G.K.Y. hierarchy in the form of equation (IV-B-26)

i.e. $$\frac{\partial F_s}{\partial t} + \varepsilon \mathcal{H}_s F_s = \varepsilon \mathcal{L}_s F_{s+1} \qquad \text{(IV-B-26)}$$

and performing the usual expansion in powers of the label parameter

i.e. $$F_s = F_s^{(0)} + \varepsilon F_s^{(1)} + \varepsilon^2 F_s^{(2)} + \ldots$$

such that substituting the above equation into the hierarchy and collecting orders of ε , one retains the following perturbed equations

$$\frac{\partial F_s^{(0)}}{\partial t} = 0 \qquad \text{(IV-B-29-0)}$$

$$\frac{\partial F_s^{(1)}}{\partial t} = - \mathcal{H}_s F_s^{(0)} + \mathcal{L}_s F_{s+1}^{(0)} \qquad \text{(IV-B-29-1)}$$

$$\frac{\partial F_s^{(k)}}{\partial t} = - \mathcal{H}_s F_s^{(k-1)} + \mathcal{L}_s F_s^{(k-1)} \qquad \text{(IV-B-29-k)}$$

Integrating (IV-B-29-0) over the interval $(t-\Delta t, t)$, we obtain the following trivial solution

$$F_s^{(0)}(\vec{x}_s, t) = F_s^{(0)}(\vec{x}_s, t-\Delta t) \qquad \text{(V-B-14)}$$

The simplicity of this solution becomes, in fact, somewhat disconcerting since the absence of a streaming operator on the right hand side of (V-B-14) prevents us from imposing suitable boundary conditions which could transform the solution into a viable explicit, or implicit, solution in time. Consequently, one must reluctantly conclude that, for weakly coupled system, as defined in the present thesis, one cannot derive a useful kinetic equation via a perturbation approach. Indeed, one would

face the very same dilemna if a Bogoliubov, (MTS), or Harris and Lewis expansion of (IV-B-26) had been attempted. In spite of this conclusion, one may find in the literature numerous perturbational derivations of kinetic equations for uniform weakly coupled systems. However, as previously emphasized these derivations are generally founded on faulty dimensional analyses which dubiously assign a greater weight to the momentum streaming term $\sum \frac{\vec{p}_i}{m} \frac{\partial F_s}{\partial \vec{q}_i}$ than the remaining interaction and mixing terms $\sum \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_s}{\partial \vec{p}_i}$, $\mathcal{L}_s F_{s+1}$. Such a peculiar scaling could, in fact, only hold temporarily as the result of strong initial correlations. Naturally, if one accepts the ideas of Bogoliubov, such correlations would be forgotten when the kinetic regime established itself. Consequently, any kinetic equation founded on this special ordering of terms would seem rather suspect.

c) Simple Uniform Brownian System.

As a final illustration of the reinitialization perturbation method for spatially uniform systems, consider the special case of a single heavy Brownian particle coexisting with a bath of N identical light particles. For this purpose, let us recall the B.B.G.K.Y. hierarchy for the single Brownian particle and the full Liouville equation as given by equations (IV-B-44) and

(IV-B-45) respectively

$$\frac{\partial F_{\{0,1\}}}{\partial t} = \varepsilon \mathcal{L} F_{\{1,1\}} \qquad \text{(IV-B-44)}$$

$$\frac{\partial F_{\{N,1\}}}{\partial t} + \left\{ \mathcal{H}^{I}_{\{N,1\}} + \varepsilon \mathcal{H}^{II}_{\{N,1\}} \right\} F_{\{N,1\}} = 0 \qquad \text{(IV-B-45)}$$

where

$$\mathcal{L} = N \int\int \frac{\partial \phi^{B,b}_{1,1}}{\partial \vec{q}_1^{\,B}} \cdot \frac{\partial}{\partial \vec{p}_1^{\,B}} \, d\vec{r}^{\,B}_{1,1} \, d\vec{p}_1^{\,b} \qquad \text{(IV-B-46)}$$

$$\left.\begin{aligned} \mathcal{H}^{I}_{\{N,1\}} &= \sum_{i=1}^{N} \frac{\vec{p}_i^{\,b}}{m_b} \cdot \frac{\partial}{\partial q_i^{b}} - \sum_{i=1}^{N} \left[\left(\sum_{j=1}^{N} \frac{\partial \phi^{bb}_{i,j}}{\partial \vec{q}_i^{\,b}} \right) \right. \\ &\left. + \frac{\partial \phi^{b\,B}_{i,1}}{\partial \vec{q}_i^{\,B}} \right] \cdot \frac{\partial}{\partial \vec{p}_i^{\,b}} \\ \mathcal{H}^{II}_{\{N,1\}} &= \frac{\vec{p}_1^{\,B}}{m_B} \cdot \frac{\partial}{\partial \vec{q}_1^{\,B}} - \sum_{i=1}^{N} \frac{\partial \phi^{B,b}_{1,i}}{\partial \vec{q}_1^{\,B}} \cdot \frac{\partial}{\partial \vec{p}_1^{\,B}} \end{aligned}\right\} \qquad \text{(IV-B-47)}$$

Expanding $F_{\{s,1\}}$, as in the previous chapter, in powers of the label parameter ε and substituting into (IV-B-44) and (IV-B-45) we then retain, after collection of terms, the following equations for $F^{(k)}_{\{0,1\}}$ and $F^{(k)}_{\{N,1\}}$

$$\left.\begin{aligned} \frac{\partial F^{(0)}_{\{0,1\}}}{\partial t} &= 0 \\ \frac{\partial F^{(1)}_{\{0,1\}}}{\partial t} &= \mathcal{L} F^{(0)}_{\{1,1\}} \\ &\vdots \\ \frac{\partial F^{(k)}_{\{0,1\}}}{\partial t} &= \mathcal{L} F^{(k-1)}_{\{N,1\}} \end{aligned}\right\} \qquad \text{(IV-B-49)}$$

$$\left.\begin{aligned}
&\frac{\partial F^{(0)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(0)}_{\{N,1\}} = 0 \\
&\frac{\partial F^{(1)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(1)}_{\{N,1\}} = -\mathcal{H}^{II}_{\{N,1\}} F^{(0)}_{\{N,1\}} \\
&\vdots \\
&\frac{\partial F^{(k)}_{\{N,1\}}}{\partial t} + \mathcal{H}^{I}_{\{N,1\}} F^{(k)}_{\{N,1\}} = -\mathcal{H}^{II}_{\{N,1\}} F^{(k-1)}_{\{N,1\}}
\end{aligned}\right| \qquad \text{(IV-B-50)}$$

Following an outline similar to that used for the non-dense system we shall integrate (IV-44-0) and (IV-B-50-0) over the time interval $[t-\Delta t, t]$ where Δt will be chosen as short as possible to preserve the validity of the following solutions

$$F^{(0)}_{\{0,1\}}(\vec{P}_1, t) = F^{(0)}_{\{0,1\}}(\vec{P}^B_1, t-\Delta t) \qquad \text{(V-B-15)}$$

$$F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}}, t) = e^{-\mathcal{H}^{I}_{\{N,1\}}\Delta t} F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}}, t-\Delta t) \qquad \text{(V-B-16)}$$

Now, since $e^{-\mathcal{H}^{I}_{\{N,1\}}\Delta t}$ simply streams the bath particles back in time in the presence of the Brownian particle, we shall assume that there exists a relaxation time τ_b such that for $\Delta t > \tau_b$ these light particles will have reached an equilibrium state with the larger particle. In other words we shall assume the following boundary condition

$$e^{-\mathcal{H}^{I}_{\{N,1\}}\Delta t} F_{\{N,1\}}(\vec{X}_{\{N,1\}}, t) = e^{-\mathcal{H}^{I}_{\{N,1\}}\Delta t} F_{\{N,0\}\,eq.} F_{\{0,1\}}(\vec{P}^B_1, t)$$

$$= F_{\{N,0\}\,eq.} F_{\{0,1\}}(\vec{P}^B_1, t)$$

$$\Delta t > \tau_b$$

where $F_{\{N,0\}_{eq}}$ denotes the equilibrium distribution for the bath particles as defined by (IV-B-56). Now substituting the expansions for $F_{\{N,1\}}$ and $F_{\{0,1\}}$ into (V-B-17) and collecting orders of ε one then emerges with the following boundary condition for

$$e^{-\mathcal{H}^I_{\{N,1\}}\Delta t} F^{(k)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t)^\circ = e^{-\mathcal{H}^I_{\{N,1\}}\Delta t} F_{\{N,0\}_{eq}} F^{(k)}_{\{0,1\}}(\vec{p}^B_1,t) \qquad \Delta t > \tau_c \qquad \text{(V-B-18)}$$

Consequently if we further assume that the time interval Δt remains sufficiently short to preserve the validity of the expansion we may then rewrite the zeroth order solution (V-B-18) as:

$$F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = F_{\{N,0\}_{eq}} F^{(0)}_{\{0,1\}}(\vec{p}^B_1,t-\Delta t)$$

$$= F_{\{N,0\}_{eq}} F^{(0)}_{\{0,1\}}(\vec{p}^B_1,t) \qquad \text{(V-B-19)}$$

which simply states that, in the zeroth order approximation the bath particles may be considered in equilibrium with themselves and the Brownian particle although the latter remains in a state of nonequilibrium.

We may now derive a first order kinetic equation by integrating $F^{(0)}_{\{N,1\}}$ over the coordinates and momenta of all but one bath particle so as to obtain a suitable zeroth order solution for the two particle distribution $F^{(0)}_{\{1,1\}}(\vec{q}^b_1,\vec{p}^b_1,\vec{q}^B_1,\vec{p}^B_1,t)$. Performing this integration one then obtains

$$F^{(0)}_{\{1,1\}}(\cdot,t) = \int\cdots\int F^{(0)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t)\prod_{k=2}^{N} dq_k^b\, dp_k^b$$

$$= F_{\{0,1\}}(\vec{p}_1^{\,B},t)\, F^{(0)}_{\{1,0\}eq} \qquad \text{(V-B-20)}$$

where $F_{\{1,0\}eq}$ denotes the Maxwellian distribution defined in (IV-B-63). Substituting (V-B-20) into (IV-B-49-1) one emerges with the following trivial kinetic equation

$$\frac{\partial F^{(1)}_{\{0,1\}}}{\partial t} = 0 \qquad \text{(V-B-21)}$$

which, as usual, shall be integrated over the interval $[t-\Delta t, t]$ to yield

$$F^{(1)}_{\{0,1\}}(\vec{p}_1^{\,B},t) = F^{(1)}_{\{0,1\}}(\vec{p}_1^{\,B}, t-\Delta t) \qquad \text{(V-B-22)}$$

Now proceeding to the first order equation for $F_{\{N,1\}}$ let us integrate (IV-B-50-1) over the interval $[t-\Delta t, t]$ and recall (V-B-22) and the boundary condition (V-B-18) so as to obtain the following solution

$$F^{(1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = F_{\{N,0\}eq}\, F^{(1)}_{\{0,1\}}(\vec{p}_1^{\,B},t)$$
$$-\int_0^{\Delta t} e^{-\mathcal{H}^{I}_{\{N,1\}}t'}\,\mathcal{H}^{II}_{\{N,1\}}\, F_{\{N,0\}eq}\, F^{(0)}_{\{0,1\}}(\vec{p}_1^{\,B},t)\,dt' \qquad \text{(V-B-23)}$$

which, after some manipulation may also be written as

$$F^{(1)}_{\{N,1\}}(\vec{X}_{\{N,1\}},t) = F_{\{N,0\}_{eq}} F^{(1)}_{\{0,1\}}(\vec{p}_1^{\,2},t)$$

$$- \int_0^{\Delta t} \vec{SF}(-t')\,dt' \cdot \left(\frac{\vec{p}_1^{\,2}}{m_B K T} + \frac{\partial}{\partial \vec{p}_1^{\,2}} \right) F_{\{N,0\}_{eq}} F^{(0)}_{\{0,1\}}(\vec{p}_1^{\,2},t)$$

(V-B-24)

where

$$\vec{SF}(-t') = e^{-\mathcal{H}^I_{\{N,1\}} t'} \vec{SF}$$

$$\vec{SF} = -\sum_{j=1}^{N} \frac{\partial \phi^{Bb}_{1,j}}{\partial \vec{q}_1^{\,2}}(|\vec{r}^{\,Bb}_{1,1}|) = \sum_{j=1}^{N} \vec{SF}_j$$

Now integrating this solution over the coordinates and momenta of all, but one, bath particles, we may then express $F^{(1)}_{\{1,1\}}$ as follow:

$$F^{(1)}_{\{1,1\}} = -\int_0^{\Delta t} \int\cdots\int \vec{SF}(-t')\, F_{\{N,0\}_{eq}} \prod_{K=2}^{N} d\vec{q}_K^{\,B}\, d\vec{p}_K^{\,B}\, dt'$$

$$\cdot \left(\frac{\vec{p}_1^{\,2}}{m_B K T} + \frac{\partial}{\partial \vec{p}_B} \right) F^{(0)}_{\{0,1\}}(\vec{p}_1^{\,2},t)$$

such that substituting this solution into (V-B-49-2) for $F_{\{0,1\}}$ and assigning, once more, no distinction between bath particles we may then arrive at the following rate equation for $F^{(2)}_{\{0,1\}}$

$$\frac{\partial F^{(2)}_{\{0,1\}}}{\partial t} = \int_0^{\Delta t} \langle \vec{SF}\, \vec{SF}(-t') \rangle_{eq}\, dt'$$

$$: \frac{\partial}{\partial \vec{p}_1^{\,2}} \left(\frac{\vec{p}_1^{\,2}}{m_B K T} + \frac{\partial}{\partial \vec{p}_1^{\,2}} \right) F^{(0)}_{\{0,1\}}(\vec{p}_1^{\,2},t) \qquad \text{(V-B-26)}$$

$\Delta t > \tau_b$

Finally since Δt must be chosen larger than the time required for the bath particles to reach an equilibrium with the Brownian particle, which is characterized by a much longer relaxation time, τ_B, it would seem reasonable to also assume that the autocorrelation function $\langle \vec{\mathcal{F}} \cdot \vec{\mathcal{F}}(t') \rangle$ should become vanishingly small for $t' > \tau_b$. Consequently, with this further assumption one may rewrite (V-B-26) as

$$\frac{\partial F^{(2)}_{[0,1]}}{\partial t} = \bar{\bar{b}} : \frac{\partial}{\partial \vec{p}_1^B} \left[\frac{\vec{p}_1^B}{m_B kT} + \frac{\partial}{\partial \vec{p}_1^B} \right] F^{(0)}_{[0,1]} \quad .$$

where

$$\bar{\bar{b}} \equiv \int_0^\infty \langle \vec{\mathcal{F}} \, \vec{\mathcal{F}}(t') \rangle_{eq} \, dt' \qquad \text{(V-B-27)}$$

Consequently combining this equation with the lower order equations (V-B-21) and (IV-B-49-0) one emerges with the following kinetic equation

$$\frac{\partial F_{[0,1]}}{\partial t} = J_{F.P.}\left(F_{[0,1]}\right) + O[\varepsilon^3]$$

$$J_{F.P.} = \bar{\bar{b}} : \frac{\partial}{\partial \vec{p}_1^B} \left[\frac{\vec{p}_1^B}{m_B kT} + \frac{\partial}{\partial \vec{p}_1^B} \right]$$

which is, of course, the well known Fokker Planck equation for Brownian Motion.

C. SUMMARY AND CONLUSIONS

This chapter has reviewed some of the alternate perturbation schemes which have been used in the past to

derive non divergent kinetic equations. It has also developed a simplified expansion approach, emerging as a natural extension of the initial value perturbation scheme, which hopefully clarifies some of the limitations and subtle ambiguities encountered in these earlier methods. In this review, three particular approaches have been considered: Bogoliubov's functional expansion [12], Frieman's multiple time scale (MTS) perturbation scheme [24] and finally Lewis and Harris' time expansion method [39]. Furthermore, for the sake of illustration, each technique has been applied to the simple spatially uniform non-dense system.

The Bogoliubov approach rests on the assumption that for $t \gg r_0/v_0$, $F_s(s\pi/2)$ bears a time dependence only through a functional dependence on F_1 and hinges, in its derivation of the Boltzmann equation, on the boundary condition

$$\lim_{\tau\to\infty} e^{-\mathcal{H}_2\tau} F_2(\vec{x}_i,\vec{x}_j|F_1) = \lim_{\tau\to\infty} e^{-\mathcal{H}_2\tau} F_1(\vec{p}_i,t) F_1(\vec{p}_j,t) \qquad \text{(V-C-1)}$$

The MTS expansion, on the other hand, replaces the real time t by a set of progressively slower time scales $t_0, t_1, t_2, \cdots$,

$$\text{where } t = t_0 = t_1/\varepsilon = t_2/\varepsilon^2 = \cdots t_i/\varepsilon^i \qquad \text{(V-C-2)}$$

and derives the Boltzmann equation on the slow t_1 scale,

by imposing on the fast t_0 scale the boundary condition[1]

$$\lim_{t_0\to\infty} e^{-\mathcal{H}_2 t_0} F_2^{(0)}(\vec{x}_1,\vec{x}_2,0,t_1,t_2) = \lim_{t_0\to\infty} e^{-\mathcal{H}_2 t_0} F_1^{(0)}(\vec{p}_1,0,t_1,t_2\cdots) F^{(0)}(\vec{p}_2,0,t_1,t_2\cdots) \qquad \text{(V-C-3)}$$

and setting to zero the sum of all terms growing linearly with t_0, as $t_0\to\infty$, in the solution for F_1. The strength of both of these expansion methods would seem to rest on the added flexibility alloted by the introduction of auxiliary time variables such as τ in the Bogoliubov approach and $t_0, t_1, \ldots$ in the MTS method. Whereas in the former expansion the arbitrary independent time variable τ allows one to seek a particular boundary condition in the limit $\tau\to\infty$ without naturally imposing a similar limit in the real time t, the discrete set of time scales in the latter approach allows the derivation of a kinetic equation on a slow time scale through the elimination of secular terms on a faster time scale. Unfortunately, these auxiliary time scales also carry with them a certain level of arbitrariness and at times, a definite degree of inconsistency. For example the particular choice by Bogoliubov of the limit $\tau\to\infty$ in the boundary condition (V-C-1) represents one not only of insight, but of convenience. Indeed, as

1 This boundary condition has occasionally been replaced by the initial condition on the t_0 time scale [25].

$$F_2^{(0)}(\vec{x}_1,\vec{x}_2,0,t_1,t_2) = F_1^{(0)}(\vec{p}_1,0,t_1,t_2\cdots) F_1^{(0)}(\vec{p}_2,0,t_1,t_2\cdots)$$

first noted by Cohen and Berlin [23] the seemingly equally plausible assumption that

$$\lim_{\tau\to-\infty} e^{-\mathcal{H}_2(i,j)\tau} F_2(\vec{x}_i,\vec{x}_j|F_1) = \lim_{\tau\to-\infty} e^{-\mathcal{H}_2(i,j)\tau} F_1(\vec{p}_i,t)\,F_1(\vec{p}_j,t) \qquad \text{(V-C-4)}$$

leads to a so-called "anti-Boltzmann" characterized by a negative collision term and a time evolution with decreasing entropy. Such an equation, with its irreversibility seemingly pointing the "wrong way", could also be extracted from the MTS scheme by imposing the seemingly reasonable boundary condition

$$\lim_{t_0\to-\infty} e^{-\mathcal{H}_2(i,j)t_0} F_2^{(0)}(\vec{x}_i,\vec{x}_j,0,t_1,t_2) = \lim_{t_0\to-\infty} e^{-\mathcal{H}_2(i,j)t_0} F_1^{(0)}(\vec{p}_i,0,t_1,t_2)\,F_1^{(0)}(\vec{p}_j,0,t_1,t_2) \qquad \text{(V-C-5)}$$

and eliminating secular terms appearing in the limt $t_0\to-\infty$ Furthermore, due to equation (V-C-2) relating the various time scales with themselves and the real time one cannot, strictly speaking, consider such variables as independent and consequently take a limit $t_0\to\pm\infty$ without implying similar limits on $t_1, t_2 \ldots$ Finally, in terms of possible applications, the MTS approach suffers from the fact that kinetic equations emerge only if the exact form of the secular terms on the fast time scale may be derived. Unfortunately, since such a task becomes extremely difficult in the case of a non uniform system, the derivation of kinetic equations, using

the MTS scheme has generally been restricted to uniform (or quasiuniform) systems.

