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Molecular Dynamics Characterization of Temperature and Pressure Effects on the Water-Methane Interface

Abstract

The water-methane interface plays an important role in mass transfer between the phases. In this work, we employ molecular dynamics to investigate and characterize the mechanics, thermodynamics, and composition of water-methane interfaces applying a unique methodology known as the NP_NAT ensemble. We systematically increase the pressure (1-50 MPa) and temperature (25-105°C) to calculate the interfacial tension from its mechanical definition. We predict the surface tension via pressure and temperature relations in agreement with the classical scaling laws such as the Eötvös rule. It is found that the surface adsorbs methane molecules as per high interfacial excess and local density of methane. The methane practically remains insoluble in water due to favorable interactions with a dense hydrogen bonded region near the surface. The obtained macroscopic interfacial tension properties and sensitivity to pressure and temperature and the corresponding molecular mechanisms contribute to the evolving understanding and practical applications of this important interface.

Keywords: water-methane mixture; surface tension; molecular dynamics simulation; NP_NAT ensemble

Introduction

Interfacial thermodynamics and transport phenomena are central to many engineering and chemical processes. In particular, the interfacial tension drives the mass transport across the interface and significantly influences the capillary pressure governing the fluid transport in petroleum reservoirs, which is considered vital for the exploration, production, and high pressure processes [1, 2]. The interfacial tension mainly depends on structural and thermodynamic properties such as pressure, temperature, and chemical compositions, which are currently poorly

understood but cannot be ignored in the study of aqueous mixtures which contains water and gaseous alkanes [3]. As fossil energy resources are diminishing, we need to optimize extraction and use processes based on molecular-level understanding of the physical properties of hydrocarbon-water systems.

Water-methane interfaces are ubiquitous as the latter is the most common and lightest component of the natural gas. The interaction of co-exiting methane and water bulk phases in natural and industrial environments might cause the formation of clathrate hydrates promoting the motives of our work [4]. Clathrate hydrates, gas hydrates, or simply hydrates are ice-like crystalline solids that consist of water molecules stable cages (cavities), called hosts. The gas molecule, which is effectively compressed inside of the water cage is the guest or hydrate former. Gas hydrates have a wide range of applications in different industries including: flow assurance, transportation, new energy resources, gas storage, environmental crisis like global warming arisen by release of methane gas [4-6]. Hydrate formation process typically initiates at the surface, whose materials physics are not well understood [7]. Classical nucleation theory postulates the formation of a new cluster phase consisting of n crystal unit cells which needs work to compensate for the energy consumed for a combination of interfacial energy and the creation of a new phase that occupies space. The formation work is given by [7]:

$$W(J) = -n\Delta\mu + c(n\nu_h)^{\frac{2}{3}}\sigma, \qquad (1)$$

where $\Delta \mu(J)$, c, v_h , and $\sigma_{ef}(J/m^2)$ are supersaturation, shape factor, hydrate volume, and surface energy, respectively. For an anisotropic system, the surface energy is clearly not a scalar quantity. To obtain the interfacial energy between different phases, most significantly liquid-gas, we need a clear knowledge of the pressure tensor governing the surfaces. This knowledge is required to explain phase transitions, thermodynamic stability, morphology, nucleation, and the growth rate of gas hydrates. This is imperative in order to understand the basic theory of hydrate formation and find ways of inhibiting or promoting their formation, depending on the application. Furthermore, water-methane studies give better insight into water-heavier alkanes mixtures due to the similar nature of interfacial interactions such as surface tension which is predominantly influenced by molecular structure than weight.

In distinction to the bulk region, interfacial atoms and molecules are not strongly bound, allowing for molecular re-organizations at the interface [3] demanding new experimental, computational, and theoretical characterization techniques. Experimentally, it is difficult to

