

Molecular Dynamics Calculations of Near-Critical LOX Droplet Surface Tension

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Surface tension is an important concept when considering any aspect of droplet behavior. Surface tension causes the spherical geometry that droplets form and determines the liquid pressure within the droplet as a function of droplet size. As the critical point for the liquid is approached the surface tension goes to zero and droplets no longer form, a defining aspect for supercritical conditions. The surface tension of liquid oxygen droplets in gaseous oxygen and helium environments at a variety of pressures was calculated in the course of a molecular dynamics (MD) simulation. The surface tension was calculated by averaging the net interatomic attractive force experienced by atoms in the simulation. The calculated values of surface tension as a function of pressure compared well with theoretical and experimentally measured values found in the literature. The effect of the helium environment in raising the critical point of the oxygen was reproduced by the simulations.

1. Introduction

Surface tension is an important concept when considering any aspect of droplet behavior. Surface tension causes the spherical geometry that droplets form and determines the liquid pressure within the droplet as a function of droplet size. As the critical point for the liquid is approached the surface tension goes to zero and droplets no longer form, a defining aspect for supercritical conditions. The surface tension of a liquid in equilibrium with its vapor as a function of temperature and pressure can be found in the literature. But the surface tension of a liquid in contact with a gas of another species under nonequilibrium conditions such as vaporization or approaching the critical point of the liquid has previously only been obtainable from experimental measurements [1].

On a molecular level surface tension can be explained as the result of unequal attractive forces exerted on surface molecules in the droplet [2]. Molecules in a uniformly dense system experience attractive forces due to neighboring molecules, but they have no net effect because the force field is symmetrical. But when two phases coexist, the molecules on the interface region will experience a net attraction toward the more dense phase. This is due to the large number of neighboring molecules exerting an attractive force on the liquid side of the interface, while very few molecules on the gas side will be close enough to exert any force. This explanation suggests that molecular dynamics (MD) can be easily used to determine the surface tension under any conditions. Because the force on any given molecule is calculated at each time step in a MD simulation, the net attractive force on each

molecule gives an indication of the surface tension. MD has been shown to be an appropriate method for modeling other thermodynamic properties of systems near or above the critical point [3-5].

2. Molecular Dynamics Simulation

The case described here is that of a liquid oxygen (LOX) droplet evaporating in a warmer quiescent oxygen or helium gas under conditions approaching the critical point. The computer code used was the one developed by Kaltz et al [6] to simulate subcritical and supercritical LOX droplet vaporization. All interatomic potentials used were the Lennard-Jones 12-6 two parameter potential

$$u_{ij}(r_{ij}) = 4\epsilon \left(\frac{\sigma}{r_{ij}} \right)^{12} - \frac{\sigma}{r_{ij}}^6 \quad (1)$$

where u_{ij} is the potential between two atoms i and j and r_{ij} is the interatomic distance. The Lennard-Jones 12-6 potential is characterized by a strong repulsive force at very short range and a weak attractive force at intermediate range. It contains two parameters: σ , the zero energy separation distance, roughly equivalent to atomic diameter, and ϵ , the minimum energy. The force on atom i from atom j is given by the gradient of the potential. The Lennard-Jones parameters for interactions between unlike atoms were obtained by the Lorentz-Berthelot mixing rules [7], which are expressed as

$$\sigma_{AB} = \frac{1}{2} (\sigma_{AA} + \sigma_{BB}) \quad (2)$$

$$\epsilon_{AB} = (\epsilon_{AA} \epsilon_{BB})^{1/2}$$

Table 1 lists the potential parameters, bond length and critical temperature and pressure for the oxygen and helium simulated in this study.