It has become quite evident since the development of the Bogoliubov and MTS expansions that such methods remain in their mathematical form incomplete without a proper interpretation of the assumptions and auxiliary time scales involved. Hence, as will be discussed shortly, the resolution of the inconsistencies mentioned above lies beyond their detailed mathematical manipulations into what we shall very loosely refer to as their inherent "physical spirit"... In fact it was presumably in the hope of clarifying this "physical spirit" of these schemes that Lewis and Harris presented an alternate derivation of kinetic equations for nondense systems which they believed to be "physically more transparent than other methods." The Lewis and Harris scheme essentially consisted of expressing the s particle distribution in terms of correlation functions and performing a double expansion in density and time on the B.B.G.K.Y. hierarchy. Without reviewing the detailed description of this method, which is included in the main text of this chapter, suffice it to say that, due to the complex form these correlation functions give to the B.B.G.K.Y. hierarchy, along with the cumbersome double expansion, the Lewis and Harris approach does not represent, in mathematical terms, the simplest method of deriving kinetic equations. Furthermore, due to the

intricate form of the higher level correlation functions such a method would not lend itself very well, for example, to the study of Brownian motion involving the simultaneous interaction between a large number of particles. Nevertheless the joint use of the correlation functions and the additional time expansion inherently allows one, for $|r_{ij}| < r_0$, to limit all time integrations over a time much shorter than λ/ω_0 thus avoiding the secular terms encountered in the IVP scheme without artificially introducing auxiliary time variables as in the Bogoliubov and MTS methods. It is in fact this aspect of limiting the range of the time integration which suggests an alternate mathematically simple and physically clear extension of the IVP scheme leading to a straightforward truncation of the B.B.G.K.Y. hierarchy, which we shall now discuss.

The breakdown of the IVP, when applied to a uniform non-dense system for $t \sim o[\tau_1] \sim o[\lambda/\omega_0]$, would suggest an alternate scheme in which integrals would be performed over a time interval of $\Delta t \ll \tau_1$ so as to maintain reasonable accuracy yet much longer than $\tau_0 \sim o[r_0/\omega_0]$ as to impose suitable boundary conditions. With such an approach one could then write the zeroth order solutions for F_1 and F_2 as:

$$F_1^{(0)}(\vec{p}_1, t) = F^{(0)}(\vec{p}_1, t-\Delta t) \quad ; \Delta t \ll \tau_1 \qquad \text{(V-C-6)}$$

$$F_2^{(0)}(\vec{x}_1, \vec{x}_2, t) = e^{-\mathcal{H}_2(1,2)\Delta t} F_2^{(0)}(\vec{x}_1, \vec{x}_2, t-\Delta t); \Delta t \ll \tau_1 \qquad \text{(V-C-7)}$$

and impose, for $\Delta t \gg \tau_0$, the following boundary condition:

$$e^{-\mathcal{H}_2(i,j)\Delta t} F_2(\vec{x}_i,\vec{x}_j,t) = \lim_{\tau\to\infty} e^{-\mathcal{H}_2(i,j)\tau} F_1(\vec{p}_i,t) F_1(\vec{p}_j,t) \qquad (V\text{-}C\text{-}8)$$

$\Delta t \gg \tau_0$

Hence selecting $\tau_0 \ll \Delta t \ll \tau_1$ one then emerges with the familiar zeroth order solution

$$F_2^{(0)}(\vec{x}_i,\vec{x}_j,t) = \lim_{\tau\to\infty} e^{-\mathcal{H}_2(i,j)\tau} F_1(\vec{p}_i,t) F_1(\vec{p}_j,t) \qquad (V\text{-}C\text{-}9)$$

and the well known Boltzmann equation for F_1. In this method the initial conditions in the IVP scheme are substituted by reasonable boundary conditions and each equation is integrated over a short time $[t-\Delta t, t]$, rather than the full time interval $[0,t]$ so as to constantly reinitialize the system. Furthermore the time interval Δt in the method of "reinitialization" represents a real time interval which is carefully chosen so as to optimize the eventual solution. The criteria for such an optimization are also conceptually quite clear since one wished, on one hand, to minimize Δt to a value much shorter than τ_1 so as to maximize the accuracy of the approximate equations (V-C-6) and (V-C-7) and, on the other hand, maintain Δt sufficiently large to allow the interacting particles to decouple and, hence, uncorrelate under the backward streaming operation $e^{-\mathcal{H}_2(i,j)\Delta t}$. It is in fact these criteria for optimization which prevent one from writing the solution (V-C-6) and (V-C-7) in the form:

$$F_1^{(0)}(\vec{p}_i,t) = F_1^{(0)}(\vec{p}_i,t+\Delta t) \qquad (V\text{-}C\text{-}10)$$

$$F_2^{(0)}(\vec{x}_i,\vec{x}_j,t) = e^{\mathcal{H}_2(i,j)\Delta t} F_2^{(0)}(\vec{x}_i,\vec{x}_j,t+\Delta t) \qquad (V\text{-}C\text{-}11)$$

and derive the alternate solution:

$$F_2^{(0)}(\vec{x}_i,\vec{x}_j,t) = \lim_{\tau\to-\infty} \mathcal{L}^{-\mathcal{H}_2\tau} F_1(\vec{p}_i,t)\,F_1(\vec{p}_j,t) \qquad \text{(V-C-12)}$$

which would result in the infamous anti-Boltzmann equation. One may fully appreciate this fact by reviewing the effect of the backward streaming operator $\mathcal{L}^{-\mathcal{H}_2(ij)\Delta t}$ on $F_2(\vec{x}_i,\vec{x}_j,t)$ for $|r_{ij}| < r_0$ and all real values of Δt.

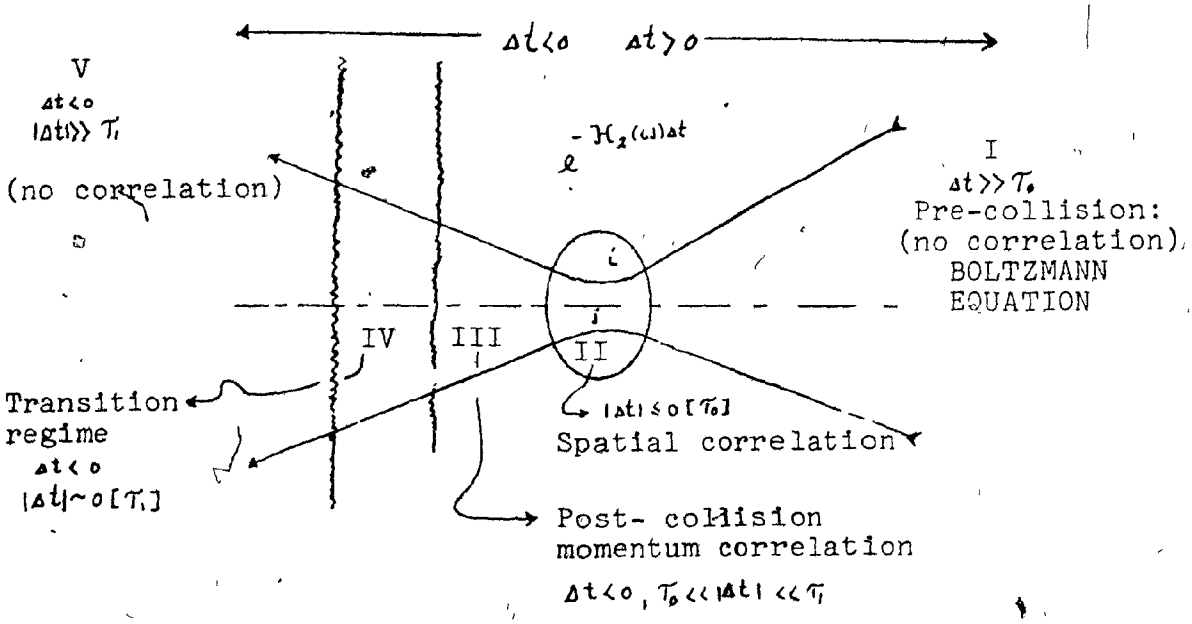

Fig. V-6

As illustrated in figure V-6 there exists for the full range of Δt five domains of interest. When $\Delta t \gg \tau_0$, the operator $\mathcal{L}^{-\mathcal{H}_2(ij)\Delta t}$ streams the particle i and j outside their mutual range of interaction into a pre-collision configuration. In such a state, one may reasonably assume a complete lack of correlation between the positions and momenta of the two

particles and hence impose the boundary condition (V-C-8) which will result in the Boltzmann kinetic equations. On the other hand for $\Delta t < 0$ and $\tau_0 \ll |\Delta t| \ll \tau_1$, the streaming operator $e^{-\mathcal{H}_2(ij)\Delta t}$ once again streams the particles outside their mutual range of interaction but this time in a state of post-collision. As suggested by Cohen and Berlin[23] one must assume, in such a configuration, the existence of momentum correlations between these two particles. Hence for this case the use of the forward boundary condition

$$e^{\mathcal{H}_2(ij)\Delta t} F_2(\vec{x}_1, \vec{x}_2, t) = \lim_{\tau \to \infty} e^{\mathcal{H}_1(ij)\tau} F_1(\vec{p}_1, t) F_1(\vec{p}_2, t)$$

$$\tau_0 \ll \Delta t \ll \tau_1$$

in the reinitialization approach to derive anti-Boltzmann equation would seem invalid. The above reasoning would of course break down if, as suggested by Cohen and Berlin, two molecules were in fact very peculiarly correlated prior to their collision that their subsequent interaction would result in a post-collision uncorrelated state. Such an event would, for example, happen if the motion of the individual particles were at some time reversed in direction such that correlations created in the forward collision would once again vanish after the reverse encounter. Naturally, as first noted by Loschmidt, if such a reversal of motion should occur one would indeed expect the system to display an irreversibility which, from our experience, is proceeding the "wrong way". Confronted with such a possibility let us simply

follow Boltzmann and hope that such a reversal of motion is highly improbable and suggest that the second law of thermodynamics represents one of high probability rather than of certainty. ... Pursuing in our analysis of the possible domains in fig. (V-6) let us now consider the particular choice of $\Delta t < 0$ with $|\Delta t| \gg \tau_1$. In this case the operator $e^{-\mathcal{H}_2(i,j)\Delta t}$ not only streams the particles forward outside of their mutual range of interaction but displaces them with a separation much larger than the mean free path of the gas. Because of the presence of other molecules one can hardly consider the resulting configuration as one of post-collision since in the real system it is highly improbable that particles in such a state actually interacted in their recent past. Consequently for $\Delta t < 0$, $|\Delta t| \gg \tau_1$ one could justifiably impose the boundary condition:

$$e^{-\mathcal{H}_2(i,j)\Delta t} F_2(\vec{x}_i, \vec{x}_j, t) = \lim_{\tau \to \infty} e^{\mathcal{H}_2 \tau} F_1(\vec{p}_i, t) F_1(\vec{p}_j, t)$$

$$\Delta t < 0 \,, \quad |\Delta t| \gg \tau_1 \qquad \text{(V-C-13)}$$

However, since the IVP scheme completely breaks down for such large values of Δt, the above forward boundary condition cannot be used in the solution (V-C-11), valid only for $|\Delta t| \ll \tau_1$ to render an anti-Boltzmann equation. Finally, since the regions $|\Delta t| \leq o[\tau_0]$ (II) and $\Delta t < 0$, $|\Delta t| \sim o[\tau_1]$ (III) do not represent proper domains for the existence of suitable boundary conditions which would allow one to express F_2 as a

functional of F_1, we thus conclude from figure V-6 and the range of validity of the reinitialized solution (V-C-6) that, at the zeroth order of the expansion, the domain $\tau_0 \ll \Delta t \ll \tau_1$ leading to the Boltzmann equations represents the optimal choice in the expansion.

It would appear that the restriction $|\Delta t| \ll \tau_1$ inspired by the breakdown of the IVP scheme not only allows the derivation of non secular kinetic equations but also indicates the proper choice of boundary conditions. We should also note that this limitation on the magnitude of Δt is also implied by the nondimensionalization performed in Chapter III of the present thesis since the results of that analysis essentially indicate that the mixing term of the B.B.G.K.Y. hierarchy is only dominated, on the average, by the remaining momentum convection and interaction terms over a physical volume $V_1 \ll n^{-1}$. Hence any solution of the form:

$$F_2(\vec{x}_1, \vec{x}_2, t) = e^{-\mathcal{H}_2(1,2)\Delta t} F_2(\vec{x}_1, \vec{x}_2, t-\Delta t) \quad , |r_{12}| \ll r_0$$

should restrict itself to time intervals sufficiently short to prevent the operator $e^{-\mathcal{H}_2(1,2)\Delta t}$ from streaming the particles outside this volume. Consequently the scaling arguments suggest a limitation $\Delta t \ll \frac{1}{\sqrt[3]{n}\, v_0} \ll \tau_1$. With the above simple expansion method which completely avoids the artificial introduction of auxiliary time variables we may now attempt to interpret some of the ambiguities encountered in the Bogoliubov and MTS schemes. We recall that due to the

equation (V-C-2)

$$t = t_0 = t_1/\varepsilon = t_2/\varepsilon^2 = \ldots \qquad \text{(V-C-2)}$$

relating the time scales $t_0, t_1, \ldots$ to themselves and the real time, it becomes mathematically inconsistent to treat these variables as truly independent and impose a limit $t_0 \to \infty$ without imposing a similar limit on the remaining time scales. For this reason some authors[26] have opted to treat the independence of the various time scales as an approximation which becomes quite adequate if one remains reasonably close to the physical line defined by equation (V-C-2). Now since this latter equation states that if the real and fast time scales t and t_0 are scaled on a unit of time, τ_0, the slower time t_1 should consequently scale itself on a longer time $\varepsilon \tau_0 = \varepsilon \, n_0/\nu_0 = \frac{n r_0^2}{\nu_0} \sim o[\frac{\lambda}{\nu_0}] = \tau_1'$, it would then follow that to remain reasonably close to the "physical line", any limit $t_0 \to \infty$ should really bear the physical interpretation $t_0 \to \tau^{\circledast}$ where $\tau_0 \ll \tau^{\circledast} \ll \tau_1$. Hence the auxiliary time variable t_0 in the MTS scheme would seem to play the same role and bear the same restrictions in magnitude as the time interval Δt in the reinitialization approach. With this interpretation the MTS scheme then becomes exempt from the possibility of deriving the intriguing yet embarrassing anti-Boltzmann equation. Similarly, by pure comparison of the mathematical form between the Bogoliubov and the reinitialization scheme one could tentatively argue that the auxiliary

time scale in the former scheme and the time interval Δt in the latter share a close resemblance in roles. However, there does not exist in the Bogoliubov approach any mathematical reasons for restricting the magnitude of τ within the range $\tau_0 \ll \tau \ll \tau_1$ and hence avoid the limit $\tau \to -\infty$ which leads to the anti-Boltzmann equation. Indeed if any restriction exists it can only be found in the "spirit" of the assumptions of Bogoliubov suggesting the occurrence of two distinct time scales, one which is dynamic, $\sim o[\tau_0]$, governing the early development of $F_s(\vec{X}_s, t)$ s>1 and the other kinetic $\sim o[\tau_1]$ which paces the evolution of F_1 and the later development of $F_s(\vec{X}_s | F_1)$. Consequently if one identifies τ as the dynamic time variable, the limitation $|\tau| \ll \tau_1$ would follow and the possibility of a forward boundary condition and an anti-Boltzmann equation would seem to have been intuitively eliminated.

In Appendix III we have pursued the reinitialization expansion to derive a second order kinetic equation which was initially obtained by Choh[16] using a Bogoliubov perturbation scheme. The derivation of such an equation essentially requires a first order solution for F_2 which is in turn expressed in terms of a zeroth order solution for F_3. Unfortunately one notes that, over a physical volume $r^3 \ll V_1 \ll \lambda_1^3$, a boundary condition of the type:

$$\underset{\Delta t > \tau}{\ell} \; e^{-\mathcal{H}_3((i)(k))\Delta t} F_3(\vec{x}_i, \vec{x}_j, \vec{x}_k, t) = \lim_{\tau \to \infty} e^{-\mathcal{H}_3((i)(k))\tau} F_1(\vec{p}_i, t) F_1(\vec{p}_j, t) F_1(\vec{p}_k, t) \qquad \text{(V-C-14)}$$

which one requires for zeroth order 3 particle distribution cannot be imposed for a time $\tau^{\circledast} \ll \tau_1$. Indeed, as noted by Cohen [21] and others [26], and illustrated in figure V-6 there exists configurations for which the complete set of reverse interactions occur over a path much larger than the mean free path.