measure surface tension in perfect samples with controlled purity. Moreover, experiments typically require high pressure for hydrate formation, which are extremely difficult and involve expensive instrumentation. Generally, surface energy cannot be precisely obtained from only experiments [8, 9]. In addition, we need microscopic understanding of the system, which experimental work lacks, leaving molecular simulations as a very effective option to provide all the necessary information concerning the interfacial regions. Likewise, computer simulations encounter their own challenges when the system contains liquid-gas interfaces. First, the interface separating liquid and gas phases is extremely thin leading to essential discontinuities in macroscopic fields. Second, local densities largely change across the interface. Liquids have high density with constant volume in addition to spontaneous interfacial contraction, while gases develop an apparent elastic skin with large molecular mobility in much lower density regimes. Third, the interface imposes a localized surface tension force on the liquid phase. Fourth, we experience a phase transition and topology changes at the interface, which import disturbance and poor statistics into the system properties relative to the number of molecules. Lastly, time and length scales should be sufficiently long to tailor realistic models. The most important challenge is to narrow the gap between experiments, theory and simulation predictions on interfacial tension and its dependence on temperature and pressure.

This challenge is even more highlighted for the water-methane systems. Even in the most stable conditions, the water-hydrophobic gas surface is not flat showing nanoscopic waves scattering light with low intensity. The ionization properties, dipole moment, and dielectric permittivity of water phase vary from its bulk to surface over infinitesimal distances. The organization of water molecules at the surface simply adapts with thermodynamic parameters and ions binding. Furthermore, robust hydrogen bonding and charges holding between molecules complicate water mixtures. In general, liquid water in contact with gas or solid phase exhibits two distinct thermodynamic behaviors at the interface and bulk [10, 11].

In recent years, with the use of very powerful computing resources and improved computational models, molecular simulation techniques can leverage theoretical tools combined with statistical mechanics to accurately capture the dynamics of interfacial systems at length and time scales difficult to access experimentally. In this paper, we use molecular dynamic (MD) techniques in conjunction with interfacial thermodynamics of gas-liquid interfaces and surface physics to provide an accurate characterization of the complex water-methane-interface as a function of temperature and applied pressure. In particular, classical scaling laws of utility to applications are derived and the molecular underpinnings are revealed.

Use of powerful computing resources allows utilization of sufficiently long time and length scales to mimic realistic models. The key aspect of the MD approach is to completely control a pure water-methane mixture with no external disturbances, as opposed to experiments, to investigate the thermodynamics and mechanics of the system. We can observe macromolecular structures to better understand the physics and theory behind the phase transitions from microscopic to macroscopic level. With molecular dynamics, we can also readily obtain the crucial interfacial tension parameters from stress tensor analysis and characterize the temperature and pressure effects.

In an aniso-diametric system, the physical and thermodynamic parameters such as the local density are not uniform along the normal direction to the planar surface. One of the challenges in the calculation of the interfacial tension is to address an appropriate statistical ensemble as we intend to predict sensible values. In the NVT ensemble the system volume should be adjusted manually, consequently, great knowledge over the system volume at equilibrium is always required. On the other hand, the standard NPT ensemble cannot properly predict the interfacial tension as the tangential pressure is negative and not constant along the interface. The pressure cannot be chosen to be isotropic for systems with multiple phases, whose interfaces have thermodynamic differences between the lateral and normal directions. Therefore, conventional NVT and NPT ensembles are not precise enough for interfacial tension calculations. We need specific ensembles that controls the pressure across the system to avoid the disturbances in the interfacial area. To obtain sensible values, we use the NP_NAT ensemble, since we cope with a constant normal pressure P_N imposed to the planar surface with a specific cross sectional area (A). This novel ensemble provides the most reliable predictions of liquid-gas systems [12, 13] and lipid membranes in cell biology [14]. In recent computational studies, the thermodynamic definition is used to calculate the surface tension of mixtures [15, 16]. According to this definition, the interfacial tension is the derivative of the free energy with respect to the interfacial area. This method effectively estimates more global than local properties [17], even though we intend to study the system from both perspectives. Besides, the NP_NAT ensemble holds the interfacial area static throughout the simulations. Hence, the thermodynamic definition is unable to predict the interfacial tension. Herein, we use the local components of the stress tensor to follow the Kirkwood

and Buff method for calculating the interfacial tension (γ_{KB}) from the mechanical definition at the water-methane interface [18].

The organization of this paper is as follows. In the next section, we describe the model and briefly state the computational MD simulations details. In addition, we elaborate on the novel approach for interfacial tension calculation. In the results section, we discuss the pressure and temperature effects on the interfacial density, tension, thickness, and molecular composition. Lastly, the main conclusions and their significance are presented.

