Experimental measurements and numerical modelling of interfacial tension in water-methane systems

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Abstract: - The interfacial tension between water and methane were estimated for a model molecular system in the NPT ensemble. We have explored the effects of the system size and long-range corrections. It has been shown that the combination of one-sited OPLS methane model and SPC/E water model yielded interfacial tension properties in good agreement with the experimental data. The results were compared to the literature data and modelled with the linear gradient theory approach.

Key-Words: - methane; water; interfacial tension; molecular modelling

1 Introduction

While the interfacial tension of hydrocarbon-water systems is of theoretical and practical interest, there is a paucity of data available in the open literature. If we consider the major component in reservoir fluids, methane, nearly all of the published data sets clearly show discrepancies when compared with each other. As such, there is a definite need to collect and critically evaluate the data for this system and for the other components found in hydrocarbon – water systems.

Molecular dynamics simulations can be a powerful tool in evaluation of the existing data set and in the further development of technique to predict the interfacial tensions of the studied systems in an attempt to supplement the experimental measurements. The amount and range of reliable data (from previous investigations and those predicted with MD simulations) is imperative to development/validation of the existing experimental data and the models used in engineering design.

This work is a contribution to the critical assessment of the hydrocarbon-water interfacial tension experimental data and to the evaluation of engineering models needed to accurately determine the interfacial tension of these systems. The results from this study will be used to evaluate the potential of MD simulations to predict the interfacial tension of hydrocarbon-water systems and subsequently used to fill in voids in the existing data set. This new data set will be used in the future development and validation of interfacial tension models for this important system.

The paper is organized as follows. The molecular dynamics simulations are described in section 2 followed by description of a simplified theoretical approach and corresponding comparisons between experimental results, simulated results and results form the simplified theoretical approach. Our conclusions are given in section 4.

2 Molecular Dynamics Simulations

Simulation details

Two methane models were considered, a five-site all-atom AMBER force field (supposedly the more realistic one) and a united-atom one-site OPLS model proposed by Jorgensen *et al* [1]. The water models used for the simulations in this work included SPC/E (Simple Point Charge/Extended) model and TIP4P water models. The molecular dynamics used the constant-temperature, constant-pressure algorithm from MDynaMix package of Lyubartsev and Laaksonen [2]. As opposed to the customary practice when we would construct the interfacial system from two slabs of bulk water and methane, set side by side, we exploited the almost complete immiscibility of water and methane and started from a uniform mixture of water and methane in the case of smaller systems. The time step was set to 0.5 femtosecond (fs). The cut off radius, r_c, for the short-range forces was set to half the smallest side length in the simulation box. The Nose-Hoover thermostat parameters [3, 4] were set to 21 fs and 43 fs for the rotational and translational modes, respectively (see [5]). Each run was equilibrated for 250 picoseconds (ps) before the production began. Each production run lasted for at least 250 ps.

Linux-based Message Passing Interface (MPI) for parallel computation was used on a cluster of dual-processor PCs. Number of processors ranged from 12 to 16. Hydrogen bonding identified by means of distance-angle criterion of the VMD package [6].

Eight preliminary simulations of small systems containing 125 molecules of each species were performed first. The system sizes were then increased due to pronounced size dependencies. A total of 24 simulations of interfacial tension of systems containing water and methane models were performed at constant pressure, temperature, and number of particles conditions (NPT ensemble). The number of molecules and type of molecule models varied. The models used included SPC/E and TIP4P models for water, and united-atom and all-atom for methane. The interfacial tension, γ, was evaluated by the common method which used the normal and tangential pressures to the interface and took into account the fact that the model systems had two interfaces normal to the z-axis.

Smaller systems

To see whether it was possible to reproduce true interfacial systems with a small number of molecules, four simulations at four different phase points were conducted for a system which contained 125 molecules of each species. In this case, all-atom methane and TIP4P water model were used.

Both the all-atom and united-atom systems underestimated the interfacial tension in all the phase points and did not show any experimentally-observed pressure dependencies [6]. The significant difference between the two systems was the density. The system containing the 5-site methane predicted a much higher density in all the phase points, while the united-atom reproduced the experimental value (0.2% underestimation). We concluded that the number of water molecules was too small to provide a proper bulk phase. As such, it was decided to double the number of water molecules in the system.