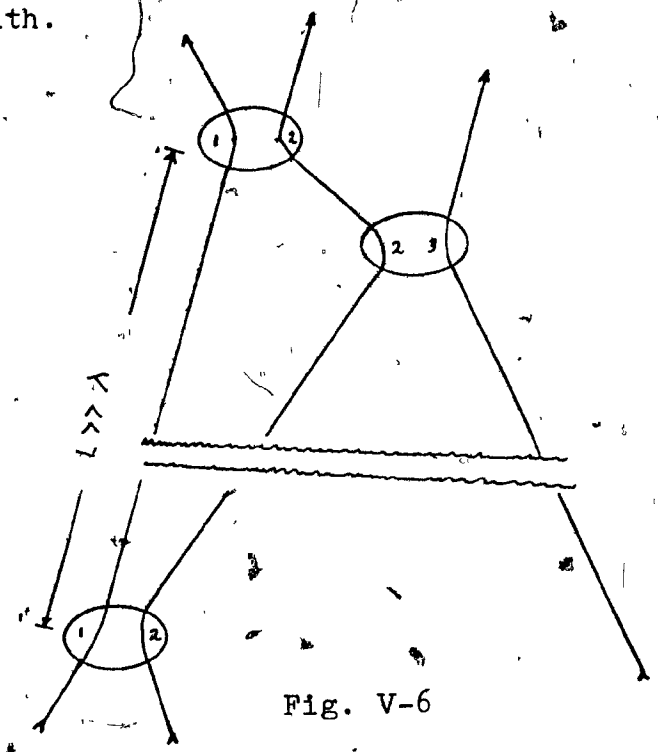

Fig. V-6

Consequently in the reinitialization scheme which attempts to minimize the time interval of integration and explicitly prohibits any $\Delta t \gtrsim o[\tau_1]$ no reasonable optimal choice for this interval exists. As a compromise one is therefore forced to limit the range of integration over $\vec{x}_k$ in the $F_2^{(1)}$ solution to the phase volume where the boundary condition (V-C-14) may be applied for a $\Delta t \ll \tau_1$. Naturally this procedure which ignores the domain for which we have no accurate solution for

$F_s^{(0)}$ strives on the hope that the error committed remains minimal.

The expansion method described above has also been applied to the uniform weakly coupled system which, for reasons given in Chapter III, is characterized by the similarly small contributions from the momentum convection, interaction and mixing terms in its B.B.G.K.Y. hierarchy. Consequently a simple expansion neglecting these terms at the zeroth order yields the following trivial equation for $F_s^{(0)}$.

$$\frac{\partial F_s^{(0)}}{\partial t} = 0 \qquad \text{(V-C-15)}$$

or $$F_s(\vec{x}_s, t) = F_s(\vec{x}_s, t-\Delta t)$$

Clearly, with no operator in the above solution to stream the particles outside their mutual range of interaction and correlation we cannot in this case, for any choice of Δt, find an explicit solution for F_2 in terms of F_1. Consequently we find ourselves unable to derive a suitable kinetic equation for this system via a perturbation approach. Indeed with the ordering of terms suggested in Chapter III, other methods including the Bogoliubov and MTS perturbation schemes should lead to the same disappointing conclusion.

Finally, we have considered in the present chapter the case of Brownian motion for which, as previously stated, we assume the root mass ratio $\gamma = \sqrt{\frac{m_b}{m_B}}$ between the light (b) bath particles and heavy (B) single Brownian particle to dictate the relative magnitude of the verious terms in the dimen-

sionless Liouville equation for the complete system and the B.B.G.K.Y. hierarchy governing the single Brownian particle distribution $F_1(\vec{p}^B, t)$. By so doing all terms associated with the motion of the heavy Brownian particle are neglected at the zeroth order of the expansion. Consequently we have at the zeroth order for the full $N(b)+1(B)$ particle distribution $F_{(N,1)}(\vec{X}_{(N,1)}, t)$ the following equation:

$$\frac{\partial F^{(0)}_{(N,1)}}{\partial t} + \mathcal{H}^{I}_{(N,1)} F^{(0)}_{(N,1)} = 0 \qquad \text{(V-C-16)}$$

with the solution expressed as:

$$F^{(0)}_{(N,1)}(\vec{X}_{(N,1)}, t) = e^{-\mathcal{H}^{I}_{(N,1)} \Delta t} F^{(0)}_{(N,1)}(\vec{X}_{(N,1)}, t-\Delta t) \qquad \text{(V-C-17)}$$

where $\mathcal{H}^{I}_{(N,1)}$ represents the Hamiltonian operator of the N bath particles interacting with themselves and the heavy Brownian particle and, consequently, $e^{-\mathcal{H}^{I}_{(N,1)}}$ streams these light particles back in time without operating on the coordinates or momentum of the heavy Brownian particle. Now we recall from the discussions in the Chapter III that this particular expansion is, in many ways, blind since we do not know over what region in $\Gamma_{(N,1)}$ space, if any, our assumption regarding the relative weight of the various terms in the governing equation remains valid. We do know however that the initial value expansion does yield divergent solutions and, hence, eventually completely breaks down. It would therefore seem reasonable to seek a suitable boundary condition which would yield an explicit

solution for $F_{(N,1)}$ as a functional of F_1 while keeping the time interval Δt to a minimum. With this goal in mind we have assumed that there exists a time τ_b much shorter than the relaxation time τ_B of the slow Brownian particle, during which the bath particles reach an equilibrium with themselves and the Brownian particle. By thus assuming that

$$e^{-\mathcal{H}^I_{(N,1)}\,\Delta t} F_{(N,1)}(\vec{X}_{(N,1)}, t) = F_{(N,0)}(\vec{X}_N)_{eq}\, F_{(0,1)}(\vec{p}', t) \quad \text{(V-C-18)}$$

one obtains a solution for $F_{(N,1)}$ which results in a kinetic equation for F_1. As this latter equation is convergent and bears the form of the well known Fokker-Planck equation commonly and successfully used to describe Brownian motion, we then conclude that our approach, in spite of its limitations, does yield a reasonable result.

CHAPTER VI

DERIVATION OF KINETIC EQUATIONS FOR NON-UNIFORM MIXTURES

The previous chapter has illustrated some of the main features of the reinitialization expansion by applying this technique to very simple molecular systems. It would now seem appropriate, in order to fully appreciate the scope, and limitations, of this approach, to probe into slightly more complex and general molecular mixtures. For this purpose, let us, then, reconsider the non-uniform, non-dense, and Brownian mixtures previously defined in the third chapter of the present thesis.

A. NON-UNIFORM NON-DENSE MIXTURES

The non-uniform, non-dense mixture, we recall, can be described by the dimensionless B.B.G.K.Y. hierarchy (III-C-52), which may also be written as:

$$\frac{\partial F^*_{\{s\}}(\vec{X}^*_{\{s\}}, t^*)}{\partial t^*} + \left(\mathcal{H}^{I\,*}_{\{s\}} + \mathcal{H}^{II\,*}_{\{s\}} \right) F^*_{\{s\}} = \sum_{\beta=1}^{M} \sum_{\alpha=1}^{M} \left({}^{I}\mathcal{L}^{\alpha\beta\,*}_{s_\alpha} + {}^{II}\mathcal{L}^{\alpha\beta\,*}_{s_\alpha} \right) F^*_{\{s, s_\beta+1\}} \qquad \text{(VI-A-1)}$$

where

$$\mathcal{H}^{I^*}_{\{s\}} = \sum_{\alpha=1}^{M} \gamma^\alpha \mathcal{K}_{\{s\}} \sum_{i=1}^{S_\alpha} \vec{p}_i^{\alpha *} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha *}}$$

$$- \sum_{\beta=1}^{M} \sum_{\alpha=1}^{M} \sum_{j=1}^{S_\beta} \sum_{i=1}^{S_\alpha} \gamma^\alpha \left({}^{I}\mathcal{R}^{\alpha\beta} \cdot \frac{\partial {}^{I}\phi_{ij}^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}} + \varepsilon_1^{\alpha\beta} {}^{II}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{II}\phi^{\alpha\beta *}}{\partial \vec{q}_i^{\alpha *}} \right) \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \qquad \text{(VI-A-2)}$$

$$\mathcal{H}^{II^*}_{\{s\}} = \sum_{\alpha=1}^{M} \sum_{i=1}^{S_\alpha} \gamma^\alpha A^\alpha \chi^\alpha \frac{\partial U^{\alpha *}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \qquad \text{(VI-A-3)}$$

$${}^{I}\mathcal{L}^{\alpha\beta *}_{\{s\}} \equiv {}^{I}\varepsilon^{\alpha\beta}_{2\{s\}} {}^{I}\mathcal{R}^{\alpha\beta} \gamma^\alpha \mu_{eq}$$

$$\times \sum_{i=1}^{S_\alpha} \iint \frac{\partial {}^{I}\phi^{\alpha\beta *}_{i,s_\beta+1}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \, d^3 \vec{r}^{\,\alpha\beta *}_{i,s_\beta+1} \, d\vec{p}^{\,\beta *}_{s_\beta+1} \qquad \text{(VI-A-4)}$$

$${}^{II}\mathcal{L}^{\alpha\beta *} \equiv {}^{II}\varepsilon^{\alpha\beta}_{2\{s\}} \varepsilon_1^{\alpha\beta} {}^{II}\mathcal{R}^{\alpha\beta} \gamma^\alpha \mu_{eq}$$

$$\times \sum_{i=1}^{S_\alpha} \iint \frac{\partial {}^{II}\phi^{\alpha\beta *}_{i,s_\beta+1}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \, d^3 \vec{r}^{\,\alpha\beta *}_{i,s_\beta+1} \, d\vec{p}^{\,\beta *}_{s_\beta+1} \qquad \text{(VI-A-5)}$$

Now, the dimensional arguments of chapter III indicate that for

$$\vec{X}^{**}_{\{s\}} \in V^*_{\{s\}}$$

where

$$V^*_{\{s\}} = V_{\{s\}} \Big/ V_c^{s} \prod_{\alpha=1}^{m} \left(\sqrt{m_\alpha \kappa T}\right)^{3s_\alpha} \qquad \text{(VI-A-6)}$$

with

$${}^{x}\bar{r} \ll r_c \ll \eta^{-1/3}$$

one has, for a non-dense system

$$\mathcal{E}^{\alpha\beta}_{2\{s\}} \ll 1$$

and

$$\mathcal{E}^{\alpha\beta}_{1} \to 0$$

Furthermore, if the external field is weak, one may also assume that

$$\chi^{\alpha} \ll 1$$

Consequently, writing (VI-A-1) in the more convenient dimensional form

$$\frac{\partial F_{\{s\}}}{\partial t} + \left(\mathcal{H}^{I}_{\{s\}} + \varepsilon\, \mathcal{H}^{II}_{\{s\}}\right) F_{\{s\}}\left(\vec{X}_{\{s\}}, t\right) = \varepsilon \sum_{\beta=1}^{M}\sum_{\alpha=1}^{M} \mathcal{L}^{\alpha\beta}_{s_\alpha, s_\beta} F_{\{s, s_\beta+1\}} \qquad \text{(VI-A-7)}$$

where

$$\mathcal{H}^{I}_{\{s\}} = \sum_{\alpha=1}^{M}\sum_{i=1}^{s_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha}} - \sum_{\alpha=1}^{M}\sum_{i=1}^{s_\alpha}\sum_{\beta=1}^{M}\sum_{j=1}^{s_\beta} \frac{\partial \Phi^{I\,\alpha\beta}_{ij}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \qquad \text{(VI-A-8)}$$

$$\mathcal{H}^{II}_{\{s\}} = -\sum_{\alpha=1}^{M}\sum_{i=1}^{s_\alpha} \frac{\partial U^{\alpha}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \qquad \text{(VI-A-9)}$$

$$\mathcal{L}^{\alpha\beta}_{s_\alpha} = (N_\beta - s_\beta)\sum_{i=1}^{s_\alpha} \int\!\!\int \frac{\partial \Phi^{I\,\alpha\beta}_{i,s_\beta+1}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}}\, d\vec{r}^{\,\alpha\beta}_{i\,s_\beta+1}\, d\vec{p}^{\,\beta}_{s_\beta+1} \qquad \text{(VI-A-10)}$$

we will attempt, as in the simple uniform system, the following expansion in powers of the label parametic ε

i.e.

$$F_{\{s\}}(X_{\{s\}},t) = F^{(0)}_{\{s\}} + \varepsilon F^{(1)}_{\{s\}} + \varepsilon^2 F^{(2)}_{\{s\}} + \dots \quad \text{(VI-A-11)}$$

Substituting (VI-A-11) into (VI-A-7) and collecting orders of ε, one then obtains the following set of rate equations

$$\frac{\partial F^{(0)}_{\{s\}}}{\partial t} + \mathcal{H}^{I}_{\{s\}} F^{(0)}_{\{s\}} = 0 \quad \text{(VI-A-12-0)}$$

$$\frac{\partial F^{(1)}_{\{s\}}}{\partial t} + \mathcal{H}^{I}_{\{s\}} F^{(1)}_{\{s\}} = -\mathcal{H}^{II}_{\{s\}} F^{(0)}_{\{s\}} + \sum_{\beta=1}^{M}\sum_{\alpha=1}^{M} \mathcal{L}^{\alpha\beta}_{s_\alpha} F^{(0)}_{\{s,s_{\beta+1}\}} \quad \text{(VI-A-12-1)}$$

$$\vdots$$

$$\frac{\partial F^{(k)}_{\{s\}}}{\partial t} + \mathcal{H}^{I}_{\{s\}} F^{(k)}_{\{s\}} = -\mathcal{H}^{II}_{\{s\}} F^{(k-1)}_{\{s\}} + \sum_{\beta=1}^{M}\sum_{\alpha=1}^{M} \mathcal{L}^{\alpha\beta}_{s_\alpha} F^{(0)}_{\{s,s_{\beta+1}\}} \quad \text{(VI-A-12-)}$$

Let us now proceed with the reinitialization approach and integrate the above equations over a time interval Δt much shorter than the mean time between collisions τ_1. At the zeroth order, this integration yields

$$F^{(0)}_{\{s\}}(X_{\{s\}},t) = e^{-\mathcal{H}^{I}_{\{s\}}\Delta t} F^{(0)}_{\{s\}}(X_{\{s\}},t-\Delta t). \quad \text{(VI-A-13)}$$

Furthermore, assuming, as in the previous chapter, that for a given $\tau_{\{s\}} \ll \tau_1$, there exists a volume $V^{+}_{\{s\}} \subset V_{\{s\}}$ in $\Gamma_{\{s\}}$ space for which the backward streaming operator will stream the s particles permanently outside of their mutual range of interaction and correlation, we

may then impose the boundary conditions

$$\ell^{-\mathcal{H}^{I}_{\{s\}}\Delta t} F_{\{s\}} = \ell^{-\mathcal{H}^{I}_{\{s\}}\Delta t} \prod_{\alpha=1}^{M} \prod_{i=1}^{S_\alpha} F_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) \qquad \text{(VI-A-14)}$$

$$\Delta t > \tau_{\{s\}} \; ; \; \vec{X}_{\{s\}} \in V^{+}_{\{s\}}(\tau_{\{s\}})$$

Substituting (VI-A-11) into (VI-A-14) and collecting orders of ε one then obtains the following particular boundary conditions for $F^{(0)}_{\{i,\alpha;j,\beta\}}$, $F^{(0)}_{\{i,\alpha,j,\beta;k,\gamma\}}$ and $F^{(1)}_{\{i,\alpha,j,\beta\}}$

$$\ell^{-\mathcal{H}^{I}_{\{i,\alpha;j,\beta\}}\Delta t} F^{(0)}_{\{i,\alpha,j,\beta\}}(\dots,t) = \ell^{-\mathcal{H}^{I}_{\{i,\alpha,j,\beta\}}\Delta t} F^{(0)}_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) F^{(0)}_{\{j,\beta\}}(\vec{q}_j^{\,\beta}, \vec{p}_j^{\,\beta}, t)$$

$$\vec{X}_{\{i,\alpha,j,\beta\}} \in V^{+}_{\{i,\alpha,j,\beta\}} \; ; \; \Delta t > \tau_{\{i,\alpha,j,\beta\}} \qquad \text{(VI-A-15)}$$

$$\ell^{-\mathcal{H}^{I}_{\{i,\alpha,j,\beta;k,\gamma\}}\Delta t} F^{(0)}_{\{i,\alpha;j,\beta;k,\gamma\}}(\dots t) = \ell^{-\mathcal{H}^{I}_{\{i,\alpha,j,\beta,k,\gamma\}}\Delta t} F^{(0)}_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) F^{(0)}_{\{j,\beta\}}(\vec{q}_j^{\,\beta}, \vec{p}_j^{\,\beta}, t) F^{(0)}_{\{k,\gamma\}}(\vec{q}_k^{\,\gamma}, \vec{p}_k^{\,\gamma}, t)$$

$$\vec{X}_{\{i,\alpha,j,\beta;k,\gamma\}} \in V^{+}_{\{i,\alpha;j,\beta,k,\gamma\}} \; ; \; \Delta t > \tau_{\{i,\alpha;j,\beta;k,\gamma\}} \qquad \text{(VI-A-16)}$$

$$\ell^{-\mathcal{H}^{I}_{\{i,\alpha;j,\beta\}}\Delta t} F^{(1)}_{\{i,\alpha,j,\beta\}}(\dots t) = \ell^{-\mathcal{H}^{I}_{\{i,\alpha;j,\beta\}}\Delta t} \left[F^{(0)}_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) F^{(1)}_{\{j,\beta\}}(\vec{q}_j^{\,\beta}, \vec{p}_j^{\,\beta}, t) + F^{(0)}_{\{j,\beta\}}(\vec{q}_j^{\,\beta}, \vec{p}_j^{\,\beta}, t) F^{(1)}_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) \right]$$

$$\vec{X}_{\{i,\alpha,j,\beta\}} \in V^{+}_{\{i,\alpha;j,\beta\}} \; ; \; \Delta t > \tau_{\{i,\alpha;j,\beta\}} \qquad \text{(VI-A-17)}$$

Combining (VI-A-15) and (VI-A-16) with (VI-A-14) we then emerge with the following zeroth order solutions

$$F^{(o)}_{\{i,\alpha\}}(\vec{q}^{\alpha}_i, \vec{p}^{\alpha}_i, t) = e^{-\mathcal{H}^{I}_{\{i,\alpha\}}\Delta t} F^{(o)}_{\{i,\alpha\}}(\vec{q}^{\alpha}_i, \vec{p}^{\alpha}_i, t-\Delta t)$$

$$\Delta t \ll \tau_i \qquad \text{(VI-A-18)}$$

$$F^{(o)}_{\{i,\alpha;j,\beta\}}(\vec{X}_{\{i,\alpha,j,\beta\}}) =$$

$$e^{-\mathcal{H}^{I}_{\{i,\alpha,j,\beta\}}\Delta t} e^{\mathcal{H}^{I}_{\{i,\alpha\}}\Delta t} e^{\mathcal{H}^{I}_{\{j,\beta\}}\Delta t} \{F^{(o)}_{\{i,\alpha\}}(\vec{q}^{\alpha}_i, \vec{p}^{\alpha}_i, t) F^{(o)}_{\{j,\beta\}}(\vec{q}^{\beta}_j, \vec{p}^{\beta}_j, t)\}$$

$$\vec{X}_{\{i,\alpha,j,\beta\}} \in V^{+}_{\{i,\alpha;j,\beta\}} \; ; \; \tau_{\{i,\alpha,j\beta\}} \ll \Delta t \ll \tau_i \qquad \text{(VI-A-19)}$$

$$F^{(o)}_{\{i,\alpha,j,\beta,k,\gamma\}}(\vec{X}_{\{i,\alpha,j,\beta,k\gamma\}}, t) =$$

$$e^{-\mathcal{H}^{I}_{\{i,\alpha,j,\beta,k,\gamma\}}\Delta t} e^{\mathcal{H}^{I}_{\{i,\alpha\}}\Delta t} e^{\mathcal{H}^{I}_{\{j,\beta\}}\Delta t} e^{\mathcal{H}^{I}_{\{k,\gamma\}}\Delta t}$$

$$\{F^{(o)}_{\{i,\alpha\}}(\vec{X}_{\{i,\alpha\}}, t) F^{(o)}_{\{j,\beta\}}(\vec{X}_{\{j,\beta\}}, t) F^{(o)}_{\{k,\gamma\}}(\vec{X}_{\{k,\gamma\}}, t)$$

$$\vec{X}_{\{i,\alpha,j,\beta,k,\gamma\}} \in V^{+}_{\{i,\alpha,j,\beta,k,\gamma\}} \; ; \; \tau_{\{i,\alpha,j,\beta,k,\gamma\}} \ll \Delta t \ll \tau_i \qquad \text{(VI-A-20)}$$