Model and Simulation Methods

In this work, we use molecular dynamics simulations to study the classical thermodynamic behavior of the water-methane mixture at various pressures and temperatures. To calculate the interfacial tension, we follow the common computational method that confines the liquid water phase between two methane gas phases [18, 19]. We model the simulation box with an initial size of 36×36×120 Å in three dimensions. Knowledge of the initial value for the box length in the z direction (L_z) is not required as L_z can freely fluctuate, adjusting the system volume to reach the prescribed bulk density for each phase. Fixing box lengths in the x and y dimensions with independent dilation or contraction in only the z dimension provides a constant cross section (i.e., $A = L_x L_y$), essential for the NP_NAT ensemble [20]. To reach the desired target pressure, the system volume, and consequently, the coexisting densities of the components should be able to change towards equilibration. Periodic boundary conditions are applied throughout. We randomly place 3710 water molecules in a slab in the middle of the simulation box and surround this slab with 200 methane molecules on both sides. Fig. 1 shows a snapshot of a typical initial configuration of the system. To model the force field for water and methane molecules, we use the transferable intermolecular potential with the four points (TIP4P) model [21] and united atom optimized potentials for liquid simulations (OPLS-UA) model [22], within the LAMMPS simulation package [23]. We use the Lennard-Jones (LJ) potential with Lorentz-Berthelot mixing rules to represent the intermolecular interactions:

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$
(2)

In the Lorentz-Berthelot approach, an arithmetic mixing rule calculates the essential LJ parameters for the unlike particles, as given below:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}},\tag{3}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2},\tag{4}$$

where ε , σ , and r are the depth of the potential well, the finite distance with zero potential, and the distance between the particles, respectively.

We apply the particle-particle particle-mesh (PPPM) technique introduced by Hockney and Eastwood [24, 25] with an accuracy of 10⁻⁵ for the errors in force calculations to obtain the Coulombic electrostatic interactions. The cut-off distance for LJ and short range electrostatic interactions are 12Å and partial electron charges, the distance and the angles between atoms or charge sites, and LJ potential parameters used for the simulation can be found in Table 1 [21, 22]. Furthermore, we use the Shake algorithm to apply an additional constraining force to the specified bonds and angles associated with the water molecules. This force guarantees the OH bond length and the HOH angle remain constant throughout the simulations.

	Mass(g/mol)	$\sigma(\text{\AA})$	ε(Kcal/mol)	charge(e)
0	15.9994	3.16435	0.16275	-1.0484
Н	1.008	0	0	0.5242
CH ₄	16.0425	3.73	0.29391	0
OH bond length	0.9572			
HOH angle	104.52			
OM distance	0.125			

Table 1. Simulation parameters including: partial electron charges, distance and angles between atoms or charge sites, and Lennard-Johns potential well depth (ε) and finite distance (σ).

We then integrate the non-Hamiltonian equations of motion by using the Verlet algorithm and velocity rescaling for temperature control to sample the particles positions and velocities from the desired ensemble. The pressure and temperature is then regulated and include the inherent fluctuations using Nosé-Hoover thermostat and Parrinello-Rahman barostat, which couple some



Fig. 1 (a) Schematic showing one grey zone containing the water molecules and two white zones containing the methane molecules to form the liquid respectively. gas phases, (b) and Initial configuration of the system. The green, red, and white particles represent the methane molecules, the and the hydrogen oxygen atoms, atoms. respectively. Two brown regions represent the interfaces between the liquid and gas phases.

dynamic variables to the equations of motion. The time step is fixed at 2 fs and all simulations are performed for 4 ns in order to reach equilibrium. This simulation time is set sufficiently long to provide accurate results for the surface tension as opposed to previous MD studies. The damping constant for temperature and pressure regulation is chosen to be 4 ps. We estimate that the system reaches equilibration during the first 3 ns since there is no significant change in the behavior of the thermodynamic and mechanical properties such as temperature and pressure. The correlation factor calculated for the system energy rapidly approaches zero to support the equilibrium state. In the last 1 ns of the simulations, once the equilibration is assured, we begin to collect the simulation outcome for further analysis.