Large systems

Two new systems were then constructed, both containing 125 1-site methane models (the 5 site methane model was rejected due to poor density reproduction), and 256 water molecules, the first system contained TIP4P water and the second one, SPC/E water. In this case, the system was formed from water and methane slabs. Same phase points as the smaller systems were used. These runs showed that system that contained SPC/E water reproduced the interfacial tension slightly better than TIP4P water. Therefore, several even larger water–methane systems were set up and simulated under additional T and P conditions.

These systems were initially constructed by stacking together slabs of water (2500 and 2310 SPC/E molecules) and methane (144 molecules at 275 K and 65 atm, 684 molecules at 473 K and 1000 atm). Experimental densities were used for water and methane. Both systems ranged 42Å x42Å x82Å in size.
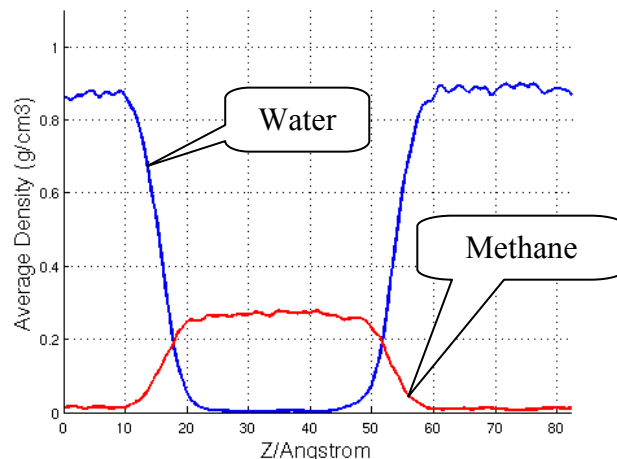

Figure 1. Density profiles for a larger system containing SPC/E water and methane at 65 atm and 273 K. Higher densities correspond to water, lower, methane.
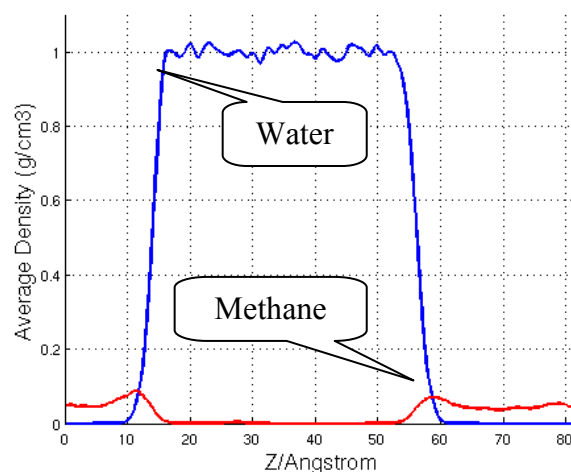

Figure 2. Density profiles for a larger system containing SPC/E water and methane at 1000 atm and 473 K. Higher densities correspond to water, lower, methane.

Figures 1 and 2 presents the density profiles of OPLS–SPC/E systems at (Fig. 1) 65 atm and 275 K, and (Fig. 2) 473 K and 1000 atm. Both systems display well-defined regions of bulk water, and it should be noted that while the thickness of the initial water slab was the same for the two P-T sets, the interface width showed a dramatic dependence on the temperature and pressure. The width of the interface is around 8-10 Å in the low-temperature system, with the corresponding 30-Å bulk

System	P (atm)	T (K)	Box size x/y/z (Å)			ρ (g/cm3)	γ (mN/m)	$\frac{sim-exp^1}{exp}$(%)
Amber-SPC/E	100	296.5	19.73	19.73	69.89	0.4037	50.7 ± 4.0	-21
Amber-SPC/E	300	296.5	19.73	19.73	53.12	0.5313	47.7 ± 4.0	-12
Amber-SPC/E	100	373.2	19.73	19.73	120.71	0.2337	38.9 ± 3.5	-22
Amber-SPC/E	300	373.2	19.73	19.73	67.24	0.4197	39.0 ± 3.5	-11
OPLS-SPC/E	100	296.5	19.72	19.72	71.23	0.3968	55.2 ± 4.5	-14
OPLS-SPC/E	200	296.5	19.72	19.72	59.52	0.4748	52.7 ±4.5	-9
OPLS-SPC/E	300	296.5	19.72	19.72	53.22	0.531	53.6 ±4.5	-1
OPLS-SPC/E	400	296.5	19.72	19.72	50.78	0.5566	53.4 ±4.5	3
OPLS-SPC/E	100	373.2	19.72	19.72	112.04	0.2523	44.8 ±4.5	-11
OPLS-SPC/E	200	373.2	19.72	19.72	77.57	0.3643	44.3 ±4.0	-1
OPLS-SPC/E	300	373.2	19.72	19.72	66.58	0.428	43.1 ±3.8	-1
OPLS-SPC/E	400	373.2	19.72	19.72	60.50	0.4672	41.9 ±4.0	0
OPLS-SPC/E	100	449.9	19.72	19.72	174.05	0.1624	30.6 ±4.1	-13
OPLS-SPC/E	200	449.9	19.72	19.72	107.33	0.2633	29.8 ± 3.7	-11
OPLS-SPC/E	300	449.9	19.72	19.72	85.16	0.3319	29.4 ± 3.9	-8
OPLS-SPC/E	400	449.9	19.72	19.72	74.67	0.3785	30.0 ±4.0	-6
OPLS-SPC/E	65	275.15	42.0	42.0	82.40	0.5409	57.0 ±1.0	-11
OPLS-SPC/E	1000	473.15	42.0	42.0	82.39	0.6008	28.0 ±1.0	+0.4

