MOLECULAR DYNAMICS SIMULATION OF INTERFACIAL TENSION OF ULTRA-THIN LIQUID FILMS ON A SOLID SURFACE

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ABSTRACT
The effect of wall proximity on the interfacial tension of ultra-thin liquid films of Lennard-Jones (12,6) fluid has been studied using Molecular Dynamics Simulation. The wall’s presence can potentially affect drop-wise condensation and other phase change phenomena such as boiling. Initially the Lennard-Jones atoms are placed near a solid wall with FCC lattice structure in a doubly periodic box. Once equilibrated at a desired temperature, a thin liquid film forms on the solid wall. The surface tension of the liquid-vapor interface is computed statistically. When the film is thick (> 40 Å), surface tension at the liquid-vapor interface is found to be unaffected by the presence of the solid wall and matches bulk values reported for Argon. However for thinner films (< 15 Å), surface tension of the liquid-vapor interface deviates from the macroscopic value. This has been investigated for various temperatures ranging from the triple point to the critical point. As the film thins further (1-2 molecules thickness), the liquid-vapor interface resembles a solid-vapor interface. Surface tension of this solid-vapor interface is evaluated for a solid wall modeled both by an equivalent interacted potential and discrete atoms. The two cases are found to yield different results. The Equivalent potential for the wall gives lower surface tension and liquid density near the solid wall compared to the discrete atoms case.

NOMENCLATURE
A Surface Area
$L_x, L_y, L_z$ Length of the simulation box along $x, y$ and $z$ axes respectively

$R_0$ Lattice constant
$T$ Temperature of the system
$d$ Interfacial thickness
$f$ Force
$k_B$ Boltzmann constant
$m$ Atomic mass
$r$ Separation distance between atoms
$r_c$ Cutoff radius for the Lennard-Jones potential
$v$ Velocity

Greek
$\delta_f$ Film thickness
$\epsilon$ Lennard-Jones energy parameter
$\epsilon_r$ Relative strength of the wall, $\epsilon_{sf}/\epsilon_{ff}$
$\phi$ Potential function
$\gamma$ Surface tension
$\rho$ Density
$\sigma$ Lennard-Jones length parameter
$\psi$ Wall potential
$\Delta t$ Time step

Superscripts
* Non-dimensional parameters

Subscripts
$i,j$ Atoms index
$l$ Liquid
$N$ Normal to the interface
$T$ Tangent to the interface
$\nu$ Vapor
x Co-ordinate in the plane of interface
y Co-ordinate in the plane of interface
z Co-ordinate normal to interface

INTRODUCTION

Surface tension is an important factor in various phase change phenomena (boiling and condensation), wetting and drying of a solid wall, and capillary effects in narrow channels. However, experimental investigation of surface tension has been limited to macroscopic study due to the difficulty of making measurements at sub-micron scale even though many processes occur at sub-micron scale, such as thin fluid film coating and micro layer dynamics underneath vapor bubble. The dynamics at these small scales need to be quantified.

Surface tension can be defined thermodynamically as the isothermal work of formation of unit area of interface. However, Kirkwood and Buff [1] expressed surface tension as the integrated imbalance of normal and tangential pressures near the interface and thus enabling the evaluation of surface tension in molecular simulations. Pressure stresses are evaluated near the interface. All components of pressure tensor are the same in bulk liquid and vapor phases. However, near the interface, they differ from each other. The surface tension is computed by integrating the difference between pressure components across the interface. This method has been used extensively in the past to study the interfacial properties for Lennard-Jones fluid placed in a triply periodic box free from any external field [2; 3; 4; 10]. These studies showed that a cutoff radius of 4.5 – 5σ, which is significantly larger than the 2.5σ cutoff typically used, was required in addition to appropriate tail correction for the potential [6; 7] to accurately predict surface tension. However, the effect of external potential, a solid wall in our case, on surface tension has not been investigated.

In this work, we study the effect of film thickness on interfacial properties. In the following sections, we derive the surface tension accounting for an externally applied potential, provide simulation details, and present and discuss results.