Now, since we may derive a first order kinetic equation with only the knowledge of $F^{(o)}_{\{i,\alpha,j,\beta\}}$ for $|\vec{r}^{\alpha\beta}_{ij}| < {}^{I}r^{\alpha\beta} \sim o[{}^{I}r^{\beta\gamma}] \sim o[{}^{I}r]$ we may, for this restricted domain, where $\tau_{\{i,\alpha,j,\beta\}} \sim o[{}^{I}r/v_o] \sim o[\tau_o]$, rewrite (VI-A-19) as

$$F^{(o)}_{\{i,\alpha,j,\beta\}}(\vec{X}_{\{i,\alpha,j\beta\}}, t) =$$

$$F^{(o)}_{\{i,\alpha\}}(\underset{\sim}{\vec{Q}}^{\alpha}_i(\Delta t), \underset{\sim}{\vec{P}}^{\alpha}_i(\Delta t), t) F^{(o)}_{\{j,\beta\}}(\underset{\sim}{\vec{Q}}^{\beta}_j(\Delta t), \underset{\sim}{\vec{P}}^{\beta}_j(\Delta t), t) \qquad \text{(VI-A-21)}$$

where:

$$\underset{\sim}{\vec{Q}}^{\alpha}_i(\Delta t) = e^{-\mathcal{H}^{I}_{\{i,\alpha;j,\beta\}}\Delta t} e^{\mathcal{H}^{I}_{\{i,\alpha\}}\Delta t} \vec{q}^{\alpha}_i$$

$$\underset{\sim}{\vec{P}}^{\alpha}_i(\Delta t) = e^{-\mathcal{H}^{I}_{\{i,\alpha;j,\beta\}}\Delta t} e^{\mathcal{H}^{I}_{\{i,\alpha\}}\Delta t} \vec{p}^{\alpha}_i$$

$$\vec{Q}^{\beta}_{j(\alpha)} = e^{-H^{I}_{\{i,\alpha;j,\beta\}}\Delta t}\, e^{H^{I}_{\{j,\beta\}}\Delta t}\, \vec{q}^{\beta}_{j}$$

$$\vec{P}^{\beta}_{j(\alpha)} = e^{-H^{I}_{\{i,\alpha;j,\beta\}}\Delta t}\, e^{H^{I}_{\{j,\beta\}}\Delta t}\, \vec{p}^{\beta}_{j} \qquad \text{(V-A-22)}$$

in equation (VI-A-21) represent the coordinates and momenta of particles $\{i,\alpha\}$ and $\{j,\beta\}$ after they have been streamed forward, in the absence of any interaction, by $e^{H^{I}_{\{i,\alpha\}}\Delta t}$ and $e^{H^{I}_{\{j,\beta\}}\Delta t}$ respectively, and streamed back in time, with a mutual interaction $e^{-H^{I}_{\{i,\alpha,j,\beta\}}\Delta t}$. For $\vec{r}^{\alpha\beta}_{ij} < {}^{I}r^{\alpha\beta}$, the final outcome of these streaming operations becomes independent of Δt, for $\Delta t \gg \tau_0$. Consequently one may write the zeroth order solution for $F_{\{i,\alpha,j,\beta\}}$ as:

$$F^{(0)}_{\{i,\alpha;j,\beta\}} = F^{(0)}_{\{i,\alpha\}}(\vec{Q}^{\alpha}_{i}(\infty), \vec{P}^{\alpha}_{i}(\infty), t)\, F^{(0)}_{\{j,\beta\}}(\vec{Q}^{\beta}_{j}(\infty), \vec{P}^{\beta}_{j}(\infty), t) \qquad \text{(VI-A-23)}$$

Furthermore since

$$e^{H^{I}_{\{k,\gamma\}}\Delta t}\, \vec{p}^{\gamma}_{k} = \vec{p}^{\gamma}_{k} \qquad \text{(VI-A-24)}$$

we then have

$$\vec{P}^{\alpha}_{i}(\infty) = \lim_{\Delta t\to\infty} e^{-H^{I}_{\{i,\alpha,j,\beta\}}\Delta t}\, \vec{P}^{\alpha}_{i} = \vec{P}^{-\alpha}_{i}(\infty)$$

$$\vec{P}^{\beta}_{j}(\infty) = \lim_{\Delta t\to\infty} e^{-H^{I}_{\{i,\alpha,j,\beta\}}\Delta t}\, \vec{P}^{\beta}_{j} = \vec{P}^{-\beta}_{j}(\infty) \qquad \text{(VI-A-25)}$$

such that

$$F^{(0)}_{\{i,\alpha;j,\beta\}}(\vec{X}_{\{i,\alpha;j,\beta\}},t) = F^{(0)}_{\{i,\alpha\}}(\vec{\underset{\sim}{Q}}^{\alpha}_{i(\infty)},\vec{P}^{\alpha}_{i(\infty)},t)\,F_{\{j,\beta\}}(\vec{Q}^{\beta}_{j(\infty)},\vec{P}^{\beta}_{j(\infty)},t)$$

(VI-A-26)

Substituting this last equation into (VI-A-12-1) one then obtains the following rate equation for $F^{(1)}_{\{i,\alpha\}}(\vec{q}^{\alpha}_{i},\vec{p}^{\alpha}_{i},t)$.

$$\frac{\partial F^{(1)}_{\{i,\alpha\}}}{\partial t} + \mathcal{H}^{I}_{\{i,\alpha\}} F^{(1)}_{\{i,\alpha\}} + \mathcal{H}^{II}_{\{i,\alpha\}} F^{(0)}_{\{i,\alpha\}} =$$

$$\sum_{\beta=1}^{M} \mathcal{L}^{\alpha\beta}_{\{i,\alpha\}} F^{(0)}_{\{i,\alpha\}}(\vec{\underset{\sim}{Q}}^{\alpha}_{i}(\infty),\vec{P}^{\alpha}_{i}(\infty),t)\,F^{(0)}_{\{j,\beta\}}(\vec{\underset{\sim}{Q}}^{\beta}_{j}(\infty),\vec{P}^{\beta}(\infty),t)$$

(VI-A-27)

Which, when combined with the zeroth order rate equation (VI-A-12-0) and the expansion (VI-A-11), renders the following set of coupled first order kinetic equations for

$$\frac{\partial F_{\{i,\alpha\}}}{\partial t} + (\mathcal{H}^{I}_{\{i,\alpha\}} + \mathcal{H}^{II}_{\{i,\alpha\}})F_{\{i,\alpha\}} =$$

$$\sum_{\alpha=1}^{M} \mathcal{L}^{\alpha,\beta}_{\{i,\alpha\}} F_{\{i,\alpha\}}(\vec{\underset{\sim}{Q}}^{\alpha}_{i}(\infty),\vec{P}^{\alpha}_{i}(\infty),t)\,F_{\{j,\beta\}}(\vec{\underset{\sim}{Q}}^{\beta}_{j}(\infty),\vec{P}^{\beta}_{j},t)$$

(VI-A-28)

Now, since the right hand side of (VI-A-28) vanishes for $|\vec{r}^{\alpha\beta}_{ij}| > {}^{I}r^{\alpha\beta} \sim o[{}^{I}r]$ and $|\vec{\underset{\sim}{Q}}^{\alpha}_{i} - q^{\alpha}_{i}| \sim o[{}^{I}r^{\alpha\beta}] \sim o[{}^{I}r]$,

one may simplify this equation by neglecting the variation of the single particle distributions over a length scale $L \sim O[r_I]$. Consequently, if one assumes moderate spatial nonuniformities, one may rewrite equation (VI-A-28) as

$$\frac{\partial F_{\{i,\alpha\}}}{\partial t} + \left(\mathcal{H}^{I}_{\{i,\alpha\}} + \mathcal{H}^{II}_{\{i,\alpha\}}\right) F_{\{i,\alpha\}} = \sum_{\beta=1}^{M} \mathcal{L}^{\alpha\beta}_{\{i,\alpha\}} F_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{P}_i^{\,\alpha}(\infty), t) F_{\{j,\beta\}}(\vec{q}_i^{\,\alpha}, \vec{P}_j^{\,\beta}(\infty), t) \tag{VI-A-29}$$

which, using arguments similar to those found in appendix I, may be reduced to the following Boltzmann form

$$\frac{\partial f_{\{i,\alpha\}}}{\partial t} + \left(\mathcal{H}^{I}_{\{i,\alpha\}} + \mathcal{H}^{II}_{\{i,\alpha\}}\right) f_{\{i,\alpha\}} = \sum_{\beta=1}^{M} J_B^{\beta}\left(f_{\{i,\alpha\}}, f_{\{j,\beta\}}\right) \tag{VI-A-30}$$

$$J_B^{\beta} = \frac{m_\alpha}{m} \int_{-\infty}^{\infty}\int_{0}^{2\pi}\int_{0}^{\infty} \left|\frac{\vec{p}_j^{\,\beta}}{m_\beta} - \frac{\vec{p}_i^{\,\alpha}}{m_\alpha}\right| \left[f_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, p_i'^{\alpha}, t) f_{\{j,\beta\}}(q_j^{\beta}, \vec{p}_j'^{\beta}, t) - f_{\{i,\alpha\}}(\vec{q}_i^{\,\alpha}, \vec{p}_i^{\,\alpha}, t) f_{\{j,\beta\}}(\vec{q}_j^{\,\beta}, \vec{p}_j^{\,\beta}, t)\right] b\,db\,d\phi\,d\vec{p}_j^{\,\beta} \tag{VI-A-31}$$

and

$$f_{\{i,\alpha\}} = N F_{\{i,\alpha\}} \tag{VI-A-32}$$

The above kinetic equations (VI-A-28) and (VI-A-30) for non-uniform non-dense mixtures could, of course, have

been derived with other expansion methods than the reinitialization technique presented here. Braun, Flores and Garcia-Colin [34] have treated non-uniform non-dense binary mixtures using a Bogoliubov functional expansion with slightly modified boundary conditions. Lewis and Harris[39] have also presented an expansion for simple non-uniform, non-dense systems which would certainly be extended to include mixtures. As previously mentioned however, the simple reinitialization approach does offer the advantage of avoiding the functional assumption of the Bogoliubov scheme and the mathematical complexity of the Lewis and Harris approach.

B. NON-UNIFORM BROWNIAN MIXTURES

Let us now consider, as a final example of this thesis, a non-uniform mixture of Brownian particles interacting with a weak external field and coexisting with a bath of light particles which are free from any externally imposed force field. If species $\alpha = M_0, \ldots M$ represent the Brownian particles, while species $\alpha = 1, \ldots M_0 - 1$ denote the light bath particles, the dimensionless Liouville equation (II-C-37) may be written in the following form

$$\frac{\partial F^{*}_{\{N\}}}{\partial t^{*}} + \left[\mathcal{H}^{I\,*}_{\{N\}} + \mathcal{H}^{II\,*}_{\{N\}} + \mathcal{H}^{III\,*}_{\{N\}} \right] F^{*}_{\{N\}} = 0 \qquad \text{(VI-B-1)}$$

where

$$\mathcal{H}^{I\,*}_{\{N\}} = \sum_{\alpha=1}^{M_0-1} \sum_{i=1}^{N_\alpha} {}^{*}K^{\alpha}\, \gamma^{\alpha}\, \vec{p}_i^{\,\alpha *} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha *}}$$

$$- \sum_{\alpha=1}^{M_0-1} \sum_{i=1}^{N_\alpha} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \gamma^{\alpha} \left({}^{I}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{I}\phi^{\alpha\beta *}}{\partial \vec{q}_i^{\,\alpha *}} + {}^{II}\mathcal{R}^{\alpha\beta}\, \varepsilon_i^{\alpha\beta} \frac{\partial {}^{II}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\,\alpha *}} \right) \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha *}}$$

(VI-B-2)

$$\mathcal{H}^{II\,*}_{\{N\}} = \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} {}^{*}K^{\alpha}\, \gamma^{\alpha}\, \vec{p}_i^{\,\alpha *} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha *}}$$

$$- \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \gamma^{\alpha} \left({}^{I}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{I}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\,\alpha *}} + {}^{II}\mathcal{R}^{\alpha\beta}\, \varepsilon_i^{\alpha\beta} \frac{\partial {}^{II}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\,\alpha *}} \right) \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha *}}$$

(VI-B-3)

$$\mathcal{H}^{III\,*}_{\{N\}} = - \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \gamma^{\alpha} A^{\alpha} \chi^{\alpha} \frac{\partial u^{\alpha *}}{\partial \vec{q}_i^{\,\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha *}} \qquad \text{(VI-B-4)}$$

Similarily the B.B.G.K.Y. equation governing the distribution $F_{\{N_B\}}$ of all the Brownian particles may be written as

$$\frac{\partial F^{*}_{\{N_B\}}}{\partial t^{*}} + \left[\mathcal{H}^{A\,*}_{\{N_B\}} + \mathcal{H}^{B\,*}_{\{N_B\}} \right] F^{*}_{\{N_B\}}$$

$$= \sum_{\beta=1}^{M_0-1} \sum_{\alpha=M_0}^{M} \left({}^{I}\mathcal{L}^{\alpha\beta}_{\{N_B\}} + {}^{II}\mathcal{L}^{\alpha\beta}_{\{N_B\}} \right) F^{*}_{\{N_B;(1,\beta)\}} \qquad \text{(VI-B-5)}$$

where

$$\mathcal{H}^{1*}_{\{N_\beta\}} = \sum_{\alpha=M_0}^{M} \gamma^\alpha \mathcal{K}^\alpha_{\{N_\beta\}} \sum_{i=1}^{N_\alpha} \vec{p}_i^{\alpha *} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha *}}$$

$$- \sum_{\beta=M_0}^{M} \sum_{j=1}^{N_\beta} \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \gamma^\alpha \left({}^{I}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{I}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\alpha *}} + \varepsilon_1^{\alpha\beta} {}^{II}\mathcal{R}^{\alpha\beta} \frac{\partial {}^{II}\phi^{\alpha\beta}_{ij}}{\partial \vec{q}_i^{\alpha *}} \right) \cdot \frac{\partial}{\partial \vec{P}_i^{\alpha *}}$$

(VI-B-6)

$$\mathcal{H}^{3}_{\{N_\beta\}} = - \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \gamma^\alpha \mathcal{A}^\alpha \chi^\alpha \frac{\partial \mathcal{U}^{\alpha *}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}}$$

(VI-B-7)

and

$${}^{I}\mathcal{L}^{\alpha\beta *}_{\{N_\beta\}} = {}^{I}\varepsilon_{2\{N_\beta\}}{}^{\alpha\beta} \, {}^{I}\mathcal{R}^{\alpha\beta} \gamma^\alpha \mu_{\alpha q}$$

$$\sum_{i=1}^{N_\alpha} \int\int \frac{\partial {}^{I}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \, d{}^{I}\vec{\Gamma}^{\alpha\beta *}_{i,1} \, d\vec{p}_1^{\beta *}$$

(VI-B-8)

$${}^{II}\mathcal{L}^{\alpha\beta *}_{\{N_\beta\}} = {}^{II}\varepsilon_{2\{N_\beta\}}{}^{\alpha\beta} \varepsilon_1^{\alpha\beta} \, {}^{II}\mathcal{R}^{\alpha\beta} \gamma^\alpha \mu_{\alpha q}$$

$$\sum_{i=1}^{N_\alpha} \int\int \frac{\partial {}^{II}\phi^{\alpha\beta *}_{ij}}{\partial \vec{q}_i^{\alpha *}} \cdot \frac{\partial}{\partial \vec{p}_i^{\alpha *}} \, d{}^{II}\vec{\Gamma}^{\alpha\beta *}_{i,1} \, d\vec{p}_1^{\beta *}$$

(VI-B-9)

Let us now assume that $\gamma^\alpha \sim o[\gamma^\beta] \sim o[\chi^\alpha] \sim o[\chi^\beta] \ll 1$, for $\alpha, \beta = M_0 \ldots M$, and rewrite the above dimensionless Liouville and B.B.G.K.Y. equations in the following convenient dimensional form

$$\frac{\partial F_{\{N\}}}{\partial t} + \left[\mathcal{H}^{I}_{\{N\}} + \varepsilon \mathcal{H}^{II}_{\{N\}} + \varepsilon^2 \mathcal{H}^{III}_{\{N\}} \right] F_{\{N\}} = 0 \qquad \text{(VI-B-10)}$$

$$\frac{\partial F_{\{N\beta\}}}{\partial t} + \left[\varepsilon \mathcal{H}^{A}_{\{N_\beta\}} + \varepsilon^2 \mathcal{H}^{B}_{\{N_\beta\}} \right] F_{\{N\beta\}} =$$

$$\varepsilon \sum_{\beta=1}^{M_0-1} \sum_{\alpha=M_0}^{M} \mathcal{L}^{\alpha\beta}_{\{N_\beta\}} F_{\{N_\beta,(1,\beta)\}} \qquad \text{(VI-B-11)}$$

where

$$\mathcal{H}^{I}_{\{N\}} = \sum_{\alpha=1}^{M_0-1} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha}}$$

$$- \sum_{\alpha=1}^{M_0-1} \sum_{i=1}^{N_\alpha} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \qquad \text{(VI-B-12)}$$

$$\mathcal{H}^{II}_{\{N\}} = \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha}}$$

$$- \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \sum_{\beta=1}^{M} \sum_{j=1}^{N_\beta} \frac{\partial \phi_{ij}^{\alpha\beta}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \qquad \text{(VI-B-13)}$$

$$\mathcal{H}^{III}_{\{N_\beta\}} = - \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \frac{\partial U^{\alpha}}{\partial \vec{q}_i^{\,\alpha}} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\alpha}} \qquad \text{(VI-B-14)}$$

$$\mathcal{H}^{A}_{\{N_\beta\}} = \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_i^{\,\alpha}}{m_\alpha} \cdot \frac{\partial}{\partial \vec{q}_i^{\,\alpha}} \quad - \quad \Rightarrow$$

$$\sum_{\alpha=M_0}^{M}\sum_{L=1}^{N_\alpha}\sum_{\beta=M_0}^{M}\sum_{j=1}^{N_\beta} \frac{\partial \phi_{Lj}^{\alpha\beta}}{\partial \vec{q}_L^{\alpha}} \cdot \frac{\partial}{\partial \vec{p}_L^{\alpha}} \qquad \text{(VI-B-15)}$$

$$\mathcal{H}^{\beta}_{|N\beta|} = -\sum_{\alpha=M_0}^{M}\sum_{L=1}^{N_\alpha} \frac{\partial u^{\alpha}}{\partial \vec{q}_L^{\alpha}} \qquad \text{(VI-B-16)}$$

$$\mathcal{L}^{\alpha\beta}_{|N\beta|} = N_\beta \sum_{L=1}^{N_\alpha} \iint \frac{\partial \phi_{Lj}^{\alpha\beta}}{\partial \vec{q}_L^{\alpha}} \cdot \frac{\partial}{\partial \vec{p}_L^{\alpha}} \, d\vec{r}_{Lj}^{\alpha\beta} \, d\vec{p}_j^{\beta} \qquad \text{(VI-B-17)}$$

