

Pressure Analyses at the Planar Surface of Liquid-Vapor Argon by a Test-Area Molecular Dynamics Simulation

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Pressure tensors at the planar surface of liquid-vapor argon are evaluated from the virial theorem, Irving-Kirkwood, and Harasima versions using a test-area molecular dynamics simulation method through a Lennard-Jones intermolecular potential at two temperatures. We found that the normal and transverse components of the pressure tensor, $p_N(z)$ and $p_T(z)$, obtained from the virial theorem and Harasima version are essentially the same. The normal component of the pressure tensor from Irving-Kirkwood version, $p_N^{IK}(z)$, is shown to be a nearly constant at the lower temperature, independent of z , as agreed in a previous study, but not for $p_N^H(z)$, while the transverse components, $p_T^{IK}(z)$ and $p_T^H(z)$, are almost the same. The values of surface tension for both versions computed from $p_N(z) - p_T(z)$ are also the same and are fully consistent with the experimental data.

Key Words : Irving-Kirkwood pressure, Harasima pressure, Test-area simulation method, Surface tension

Introduction

The surface tension between a liquid and its vapor or two coexisting liquids is the key quantity among the other interfacial properties such as coexisting curves of liquid and vapor densities, which is of central importance in understanding capillary rise and the solubilization of immiscible fluids. There are a number of different approaches that can be used in the calculation of the surface tension. Molecular theories of inhomogeneous systems are now well developed¹⁻³ with major advance since the pioneering work of van der Waals⁴ and molecular dynamics simulation techniques are also routinely used to examine inhomogeneous systems.

The most widespread class of technique to determine the surface tension γ involves a mechanical routine which requires the calculation of the tensional components of the pressure.¹ In the case of a planar interface perpendicular to the z axis, the surface tension is given by,

$$\gamma = \int_{-\infty}^{\infty} dz [p_N(z) - p_T(z)], \quad (1)$$

where $p_N(z)$ and $p_T(z)$ are the normal and transverse components of the pressure tensor at position z , respectively: $p_N(z) = p_{zz}(z)$ and $p_T(z) = [p_{xx}(z) + p_{yy}(z)]/2$ at a planar interface. Considering two vapor-liquid interfaces in this test-area molecular dynamics simulation method, γ turns out to be

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} dz [p_N(z) - p_T(z)]. \quad (2)$$

Therefore the accurate evaluation of the normal and transverse components of the pressure tensor, $p_N(z)$ and $p_T(z)$, is essential. The pressure tensor of each slab of width Δz is simply defined from the virial theorem by⁵

$$p_{\alpha\beta}^V(z) = \frac{1}{V} \sum_i p_{i\alpha\beta}(z_i) \delta(z - z_i) \\ = \frac{1}{V} \sum_i [m v_{i\alpha}(z_i) \cdot v_{i\beta}(z_i) + \sum_{j>i} r_{ij\alpha}(z_i) \cdot f_{ij\beta}(z_i)] \delta(z - z_i), \quad (3)$$

where v is the volume of each slab ($v = A \cdot \Delta z$ with the surface area A), p_i is considered as the stress of particle i though the pressure is a property of system⁶ and $\delta(z - z_i)$ is the Dirac delta function. Hence the normal and transverse components of the pressure tensor at position z are given by, respectively,

$$p_N^V(z) = p_{zz}^V(z) \quad (4)$$

and

$$p_T^V(z) = [p_{zz}^V(z) + p_{yy}^V(z)]/2. \quad (5)$$

The pressure tensor of a fluid is the negative of the equilibrium average of the microscopic stress tensor and it is not well-defined in an inhomogeneous fluid.⁷ This is composed of two parts in a fluid of spherical molecules, a kinetic part that arises from the linear momentum of the molecules, and a configurational part that arises from the central intermolecular forces. The first part is well-defined, but in an inhomogeneous fluid the second is not, since there is no unambiguous way of deciding where in the fluid a particular intermolecular force is acting. Similarly, there is no unambiguous way of deciding which molecular pairs contribute to the stress across any microscopic element of area. This ambiguity was first recognized implicitly by Kirkwood, for two different forms of the configurational part of the pressure are to be found in his 1949 paper with Buff⁸ and his 1950 paper with Irving.⁹ The ambiguity was described explicitly by Harasima in 1958,¹⁰ and re-iterated by Ono and Kondo in their review,¹¹ and its implications have been continually explored later on.¹²⁻¹⁴