SURFACE TENSION: WITH AN EXTERNAL FIELD

Kirkwood and Buff’s expression for surface tension is

\[
\gamma = \int_{\text{phase 1}}^{\text{phase 2}} [P_N(z) - P_T(z)]dz. \quad (1)
\]

For a plane interface perpendicular to the z axis, tangential and normal pressure components are

\[
P_N(z) = P_{zz}(z), \quad \text{and,} \quad P_T(z) = \frac{P_{xx}(z) + P_{yy}(z)}{2}, \quad (3)
\]

where, the pressure tensor is defined in terms of molecular positions r, velocities v and inter-atomic forces f as

\[
P_{xx} = \frac{1}{V} \sum_j m_j v_{xj} v_{xj} + \frac{1}{2} \sum_{i\neq j} \sum_{j \geq i} r_{ij} f_{ij} \quad (4)
\]

\[
P_{xy} = \frac{1}{V} \sum_j m_j v_{xj} v_{yj} + \sum_{i \geq j} \sum_{j} r_{ij} f_{ij},
\]

\[
P_N(z) = kT \langle \rho(z) \rangle - \sum_{i>j} \sum_{j} \frac{z_j^2 \psi_{ij}'}{Adz r_{ij}} - \sum_{j} \frac{z_j \psi'(z)}{Adz}, \quad (5)
\]

\[
P_T(z) = kT \langle \rho(z) \rangle - \sum_{i>j} \sum_{j} \frac{z_j^2 \psi_{ij}'}{2Adz r_{ij}}, \quad (6)
\]

where ϕ and ψ are potential function for fluid-fluid and fluid-solid interactions respectively and A is the cross-sectional area of the box (A = LxLy). Combining (1), (5) and (6) we get the surface tension of the liquid-vapor interface

\[
\gamma = \sum_{i>j} \frac{z_j^2 \psi_{ij}'}{2A r_{ij}} - \sum_{j} \frac{z_j \psi'(z)}{A}. \quad (7)
\]

The second term in the above expression shows that an external field can alter the surface tension. A similar expression was derived for solid-liquid interface by Navascues and Barry [8].

SIMULATION DETAIL

In this work, the atoms are modelled using the Lennard-Jones 12–6 potential,

\[
\phi(r) = 4\varepsilon_{ff} \left[ \left( \frac{\sigma_{ff}}{r} \right)^{12} - \left( \frac{\sigma_{ff}}{r} \right)^6 \right], \quad (8)
\]

where r is the inter-atomic distance, \(\varepsilon_{ff} (\varepsilon/k_B = 119.89K)\) is the well of the potential and \(\sigma_{ff} (\sigma = 3.405\text{Å})\) is the length scale.
Interatomic forces are truncated at \( r_c = 4.5\sigma \). A rectangular box of volume \( L_x \times L_y \times L_z \) is used for the simulation. Side lengths are varied to change the film thickness and keeping the same number of atoms in the simulation domain. The domain is periodic in \( x \) and \( y \) direction and has mirror boundary condition in \( z \) direction as seen in Fig. (1). A FCC(111) solid Platinum wall is represented at \( z = 0 \). Fluid and solid wall atoms interact with Lennard-Jones 12-6 potential as in (8) but different well parameters, \( \epsilon_{sf} \) and length scale, \( \sigma_{sf} \). The Argon-Platinum interaction is modeled as \( \sigma_{sf} = 0.8\sigma_{ff}, \epsilon_{sf} = 0.6\epsilon_{ff} \) with lattice constant \( R_0 = 0.8147\sigma_{ff} \). Integrating the effect of all solid atoms in \( x, y \) and \( z \) directions, we get an equivalent bulk wall potential \( \psi \) at height \( z \)

\[
\psi(z) = \frac{4\pi}{45\sqrt{3}} \frac{\epsilon_{sf}\sigma_{sf}^3}{R_0^3} \left[ 2 \left( \frac{\sigma_{sf}}{z} \right)^9 - 15 \left( \frac{\sigma_{sf}}{z} \right)^5 \right].
\]  

(9)