Table 1. Estimated interfacial tension in the larger systems

water region. On the other hand, the water–methane interface was broadened almost by half in the supercritical system, reaching about 12 Å in thickness. In yet another departure from ambient behaviour, methane solubility in water and water solubility in methane both showed dramatic increase compared to normal water in this model system. This agrees well with the experimental data presented by Yarrison *et al.* [7] that showed that while water solubility in methane amounted only to 0.002209 at 310.9 K and P= 3.45 MPa, it increased by a factor of more than 20 at 477.5 K and P= 96.53 MPa (close to our simulation point).

In case of SPC/E water, the comparison of systems that employed the same force fields, temperatures and pressures but differed in the number of water molecules has shown significant variations of the estimated interfacial tension. Systems that contained TIP4P water did not exhibit any significant differences at 296.5 K but yielded slightly poorer estimations at 373.2 K than the smaller systems studied. Comparison between the large systems showed that OPLS–SPC/E combination of force fields resulted in better estimates. Based on this, this approach was used at several other

phase points as shown in Table 1. Both systems that contained TIP4P and SPC/E water showed slight pressure dependence at 296 K. At 373 K, only the OPLS-SPC/E system exhibited pressure dependence.

Proper tail correction

At conditions away from ambient, the SPC/E water model has been known to perform well, especially for calculating bulk properties. This is also holds true for the OPLS methane model.

On the other hand, several studies have indicated that applying a straightforward long-range Lennard-Jones correction resulted in an error due to non-uniform densities outside the cut-off area. We have followed in the approach of Alejandre et al [8], where the proper tail correction was evaluated by the method of Chapela et al [9]. In this work, the tail correction was estimated through interpolations of values calculated for a pure SPC/E water system, and extended to the mixture of SPC/E water and OPLS methane with the application of dimensional arguments used to derive analogues of the pure fluid properties in the case of mixtures.

Corrected interfacial tensions plotted in Figure 3 shows that results obtained with proper tail corrections exhibit pressure dependences closer to that of the experimental data. However, it is not possible to conclude outright that the corrected results offer a real improvement since the tail corrections were estimated with a number of assumptions. On the other hand, the application of the tail correction raised the estimated interfacial tension at all phase points, and introduced pressure dependence similar to those exhibited in experimental results. To put it another way, the tail corrections might have failed to bring the results into a perfect quantitative agreement with experimental results but it certainly improved the results qualitatively.
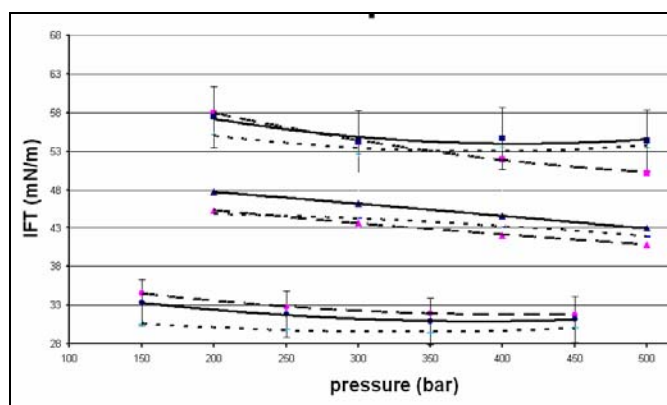

Figure 3. Interfacial tensions at pressures corresponding to experimental methane densities. Stippled lines -- experimental values; dotted lines – simulated values with the tail correction applied; full lines – without tail correction.