The Irving-Kirkwood versions⁹ of pressure tensor are

$$p_N^{\text{IK}}(z) = \rho(z)kT - \frac{1}{A} \left\langle \sum_{j>i} \frac{z_{ij}^2}{r_{ij}} u'(r_{ij}) \frac{1}{|z_{ij}|} \theta\left(\frac{z-z_i}{z_{ij}}\right) \theta\left(\frac{z_i-z}{z_{ij}}\right) \right\rangle \quad (6)$$

and

$$p_T^{\text{IK}}(z) = \rho(z)kT - \frac{1}{A} \left\langle \sum_{j>i} \frac{x_{ij}^2 + y_{ij}^2}{2r_{ij}} u'(r_{ij}) \frac{1}{|z_{ij}|} \theta\left(\frac{z-z_i}{z_{ij}}\right) \theta\left(\frac{z_i-z}{z_{ij}}\right) \right\rangle, \quad (7)$$

where k is the Boltzmann constant, A is the surface area, $u(r_{ij})$ is the intermolecular potential, and $\theta(x)$ is the unit step-function. The distance z_{ij} is divided into N_s slabs of Δz and the molecules i and j contribute to the surface tension if the slab contains the line that connects them. Each slab has $1/N_s$ of the total contribution from the i - j interaction.

Harasima's choice of contour^{7,13} gives similarly

$$p_N^{\text{H}}(z) = \rho(z)kT - \frac{1}{v} \left\langle \sum_{j>i} \frac{z_{ij}^2}{r_{ij}} u'(r_{ij}) \delta(z-z_i) \right\rangle \quad (8)$$

and

$$p_T^{\text{H}}(z) = \rho(z)kT - \frac{1}{v} \left\langle \sum_{j>i} \frac{x_{ij}^2 + y_{ij}^2}{2r_{ij}} u'(r_{ij}) \delta(z-z_i) \right\rangle. \quad (9)$$

Unlike the IK version, each slab containing i -th molecule has the total contribution from the i - j interaction.

Test-Area Molecular Dynamics Simulation Method. In a recent paper¹⁵ we performed test-area MD simulations of two states of liquid argon as shown in Table 1. First, the systems of $N = 2400$ argon molecules are fully equilibrated in cubic boxes with the usual periodic boundary condition: The usual Lennard-Jones (LJ) 12-6 potential for the interaction between argon molecules is used with LJ parameters, $\sigma = 0.34$ nm and $\varepsilon/k = 120$ K. The inter-atomic potential is truncated at $r_c = 4\sigma$ and long-range corrections are applied to the energy, pressure, *etc.* due to the potential truncation.¹⁶ The time integrations for the equation of translational motion is solved using the velocity-Verlet algorithm¹⁷ with a time step of 5×10^{-15} second (5 fs). The temperature is kept constant by using a Nose-Hoover^{18,19} thermostat.

Second, in order to simulate the liquid-vapor interface, a slab of well equilibrated systems of liquid argon is placed in between two empty regions. MD simulations are carried out at constant T and volume V in a rectangular box of dimensions $L_x = L_y \approx 4.8\text{--}5.2$ nm according to the system density at a given temperature (see Table 1), and $L_z = 10$ nm with the usual periodic boundary condition of the x -, y -, and z -

Table 1. Two chosen states of liquid argon. L is the length of initial cubic simulation box. ρ_v and ρ_l are the densities of the vapor and liquid phases. z_0 is the position of the Gibbs' dividing surface and d is a parameter for thickness of the interface in Eq. (10). Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis

