



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



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## 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  $NP_{\mu}AT$  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.

## 1. 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-existing 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]:

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

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

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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<sub>N</sub>AT* 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<sub>N</sub>AT* 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 ( $\gamma_{KB}$ ) 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.

## 2. 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  $36 \times 36 \times 120$  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<sub>N</sub>AT* ensemble [20]. To reach the desired target pressure, the system volume, and consequently, the co-existing 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:

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

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

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (3)$$

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