Interface roughness and the capillary wave theory

When it comes to the calculation of interfacial tension basing on the properties of the interface between two fluids, an alternative approach exists – the capillary wave theory. This theory suggests the following relationship between the interfacial free energy, γ, and the roughness of the interface in terms of its average surface fluctuations, σ^2 [10, 11]:

$$\sigma^2 = \sum \left(h_{ij} - \left\langle h_{ij} \right\rangle \right)^2 \qquad (1)$$

$$\sigma^2 = \frac{k_B T}{2\pi\gamma} \ln\left[\frac{1 + \left(2\pi l_c / \varepsilon_b\right)^2}{1 + \left(2\pi l_c / L\right)^2} \right] \qquad (2)$$

where h_{ij} is the position of the interface between fluids i and j; k_B, the Boltzmann constant; T, absolute temperature; $l_c = [\gamma/g(\rho_w - \rho_{CH4})]^{1/2}$; ρ_w and ρ_{CH4} are measured densities of water and methane, respectively, respectively; g, the acceleration of gravity; and L and ε_b are the upper and lower wavelength limits determined by the size of the interface (Lx) and the bulk correlation length, respectively.
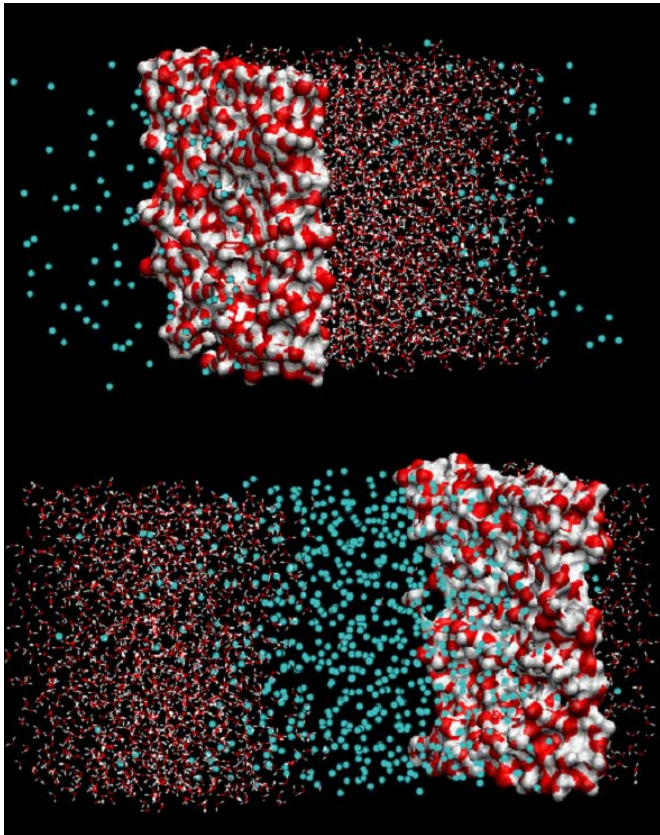

Figure 4. Water–methane interface between water–methane systems at 275 K and 65 atm (top) and 473 K and 1000 atm (bottom). The simulation cell has been duplicated along the axis normal to the interface. See text for details and discussion.

The capillary wave function technique has been proven to work quite well in case of water-supercritical CO_2 (see Rocha *et al.* [12, 13]). Figure 4 offers the comparison between water–methane surfaces at 275 K and 65 atm (top) and 473 K and 1000 atm (bottom). The first of the two has much higher interfacial tension than the supercritical one (57 mN/m as opposed to 28 mN/m), and this difference is clearly reflected in the relative heights of finger like interface protrusions. Thus we have concluded that given the sharp interface between water and methane, the capillary wave approach is well suited for interfacial tension estimation in systems where one of the fluids has low density and is worth considering alongside with the density-gradient theories.

3   Engineering calculations using the gradient theory approach

There are a number of techniques to model the interfacial tension, which range from the simple empirical correlations to those based on statistical thermodynamics. Unfortunately, the simpler methods, such as the Parachor method, suffer in their accuracy to model the hydrocarbon + water systems [14]. The techniques derived from statistical thermodynamics and the theory of inhomogeneous fluids has been shown to be more theoretically sound, accurate and robust calculation method. However, due to their complexity, a number of the methods used to predict interfacial tensions are unsuitable for engineering applications.

