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Studies on the effect of curvature on the surface properties of nanodrops

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ABSTRACT

We present the results from the molecular dynamics (MD) simulations of nanodrops. A thermodynamic based method known as test area simulation method (TASM) developed by Gloor et al. [J. Chem. Phys. 123, 134703 (2005)] is employed to determine the surface tension. The results show that the value of surface tension decreases with the decrease of size of the drop. We have also determined the Tolman's gap and surface entropy of nanodrop–vapor interfaces for a better understanding of curvature effects on surface tension. Both these parameters are found to be size dependent properties. The thermodynamic perturbation theory (TPT) method is employed to validate the size effect of drops on surface tension. Second order approximation of TPT is found to be in good agreement with central difference TASM results.

1. Introduction

For temperatures and pressures below the values at critical point, a fluid can exist in the form of a dense liquid coexisting with its vapor phase. The surface tension of droplet–vapor interface is an important chemico-physical property which plays an important role in the phenomenon such as nucleation, wetting, capillarity, etc. The earliest studies on liquid droplet surrounded by a vapor phase were done by Laplace, wherein it was proved that the surface tension of this liquid–vapor interface is the source for the spherical surface of the droplet [1,2].

According to this theory, when two fluids in equilibrium are separated by a spherical interface of radius R, the pressure of the fluid inside, p^α, differs from that of fluid outside, p^β. The condition for mechanical equilibrium is established by a simple relation given as:

$$\Delta P = p^\alpha - p^\beta = \frac{2\gamma}{R}. \tag{1}$$

The droplet is thus stabilized by a pressure difference over the curved interface which is balanced by the surface tension (γ), that acts as the contracting force. For a planar interface, the surface tension (γ_∞) can be considered as the integral taken over the interface zone (along z-axis) of the differences between the normal (P_N) and tangential pressures (P_T) to the interface [3].

$$\gamma_\infty = \int_{-\infty}^{\infty} [P_N(z) - P_T(z)]dz \tag{2}$$

For a homogeneous phase, the above expression becomes zero, while at the interface the difference in pressure tensor creates the 'surface tension' effect. By hypothetically strip cutting the surface of drop, the above equation can be applied to spherical drops as [4]:

$$\gamma_s = \int_0^\infty \left(\frac{r}{R_s}\right)^2 [P_N(r) - P_T(r)]dr. \tag{3}$$

The effect of the surface curvature on the properties of small drops has been studied previously using MD [5–7]. Studies have shown that the pressure tensor difference can be considered as a function of the drop radius [8,9]. Surface tension values in these studies were obtained using the Kirkwood–Buff relation [3] for the pressure tensor.

However for the above mentioned method, it is necessary to have a description of the interface which remains meaningful on a molecular scale. For planar interfaces, the stress tensor description can be easily applied and most of the studies reported in literature have been obtained using this method. On the contrary, when the interface is curved, the evaluation of stress-tensor becomes tedious, especially at the nanoscale interfaces. Also it is important to understand how the surface energy varies with curvature, which is difficult to be analyzed using pressure tensor methods. Free energy method, based on the thermodynamic definition is thus an alternate option to determine surface tension.

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Thermodynamic based methods are expected to provide better understanding on the effect of the curvature on the surface tension.

Generally, interfaces do not assume planar shape but rather exhibit some curvatures and the magnitude of surface tension is affected by interfacial curvature. Hence the concept of Tolman's length (δ_L) is used, which is defined as the extent by which the surface tension of a small liquid drop (γ_s) deviates from its planar value (γ_∞).

From the Gibbs–Tolman–Koening–Buff equation:

$$\frac{1}{\gamma_s}\frac{d\gamma_s}{dR_s} = \frac{\frac{2\delta_G}{R_s^2}\left[1+\frac{\delta_G}{R_s}+\frac{1}{3}\left(\frac{\delta_G}{R_s}\right)^2\right]}{1+\frac{2\delta_G}{R_s}\left[1+\frac{\delta_G}{R_s}+\frac{1}{3}\left(\frac{\delta_G}{R_s}\right)^2\right]} \tag{4}$$

where δ_G is known as the Tolman's gap and is defined as: $\delta_G = R_e = R_s$. The Tolman's gap is a function of surface of tension (R_s) and temperature. This surface of tension is the distance parameter at which Laplace equation (Eq. (1)) is satisfied. The equimolar radius (R_e) is the location of the equimolar dividing surface, where the density becomes the average of bulk gas (ρ_{gas}) and bulk liquid densities (ρ_{liq}). The equimolar radii of the drop are calculated using the formula:

$$R_e^3 = \frac{1}{\rho_{gas} - \rho_{liq}} \int_0^\infty r^3 \frac{d\rho(r)}{dr} dr \tag{5}$$

While the Tolman's length is related to Tolman's gap by the relation:

$$\delta_L \equiv \lim_{R_s \to \infty} \delta_G \equiv \lim_{R_s \to \infty} (R_e - R_s). \tag{6}$$

The Tolman's gap δ_G and the Tolman's length δ_L are of nanoscale dimensions.