T (K)	ρ (g/cm ³)	L (nm)	ρ_v (g/cm ³)	ρ_l (g/cm ³)	z_0 (nm)	d (nm)
94.4	1.374	4.8753	0.0122(5)	1.333(4)	2.50(1)	0.337(6)
119.8	1.176	5.1348	0.0649(15)	1.145(4)	2.51(2)	0.548(4)

directions. The equilibrium properties are averaged over 5 blocks of 200,000 time steps after equilibration for 500,000 time steps and the configuration of all the argon molecules is stored every 4 time steps for further analyses. The calculated density profile of each block along the z -direction normal to the interface is not changed with time after equilibration (see Fig. 1).

Results and Discussion

Typical density profiles at two different states of liquid and vapor argon are shown in Fig. 1. A hyperbolic tangent function of the form²⁰

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v) \tanh[(z - z_0)/d] \quad (10)$$

is fitted to the simulation results where ρ_l are ρ_v the densities of liquid and vapor argon in the bulk phases, z_0 is the position of the Gibbs' dividing surface, and d is a parameter for thickness of the interface. The fitted $\rho(z)$ are shown as dashed lines in Figure 1. The liquid and vapor equilibrium densities and the parameters used in Eq. (10) are given in Table 1 for two states of argon.

Since $\mathbf{f}_{ij} = -\frac{r_{ij}}{r_{ij}} u'(r_{ij})$ or $f_{ij\beta} = -\frac{r_{ij\beta}}{r_{ij}} u'(r_{ij})$, Eq. (3) becomes

$$\begin{aligned} p_N^{\text{V}}(z) &= p_{zz}^{\text{V}}(z) = \frac{1}{v} \sum_i \left[m v_{iz}^2(z_i) - \sum_{j>i} \frac{z_{ij}^2}{r_{ij}} u'(r_{ij}) \right] \delta(z-z_i) \\ &= \rho(z)kT - \frac{1}{v} \sum_i \sum_{j>i} \frac{z_{ij}^2}{r_{ij}} u'(r_{ij}) \delta(z-z_i) \end{aligned} \quad (11)$$

So $p_N^{\text{V}}(z)$ are $p_T^{\text{V}}(z)$ essentially equal to $p_N^{\text{H}}(z)$ and $p_T^{\text{H}}(z)$,

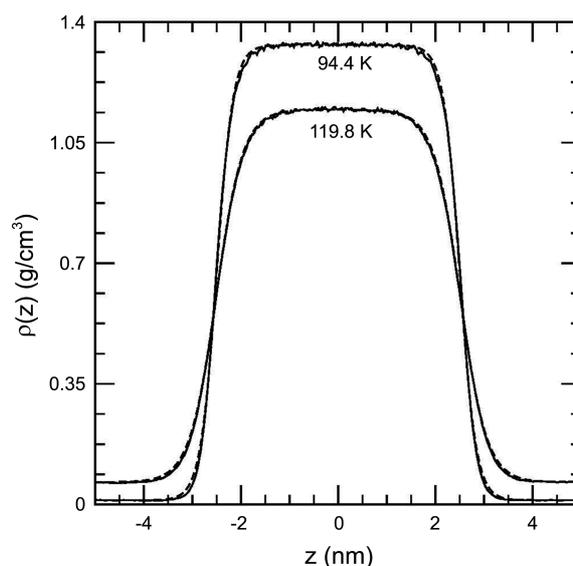


Figure 1. Vapor-liquid density profile, $\rho(z)$ in unit of g/cm³, along the z -direction normal to the interface obtained from MD simulation for two chosen states of liquid argon (94.4 K and 119.8 K). The dashed lines are for the fitted tangent hyperbolic function [Eq. (10)].