The velocity Verlet algorithm with a time step of 2.5 femtoseconds (fs) was used to calculate the position and velocity of all the atoms at each time step. Molecules such as oxygen were modeled as two separate oxygen atoms constrained to remain a fixed bond length apart. This was done using constraint dynamics as embodied in the RATTLE algorithm [8]. The simulations used between 4580 and 7200 atoms, depending on the gas density. A Verlet neighbor list and periodic boundary conditions were also used. The initial droplet diameter was approximately 6 nanometers (nm). With 7200 atoms the code ran from 22 minutes on 12 processors of a Beowulf PC cluster to only 6 minutes on 64 processors using particle decomposition to partition the computational load [9]. The initialization process involved equilibrating separately a droplet in equilibrium with its vapor and a

Table 1
Pair potential parameters, bond length and critical temperature and pressure for species modeled in the simulation

Species	σ (\AA)	ϵ / k_b (K)	d / σ	T_c (K)	P_c (MPa)
O ₂	2.95	58.0	0.42	154.58	5.04
He	2.28	10.2	-	10.2	0.227

gaseous environment at a specified temperature and pressure and then placing the droplet within the gas. The reason for using these separated steps is to guarantee that the droplet retains any surface tension of the saturated conditions and to minimize any effects due to the sudden introduction of a dense region into the dilute environment. Heat is added to the gaseous environment during the simulation to maintain a constant temperature.

Within the code the net attractive force for each molecule was averaged over 200 time steps to generate a local average force. The repulsive force was not included because the large magnitude of the repulsive forces associated with molecular collisions would dominate, and the resulting force would simply be proportional to the local density.

3. Results

3.1 Liquid oxygen/gaseous oxygen

An initial series of simulations of a liquid oxygen droplet in equilibrium with its vapor were conducted to validate the code. Simulations were conducted at pressures of 0.26, 0.4, 1.0, 2.0, 3.0 and 4.0 MPa [10]. The liquid and gaseous temperatures for each pressure was the temperature of liquid oxygen that gave the same vapor pressure as the simulation pressure. Thus the simulation temperature ranged from 100 K at 0.26 MPa to 148.4 K at 4 MPa.

Figure 1 shows a contour plot of the nondimensionalized rms force for a slice through the center of a liquid oxygen droplet in equilibrium with its vapor at 0.26 MPa. It can be seen that the force is manifested along the surface of the droplet and is zero both inside the droplet as well as in the gaseous environment. Figure 2 shows a contour plot of the nondimensionalized rms force for a slice through the center of a liquid oxygen droplet in equilibrium with its vapor at 2.0 MPa. It can be seen that the magnitude of the rms force is lower and is manifested over a larger radial range. Figure 3 shows a contour plot of the nondimensionalized rms force for a slice through the center of a liquid oxygen droplet in

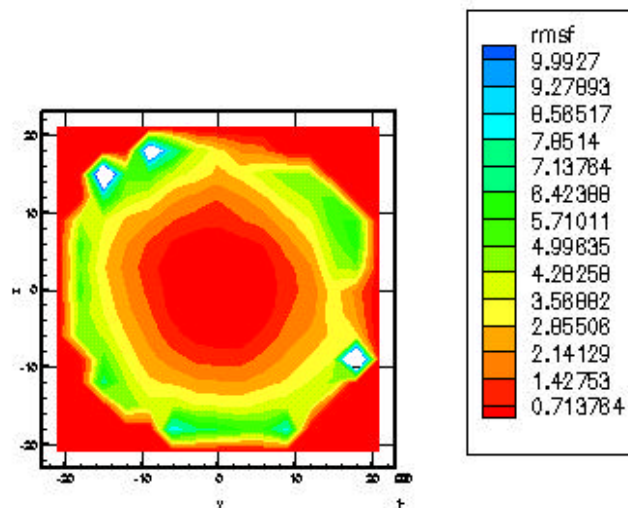


Fig. 1 Contour plot of the nondimensionalized rms force in the plane through the center of a liquid oxygen droplet in equilibrium with its vapor at 0.26 MPa.