The final expression can be reduced as:

$$\frac{\gamma_s}{\gamma_\infty} = \frac{1}{1+\frac{2\delta_L}{R_s}} + \ldots = 1 - \frac{2\delta_L}{R_s} + \ldots \tag{7}$$

where γ_∞ is the surface tension for planar interfaces.

It is difficult to estimate Tolman's length experimentally. Its dependence on temperature and its sign is still a matter of controversy.

For example, in the case of a macrodroplet or gas bubble, whether their surface tension is greater or less than the planar one, it is still an open question. Similarly for LJ fluids and the like, the classical density-functional theory (DFT) predicts $\delta_L < 0$ [10,11], whereas molecular dynamics simulation studies [6,12] and other semi-phenomenological theories [13] show that $\delta_L > 0$.

In this study, a series of MD simulations in which nanodroplets of different radii, surrounded by a saturated vapor phase, are studied. We have employed test area simulation method (TASM) [14], which is a thermodynamic based approach, to predict the surface tension and Tolman's gap of drops. Attempts have been made to validate the results using thermodynamic perturbation theory (TPT). Details of TASM and the MD simulation methodology are presented in the following sections. The included studies on TPT and surface entropy enabled a better understanding of curvature effect on surface tension and explore subtle effects of curvature free energy.

2. Methodology

2.1. TASM

The thermodynamic approach involves calculating the thermodynamic free energy difference between two systems to estimate the interfacial tension. Using TASM [14], which calculates free energy affected by slight perturbation of the reference system, the interfacial tension is calculated. In this method, the change in free energy was evaluated from the perturbation of the systems without affecting properties of reference system. Liquid–vapor interfacial tension (γ_{vl}) is thus measured by estimating the change in free energy for an infinitesimal change in area.

Finite difference techniques such as forward, backward and central difference (CD) can be used for calculating this derivative. The use of a CD approximation has been found to improve the accuracy of the computed surface tension [14]. It also allows one to circumvent the problem associated with an asymmetry in the free-energy differences which is inherent in systems of particles interacting through discontinuous potentials. For implementing the test-area method using central difference method, three simulation cells are required, each constructed with an equal number of molecules, but different surface areas. The first step of this method is to simulate a system equilibrated to a reference state system 0 with interfacial area A_0. A test-area change is then performed to generate two perturbed state systems such that $A_1 = A_0(1 + \Delta A)$ and $A_2 = A_0(1 - \Delta A)$ keeping overall volume of the system a constant.

From the thermodynamic definition of interfacial tension [1]:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{NVT} \tag{8}$$

where ∂F is the free energy change associated with area change ∂A. The change in free energy ΔF can be expressed in terms of system change 0 → 1 as:

$$\Delta F_{0\to 1} = F_1 - F_0 = -kT \ln\left(\frac{Q_1}{Q_0}\right) \tag{9}$$

where Q represents the partition function.

The partition function ratio can be written as:

$$\frac{Q_1}{Q_0} = \frac{z_1}{z_0} = \frac{\int dr^N \exp(-U_1/kT)}{\int dr^N \exp(-U_0/kT)} \tag{10}$$

where U is the configuration energy and z is the configuration integral. For a closed system, this U is the Hamiltonian of the system.

$$\frac{z_1}{z_0} = \frac{\int dr^N \exp(-U_0/kT)\exp(\Delta U/kT)}{\int dr^N \exp(-U_0/kT)} \tag{11}$$

$$\frac{z_1}{z_0} = \langle exp(-\Delta U/kT)\rangle_0 \tag{12}$$

where $\Delta U = U_1 - U_0$..

The central difference approximation for the interfacial tension can be written as:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{CD} = \frac{f(F_0 + \Delta F) - f(F_0 - \Delta F)}{2\Delta A}. \tag{13}$$

Thus for the changes in configuration energy of these perturbations denoted by $\Delta U^+ = U(A + \Delta A) - U(A)$ and $\Delta U^- = U(A - \Delta A) - U(A)$, respectively, the interfacial tension can be obtained from the expression as follows:

$$\gamma = \lim_{\Delta A \to 0} \frac{-kT}{2\Delta A}\left(\ln\left\langle \exp\left(-\frac{\Delta U^+}{kT}\right)\right\rangle - \ln\left\langle \exp\left(\frac{\Delta U^-}{kT}\right)\right\rangle\right). \tag{14}$$

2.2. Molecular dynamics (MD)

We have performed MD simulations [15–17] to model the system for estimating the nanodrop–vapor interfacial tension. The LAMMPS [18] package was utilized for the simulations. A monoatomic LJ