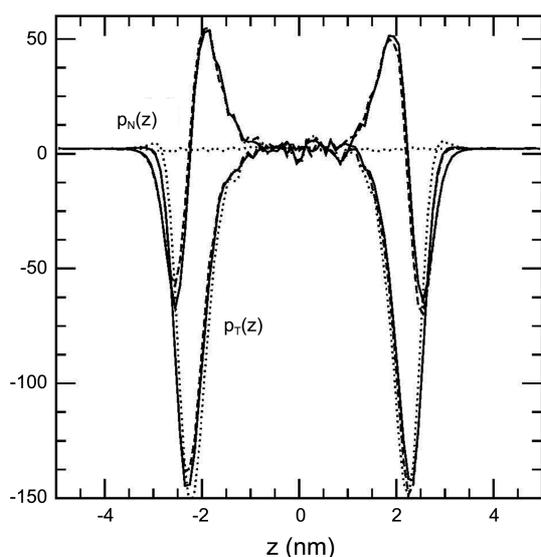


Figure 2. $p_N(z)$ and $p_T(z)$ from the virial theorem (solid lines), Irving-Kirkwood (dotted lines), and Harasima (dashed lines) versions at 94.4 K. The unit of p is [bar].

respectively.

In Figure 2 we present $p_N(z)$ and $p_T(z)$ obtained from the virial theorem (V), Irving-Kirkwood (IK), and Harasima (H) versions at 94.4 K. As discussed above, $p_N^V(z)$ and $p_T^V(z)$ are essentially equal to $p_N^H(z)$ and $p_T^H(z)$, respectively, except the difference between $\frac{1}{V} \sum_i m v_{iz}^2$ and $\rho(z)kT$. Since the vapor pressure is small at the lower temperature (94.4 K), $p_N^{IK}(z)$ is small and nearly constant, independent of z , agreed as in previous studies.^{7,21} However, $p_N^H(z)$ is negative in the interface with a minimum at z_0 , then becomes positive on the gas-side of the interface, and finally decreases as zero in the middle of liquid. The transverse components for both IK and H versions, $p_T^{IK}(z)$ and $p_T^H(z)$, are almost the same with strongly negative regions in the interfaces and zero in the middle of liquid.

The surface tension is defined as the free energy per unit volume. Since there is no external field acting on the plane sheet the pressure is isotropic everywhere except at the surface. In the interface, the change in density along the direction normal to the surface produces an asymmetry in the pressure tensor. It is easy to see from symmetry of the system that the pressure tensor has only two components, $p_N(z)$ and $p_T(z)$. Hydrostatic equilibrium imposes the condition that $p_N(z)$ is everywhere a constant and is equal to the hydrostatic pressure. $p_T(z)$ differs from $p_N(z)$ in the surface zone.

Figure 3 shows $\frac{1}{2} [p_N(z) - p_T(z)]$ and $\gamma(z) = \frac{1}{2} \int_{-\infty}^{\infty} [p_N(z) - p_T(z)] dz$ for all together obtained from the virial theorem (V), Irving-Kirkwood (IK), and Harasima (H) versions at 94.4 K. All the $\frac{1}{2} [p_N(z) - p_T(z)]$ are very similar even though $p_T^{IK}(z)$ and $p_T^H(z)$ are almost the same, and $p_N^{IK}(z)$ is nearly constant and independent of z but not for $p_N^H(z)$. All the $\gamma(z)$ are also very similar. The unit of $\gamma(z)$ is [bar·nm] which is equal to 0.1 [mN/m]. The estimated values of surface tension from the virial theorem (V), Irving-