Atomic trajectories are computed using the velocity Verlet algorithm [9] and forces are evaluated using a neighbor list method. A time step of \( \Delta t^* = \Delta t/\sigma_{ff}\sqrt{m/\epsilon_{ff}} = 0.005 \) is used in the simulation. Initially, a liquid layer is placed near the solid wall and some fluid atoms are randomly distributed in vapor region based on approximate density at the desired system temperature. The system is equilibrated using Berendsen’s thermostat [12] for 100,000 time steps. This is followed by 50,000 time steps of non-thermostat equilibration before sampling. Sampling is performed every 50 time steps for next 1 million time steps. The simulation domain is divided into 512 bins in \( z \) direction. Density and pressure components are evaluated at all bins. It should be noted that for computational efficiency, we have attributed half of the contribution of pair \((i,j)\) to bin at \( z \) in (6) and (5) when either \( i \) or \( j \), was situated in bin at \( z \) while we attribute the total contribution to that bin when both \( i \) and \( j \) are situated in that bin. Technically the pair \((i,j)\) term should be distributed to all bins in between the bins containing \( i \) and \( j \) atoms. However, using this simpler method we obtain near perfect agreement with data from experiments for thick films. Since it has been found [2] that interfacial properties are sensitive to cutoff radius used in the simulation, a tail correction [7] to the surface tension is applied

\[
\gamma_{\text{tail}} = \int_{0}^{1} \int_{r_{c}}^{\infty} 12\pi (\rho_i - \rho_v)^2 \coth \left( \frac{2r}{d} \right) \left( \frac{3s^3 - s}{r^3} \right) \, dr \, ds,
\]  

(10)

where \( \rho_i \) and \( \rho_v \) are liquid and vapor densities respectively. The parameter \( d \),

\[
d = -\left. \left( \frac{d\rho}{dz} \right) \right|_{z=0},
\]  

(11)

is the measure of interfacial thickness and \( z_0 \) is the location of \( \rho = (\rho_i + \rho_v)/2 \).

For thinner liquid films, we simulated solid wall as discrete atoms. Solid atoms were arranged in 6 layers of a FCC (111) crystal. An equivalent \( \psi(9,3) \) potential is used beyond the 6th layer. There is a three layer periodicity in FCC (111) plane. Solid-fluid interaction has \( \epsilon_{ef} \) and \( \sigma_{sf} \) as before. The solid-solid interaction is modeled by a Lennard-Jones 12-6 potential with \( \sigma_{ss} = 0.74597\sigma_{ff}, \epsilon_{ss} = 40\epsilon_{ff} \) and \( m_s = 4.8833m_f \). Motion of solid atoms is solved similar to that for the fluid atoms. The potential well depth is such that the lattice is stable.

**RESULTS AND DISCUSSIONS**

**Interfacial Tension of Thin Liquid Film**

Fig. (2) shows the local surface tension profile \( \gamma_{\text{local}} = (\rho_k(z) - \rho_f(z))\Delta z \) as a function of height \( z \) for \( T^* = 0.85 \). Surface tension values are normalized by \( \epsilon_{ff}/\sigma_{ff}^3 \). The equivalent wall potential (9) is specified at \( z^* = 0 \). \( \gamma_{\text{local}} \) is approximately zero in bulk vapor and liquid phases and non-zero at solid-liquid and liquid-vapor interfaces. Fig. (3) shows number density profile of the fluid atoms and we observe layering of liquid atoms near the wall. Density fluctuation in the liquid side decays with increasing \( z \) and asymptotically approaches to the liquid density \( \rho_l \) by \( z = 3 - 5\sigma \). At larger \( z \), we see a smooth transition from liquid to vapor region and density approaches the vapor density \( \rho_v \). Film thickness \( \delta_{f} \) is defined by the point where \( \rho(z) = (\rho_l + \rho_v)/2 \). Integrated surface tension, which is the sum of local surface tension in all bins at smaller height, is plotted in Fig. (3). We measure the liquid-vapor surface tension as the difference of the profile in bulk vapor and bulk liquid region. Tail
correction (10) is added to this simulation result and we obtain the interfacial tension.

First we simulated a thick liquid film ($\delta_f = 15\sigma_{ff}$) adjacent to the solid wall. Liquid and vapor densities are compared with experimental data for liquid Argon and data in the literature [10] at various non-dimensioned temperature in Fig. (4). In Fig. (5), we compare the interfacial tension with thermodynamic correlation (based on experimental data of Argon). This graph shows that interfacial and thermodynamic properties are mainly unaffected at $\delta_f = 15\sigma$.