In the work of Schmidt and Kvamme [15] all of the existing experimental methane-water interfacial tension data available in the open literature were reviewed and modelled with the linear gradient theory (LGT) [16], a practical version of the gradient theory [17], combined with the Peng-Robinson equation of state (PR EOS) [18] (PR-LGT). The LGT approach eliminates the need to solve the set of time consuming density profile equations that are inherent with the gradient theory approach. This speeds up the calculation procedure without significantly losing accuracy for these types of mixtures [16, 19].

Briefly, in the linear gradient theory approach, the number density, $n_i(z)$ of component i at position z is linearly distributed across the interface:

$$\frac{dn_i(z)}{dz} = D_i \qquad (3)$$

Similar to the gradient theory, the interfacial tension is determined by:

$$\gamma = \int_{n_1^{HC}}^{n_1^{W}} \sqrt{2c\left[\Phi(n)-\Phi_b\right]}\,dn_1 \qquad (4)$$

where $c, \Phi(n)$, Φ_b are the mixture influence parameter, grand thermodynamic potential energy density and negative pressure (-P). In this case, the grand thermodynamic potential energy density is determined from the PR EOS via the Helmholtz free energy, $f^{\circ}(n)$, and chemical potentials of each species, μ_i.

$$\Phi(n) = f^{\circ}(n) - \sum_{i=1}^{N} n_i \mu_i \qquad (5)$$

The PR EOS is also used to determine the equilibrium densities of each phase in contact with the interface. The PR EOS may be expressed as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \qquad (6)$$

In the LGT the mixture influence parameter is determined by:

$$c = \sum_{i=1}^{N} \sum_{j=1}^{N} c_{ij} \left(\frac{\Delta n_i}{\Delta n_1}\right)\left(\frac{\Delta n_j}{\Delta n_1}\right) \qquad (7)$$

where Δn_i is the number density of component i in the interface. The crossed influence parameter, c_{ij}, is determined from the pure component influence parameters, c_{ij} and c_{jj} and the binary interaction parameter l_{ij}, with equation 8.

$$c_{ij} = \sqrt{c_{ii}c_{jj}}\,(1-l_{ij}) \qquad (8)$$

Schmidt and Kvamme [15] discuss the determination of c_{ij}, c_{jj} & l_{ij}, the numerical results and review the available literature data in detail.

The collected literature data and the results from [15] are compared with the data obtained from the MD simulations in Figures 5 - 9. As can be seen from the figures, the PR-LGT modelling approach closely matches the experimental data over the 200 K temperature range. The simulation results are not in perfect quantitative agreement with experimental or modelled results but qualitatively the obtained results will be expanded to ensure the PR-LGT model exhibits the correct behaviour over the large pressure and temperature ranges considered. In addition, when the simulations do exhibit the correct quantitative agreement

with the modelled and literature results the resulting simulations will be considered in the context of supplementing the existing experimental database.
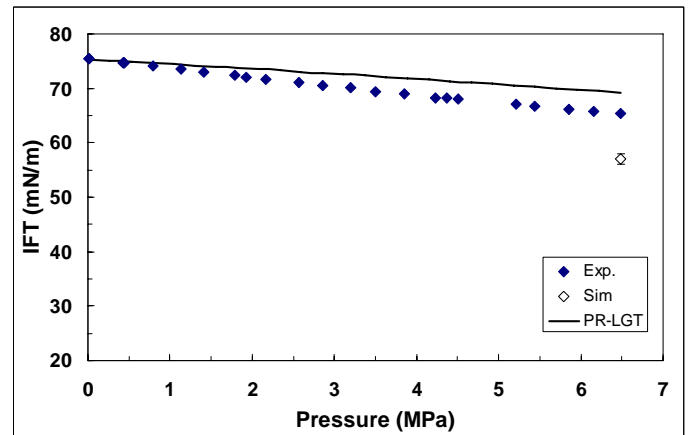