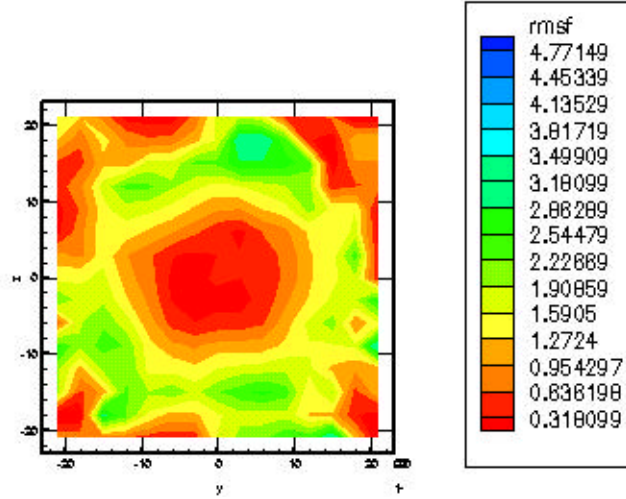


Fig. 2 Contour plot of the nondimensionalized rms force in the plane through the center of a liquid oxygen droplet in equilibrium with its vapor at 2.0 MPa.

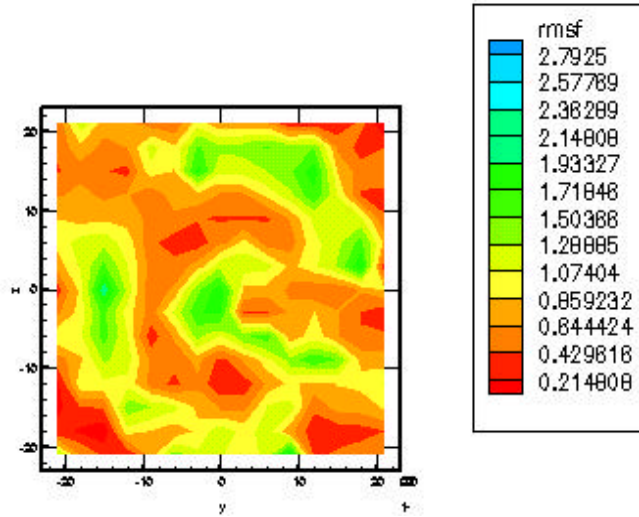


Fig. 3 Contour plot of the nondimensionalized rms force in the plane through the center of a liquid oxygen droplet in equilibrium with its vapor at 4.0 MPa.

equilibrium with its vapor at 4.0 MPa. For this case near the critical point the surface tension force has disappeared and the droplet surface, as defined by the surface tension, is indistinguishable.

Figure 4 compares the surface tension calculated from the molecular dynamics simulations to experimental values from Vieille for LOX droplets evaporating in air [1]. In these experiments the surface tension was obtained by measuring the frequency of natural oscillations of the droplets during free fall and using an expression derived by Rayleigh relating the natural frequency of the fundamental mode as a function of surface tension [11]

$$\omega^2 = \frac{8}{3\pi} \frac{\sigma}{M} \quad (3)$$

where M is the mass of the drop. The falling droplets were photographed by a fast video