According to the Kirkwood and Buff method, the surface tension for a system with a density gradient in the z direction is obtained from:

$$\gamma_{KB} = \int_{-\infty}^{+\infty} \left(P_N - P_T(z) \right) dz, \tag{5}$$

where P_N and P_T are the normal pressure and tangential pressure, respectively, and the integral is calculated over the interfacial thickness. The values for P_N and P_T can be calculated from the stress tensor [26]:

$$P_N = P_{zz} = P \tag{6}$$

$$P_T = \frac{1}{2} \left(P_{xx} + P_{yy} \right)$$
(7)

Subsequently, the surface tension is given by:

$$\gamma_{KB} = \int_{-\infty}^{+\infty} \left[P_{zz} - \frac{1}{2} \left(P_{xx} + P_{yy} \right) \right] dz$$
(8)

Ignoring the slight computational fluctuations, the normal and tangential pressures are constantly equal to the total pressure along the simulation box, except for the interface. The tangential pressure drastically decreases at the interface resulting in a nonzero positive value for the surface tension. Nevertheless, the surface tension obtained from the mechanical definition (eqn.(8)) underestimates its value owing to truncations in the interatomic interactions, particularly in inhomogeneous systems [27-29]. The cut-off distance in the LJ potential calculations diminishes the value for the surface tension in an analogous manner that attenuates the bulk pressure with a constant density. Therefore, multicomponent systems where all their components are present in all the phases require a long-range or tail correction in the interfacial energy calculation. Chapela et al. [29] introduced a well-known formula, later improved by Blokhuis et al. [28], for the tail correction to compensate for this inaccuracy:

$$\gamma_{tail} = \int_0^1 \int_{r_c}^\infty 12\pi\varepsilon \sigma^6 \left(\rho_l - \rho_g\right)^2 \left(\frac{3s^3 - s}{r^3}\right) \cot\left(\frac{rs}{d}\right) ds dr,\tag{9}$$

where r_c , s, d, and ρ_g and ρ_l are the cut-off distance, position, interfacial thickness, and molecular densities of the gas and liquid phases, respectively. Hence, the interfacial tension (γ) adopted in this work is:

$$\gamma = \gamma_{KB} + \gamma_{tail} \tag{10}$$

Results and Discussion

To calculate the interfacial tension based on the mechanical definition, we need to divide the simulation box into small slabs (i.e., cuboids with equal lengths in x and y dimensions) and subtract the normal and the tangential pressure values obtained from the components of the stress tensor in each slab. As mentioned above, the system stability requires the normal and tangential pressures to remain constant and negative at the interface, respectively, allowing the interfacial tension to achieve a positive value. However, the normal and tangential pressure difference reveals two negative peaks near the water phase, appearing on both interfaces (left and right), which implies

an edge compression regime [30-32]. This compression regime is relatively small compared to the tension regime. Previous researches reported different potential sources triggering the compression: the nature of the interfaces [31, 32], interfacial polarization [33], the choice of the force field with LJ and electrostatic truncation scheme [13, 34], or unphysical values originated from inevitable simulations errors [17, 35]. Nevertheless, the existence of such a compression zone is not yet fully understood and its full resolution and complete understanding is beyond the scope of this work.

The nonuniform behavior in the z dimension, particularly close to the interface, demands an increase in the slab size and average the macroscopic parameters to maintain the system stabilization. As we systematically increase the slab size from 0.1Å to 12Å or the temperature from 25°C to 105°C, the negative peaks associated with the presumed compression regimes weaken. Fig. 2 depicts how the slab size changes the normal and tangential pressure difference leading us to use average stress tensor components for the surface tension calculation as given below. It is noted that we divide the integral (eqn.(5)) by two as two interfaces appear between water and methane molecules along the simulation box:

$$\gamma = \frac{L_Z}{2} \left[\langle P_Z \rangle - \frac{1}{2} \left(\langle P_{xx} \rangle + \langle P_{yy} \rangle \right) \right] + \gamma_{tail}$$
(11)

On the other hand, the presence of two maximum peaks indicates that the system configuration is well defined to include two independent liquid-gas surfaces, while the tonsorial components of the pressure in the bulk phases are not involved in the interfacial energy calculation.