Figure 5. Comparison of the experimental, simulated and modelled water–methane interfacial tension at 273.2 K.
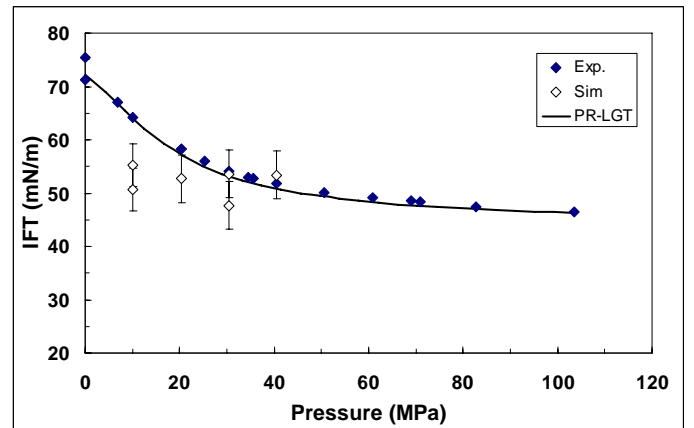

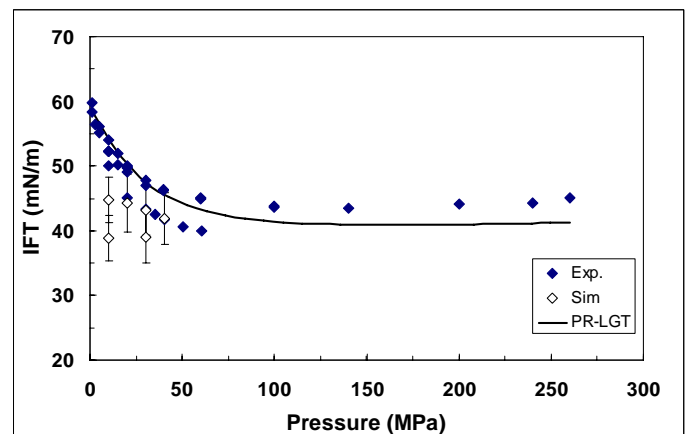Figure 6. Comparison of the experimental, simulated and modelled water–methane interfacial tension at 296.5 K.

Figure 7. Comparison of the experimental, simulated and modelled water–methane interfacial tension at 373.2 K.

4 Conclusions

Molecular-Dynamic simulations can be a powerful tool in the further development of this and other modelling approaches. The combination of the simulations, modelling results, literature database and review gives us a unique approach to understand the water+methane interfacial tension over a wide range of temperature and pressures. This investigation will be similarly performed on other hydrocarbon+water systems.
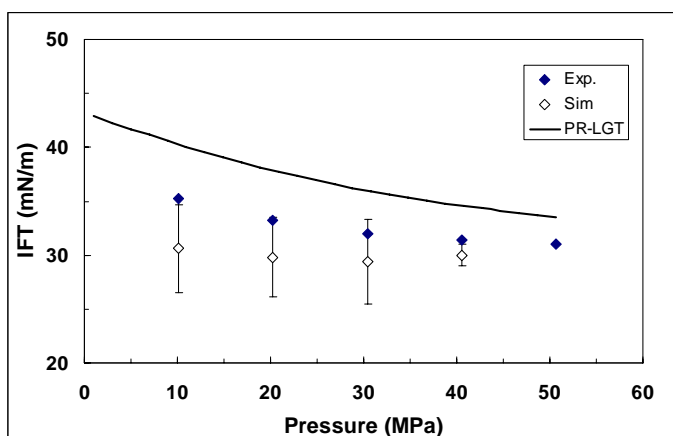

Figure 8. Comparison of the experimental, simulated and modelled water–methane interfacial tension at 449.8 K.
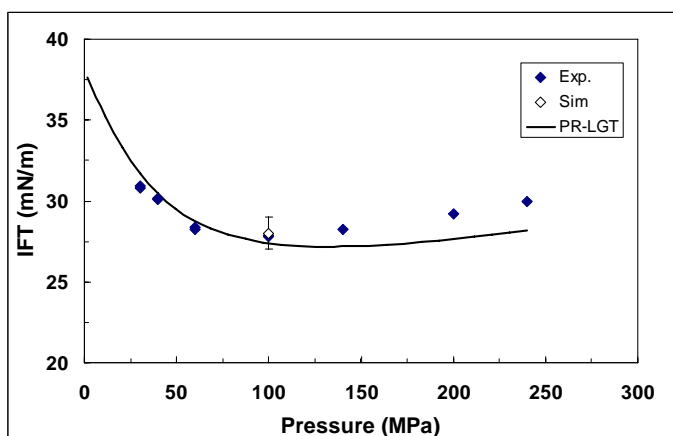

Figure 9. Comparison of the experimental, simulated and modelled water–methane interfacial tension at 473.2 K.

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