A closed rate equation for $F_{|N\beta|}$ may then be derived by expanding $F_{|ss|}$ for all $|ss|$ in powers of the label parameter ε

i.e. $$F_{|ss|} = F^{(0)}_{|ss|} + \varepsilon F^{(1)}_{|ss|} + \varepsilon^2 F^{(2)}_{|ss|} + \cdots \qquad \text{(VI-B-18)}$$

and substituting this expansion into (VI-B-10) and (VI-B-11) so as to obtain, after collection of terms, the following perturbed equations for $F_{|N|}$ and $F_{|N\beta|}$

$$\frac{\partial F^{(0)}_{|N|}}{\partial t} + \mathcal{H}^{I}_{|N|} F^{(0)}_{|N|} = 0 \qquad \text{(VI-B-19-0)}$$

$$\frac{\partial F^{(1)}_{|N|}}{\partial t} + \mathcal{H}^{I}_{|N|} F^{(1)}_{|N|} = -\mathcal{H}^{II}_{|N|} F^{(0)}_{|N|} \qquad \text{(VI-B-19-1)}$$

$$\frac{\partial F^{(2)}_{|N|}}{\partial t} + \mathcal{H}^{I}_{|N|} F^{(2)}_{|N|} = -\mathcal{H}^{II}_{|N|} F^{(1)}_{|N|} - \mathcal{H}^{III}_{|N|} F^{(0)}_{|N|} \qquad \text{(VI-B-19-2)}$$

$$\vdots$$

$$\frac{\partial F^{(k)}_{|N|}}{\partial t} + \mathcal{H}^{I}_{|N|} F^{(k)}_{|N|} = -\mathcal{H}^{II}_{|N|} F^{(k-1)}_{|N|} - \mathcal{H}^{III}_{|N|} F^{(k-2)}_{|N|} \qquad \text{(VI-B-19-k)}$$

$$\frac{\partial F^{(0)}_{\{NB\}}}{\partial t} = 0 \qquad \text{(VI-B-20-0)}$$

$$\frac{\partial F^{(1)}_{\{NB\}}}{\partial t} = -\mathcal{H}^{A}_{\{NB\}} F^{(0)}_{\{NB\}} + \sum_{\beta=1}^{M_0-1} \sum_{\alpha=M_0}^{M} \mathcal{L}^{\alpha\beta}_{\{NB\}} F^{(0)}_{\{NB;(1,\beta)\}} \qquad \text{(VI-B-20-1)}$$

$$\frac{\partial F^{(2)}_{\{NB\}}}{\partial t} = -\mathcal{H}^{A}_{\{NB\}} F^{(1)}_{\{NB\}} + \sum_{\beta=1}^{M_0-1} \sum_{\alpha=M_0}^{M} \mathcal{L}^{\alpha\beta}_{\{NB\}} F^{(1)}_{\{NB;(1,\beta)\}}$$

$$\vdots \qquad -\mathcal{H}^{B}_{\{NB\}} F^{(0)}_{\{NB\}} \qquad \text{(VI-B-20-2)}$$

$$\frac{\partial F^{(k)}_{\{NB\}}}{\partial t} = -\mathcal{H}^{A}_{\{NB\}} F^{(k-1)}_{\{NB\}} + \sum_{\beta=1}^{M_0-1} \sum_{\alpha=M_0}^{M} \mathcal{L}^{\alpha\beta}_{\{NB\}} F^{(k-1)}_{\{NB;(1,\beta)\}}$$

$$-\mathcal{H}^{B}_{\{NB\}} F^{(k-2)}_{\{NB\}} \qquad \text{(VI-B-20-k)}$$

Proceeding with the reinitialization approach, we now integrate equations (VI-B-19-0) and (VI-B-20-0) over the time interval $[t-\Delta t, t]$ where Δt will be chosen as short as possible so as to preserve the validity of the expansion. One obtains from such an equation the following solutions for $F^{(0)}_{\{N\}}$ and $F^{(0)}_{\{NB\}}$

$$F^{(0)}_{\{N\}}(\vec{X}_{\{N\}}, t) = e^{-\mathcal{H}^{I}_{\{N\}}\Delta t} F^{(0)}_{\{N\}}(\vec{X}_{\{N\}}, t-\Delta t) \qquad \text{(VI-B-21)}$$

$$F^{(0)}_{\{NB\}}(\vec{X}_{\{NB\}}, t) = F^{(0)}_{\{NB\}}(\vec{X}_{\{NB\}}, t-\Delta t) \qquad \text{(VI-B-22)}$$

As in the simple Brownian system, discussed in previous chapter, let us assume that, since $e^{-\mathcal{H}^{I}_{\{N\}}\Delta t}$ streams the light bath particles in the presence of

the heavier Brownian particles, there exists, for the bath molecules, a relaxation time τ_b, such that for $\Delta t > \tau_b$ one may impose the following boundary condition

$$e^{-\mathcal{H}^I_{|N|}\Delta t} F_{|N|}(\vec{X}_{|N|},t) = F_{|N_b|eq}\, F_{|N_B|}(\vec{X}_{|N_B|},t) \tag{VI-B-23}$$

where

$$F_{|N_b|eq} = (Z^I_{|N_B|})^{-1} e^{-H^I_{|N_b|}/kT} \tag{VI-B-24}$$

$$H^I_{|N_b|} = \sum_{\alpha=1}^{M_0-1}\sum_{i=1}^{N_\alpha} |\vec{P}^\alpha_i|^2/2m_\alpha + \frac{1}{2}\sum_{\beta=1}^{M_0-1}\sum_{j=1}^{N_\beta}\sum_{\alpha=1}^{M_0-1}\sum_{i=1}^{N_\alpha}\Phi^{\alpha\beta}_{ij} + \sum_{\beta=M_0}^{M}\sum_{j=1}^{N_\beta}\sum_{\alpha=1}^{M_0-1}\sum_{i=1}^{N_\alpha}\Phi^{\alpha\beta}_{ij} \tag{VI-B-25}$$

$$Z^I_{|N_B|} = \int\cdots\int e^{-H^I_{|N_B|}/kT} \prod_{\gamma=1}^{M_0-1}\prod_{k=1}^{N_\gamma} d\vec{q}^\gamma_k\, d\vec{p}^\gamma_k \tag{VI-B-26}$$

represents the equilibrium distribution for the bath particles under the influence of the neighboring Brownian particles. Substituting the expansions for $F_{|N|}(\vec{X}_{|N|},t)$ and $F_{|N_B|}(\vec{X}_{N_B},t)$ and collecting orders of ε we may then rewrite (VI-B-23) as

$$e^{-\mathcal{H}^I_{|N|}\Delta t} F^{(k)}_{|N|}(\vec{X}_{|N|},t) = F_{|N_b|eq}\, F^{(k)}_{|N_B|}(\vec{X}_{|N_B|},t) \tag{VI-B-27}$$

Consequently if τ_b remains sufficiently short to preserve the validity of the expansion the solution for

$F^{(0)}_{\{N\}}(\vec{X}_{\{N\}},t)$ becomes

$$F^{(0)}_{\{N\}}(X_{\{N\},t}) = F_{\{N_b\}eq}\, F^{(0)}_{\{N_B\}}(\vec{X}_{\{N_B\}},t-\Delta t)$$

$$= F_{\{N_b\}eq}\, F^{(0)}_{\{N_B\}}(\vec{X}_{\{N_B\}},t) \qquad \text{(VI-B-28)}$$

Integrating the above solution over all bath particles except $\{1,\beta\}$; one may also obtain the following solution for $F^{(0)}_{\{N_B\}(1,\beta)}$

$$F^{(0)}_{\{N_B,(1,\beta)\}} = F^{(0)}_{\{N_B\}}(X_{\{N_B\},t})\, F_{\{1,\beta\}eq} \qquad \text{(VI-B-29)}$$

where

$$F_{\{1,\beta\}eq} = Z^{-1}_{\{1,\beta\}}\, e^{-H_{\{1,\beta\}}/KT} \qquad \text{(VI-B-30)}$$

$$H_{\{1,\beta\}} = |\vec{P}_1^{\,\beta}|^2/2m_\beta + \sum_{\alpha=M_0}^{M}\sum_{i=1}^{N_\alpha} \phi^{\alpha\beta}_{i1} \qquad \text{(VI-B-31)}$$

$$Z_{\{1,\beta\}} = \int\int e^{-H_{\{1,\beta\}}/KT}\, d\vec{q}_1^{\,\beta}\, d\vec{P}_1^{\,\beta} \qquad \text{(VI-B-32)}$$

This solution may then be substituted into (VI-B-20-1) to render the following rate equation for $F^{(1)}_{\{N_B\}}$

$$\frac{\partial F^{(1)}_{\{N_B\}}}{\partial t} + \mathcal{H}^{A}_{\{N_B\}} F^{(0)}_{\{N_B\}} = \sum_{\alpha=M_0}^{M}\sum_{\beta=1}^{M_\alpha-1} \mathcal{L}^{\alpha\beta}_{\{N_B\}}\, F^{(0)}_{\{N_B;(1,\beta)\}} \qquad \text{(VI-B-33)}$$

which, using the definitions for $\mathcal{H}^{A}_{\{N_B\}}$ and $\mathcal{L}^{\alpha\beta}_{\{N_B\}}$

may also be written as

$$\frac{\partial F^{(1)}_{\{N\beta\}}}{\partial t} + \mathcal{H}^{+}_{\{N\beta\}} F^{(0)}_{\{N\beta\}} = 0 \qquad \text{(VI-B-34)}$$

where:

$$\mathcal{H}^{+}_{\{N\beta\}} = \mathcal{H}^{A}_{\{N\beta\}} + \sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \langle \delta\vec{F}^{i\alpha} \rangle_{eq} \cdot \frac{\partial}{\partial \vec{q}_i^{\alpha}} \qquad \text{(VI-B-35)}$$

and

$$\langle \delta\vec{F}^{i\alpha} \rangle_{eq} = -N_\beta \sum_{\beta=1}^{M_0-1} \int\int \frac{\partial \phi^{i\alpha}_{j\beta}}{\partial \vec{q}_i^{\alpha}} F_{\{1,\beta\}eq} \, d\vec{q}_j^{\beta} \, d\vec{p}_j^{\beta}$$

$$= \sum_{\beta=1}^{M_0-1} \sum_{j=1}^{N_\beta} \langle \delta\vec{F}^{i\alpha}_{j\beta} \rangle \qquad \text{(VI-B-36)}$$

represents the average force exerted by all the bath particles on the Brownian particle $\{i,\alpha\}$ when the former are in equilibrium with the field exerted by all the Brownian particles. Naturally if the latter are seperated by distances much larger than the typical Brownian-bath range of interaction, this average force vanishes. Combining (VI-B-34) and (VI-B-20-0) one may then write the following first order rate equation for

$$\frac{\partial F_{\{N\beta\}}}{\partial t} + \mathcal{H}^{+}_{\{N\beta\}} F_{\{N\beta\}} = 0 \qquad \text{(VI-B-37)}$$

One may pursue this expansion to a higher order by recalling equation (VI-B-19-1) and integrating it over the time interval $[t-\Delta t, t]$ so as to obtain

$$F^{(1)}_{(N)}(\vec{X}_{(N)},t) = e^{-\mathcal{H}^{I}_{(N)}\Delta t} F^{(1)}_{(N)}(\vec{X}_{(N)},t-\Delta t)$$
$$= \int_0^{\Delta t} e^{-\mathcal{H}^{I}_{(N)}t'} \mathcal{H}^{II}_{(N)} F^{(0)}_{(N)}(\vec{X}_{(N)},t-t')\,dt'$$

(VI-B-38)

Choosing $\Delta t > \tau_b$, and combining equations (VI-B-27), (VI-B-28) and (VI-B-34), this solution may also be written as

$$F^{(1)}_{(N)}(\vec{X}_{(N)},t) = F_{(N_b)eq}\left[F^{(1)}_{(N_B)}(\vec{X}_{(N_B)},t) + \mathcal{H}^{+}_{(N_B)} F^{(0)}_{(N_B)}(X_{(N_B)},t)\,\Delta t\right]$$
$$- \int_0^{\Delta t} e^{-\mathcal{H}^{I}_{(N)}t'} \mathcal{H}^{II}_{(N)} F^{(0)}_{(N_B)}(X_{(N_B)},t)\,F_{(N_b)eq}\,dt'$$

(VI-B-39)

or, after some manipulation, as

$$F^{(1)}_{(N)}(\vec{X}_{(N)},t) = F_{(N_b)eq}\,F^{(1)}_{(N_B)}(\vec{X}_{(N_B)},t)$$
$$- \int_0^{\Delta t} \sum_{\alpha=M_0}^{M}\sum_{i=1}^{N_\alpha} \left(\vec{SF}^{i\alpha}(-t'),-\langle \vec{SF}^{i\alpha}\rangle_{eq}\right)dt'\,F_{(N_b)eq}$$
$$\cdot\left\{\frac{\vec{p}_i^{\,\alpha}}{m_\alpha KT} + \frac{\partial}{\partial \vec{p}_i^{\,\alpha}}\right\} F^{(0)}_{(N_B)}(\vec{X}_{(N_B)},t)$$
$$- \sum_{\alpha=M_0}^{M}\sum_{\mu=1}^{N_\alpha} \langle \vec{SF}^{i\alpha}\rangle_{eq} \cdot \frac{\vec{p}_i^{\,\alpha}}{m_\alpha KT}\,F_{(N_b)eq}\,F^{(0)}_{(N_B)}(X_{(N_B)},t)\,\Delta t$$

(VI-B-40)

where

$$\vec{SF}^{i\alpha}(-t) = e^{-\mathcal{H}^{I}_{\{N\}} t} \vec{SF}^{i\alpha}$$

(VI-B-41)

Integrating this solution over the coordinates and momenta of all bath molecules, except $\{1,\beta\}$ one then obtains the following expression for

$$F^{(1)}_{\{N_B,(1,\beta)\}} = F_{\{1,\beta\}eq}\, F^{(1)}_{\{N_B\}}(\vec{X}_{\{N_B\}},t)$$
$$- \int_0^{\Delta t} \int\cdots\int \sum_{\alpha=M_0}^{M}\sum_{i=1}^{N_\alpha} (\vec{SF}^{i\alpha}(-t') - \langle \vec{SF}^{i\alpha}\rangle_{eq})\, F_{\{N_\alpha\}eq}$$
$$\cdot \left\{ \frac{\vec{p}_i^{\alpha}}{m_\alpha KT} + \frac{\partial}{\partial \vec{p}_i^{\alpha}} \right\} F^{(0)}_{\{N_B\}}(X_{\{N_B\}},t) \prod_{\substack{\gamma=1\\ \{k,\gamma\}\neq\{1,\beta\}}}^{M_0-1}\prod_{k=1}^{N_\gamma} d\vec{q}_k^{\gamma}\, d\vec{p}_k^{\gamma}\; dt'$$
$$- \sum_{\alpha=M_0}^{M}\sum_{i=1}^{N_\alpha} \langle \vec{SF}^{i\alpha}\rangle_{eq} \cdot \frac{\vec{p}_i^{\alpha}}{m_\alpha KT} F_{\{1,\beta\}eq}\, F_{\{N_B\}}(X_{\{N_B\}},t)\,\Delta t$$

(VI-B-42)

which, after substitution into (VI-B-20-2), leads to the following rate equation for $F^{(2)}_{\{N_B\}}$

$$\frac{\partial F^{(2)}_{\{N_B\}}}{\partial t} + \mathcal{H}^{+}_{\{N_B\}} F^{(1)}_{\{N_B\}} + \mathcal{H}^{B}_{\{N_B\}} F^{(0)}_{\{N_B\}} =$$
$$\sum_{\alpha=M_0}^{M}\sum_{i=1}^{N_\alpha}\sum_{\alpha'=M_0}^{M}\sum_{i'=1}^{N_{\alpha'}} \left\{ \int_0^{\Delta t} \langle \vec{SF}^{i\alpha} (\vec{SF}^{i'\alpha'}(-t') - \langle \vec{SF}^{i'\alpha'}\rangle_{eq})_{eq}\, dt' \right.$$
$$: \frac{\partial}{\partial \vec{p}_i^{\alpha}} \left[\frac{\vec{p}_{i'}^{\alpha'}}{m_{\alpha'}KT} + \frac{\partial}{\partial \vec{p}_{i'}^{\alpha'}} \right] F^{(0)}_{\{N_B\}}(\vec{X}_{\{N_B\}},t)$$
$$\left. + \langle \vec{SF}^{i\alpha}\rangle_{eq} \langle \vec{SF}^{i'\alpha'}\rangle_{eq} : \frac{\partial}{\partial \vec{p}_i^{\alpha}} \left[\frac{\vec{p}_{i'}^{\alpha'}}{m_{\alpha'}KT} F^{(0)}_{\{N_B\}}(\vec{X}_{\{N_B\}},t) \right] \Delta t \right\}$$

(VI-B-43)

Furthermore, defining

$$\Delta \vec{\mathcal{F}}^{(\alpha)} = \vec{\mathcal{F}}^{(\alpha)} - \langle \vec{\mathcal{F}}^{(\alpha)} \rangle_{eq} \qquad \text{(VI-B-44)}$$

and noting that

$$\langle \vec{\mathcal{F}}^{(\alpha)}(-t) \rangle_{eq} = \langle \vec{\mathcal{F}}^{(\alpha)} \rangle_{eq} \qquad \text{(VI-B-45)}$$

we may also rewrite (VI-B-43) as

$$\frac{\partial F^{(2)}_{(N_B)}}{\partial t} + \mathcal{H}^{+}_{(N_B)} F^{(1)}_{(N_B)} + \mathcal{H}^{II}_{(N_B)} F^{(0)}_{(N_B)} =$$

$$\sum_{\omega=M_0}^{M} \sum_{i=1}^{N_\omega} \sum_{\omega'=M_0}^{M} \sum_{i=1}^{N_{\omega'}} \left\{ \int_0^{\Delta t} \langle \Delta \vec{\mathcal{F}}^{(i\omega)} \, \Delta \mathcal{F}^{(i'\omega')}(-t') \rangle_{eq} \, dt' \right.$$

$$\cdot \frac{\partial}{\partial \vec{p}_i^{\,\omega}} \left[\frac{\vec{p}_i^{\,\omega}}{m_\omega KT} + \frac{\partial}{\partial \vec{p}_{i'}^{\,\omega'}} \right] F^{(0)}_{(N_B)}(\vec{X}_{(N_B)}, t)$$

$$\left. + \langle \vec{\mathcal{F}}^{(i\omega)} \rangle_{eq} \langle \vec{\mathcal{F}}^{(i'\omega')} \rangle_{eq} \cdot \frac{\partial}{\partial \vec{p}_i^{\,\omega}} \left[\frac{\vec{p}_i^{\,\omega}}{m_\omega KT} F^{(0)}_{(N_B)}(\vec{X}_{(N_B)}, t) \right] \Delta t \right\}$$