Fig. 2 Choosing different size for the slabs changes the difference of the normal and tangential pressures (reported in units of mN/m^2). This change might even lead to unreliable surface tension values. Blue and black lines represent the simulations with the slab lengths of 0.1Å and 6Å (as example) in the z dimension, respectively. The pressure of the system is 10 MPa and the temperatures are 25°C (a) and 105°C (b). In addition, the blue line in plot (b) clearly shows how increasing temperature damps the two negative edge peaks associated with compression [30,32].

The mass density is now characterized to better understand the temperature and pressure effects on the interfacial molecular-level behavior, noting that an accurate density profile from experiments may not be trivial. We also require the density profile for both water and methane phases to calculate tail corrections. The temperature is then systematically incremented from 25°C to 105°C. In summary, a sudden expansion initially occurs in the z dimension, which causes the local mass density of both components to dramatically decrease at the interface until the system is sufficiently expanded to allow the local densities to fluctuate around an approximate plateau. In contrast with the effect of the temperature, increasing the system pressure compresses both phases leading to larger local densities. This enlarging shift is almost negligible on the water side suggesting pressure independency. The compressive forces predominantly impact the gas components as expected, which implies preferred adsorption of methane molecules on the water phase. Additionally, we fit the density profiles with hyperbolic tangent functions to obtain the surface excess at 25°C from [36]:

$$\Gamma(\mathrm{mol}/m^2) = \frac{1}{A} \int_{-\infty}^{\infty} \{\rho_m(z) - \rho_{m,l} \Theta(-z) - \rho_{m,\nu} \Theta(z)\} dz, \qquad (12)$$

where ρ_m , $\rho_{m,l}$, $\rho_{m,v}$, and $\Theta(z)$ are the methane density profile, bulk density in water and methane phases, and Heaviside step function, respectively. The calculated surface excesses of 2.8×10^{-6} and



Fig. 3 The plots depict the values for the local density (g/cm^3) of the water (a) and the methane (b) molecules at the interface versus the temperature (°C) of the system. The plus sign, circle, star, square, and triangle markers represent the system pressure of 10, 20, 30, 40, and 50 MPa, respectively. When the system is exposed to a temperature upturn, a sudden decrease is observed for the local density of both components, especially in the systems with higher pressure regime (>30 MPa).

 3.5×10^{-6} mol/m² at 10 and 15 MPa, respectively, in combination with increase of methane local density, suggest ideal methane enrichment in the surface. This dense methane film can explain lower interfacial energy by the Gibbs equation compared to the pure water liquid-vapor system. A similar trend can be obtained for the methane density profile in systems in a lower temperature

regime. For instance, the surface excess of methane at 0° C and 10 MPa is 3.9×10^{-6} mol/m², which reveals more noticeable methane adsorption onto the surface. This anomalous adsorption suggests heterogeneous nucleation for methane hydrate, which occurs at the surface.

With robust knowledge of the interfacial density profile, we can now calculate the interfacial tension between the liquid and gas phases from Eqn. 11. Fig. 4 shows that the interfacial tensions of the water-methane mixture from MD simulations are in very good agreement with experiments and previous computational work. The average absolute deviations (AAD) are in a range of 1.38% to 5.59% computed from the given formula:

$$AAD = \frac{1}{N} \sum_{i=1}^{N} |\gamma_i - \langle \gamma_{ref} \rangle| \times 100, \tag{13}$$

where $\langle \gamma_{ref} \rangle$ and N denote the mean value and the number of references, respectively. Since molecular dynamics is a very sensitive technique to pressure, the systems in low pressure regime (<5 MPa) show further pressure fluctuations leading to instabilities, whereas the high-pressure regime (>10 MPa) have been commonly accepted to provide more reliable results, particularly in liquid and solid phases.



Fig. 4 Surface tension (mN/m) at the temperature of 25°C with increasing the system pressure (MPa). The plus sign, triangle, circle, and square markers denote the data obtained from the experiments by Sachs et al. and Sun et al., simulation, and present work (with blue fitting curve), respectively [36-38].