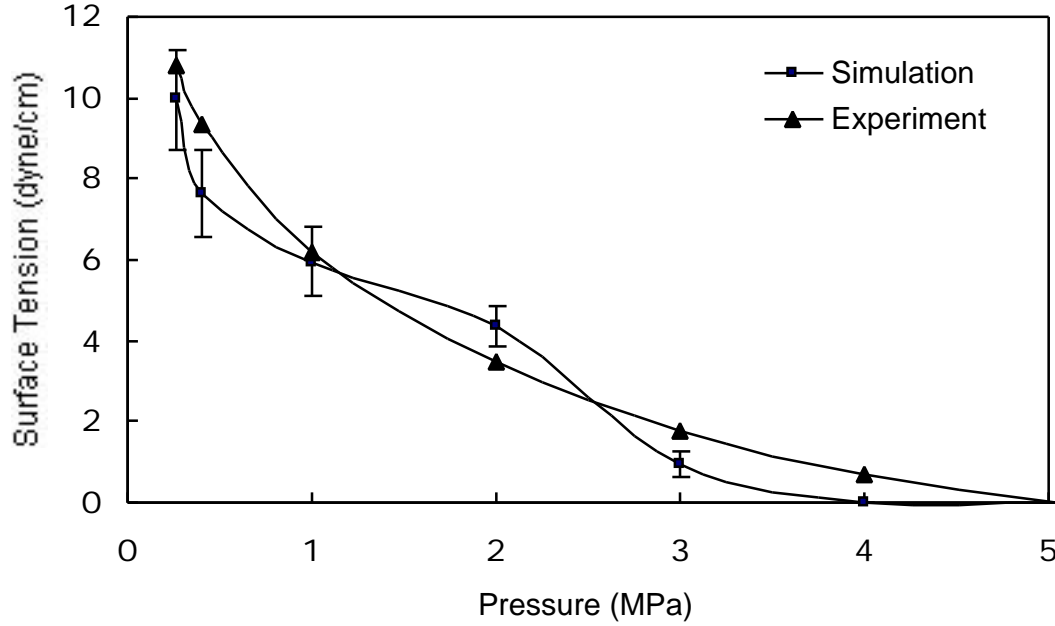


Fig. 4 Calculated and measured values of surface tension as a function of pressure for a liquid oxygen droplet in a gaseous oxygen (MD) versus air [1] environment.

camera filming at 1000 frames/s with a resolution of 80 $\mu\text{m}/\text{pixel}$. Droplet sizes were on the order of 0.5 mm. Image analysis software was used to calculate the orientation of the droplet inertial axis as a function of time and the oscillation frequency was determined both manually and by FFT for use in Equation 3. The experimentally and numerically obtained values for the surface tension can be seen to compare well.

3.2 Liquid oxygen/gaseous helium

For these simulations the initial liquid oxygen droplet temperature was 90 K and the gaseous helium temperature was 300K. Simulations were conducted at environment pressures of 0.1, 1.0, 4.0, 6.0 and 8.0 MPa. The helium environment has the effect of increasing the critical point of the oxygen. The same behavior shown in Figures 1-3 was also observed for these cases. Figure 5 compares the calculated surface tension to experimentally measured values [1]. The existence of surface tension to a higher pressure due to the helium environment can be seen. Once again the calculated results compare well to the experimentally measured values.

4. Conclusions

The surface tension of liquid oxygen droplets in gaseous oxygen and helium environments at a variety of pressures was calculated in the course of a molecular dynamics simulation. The surface tension was calculated by averaging the net interatomic attractive force experienced by atoms in the simulation. The calculated values of surface tension as a function of pressure compared well with experimentally measured values found in the literature. The

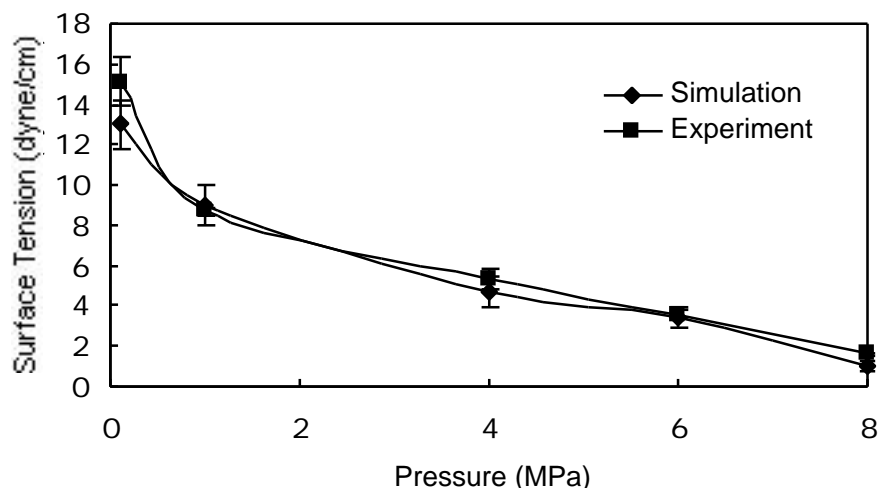


Fig. 5 Calculated and measured [1] values of surface tension as a function of pressure for a liquid oxygen droplet in a gaseous helium environment.

effect of the helium environment in raising the critical point of the oxygen was reproduced by the simulations. The molecular dynamics simulations provide a valuable tool for calculating surface tension in systems consisting of more than one species and under nonequilibrium conditions.

5. References

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