(VI-B-46)

Now, the right hand side of the above equations still bears a dependence on Δt which must be chosen larger than the relaxation time of the light bath molecules, yet sufficiently short to preserve the validity of the expansion. Unfortunately, since Δt may still assume a wide

range of values, the equation (VI-B-46) remains rather arbitrary. One may of course, partially resolve this problem by assuming that the cross correlations $\langle \Delta \vec{\mathcal{F}}^{(\alpha} \Delta \vec{\mathcal{F}}^{(\alpha'}(-t)\rangle_{eq}$ become vanishingly small for $t > \tau_b$ such that

$$\int_0^{\Delta t} \langle \Delta \vec{\mathcal{F}}^{(\alpha} \Delta \vec{\mathcal{F}}^{(\alpha'}(-t')\rangle_{eq}\, dt' = \int_0^{\infty} \langle \Delta \vec{\mathcal{F}}^{(\alpha} \Delta \vec{\mathcal{F}}^{(\alpha'}(-t')\rangle_{eq}\, dt \qquad \text{(VI-B-47)}$$

$$\Delta t > \tau_b$$

The last term in equation (VI-B-46), however, grows linearly with Δt and can only be eliminated if one restricts $\vec{X}_{(N_\beta)}$ to a volume $V^{\oplus}_{(N_\beta)}$ in which Brownian particles are sufficiently distant from each other that they cannot share any direct interaction with the same bath particle. In this volume (where Brownian particles may still interact with each other if their mutual range of interaction is much larger than their range of interaction with the bath particles) one has

$$\langle \vec{\mathcal{F}}^{(\alpha)} \rangle_{eq} = 0 \qquad \alpha = M_0 \cdots M$$

Consequently, for $\vec{X}_{(N_\beta)} \in V^{\oplus}_{(N_\beta)}$ we may write the following rate equation

$$\frac{\partial F^{(2)}_{(N_\beta)}}{\partial t} + \mathcal{H}^{A}_{(N_\beta)} F^{(1)}_{(N_\beta)} + \mathcal{H}^{B}_{(N_\beta)} F^{(0)}_{(N_\beta)} =$$

$$\sum_{\alpha=M_0}^{M} \sum_{i=1}^{N_\alpha} \sum_{\alpha'=M_0}^{M} \sum_{i'=1}^{N_{\alpha'}} \left\{ \int_0^{\infty} \langle \vec{\mathcal{F}}^{(i\alpha} \vec{\mathcal{F}}^{(i'\alpha'}(-t')\rangle_{eq}\, dt' \right. \quad \Rightarrow$$

$$\frac{\partial}{\partial \vec{p}_i^{\alpha}} \left(\frac{\vec{p}_i^{\alpha}}{m_\alpha KT} + \frac{\partial}{\partial \vec{p}_i^{\alpha}} \right) F^{(0)}_{\{N_\beta\}} (X_{\{N_\beta\}}, t)$$

$$\vec{X}_{\{N_\beta\}} \in V^{\circledast}_{\{N_\beta\}} \qquad \text{(VI-B-48)}$$

which, when combined with equations (VI-B-20-0) and (VI-B-34) renders the following second order equation:

$$\frac{\partial F_{\{N_\beta\}}}{\partial t} + \left[\mathcal{H}^{A}_{\{N_\beta\}} + \mathcal{H}^{B}_{\{N_\beta\}} \right] F_{\{N_\beta\}} = 0$$

$$\sum_{\alpha=A_0}^{M} \sum_{i=1}^{N_\alpha} \sum_{\alpha'=A_0}^{M} \sum_{i'=1}^{N_{\alpha'}} b^{i\alpha, i'\alpha'} : \frac{\partial}{\partial \vec{p}_i^{\alpha}} \left[\frac{\vec{p}_i^{\alpha}}{m_\alpha KT} + \frac{\partial}{\partial \vec{p}_i^{\alpha}} \right] F_{\{N_\beta\}}$$

$$\vec{X}_{\{N_\beta\}} \in V^{\circledast}_{\{N_\beta\}} \qquad \text{(VI-B-48)}$$

where

$$b^{i\alpha, i'\alpha'} = \int_0^{\infty} \langle \vec{SF}^{i\alpha} \vec{SF}^{i'\alpha'}(-t') \rangle_{eq} \, dt'$$

(VI-B-49)

The above equation which has a Fokker-Planck form may be viewed as a "Generalized Liouville"[42] equation for an open system of heavy particles exchanging energy and momentum with a bath of light particles. In its domain of validity, $\vec{X}_{\{N_\beta\}} \in V^{\circledast}_{\{N_\beta\}}$, this equation reduces to similar equations derived by J.M. Deutch and I. Oppenheim [36] and R. Mazo [37] using a "Projection Operator" technique developed by R.W. Zwanzig [43]

C. SUMMARY AND CONCLUSIONS

In the present chapter we have extended the analysis of the previous chapter to include more complex systems such as non uniform mixtures interacting with a weak external field. As previously noted it generally becomes quite difficult for such systems to fully assess the breakdown of the IVP solutions. Nevertheless, even in these cases, the goal of the reinitialization technique does not drastically change in principle as one still strives to minimize the time interval of integration Δt of the perturbed equations so as to assure the accuracy of their solutions. Furthermore, for non-dense systems, one should maintain $\Delta t \ll \sqrt[3]{m}\, v_0 \ll \tau$ such that the phase vector $\vec{X}(s)$ will remain within the volume $V(s)$ in $\Gamma(s)$, corresponding to a physical volume $V \ll n^{-1}$, in which the density expansion is valid. With this restriction and boundary conditions similar to those used for a uniform system one then obtains, for a non dense mixture of M species, a set of M coupled Boltzmann equations provided the external field is weak and the one particle distribution F_1 does not significantly vary spatially within the interaction sphere of the individual molecules. One may similarly consider a mixture of M_2 species of Brownian particles interacting with a weak external field and $(M - M_2)$ bath particles, by assuming that the relaxation rate for the light particles is much faster than that for the heavy particles. By further requiring that the inter Brownian particle separation is sufficiently large

to prevent two such particles from sharing a mutual interaction with a small bath particle one then obtains an equation for the N_B Brownian particle distribution $F_{(N_B)}$. In its domain of validity, this equation reduces to the Fokker-Planck equations derived by J.M. Deutch and I. Oppenheim [36] and R. Mazo [37], using a "Projection Operator" technique developed by R.W. Zwanzig [43].

CHAPTER VII

CONCLUSION

In the present thesis we have reevaluated the mathematical expansions and the physical assumptions leading to well known kinetic equations such as the Boltzmann equation for non-dense systems and the Fokker-Planck equation describing Brownian motion. Using the Hamilton, Liouville and B.B.G.K.Y. hierarchy as governing equations for a system of point particles we have firstly developed a systematic nondimensionalization of these equations which clearly reveals the relative magnitude of their various terms, over a particular volume of their respective phase space, for special classes of systems. Secondly, we have reconsidered the straightforward initial value perturbation scheme (IVP) and studied the exact form of the divergent terms which appear for spatially uniform non-dense, weakly coupled and Brownian systems. Finally, previous expansion methods such as those of Bogoliubov,[12] Frieman[24] (MTS), and Lewis-Harris[39] have been reviewed and an alternate expansion method, which emerges as a natural extension of the IVP scheme has been proposed and applied to simple uniform systems and to non-uniform mixtures interacting with a weak external field. In summary, we may offer the following conclusions.

A. UNIFORM SYSTEMS

a. Non-dense system

1. There exists, for the uniform non-dense system, a small region $V_{|s|}$ in the s particle $\Gamma_{|s|}$ space where the momentum convection term $\sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \frac{\partial F_s}{\partial \vec{q}_i}$ and the interaction term $\sum_{i=1}^{s}\sum_{j=1}^{s} \frac{\partial \phi_{ij}}{\partial q_i} \cdot \frac{\partial}{\partial p_i}$ in the B.B.G.K.Y. hierarchy dominate, on the average, over the mixing term $\mathcal{L}_s F_{s+1}$. This volume is roughly defined by the region in $\Gamma_{|s|}$ where $|\vec{p}_i| \sim o[\sqrt{mKT}]$, $(i=1,s)$, and where the s molecules may be enclosed in a spherical physical volume V_1 larger than the interaction sphere of the individual particles, yet much smaller than the specific volume n^{-1} (where n represents the average particle density). For the larger regions in $\Gamma_{|s|}$ space corresponding to a physical volume $V_2 \sim o[n^{-1}]$ the mixing term may bear the same relative weight, on the average, as the remaining momentum convection and the interaction terms.

2. Performing a simple expansion in density, which neglects the mixing term of the B.B.G.K.Y. hierarchy, in the small phase volume $V_{|s|}$, as a zeroth order approximation, and assuming that initial correlations are finite in range we then obtain, at the first order of the expansion, an equation for F_1 which bears a form identical to the Boltzmann equation with the exception that

the collision term is based on $F_1(\vec{p}_1, 0)$ rather than $F(\vec{p}_1, t)$. The time independence of this term thus leads to a divergence causing a total breakdown of the expansion when $t \sim O[\tau_1 = \lambda/v_0]$

3. The above results and a review of the Bogoliubov functional expansion, Frieman's multiple time scale perturbation scheme and Lewis and Harris's time expansion approach suggest the development of a very simple alternate perturbation scheme which follows as a natural extension of the IVP approach and which essentially consists of integrating the B.B.G.K.Y. hierarchy over a time interval $[\, t - \Delta t \,,\, t \,]$ sufficiently short to prevent breakdown yet sufficiently long to impose reasonable boundary conditions.

4. Assuming that for $|\vec{q}_1 - \vec{q}_2| < r_0$, the boundary condition:

$$e^{-\mathcal{H}_2(1,2)\Delta t} F_2(\vec{x}_1, \vec{x}_2, t) = \lim_{\tau \to \infty} e^{-\mathcal{H}_2(1,2)\tau} F_1(\vec{p}_1, t) F_1(\vec{p}_2, t)$$

is valid for $\Delta t > \tau^{\circledast}$ where $[\tau_c = r_0/v_0] \ll \tau^{\circledast} \ll [\tau_1 = \lambda/v_0]$ one recovers, at the first order of this new "reinitialization" expansion method, the familiar Boltzmann equation.

5. It is also shown that since the alternate boundary condition

$$e^{\mathcal{H}_2(1,2)\Delta t} F_2(\vec{x}_1, \vec{x}_2, t) = \lim_{\tau \to \infty} e^{\mathcal{H}_2(1,2)\tau} F_1(\vec{p}_1, t) F_1(\vec{p}_2, t)$$

should only hold for Δt much larger than the breakdown time $\sim O[\tau_1]$ of the initial value perturbation scheme,

the possibility of deriving an anti-Boltzmann equation is inherently excluded in this expansion method.

6. Pursuing the expansion to a higher order, one finds that there does not exist a $\Delta t \ll \tau_1$ sufficiently long to impose suitable boundary conditions allowing the derivation of a zeroth order solution $F_3^{(0)}$ over the domain $V_{(3)}$ contributing to a first order solution for $F_2(\vec{x}_1,\vec{x}_2,t)$ where $|\vec{q}_1-\vec{q}_2| < r_0$. This difficulty emerges from particular three particle configurations which, as noted by Cohen and others, require a time $\sim O[\tau_1]$ or longer for the reverse set of interactions induced by $e^{-\mathcal{H}_3((\cdot)R)\Delta t}$, to occur. We have essentially dealt with the problem using the pragmatic approach of deriving solutions for $F_2^{(1)}(\vec{x}_1,\vec{x}_2,t)$ using solely the domain in $\Gamma_{(3)}$ where suitable boundary conditions exist for $\Delta t \ll \tau_1$. By thus assuming that the domain neglected in $\Gamma_{(3)}$ does not significantly contribute to a second order kinetic equation, we then emerge with a Uhlenbeck-Choh equation for F_2.

b. Weakly coupled system

1. There exists, for the spatially uniform weakly coupled system, a small region $V_{(3)}$ in $\Gamma_{(3)}$ where the momentum convection, interaction and mixing terms are all very small and, on the average, of the same order of magnitude. This volume is roughly defined by the region in

$\Gamma_{(s)}$ where $|\vec{p}_i| \sim o[\sqrt{mkT}]$ $(i = 1, \ldots s)$ and where the s molecules may be enclosed in a spherical physical volume $V_i \sim o[\pi r^3]$ where πr represents the range of the weak interaction potential. For phase volumes corresponding to larger physical volumes $V >> \pi r^3$ one finds that the mixing term, however small, in fact dominates, on the average, over the remaining momentum convection and interaction terms. These results, which conflict with previous scaling arguments by Bogoliubov,[12] Sandri[25] and others,[38] emerge due to the fact that, near equilibrium, the weak potential in the interaction and mixing terms imply in $V_{(s)}$ a similarly weak correlation and hence a small gradient $\frac{\partial F_s}{\partial \vec{q}_i}$ in the momentum convection term.

2. Performing a simple initial value expansion within $V_{(s)}$ one obtains, at the first order, solutions for F_1 which diverge linearly with time if the system has initial two particle correlations. On the other hand if one assumes the system to be free of such initial correlations, one then emerges with a first order solution for F_2 which also diverges linearly with time.

3. Attempting a "reinitialization" expansion one finds that, due to the zeroth order equation:

$$\frac{\partial F_s^{(0)}}{\partial t} = 0 \quad \Rightarrow \quad F_s(\vec{x}_s, t) = F(\vec{x}_s, t - \Delta t)$$

there does not exist any choice of Δt which suggests the introduction of suitable boundary conditions which,

in turn, would allow one to express $F_s^{(0)}$ as a functional of F_1. Consequently, in contrast with the results of Bogoliubov, Sandri and others, no kinetic equation for the system should emerge, near equilibrium, via a weak coupling expansion.

c. Brownian system

1. For a system consisting of a single Brownian particle coexisting with a bath of light particles it becomes difficult to estimate, in general, the various dimensionless parameters present in the nondimensionalized Liouville and B.B.G.K.Y. equations. Consequently we have followed the pragmatic approach of Lebowitz-Resebois[9] and others[35] and assumed the root mass ratio $\gamma = \sqrt{\frac{m_1}{m_s}}$ to dictate the relative magnitude of the various terms in these equations. By so doing one essentially assigns a relatively smaller weight to these terms associated with the slow motion of the heavy Brownian particle than those corresponding to the faster motion of the light bath particles.

2. A simple initial value expansion for this system yields a first order kinetic equation for the single Brownian particle distribution $F_{(0,1)}(\vec{p}^s, t)$ which bears a form identical to the well known Fokker-Planck equation with the exception that the damping and diffusion terms are based on $F_{(0,1)}(\vec{p}^s, 0)$ rather than $F_{(0,1)}(\vec{p}^s, t)$. Consequently the solution of this equation diverges linearly with time.

3. A true Fokker Planck equation may be derived, via a reinitialized expansion, by assuming the relaxation time, τ_b, of the bath particles to be much shorter than that, τ_B, of the slower Brownian particle and by integrating the expanded equations over a time interval $[t-\Delta t, t]$ where $\tau_b \ll \Delta t \ll \tau_B$

B. NON-UNIFORM MIXTURES

Some of the results in the above analysis for simple non-uniform systems have been generalized to include non-uniform mixtures interacting with an external field. In particular, we have shown that

1. For a non-dense mixture of M species of particles one may derive a set of coupled Boltzmann equations for the single particle distribution of each specie by assuming a weak external field and integrating the expanded B.B.G-K.Y. equation over a time interval $[t-\Delta t, t]$, where $\tau_0 \ll \Delta t \ll \lambda/v_0$ and imposing boundary conditions similar to those in the spatially uniform case. This derivation, as in the Bogoliubov expansion, also requires that the spatial non-uniformities over a length scale $L \ll v_0 [\tau_0]$ may be neglected.
2. Similarly, for a mixture of M_1 species of Brownian particles interacting with a weak external field and coexisting with $(M - M_1)$ species of light bath particles, one may, with a reinitialization expansion, derive a closed

equation for the full N Brownian particle distribution $F_{(N)}$ by assuming the relaxation time for these particles to be much longer than that of the light particles. This equation which is similar to the Fokker-Planck equation derived by Deutch and Oppenheim [36] and Mazo [37] using a "Projection Operator" method of Zwanzig [43], emerges, however, only if the separation between Brownian particles is sufficiently large to prevent the latter from sharing a mutual interaction with the same light particle.

The above conclusions confirm the self-evident necessity of carefully estimating the relative importance of the various terms of the B.B.G.K.Y. hierarchy prior to performing a particular expansion for a special system. Clearly, in order to accomplish such a task, the straightforward approach, used by previous authors, of nondimensionalizing this equation with respect to a set of seemingly reasonable characteristic quantities and subsequently expanding in terms of whatever small parameter which emerges, is not at all recommended. Indeed we have shown that such a casual approach has led to major inconsistencies in previous derivations by the same authors for spatially uniform weakly coupled systems. Naturally the proper estimation of the relative importance of various terms in a complex equation such as the B.B.G.K.Y. hierarchy represents, prior to its solution, a difficult task, which

usually requires a good deal of "educated guess work". In the present thesis we have designed a nondimensionalizing scheme in which each term of the resulting dimensionless governing equation may, on the average, over a restricted volume in phase space, be written as the product of variable terms $\sim O[1]$ and a set of dimensionless parameters. The magnitude of the latter thus dictates the relative importance of each term in the equation. In any such analysis many assumptions and restrictions must of course prevail. In particular we have assumed the system of particles to be reasonably close to a canonical equilibrium and estimated average values of products of terms using products of their individual estimated average magnitude. In spite of the importance of these restrictions we nevertheless believe that such an analysis represents on one hand a true recognition of the problems of scaling in the Hamilton Liouville and B.B.G.K.Y. equations, and a first step in confronting these difficulties prior to an otherwise semi-blind perturbational derivation of a kinetic equation.