When the systems are compressed, two separated liquid and gas phases are forced to merge with each other with more condensed interfaces. Therefore, we expect the surface to lose its tension with increasing system pressure. Fig. 4 demonstrates an approximately quadratic decrease in surface tension with pressure, in agreement with both experiments and simulations [36-38]. This decreasing trend of the interfacial tension disappears at pressure greater than 50 MPa, and

subsequently the interface displays a slight tension increase with pressure upturn. The region of decreasing tension is fitted with the following quadratic polynomial (units reported in the figure): $\gamma(mN/m) = 0.0087 P^2 - 0.72 P + 68$ (14)

The 10-90 Å interfacial thickness (*t*) is representative of the surface thickness found in ellipsometric and x-ray reflectivity experiments [39, 40], which is 2.1972 times larger than the physical thickness (*d*) [41]. We obtain the physical thickness d(Å) from the hyperbolic tangent fitting curve of density profile:

$$\rho(z) = \frac{1}{2}\rho_b \left(1 - \tanh\frac{|z - z_c| - z_G}{d}\right) \tag{15}$$

where ρ_b , z_c , and z_G represent the bulk density, the center of interface, and the Gibbs dividing surface position. The physical thickness can also be calculated from fundamental thermodynamic relations:

$$d(\text{\AA}) = \left|\frac{\partial G}{\partial P}\right|_{A,T} = \left|\frac{\partial \gamma(mN/m)}{\partial P(MPa)}\right|_{A,T} \left(\frac{10^{-9}MPa}{1mN/m^2}\right) \left(\frac{10^{10}\text{\AA}}{1m}\right) = |0.174 P(MPa) - 7.2|$$
(16)

Please note that in deriving this equation using Eqn. 14 we include conversion factors for pressure and distance. The interfacial thickness obtained from these two methods at 25°C and 10 MPa has only 5.4% deviation indicating a theoretical validation for our simulations. To evaluate the temperature and pressure effects on the interface, we report the associated thickness and box length. Fig. 5 shows that interfacial thickness *t* and box length L_z substantially depend on the thermodynamic conditions of the system. L_z can largely expand and adapt as we increase the temperature. Moreover, the system can

reveal larger compression in both t and L_z along with increasing pressure. This effect of the pressure might persist so long as the system retains the conditions pertaining to its compressibility.



Fig. 5 Increasing the temperature reveals an increase in interfacial thickness t (a) and, more effectively, L_z (b) at 10 (plus signs), 20 (circles), 30 (stars), 40 (squares), and 50 (triangles) MPa. The systems at higher temperatures better manifest the box length elongation.

In addition to pressure, the interfacial tension significantly depends on the temperature of the system. When the temperature increases, the cohesive forces acting between the water molecules decrease, subsequently the interfacial tension decreases so that it approaches zero at the critical point. Fig. 6 clearly shows this trend for the surface tensions with rising temperature at constant pressures. In a system with constant pressure and cross-sectional area, a quadratic function of the temperature (K) can approximately estimate the interfacial tension:

$$\gamma(mN/m) = 0.000069 T^2 - 0.22 T + 120 \tag{17}$$

Since the second order term is almost negligible, we assume that the fitted curve is a linear function to compare the results with the classical scaling laws. Therefore, a master curve is constructed to correlate the interfacial tension and temperature with a classical equation in an improved form of the Eötvös rule given by Ramsay and Shields [42]:

$$\gamma V^{2/3} = k(T_c - T - 6), \tag{18}$$

where V, T_c , and k are the molar volume, critical temperature of the mixture, and Eötvös constant which is equal to 2.1×10^{-7} J/K.mol^{2/3}, respectively. The following linear fit reports the surface tension in units of mN/m at 10 MPa when the temperature is given in degrees K:

$$\gamma = -0.23 T + 129.4 \tag{19}$$

The binary mixture requires the molar volume of 28.37 cm³ and the critical temperature of 573.26 K to complement the fitting line. If we assume the mixture is ideal, these computed values also match the molar volume and the critical temperature of the mixture obtained from the mixing rules [43]. We note that this fitted linear function might only predict the surface tension in the



Fig. 6 The plot (a) depicts the inverse behavior of the interfacial tension (mN/m) versus temperature (°C). The plus sign, circle, star, square, and triangle markers represent the system pressure of 10, 20, 30, 40, and 50 MPa, respectively. Blue and red lines in the plot (b) display the linear and quadratic master curves, respectively, which fit the interfacial tension at 10 MPa and different temperatures (K) and whose slopes estimate the surface entropy.

specific range of pressures and temperatures as we do not examine the other factors including molecular structure, orientation, and polarity under different thermodynamic conditions.