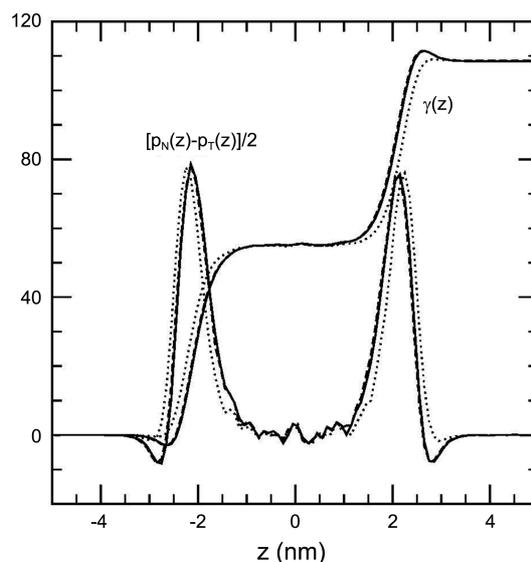


Figure 3. $\frac{1}{2} [p_N(z) - p_T(z)]$ and $\gamma(z) = \frac{1}{2} \int_{-\infty}^{\infty} [p_N(z) - p_T(z)] dz$ from the virial theorem (solid lines), Irving-Kirkwood (dotted lines), and Harasima (dashed lines) versions at 94.4 K. The unit of $\gamma(z)$ is [bar·nm] which is equal to [0.1 mN/m].

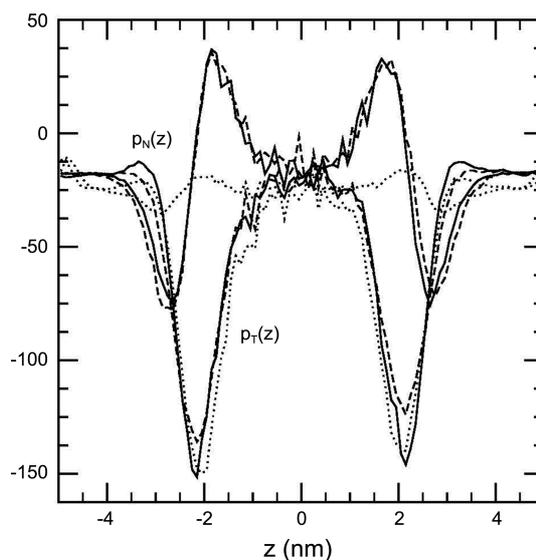


Figure 4. The same as Fig. 2 at 119.8 K.

Kirkwood (IK), and Harasima (H) versions at 94.4 K are 10.84, 10.86, and 10.86 mN/m, respectively, which are in an excellent agreement with the experimental result (10.77 mN/m).²²

The corresponding results at 119.8 K are shown in Figures 4 and 5. $p_N^{IK}(z)$ at 119.8 K is fluctuated a lot as a function of z and it is not constant in the liquid and vapor phases unlike at 94.4 K due to the increased ρ_v (0.0649 g/cm³) at 119.8 K compared with $\rho_v = 0.0122$ g/cm³ at 94.4 K. The estimated values of surface tension from the virial theorem (V), Irving-Kirkwood (IK), and Harasima (H) versions at 119.8 K are 5.23, 5.14, and 5.21 mN/m, respectively, which are also in a good agreement with the experimental result (5.00 mN/m).²²

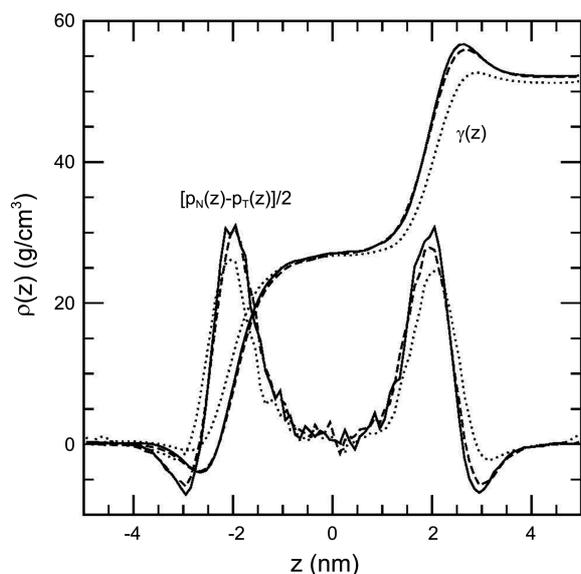


Figure 5. The same as Fig. 3 at 119.8 K.

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