The present thesis has also revealed that one may derive kinetic equations for particular systems of point particles using a very simple extension of the initial value perturbation scheme. This alternate method consists of integrating the expanded form of the B.B.G.K.Y. hierarchy over a time interval $[t-\Delta t, t]$, where Δt is sufficiently short to pre-

serve the accuracy of the expansion yet adequately long to impose reasonable boundary conditions. Hence one simply seeks an optimal value for Δt which, in the case of a uniform non-dense system, for example, must be chosen much shorter than $\tau_1 = \lambda/\bar{v}$ as suggested by the breakdown of the IVP scheme for $t > \tau_1$. This method of "reinitialization" thus avoids the introduction of auxiliary time scales as in the Bogoliubov and MTS schemes or the unnecessary use of abstract operators as in the Zwanzig projection operator approach. Furthermore, the natural constraints on Δt in this optimization, which is also implied by the small domain in phase space over which this particular expansion is valid, also suggests the proper choice of boundary conditions and inherently eliminates those which would lead to irreversible equations evolving in the "wrong" direction. We have also noted that in the derivation of the Uhlenbeck and Choh equation, which takes into account three particle interactions, the restraint on Δt also imposes a limitation on the validity of the zeroth order solution $F_s^{(0)}$ by eliminating, in Γ_{131}, regions which correspond to three particle interaction sequences occuring over a time interval $\Delta t \gg 0[\tau_1]$. For this reason we suspect that the constraint on the time interval of integration in the reinitialization scheme plays a similar role as the "damping exponential" used by some authors [21,26] to eliminate divergences at the higher orders of the density expansion.

Finally, one could also speculate that this expansion scheme may also be used to derive macroscopic laws from kinetic equations and, hence, serve as a simple alternative to the Chapman-Enskog procedure.

In many respects the present thesis represents a review, critique, simplification and clarification of a collection of concepts and ideas in the field of "nonequilibrium statistical mechanics" . Naturally, such clarifications are often somewhat personal and do not always reflect a lack of clarity in the original contribution of others. For this reason, as a final conclusion and tribute to the founder of this field, the following quotation would seem rather appropriate.

> I am concious of being only an individual struggling against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered.
>
> (L. Boltzmann) [1]

APPENDIX I

DERIVATION OF EQUATION (IV-B-18)

Equation (IV-B-17) may be transformed into (IV-B-18) by using arguments very similar to those presented by Bogoliubov [12] and Cohen [32] in their derivation of the Boltzmann equation. Let us first note that the product $F_1^{(0)}(\vec{P}_i(\infty),0)F^{(0)}(\vec{P}_j(\infty),0)$ represents a stationary solution of the zeroth order equation for $s=2$. Consequently, from the definition of $\mathcal{H}_s$, one may write

$$\frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_1^{(0)}(\vec{P}_i(\infty),0) F_1^{(0)}(\vec{P}_j(\infty),0)}{\partial \vec{P}_i}$$

$$= \left(- \frac{\partial \phi_{ij}}{\partial \vec{q}_j} \cdot \frac{\partial}{\partial \vec{P}_j} + \frac{\vec{P}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} + \frac{\vec{P}_j}{m} \cdot \frac{\partial}{\partial \vec{q}_j} \right) F_1^{(0)}(\vec{P}_i(\infty),0) F_1^{(0)}(\vec{P}_j(\infty),0) \qquad \text{(A-I-1)}$$

Substituting (A-I-1) into (IV-B-17) and noting that

$$\lim_{|\vec{P}_j| \to \infty} F_1^{(0)}(P_i(\infty),0) F_1^{(0)}(P_j(\infty),0) = 0 \qquad \text{(A-I-2)}$$

we then have

$$\frac{\partial F_1^{(1)}}{\partial t} = (N-1) \int_{-\infty}^{\infty} \int \left(\frac{\vec{P}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} + \frac{\vec{P}_j}{m} \cdot \frac{\partial}{\partial \vec{q}_j} \right) F_1^{(0)}(\vec{P}_i(\infty),0) F_1^{(0)}(\vec{P}_j(\infty),0) \, d\vec{q}_j \, d\vec{P}_j \qquad \text{(A-I-3)}$$

Furthermore, introducing the change of variable

$$\vec{q}_i = \vec{q}_i$$
$$\vec{r}_{ij} = \vec{q}_j - \vec{q}_i \qquad \text{(A-I-4)}$$

and noting that $\vec{P}_{i(\infty)}$ and $\vec{P}_{j(\infty)}$ only depend on $\vec{r}_{ij}$, $\vec{p}_i$ and $\vec{p}_j$ we may write

$$\frac{\partial F_i^{(1)}}{\partial t} = (N-1)\iint \frac{(\vec{p}_j - \vec{p}_i)}{m} \cdot \frac{\partial}{\partial \vec{r}_{ij}} F_i^{(0)}(\vec{P}_{i(\infty)}, 0) F_j^{(0)}(\vec{P}_{j(\infty)}, 0)\, d\vec{r}_{ij}\, d\vec{p}_j \qquad \text{(A-I-5)}$$

We shall now perform the spatial integration over $d\vec{r}_{ij}$ using the cylindrical coordinates (z, b, ϕ) where the z axis is chosen in the direction of the relative velocity $\vec{g}_{ij} = \frac{\vec{p}_j - \vec{p}_i}{m}$, while b and ϕ denote the radial and angular coordinates. With this geometry, equation (A-I-5) may now be rewritten as,

$$\frac{\partial F_i^{(1)}}{\partial t} = \int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{\infty}\int_{-\infty}^{\infty} \frac{|\vec{p}_j - \vec{p}_i|}{m} \frac{\partial F_i^{(0)}}{\partial g}(P_{i(\infty)}, 0) F_j^{(0)}(P_{j(\infty)}, 0)\, dg\, b\, db\, d\phi\, d\vec{p}_j =$$
$$\int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{\infty}\Big|_{g\to-\infty}^{g\to\infty} \frac{|\vec{p}_j - \vec{p}_i|}{m} F_i^{(0)}(\vec{P}_{i(\infty)}, 0) F_j^{(0)}(\vec{P}_{j(\infty)}, 0)\, b\, db\, d\phi\, dg \qquad \text{(A-I-6)}$$

Before evaluating the stationary solution $F_2^{(0)}(\vec{q}_i, \vec{r}_{ij}, \vec{p}_i, \vec{p}_j) = F_i^{(0)}(\vec{P}_{i(\infty)}, 0) F_j^{(0)}(\vec{P}_{j(\infty)}, 0)$ at the limits $g \to \pm\infty$ let us first recall that the original perturbed equation (IV-B-7) only hold for $X_s \in V_{(s)}$, or $r \ll |\vec{r}_{ij}| \ll n^{-1/3}$. Consequently it becomes totally meaningless to even use

this solution for $\beta \gtrless 0\ [n^{-1/3}]$. Fortunately, we also note that since the integrand, in the original equation (IV-B-17), vanishes when $|\vec{r}_{ij}| > {}^{I}r$, one may in fact replace the limit $\beta \to \pm\infty$ by some alternate limit $\beta \to \pm\beta^{\oplus}$ where $\beta^{\oplus}$ may be chosen within the range

$$ {}^{I}r < \beta^{\oplus} \ll n^{-1/3} \qquad \text{(A-I-7)} $$

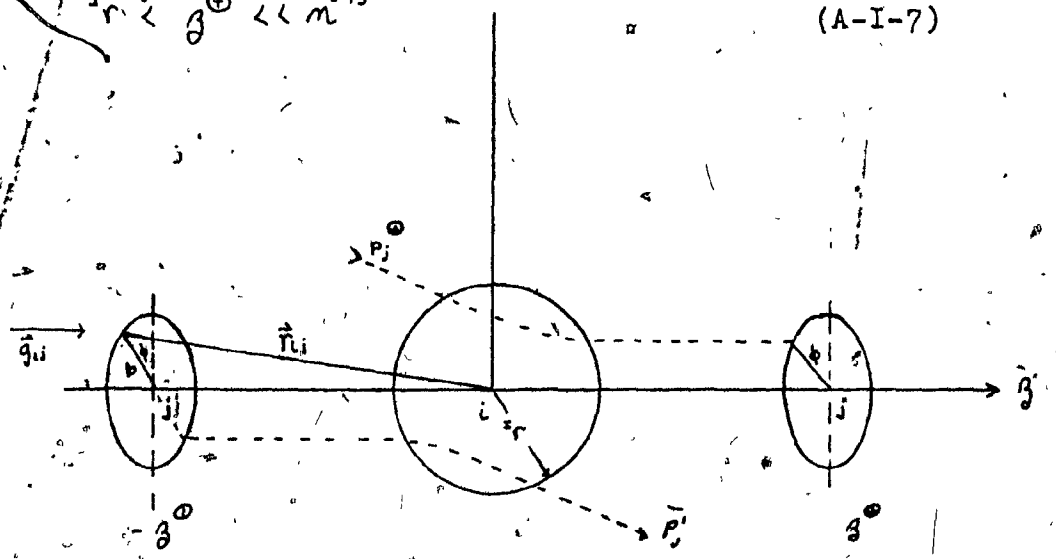

Figure A-I-1

Since, in the limit $\beta \to -\beta^{\oplus}$, we observe (see fig. A-I-1) that particles i and j approach each other such that they will not interact if streamed back in time by $\ell^{-H(i,j)t}$ we conclude that

$$ \left.\begin{aligned} &\lim_{\beta \to -\beta^{\oplus}} \vec{P}_i(\infty) = \vec{p}_i \\ &\lim_{\beta \to -\beta^{\oplus}} P_j(\infty) = p_j \end{aligned}\right\} \qquad \text{(A-I-8)} $$

On the otherhand, since in the limit $\beta \to \beta^{\oplus}$, particles i and j move away from each other such that they could interact when streamed back in time we then have

$$\lim_{\beta \to +\beta^{\oplus}} \vec{P}_i(\infty) = \vec{p}_i^{\oplus}$$

$$\lim_{\beta \to +\beta^{\oplus}} \vec{P}_j(\infty) = \vec{p}_j^{\oplus} \qquad \text{(A-I-9)}$$

where $\vec{p}_i^{\oplus}$ and $\vec{p}_j^{\oplus}$ represent the pre-collisional momenta of particles i and j . Hence, we may rewrite equation (I-6) in the following form

$$\frac{\partial F_i^{(1)}}{\partial t} = (N-1)\int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{\infty} \frac{|\vec{p}_j - \vec{p}_i|}{m}\left[F_i^{(0)}(\vec{p}_i^{\oplus},0)F_j^{(0)}(\vec{p}_j^{\oplus},0) - F_i^{(0)}(\vec{p}_i,0)F_j^{(0)}(\vec{p}_j,0)\right] b\,db\,d\phi\,d\vec{p}_j$$

(A-I-10)

Now, $\vec{p}_i^{\oplus}$ and $\vec{p}_j^{\oplus}$ also represent the post-collision momenta $\vec{p}_i'$, $\vec{p}_j'$ of two particles i and j with momenta $\vec{p}_i$ and $\vec{p}_j$ respectively in a relative configuration $\{b, \phi+\pi, -\beta^{\oplus}\}$. Consequently, since the integration in (A-I-10) is performed over the full range $0 \le \theta \le 2\pi$ of the period of the integrand, one may transform (A-I-10) into

$$\frac{\partial F_i^{(1)}}{\partial t} = (N-1)\int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{\infty} \frac{|\vec{p}_j - \vec{p}_i|}{m}\left[F_i^{(0)}(\vec{p}_i',0)F_j^{(0)}(\vec{p}_j',0) - F_i^{(0)}(\vec{p}_i,0)F_j^{(0)}(\vec{p}_j,0)\right] b\,db\,d\phi\,d\vec{p}_j$$

(A-I-11)

Finally defining $f_i(\vec{p}_i,t) = N F_i(\vec{p}_i,t)$ the above equation may be

rewritten into

$$\frac{\partial f_1}{\partial t} = J_B\left(f_1^{(0)}\right) \qquad \text{(IV-B-18)}$$

where for N large:

$$J_B\left(f_1^{(0)}\right) = \int_{-\infty}^{\infty}\int_{0}^{2\pi}\int_{0}^{\infty} \frac{|\vec{P}_j - \vec{P}_i|}{m}\left[f_1^{(0)}(\vec{P}_i',0) f_1^{(0)}(\vec{P}_j',0) - f_1^{(0)}(\vec{P}_i,0) f_1^{(0)}(\vec{P}_j,0)\right] b\,db\,d\phi\,d\vec{P}_j \qquad \text{(IV-B-19)}$$

APPENDIX II

THE INVALIDITY OF BOGOLIUBOV'S FUNCTIONAL EXPANSION FOR SIMPLE UNIFORM NON-DENSE SYSTEMS OVER LARGE PHYSICAL VOLUMES

In this appendix we shall consider the result of performing Bogoliubov's functional expansion of simple uniform non-dense system when only the original boundary conditions (II-C-4) and (II-C-6) used to derive the B.B.G.K.Y. hierarchy are applied. Let us first recall the perturbed equations (V-A-7)

$$\mathcal{H}_s F_s^{(0)}(\vec{X}_s|F_1) = 0 \qquad \text{(V-A-7-0)}$$

$$\mathcal{H}_s F_s^{(1)}(\vec{X}_s|F_1) = \mathcal{L}_s F_{s+1}^{(0)} - D^{(1)} F_s^{(0)} \qquad \text{(V-A-7-1)}$$

$$\mathcal{H}_s F_s^{(k)}(\vec{X}_s|F_1) = \mathcal{L}_s F_{s+1}^{(k-1)} - \sum_{l=1}^{k} D^{(l)} F_s^{(k-l)} \qquad \text{(V-A-7-k)}$$

where:
$$\left.\begin{aligned} D^{(k)} &= \left\{ \frac{\delta}{\delta F_1}\,,\ \mathcal{L}_{1(1)} F_2^{(k-1)}(\vec{X}_2|F_1) \right\} \\ \mathcal{H}_s &= \sum_{i=1}^{s}\left(\frac{\vec{p}_i}{m}\cdot\frac{\partial}{\partial \vec{q}_i} - \sum_{j=1}^{s} \frac{\partial \phi_{ij}}{\partial \vec{q}_i}\cdot\frac{\partial}{\partial \vec{p}_i} \right) \\ \mathcal{L}_s &= (N-s)\sum_{i=1}^{s} \iint \frac{\partial \phi_{ij}}{\partial \vec{q}_i}\cdot\frac{\partial}{\partial \vec{p}_i}\, d\vec{q}_j\, d\vec{p}_j \end{aligned}\right\} \qquad \text{(V-A-6)}$$

Now, for $s=2$, equation (V-A-2-0) may be written as

$$\frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial F_2^{(0)}}{\partial \vec{p}_i} = \left[\frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} + \frac{\vec{p}_j}{m} \cdot \frac{\partial}{\partial \vec{q}_j} - \frac{\partial \phi_{ij}}{\partial \vec{q}_j} \cdot \frac{\partial}{\partial \vec{p}_j} \right] F_2^{(0)}$$

(A-II-1)

Consequently since

$$\frac{\partial F_1}{\partial t} = \sum_k \varepsilon^k \mathcal{L}_{1(i)} F_2^{(k-1)} \qquad \text{(V-A-4)}$$

the first order equation for F_1 may be written as

$$\frac{\partial F_1}{\partial t} = \varepsilon \mathcal{L}_{1(i)} F_2^{(0)}(\vec{q}_i, \vec{p}_i, \vec{q}_j, \vec{p}_j | F_1)$$

$$= (N-1)\varepsilon \iint \left[\frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} + \frac{\vec{p}_j}{m} \cdot \frac{\partial}{\partial q_j} - \frac{\partial \phi_{ij}}{\partial q_j} \cdot \frac{\partial}{\partial p_j} \right] F_2^{(0)} d\vec{q}_j \, d\vec{p}_j$$

$$= (N-1)\varepsilon \left[\frac{\vec{p}_i}{m} \frac{\partial}{\partial \vec{q}_i} \iint F_2^{(1)} d\vec{q}_j \, d\vec{p}_j \right.$$

$$\left. + \int \frac{\vec{p}_j}{m} \Big|_{\vec{q}_j \to -\infty}^{\vec{q}_j \to \infty} F_2^{(0)} d\vec{p}_j - \int \frac{\partial \phi_{ij}}{\partial q_j} \Big|_{\vec{p}_j \to -\infty}^{\vec{p}_j \to \infty} F_2^{(0)} dq_j \right]$$

(A-II-2)

Recalling the boundary conditions (II-C-4) and (II-C-6)

$$\lim_{|\vec{q}_i| \to \infty} F_N(\vec{x}_N, t) = 0 \qquad \text{(II-C-4)}$$

and

$$\lim_{|\vec{p}_j| \to \infty} F_N(\vec{x}_N, t) = 0 \qquad \text{(II-C-6)}$$

we then conclude that

$$\lim_{|\vec{q}_i|\to\infty} F_s^{(k)}(\vec{X}_s|F_1) = 0 \qquad \text{(A-II-3)}$$

$$\lim_{|\vec{p}_i|\to\infty} F_s^{(k)}(X_s|F_1) = 0 \qquad \text{(A-II-4)}$$

such that the last two terms in (A-III-2) vanish. Furthermore, since the system has been assumed uniform, the remaining term on the right hand side of this equation must also vanish. Consequently one has at the first order of ε, the trivial kinetic equation

$$\frac{\partial F_1}{\partial t} = \varepsilon\, \mathcal{L}_{(i)}\, F_2^{(0)}(\vec{q}_i, \vec{p}_i, \vec{q}_j, \vec{p}_j|F_1) = 0 \qquad \text{(A-II-4)}$$

we also note from (V-A-6) and (A-II-5) that

$$\mathcal{D}^{(1)} = 0 \qquad \text{(A-II-6)}$$

such that the first order equation for F_2 may be written as

$$\mathcal{H}_{2(i,j)}\, F_2^{(1)}(\vec{X}_i \vec{X}_j|F_1) = \mathcal{L}_{2(i,j)}\, F_3^{(0)}(\vec{X}_i \vec{X}_j \vec{X}_k|F_1) \qquad \text{(A-II-7)}$$

where, $\mathcal{L}_{2(i,j)}\, F_3^{(0)} = (N-2)\int\int \left[\frac{\partial \Phi_{i,k}}{\partial \vec{q}_i}\cdot\frac{\partial}{\partial \vec{p}_i} + \frac{\partial \Phi_{j,k}}{\partial \vec{q}_j}\cdot\frac{\partial}{\partial \vec{p}_j}\right] F_3^{(0)}\, d\vec{q}_k\, d\vec{p}_k$

now since

$$\mathcal{H}_{3(i,j,k)}\, F_3(\vec{X}_i \vec{X}_j \vec{X}_k|F_1) = 0$$

we have

$$\left[\frac{\partial \phi_{i,k}}{\partial \vec{q}_i} + \frac{\partial \phi_{j,k}}{\partial \vec{q}_j} \right] F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k | F_1) =$$

$$\left[\mathcal{H}_2(ij) + \frac{\vec{p}_k}{m} \cdot \frac{\partial}{\partial \vec{q}_k} - \frac{\partial \phi_{ki}}{\partial \vec{q}_k} \cdot \frac{\partial}{\partial \vec{p}_k} - \frac{\partial \phi_{kj}}{\partial \vec{q}_k} \cdot \frac{\partial}{\partial \vec{p}_k} \right] F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k | F_1)$$

(A-II-8)

Consequently,

$$\mathcal{L}_2(ij) F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k | F_1) = (N-2) \left\{ \mathcal{H}_2(ij) \iint F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k | F_1) d\vec{q}_k d\vec{p}_k + \right.$$

$$\left. + \iint \left[\frac{\vec{p}_k}{m} \cdot \frac{\partial}{\partial \vec{q}_k} - \frac{\partial \phi_{ki}}{\partial \vec{q}_k} \cdot \frac{\partial}{\partial \vec{p}_k} - \frac{\partial \phi_{kj}}{\partial \vec{q}_k} \cdot \frac{\partial}{\partial \vec{p}_k} \right] F_3^{(0)}(\vec{x}_i, \vec{x}_j, x_k | F_1) d\vec{q}_k d\vec{p}_k \right.$$

(A-II-9)

The last integral of the above expression vanishes as a consequence of boundary conditions (II-C-4) and (II-C-6). Furthermore since

$$\iint F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k | F_1) d\vec{q}_k d\vec{p}_k = F_2^{(0)}(\vec{x}_i, x_j | F_1)$$

and

$$\mathcal{H}_2(ij) F_2^{(0)}(\vec{x}_i, \vec{x}_j | F_1) = 0$$

we conclude that

$$\mathcal{L}_2(ij) F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k, t) = 0$$

(A-II-10)

and $$\mathcal{H}_2(ij) F_2^{(0)}(\vec{x}_i, \vec{x}_j | F_1) = 0$$

(A-II-11)

Since $F_2^{(1)}$ obeys the same equation as $F_2^{(0)}$ we thus deduce that

$$\mathcal{L}_{1(1)} F_2^{(1)}(\vec{x}, \vec{x}; |F_1) = 0 \qquad \text{(A-II-12)}$$

and hence, to the second order of ε , F_1 , obeys the trivial kinetic equation

$$\frac{\partial F_1}{\partial t} = 0 \qquad \text{(A-II-13)}$$

Similarily one can easily see that such trivial kinetic equations should emerge at all orders of ε .