The surface entropy (S) can be calculated from the summation of two terms associated with the enthalpy and the isobaric heat capacity of the system [44]. Utilizing a more efficient approach, we assume the surface entropy only depends on the temperature at relatively constant pressure and compute it from the fundamental thermodynamic equations:

$$-S = \left(\frac{\partial G}{\partial T}\right)_{A,P} = \left(\frac{\partial \gamma}{\partial T}\right)_{A,P} \tag{20}$$

After unit conversion and multiplication by the area, we attain an entropy value of 117.98 kcal/mol at 275 K and 10 MPa, which shows very good agreement with a deviation of 6.07% from the previous studies [45].

Next, we characterize the chemical composition across the interface. Since we place the water bulk in the central region encompassed by the methane, the water mass fraction prevails over the methane mass fraction along with a decrease in the potential energy in the central region. Fig. 7 depicts pressure variation (10-50 MPa) negligibly influences the components compositions and leaves the profiles untouched, whereas it influences the local density, specifically for the methane phase. Nevertheless, increasing the temperature (25-105°C) affects the methane mass fraction, particularly under the low-pressure regime. The water molecules cope with less resistance to mobility between the phases, while lower competition from neighboring water molecules forms stronger hydrogen bonds between the polar water molecules at the surface than the bulk to interact with the nonpolar methane molecules restricting their penetration to the water phase. The hydrogen bond density near the surface in the water phase increases as per temperature drop or pressure upturn in an analogous manner to the temperature and pressure effects on the methane density profile at the interface. Therefore, the water mass fraction in the gas phase increases and methane solubility in liquid water at P>10 MPa and 25<T<105°C remains poor.



Fig. 7 Water (solid line) and methane (dashed line) mass fractions. The pressure and temperature are subject to change in the plots (a) and (b), respectively. The system temperature for the plot (a) is 25°C. Blue and red lines denote the pressure of 10 and 50 MPa, respectively. Increasing the water mass fraction, consequently, decreasing the methane mass fraction in the liquid phase exhibits a dramatic decrease in the potential energy and increase in the hydrogen bond quantity at the interface as shown in the insets. Dashed line in the inset (a) represents the interface center obtained from the inflection point of fitted density profiles. Blue and red lines in the plot (b) denote the temperature of 25°C and 105°C at 10 MPa, respectively. The insets demonstrate how the mass fractions remain constant in the liquid phase but slightly change in the gas phase when the system experiences a temperature difference so that the water molecules might enter the gas phase more frequently at high-temperature regime.

Conclusions

In this work, we used molecular dynamics to characterize the interfacial mechanics, thermodynamics, and chemical composition of liquid water and methane gas interface. Given the

chemical asymmetry and mechanical anisotropy of the methane-water interface we used a novel NP_NAT ensemble, that can keep constant normal pressure and constant cross-sectional area, both crucial to obtain reliable properties in interfacial studies. As result of this computational method, this work improved the accuracy of the predicted interfacial property data, showing less deviation from the experiments as well as generating a molecular-level characterization. Classical scaling laws were employed, such as the Eötvös rule in conjunction with fundamental thermodynamics to fully characterize the pressure and temperature dependence of the interfacial tension, interfacial thickness, and surface entropy, achieving good agreement with available experimental data. Results also concluded that the surface tension decreases as we increase the pressure up to 50 MPa and more susceptibly, the temperature. Using the adaptive ensemble, we demonstrated that the interfacial thickness and longitudinal computational box length can elongate with either temperature increase or pressure decrease. Increasing both methane surface excess and local density near the surface suggests anomalous methane adsorption onto the water-methane surface. On the other hand, the strong hydrogen bonds adjacent to the surface in the water side favorably interact with the methane molecules and withhold them in the gas phase limiting the methane solubility, particularly at high pressure (P>10 MPa). Overall, the comprehensive results provide a quantitative characterization and molecular-level description of the water-methane interface which is of importance to fundamental surface physics and energy and environmental applications.

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