Fig. (6) shows the variation of liquid and vapor density with film thickness at several temperatures. This shows that liquid and vapor density change very little (less than 5%) near the triple point $T^* = 0.72$. At higher temperatures liquid density differs from the macroscopic value by as much as 20%. Interfacial thickness $d$ is found to increase as system temperature increases. Higher interfacial thicknesses require smaller tail corrections. Change in density and interfacial thickness affects the surface tension, which is shown in Fig. (7). The surface tension does not change much for $\delta_f > 10\sigma$, but for $\delta_f \leq 8\sigma$, surface tension at the interface decreases. This difference is much more pronounced at higher temperatures.

**Interfacial Tension with Few Atoms Adsorbed on the Solid Surface**

For very thin films (1 – 3 molecules thick), no region has the bulk liquid density. In this case a more realistic solid is modeled by 2040 discrete solid atoms in 6 FCC (111) layers and 360 fluid atoms in a doubly periodic box of volume $13.85 \times 14.11 \times 28\sigma^3$. In the temperature range between triple point to critical point, local density ($\rho^*(z)$) of solid atoms is observed to be as high as 150 due to large mass of solid atoms and clustering of solid atoms in every FCC layer. Fig. (8) shows the density profile and integrated surface tension profile in the simulation box as a function of $z^*$ at

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**Figure 2.** Local surface tension profile (at $T^* = 0.85$).

**Figure 3.** Density profile and integrated surface tension profile (at $T^* = 0.85$).

**Figure 4.** Comparison of densities for $\delta_f = 15\sigma$.

**Figure 5.** Comparison of surface tension for $\delta_f = 15\sigma$.
a particular temperature $T^* = 0.847$. We can observe sharp peaks in density profile which corresponds to 6 solid layers. A very thin liquid film ($1 \sim 3\sigma$) forms adjacent to the solid wall and density sharply decays and approaches to the vapor density. For such a thin film, there is in essence only a solid-vapor interface as one to two layers of liquid atoms adsorbed on the solid surface. However, as temperature is increased, liquid density peak decreases. Local surface tension has been integrated along $z$ and is shown in Fig. (8). In the solid atom region, integrated surface tension shows large jumps at the location of each solid layer, due to large density at these layers and high potential well of solid-solid potential function. However, the effective interfacial tension of the solid-vapor interface is $\gamma'$, as shown in Fig. (10), which is the difference between the integrated surface tension value in vapor region and at the location where solid layer ends. It should be noted that $\gamma'$ is a solid-vapor interfacial tension with one to two layers of liquid atoms adsorbed on the solid surface.

If we use an equivalent wall potential for thinner film ($1 \sim 3$ monolayers thick), density profile and integrated surface tension shows deviation from the case of discrete solid atoms. Density and integrated surface tension for this case is shown in Fig. (9) at $T^* = 0.83$. The density of the wall layer fluid is smaller for this case, but we obtain the same vapor density for the both cases. Even if we are using the same number of fluid atoms, we have thicker film for equivalent wall potential case than for discrete solid atoms case. Discrete solid atom modeling is more realistic for a thinner film as fluid and solid atoms interact directly, but it is computationally more expensive. Note that we use a cutoff radius $r_c = 4.5\sigma$ for discrete solid atoms case whereas we use untruncated solid wall-fluid interaction for equivalent wall potential case. The temperature dependence of $\gamma'$ for $\delta^* = 2 \sim 3\sigma$ is plotted in Fig. (10). We observe that interfacial tension decreases with increasing temperature. The shape of the profile is similar to the liquid-vapor interfacial tension for a thick liquid film (Fig. (4)). The presence of two merged interfaces (solid-liquid and liquid-vapor) as the film gets thinner increases the effective interfacial tension of the solid-vapor interface with few fluid atoms adsorbed on it.

**CONCLUSIONS**

We have simulated Lennard-Jones fluid in thermodynamic equilibrium adjacent to an inert solid wall. An external potential field (solid wall in our case) was found to affect the interfacial properties. For thick films, $\delta_f > 40\AA$, we do not see any effect of solid wall. Interfacial and thermodynamics properties were found to be in good agreement with the experimental data. For
thinner films ($\delta_f \sim 15-20\AA$), we found that surface tension and liquid density decreases.

For ultra-thin liquid films, we found that equivalent potential for FCC (111) solid wall underpredicts interfacial tension and liquid density. For a more realistic representation, solid wall was modeled as discrete solid atoms. For films with $\delta_f = 1 \sim 3\sigma$ liquid atoms stacked near the wall atoms and density decayed rapidly to the vapor density. There were no longer distinct solid-

REFERENCES