APPENDIX III

DERIVATION OF UHLENBECK-CHOH EQUATION

The density expansion performed in chapter V may be pursued to a higher order by following the outline illustrated in fig. V-5. As a first step let us integrate (V-B-13) over a time interval $[\, t-\Delta t\,,\, t\,]$ where once again $\Delta t \ll \tau_1$ so as to obtain [1]

$$\tilde{F}_1^{(1)}(\vec{p}_1,t) = \tilde{F}_1^{(1)}(\vec{p}_1,t-\Delta t) + \int_0^{\Delta t} \tilde{\mathcal{L}}_{1(1)}\, \tilde{F}_1^{(0)}(\vec{p}_1(\infty),t-t')\, \tilde{F}_1^{(0)}(\vec{p}_2(\infty),t-t')\, dt' \qquad \Delta t \ll \tau_1 \qquad \text{(A-III-1)}$$

which, using the zeroth order solution (V-B-10) for $F_1^{(0)}$ may also be written as:

$$\tilde{F}_1^{(1)}(\vec{p}_1,t) = \tilde{F}_1^{(1)}(\vec{p}_1,t-\Delta t) + \int_0^{\Delta t} \tilde{\mathcal{L}}_{1(1)}\, \tilde{F}_1^{(0)}(\vec{p}_1(\infty),t)\, \tilde{F}_1^{(0)}(\vec{p}_2(\infty),t)\, dt' \qquad \Delta t \ll \tau_1 \qquad \text{(A-III-2a)}$$

or simply as:

$$\tilde{F}_1^{(1)}(\vec{p}_1,t) = \tilde{F}_1^{(1)}(\vec{p}_1,t-\Delta t) + \tilde{\mathcal{L}}_{1(1)}\, F_1^{(0)}(\vec{p}_1(\infty),t)\, F_1^{(0)}(\vec{p}_2(\infty),t)\, \Delta t \qquad \text{(A-III-2b)}$$

Let us now return to equation (IV-B-7-0) and rewrite the equation for $F_2^{(1)}$ in the following form:

[1] In this appendix we shall use $\tilde{F}_s = V_s F_s$ and $\tilde{\mathcal{L}}_s = n \sum_{i=1}^{s} \int\int \frac{\partial \phi_{i,s+1}}{\partial \vec{q}_i} \cdot \frac{\partial \tilde{F}_{s+1}}{\partial \vec{p}_i}\, d\vec{q}_{s+1}\, d\vec{p}_{s+1}$ with $n = \lim_{\substack{N\to\infty \\ V\to\infty}} \frac{N}{V}$.

$$\frac{\partial \tilde{F}_2^{(1)}}{\partial t} + \mathcal{H}_2(i,j)\, \tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t)$$

$$= [\tilde{\mathcal{L}}_{1(i)} + \tilde{\mathcal{L}}_{1(j)}]\, F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k, t)$$

(A-III-3)

Operating both sides of this equation by the forward streaming operator $e^{\mathcal{H}_2(i,j)t}$ and integrating over the interval $[t-\Delta t, t]$ one then obtains

$$\tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t) = e^{-\mathcal{H}_2(i,j)\Delta t}\, \tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t-\Delta t)$$

$$+ \int_0^{\Delta t} e^{-\mathcal{H}_2(i,j)t'} [\tilde{\mathcal{L}}_{1(i)} + \tilde{\mathcal{L}}_{1(j)}]\, \tilde{F}_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k, t-t')\, dt'$$

$$\Delta t \ll \tau_1$$

(A-III-4)

We recall that, in order to derive a second order kinetic equation for $F_1^{(2)}$ we only require a solution for $\tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t)$ when $|\vec{q}_i - \vec{q}_j| < r$. Further, due to the definition of $\mathcal{L}_{1(i)}$ and $\mathcal{L}_{1(j)}$, the only contribution to second term on the right hand side of (A-IV-3) lies in the region where either

$$e^{-\mathcal{H}_2(i,j)t'} |\vec{q}_i - \vec{q}_k| < r \quad \text{or} \quad e^{-\mathcal{H}_2(i,j)t'} |\vec{q}_j - \vec{q}_k| < r$$

Finally, since t' is limited to a value much shorter than the mean time between collision, it thus follows that all contributions to the integrals in $\tilde{\mathcal{L}}_{1(i)}$ and $\tilde{\mathcal{L}}_{1(j)}$ are on the whole restricted to a physical volume $V_k \ll \lambda^3$.

We also recall, however, that the zeroth order solution for $F_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k, t)$ as given by (V-B-12)

$$\tilde{F}_3^{(0)}(\vec{x}_i, \vec{x}_j, \vec{x}_k, t) = \lim_{\tau \to \infty} e^{-\mathcal{H}_3(i,j,k)\tau} \tilde{F}_1^{(A)}(\vec{p}_i, t)\, \tilde{F}_1^{(A)}(\vec{p}_j, t)\, \tilde{F}_1^{(A)}(\vec{p}_k, t)$$

(V-B-12)

is restricted to the phase volume V_{ij}^{+} in which the three particles may be streamed backwards in time by the operator $e^{-\mathcal{H}_3(i,j,k)\,\Delta t}$ outside their mutual range of correlation for $\Delta t \ll \tau_1$. Clearly, even within the small physical volume $V_R \ll \lambda^3$ there exists cases as noted by Cohen[21] and illustrated in figure (A-IV-1) where the complete reverse collision process would take a much larger time than τ_1 to be completed.

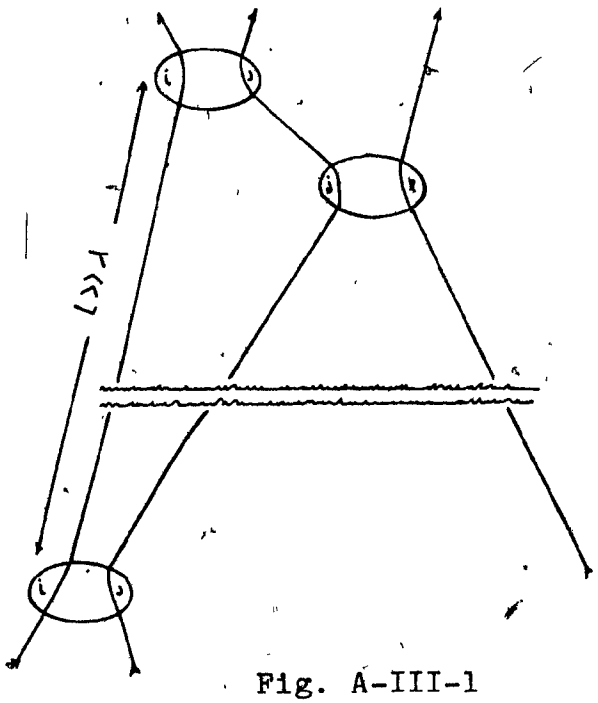

Fig. A-III-1

Hence we seem to possess a solution for $\tilde{F}_3^{(0)}$ with insufficient range of validity to offer a complete solution for $\tilde{F}_2^{(1)}$ when

$|\vec{q}_i - \vec{q}_j| < r$. Faced with this problem, let us then adopt the utilitarian approach of restricting the domain of integration of $\tilde{\mathcal{L}}_{1(i)}$ and $\tilde{\mathcal{L}}_{1(j)}$ over the domain V_{ij}^{+} where the solution (V-B-11) is valid and hope that the region ignored will not represent a significant error. Doing so, one then obtains the solution:

$$\tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t) = e^{-\mathcal{H}_2(ij)\Delta t} \tilde{F}_2^{(1)}(\vec{x}_i \vec{x}_j, t-\Delta t)$$

$$+ \int_0^{\Delta t} e^{-\mathcal{H}_2(ij)t'} \left[\tilde{\mathcal{L}}_{1(i)} + \tilde{\mathcal{L}}_{1(j)}\right] \lim_{\tau\to\infty} e^{-\mathcal{H}_3(ijk)\tau}$$

$$\tilde{F}_1^{(0)}(\vec{p}_i, t)\, \tilde{F}_1^{(0)}(\vec{p}_j, t)\, \tilde{F}_1^{(0)}(\vec{p}_k, t)\, dt'$$

$$\Delta t \ll \tau_1$$

(A-III-5)

where the zeroth order solution for $\tilde{F}_1^{(0)}(\vec{p}_i, t)$ has once again been used. Now choosing $\Delta t \gg [\tau_0 \cdot r/v_0]$, we may then, for $|\vec{q}_i - \vec{q}_j| < r$ impose the boundary condition (V-B-9) and conclude that:

$$\tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t) =$$

$$\lim_{\tau\to\infty} \left\{ e^{-\mathcal{H}_2(ij)\tau} \left[\tilde{F}_1^{(0)}(\vec{p}_i(t)\, \tilde{F}_1^{(1)}(\vec{p}_j, t) + \tilde{F}_1^{(1)}(\vec{p}_j, t)\, \tilde{F}_1^{(1)}(\vec{p}_i, t)\right.\right.$$

$$- \int_0^{\Delta t} \left(\tilde{\mathcal{L}}_1(i)\, e^{-\mathcal{H}_2(i,k)\tau} + \tilde{\mathcal{L}}_1(j)\, e^{-\mathcal{H}_2(j,k)\tau} \right) \tilde{F}_1^{(0)}(\vec{p}_i,t)\, \tilde{F}_1^{(0)}(\vec{p}_j,t)\, \tilde{F}_1^{(0)}(\vec{p}_k,t)\, dt' \Bigg]$$

$$+ \int_0^{\Delta t} e^{-\mathcal{H}_2(i,j)t'} \left(\tilde{\mathcal{L}}_1(i) + \tilde{\mathcal{L}}_1(j) \right) e^{-\mathcal{H}_3(i,j,k)\tau}\, \tilde{F}_1^{(0)}(\vec{p}_i,t)\, \tilde{F}_1^{(0)}(\vec{p}_j,t)\, \tilde{F}_1^{(0)}(\vec{p}_k,t)\, dt' \Bigg\}$$

(A-III-6)

Following Choh [16] we shall now define

$$\theta_{i,j} \equiv \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} + \frac{\partial \phi_{ij}}{\partial \vec{q}_j} \cdot \frac{\partial}{\partial \vec{p}_j} \qquad \text{(A-III-7)}$$

such that, after some manipulation we have

$$\tilde{F}_2^{(1)}(\vec{x}_i, \vec{x}_j, t) =$$

$$\lim_{\tau \to \infty} \Bigg\{ e^{-\mathcal{H}_2(i,j)\tau} \left[\tilde{F}_1^{(0)}(\vec{p}_i,t)\, \tilde{F}_1^{(1)}(\vec{p}_j,t) + \tilde{F}_1^{(0)}(\vec{p}_j,t)\, \tilde{F}_1^{(1)}(\vec{p}_i,t) \right]$$

$$+ \int_0^{\Delta t} n \iint \Big[e^{-\mathcal{H}_2(i,j)t'} \left(\theta_{i,k} + \theta_{j,k} \right) e^{-\mathcal{H}_3(i,j,k)\tau}$$

$$- e^{-\mathcal{H}_2(i,j)\tau} e^{-\mathcal{H}_2(i,k)\tau} \theta_{i,k}\, e^{-\mathcal{H}_2(i,k)\tau} e^{-\mathcal{H}_2(j,k)\tau} \Big] \theta_{j,k}\, e^{-\mathcal{H}_2(j,k)\tau} \Big]$$

$$\tilde{F}_1^{(0)}(\vec{p}_i,t)\, \tilde{F}_1^{(0)}(\vec{p}_j,t)\, \tilde{F}_1^{(0)}(\vec{p}_k,t)\, d\vec{q}_k\, d\vec{p}_k\, dt' \Bigg\}, \qquad \text{(A-III-8)}$$

$$\tau_0 \ll \Delta t \ll \tau_1$$

Finally, if we now assume that the previous restrictions on the range of integration $\iint d\vec{q}_k d\vec{p}_k$ are sufficient for the above time integral to converge within the specified limits on Δt we may then, without any error, replace Δt by the limit $\Delta t \to \infty$. Furthermore, since we may replace $\lim_{\tau\to\infty} e^{-\mathcal{H}_2(ij)\tau}$ by $\lim_{\tau\to\infty} e^{-\mathcal{H}_2(ij)(\tau+t')}$, equation (A-III-8) may also be written as:

$$
\begin{aligned}
F_2^{(1)}(\vec{x}_i, \vec{x}_j, t) = \\
\lim_{\tau\to\infty} \Bigg\{ & e^{-\mathcal{H}_2(ij)\tau} \left[\tilde{F}_1^{(0)}(\vec{p}_i, t)\, \tilde{F}_1^{(1)}(\vec{p}_j, t) + \tilde{F}_1^{(0)}(\vec{p}_j, t)\, \tilde{F}_1^{(1)}(\vec{p}_i, t) \right] \\
& + \int_0^\infty n \Bigg\{ \int_\tau e^{-\mathcal{H}_2(ij)t'} \Big[\left(\theta_{i,k} + \theta_{j,k} \right) e^{-\mathcal{H}_3(ijk)\tau} \\
& - e^{-\mathcal{H}_2(ij)\tau} \theta_{i,k}\, e^{-\mathcal{H}_3(ik)\tau} - e^{-\mathcal{H}_3(ij)\tau} \theta_{j,k}\, e^{-\mathcal{H}_2(jk)\tau} \Big] \\
& \tilde{F}_1^{(0)}(\vec{p}_i, t)\, \tilde{F}_1^{(0)}(\vec{p}_j, t)\, \tilde{F}_1^{(0)}(\vec{p}_k, t)\, d\vec{q}_k\, d\vec{p}_k\, dt'
\end{aligned}
$$

(A-III-9)

This result is very similar to that obtained by Choh[16] using the Bogoliubov scheme. Indeed, from the definition of θ_{ij}, $\mathcal{H}_2(ij)$ and $\mathcal{H}_3(ijk)$ and the identity $e^{-\mathcal{H}_2(ij)t}\, \mathcal{H}_2(ij) = -\frac{\partial}{\partial t} e^{-\mathcal{H}_2(ij)t}$, one may show after some manipulation that (A-IV-8) reduced to the simple form

$$F_2^{(1)}(\vec{x}_i, \vec{x}_j, t) =$$

$$\lim_{\tau \to \infty} \Big\{ e^{-\mathcal{H}_2(ij)\tau} \left[\tilde{F}_1^{(0)}(\vec{p}_i, t) \tilde{F}_1^{(1)}(\vec{p}_j, t) + \tilde{F}_1^{(0)}(\vec{p}_j, t) \tilde{F}_1^{(1)}(\vec{p}_i, t) \right]$$

$$+ n \int\int \Big[e^{-\mathcal{H}_3(ijk)\tau} + \mathcal{H}_2(ij)\tau - \mathcal{H}_2(ik)\tau - \mathcal{H}_2(ij)\tau$$

$$- e^{-\mathcal{H}_2(ij)\tau} - \mathcal{H}_2(jk)\tau + e^{-\mathcal{H}_2(ij)\tau} \Big]$$

$$\tilde{F}_1^{(0)}(\vec{p}_i, t) \tilde{F}_1^{(0)}(\vec{p}_j, t) \tilde{F}_1^{(0)}(\vec{p}_k, t) \, d\vec{q}_k \, d\vec{p}_k \,. \qquad \text{(A-III-10)}$$

Substituting this solution into the second order equation,

$$\frac{\partial \tilde{F}_1^{(2)}}{\partial t} = \tilde{\mathcal{L}}_{1(i)} F_2^{(1)}(\vec{x}_i, \vec{x}_j; t) \qquad \text{(A-III-11)}$$

and combining the latter with the first order and zeroth order equations one then obtains in terms of $\tilde{F}_1(\vec{p}_i, t)$ the following kinetic equation

$$\frac{\partial \tilde{F}_1}{\partial t} = n J_3(\tilde{F}_1(\vec{p}_i, t)) + n^2 J_{2c}(\tilde{F}_1(\vec{p}_i, t)) + O[\xi^3]$$

where

$\Rightarrow$

$$J_{uc} = \lim_{\tau \to \infty} \iiint \frac{\partial \phi_{ij}}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i}$$

$$\left\{ e^{-\mathcal{H}_3(ijk)\tau} - e^{-\mathcal{H}_2(ij)\tau} e^{-\mathcal{H}_2(ik)\tau} - e^{-\mathcal{H}_2(ij)\tau} e^{-\mathcal{H}_2(jk)\tau} + e^{-\mathcal{H}_2(ik)\tau} \right\}$$

$$\tilde{F}_1(\vec{p}_i, t)\ \tilde{F}_1(\vec{p}_j, t)\ \tilde{F}_1(\vec{p}_k, t)\ d\vec{q}_k\, d\vec{p}_k\, d\vec{q}_j\, d\vec{p}_j \qquad \text{(A-III-12)}$$

represents the triple collision term first derived by Choh using a Bogoliubov expansion approach.

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