Computation of surface tension of small droplets by the molecular dynamics method

G.V. Kharlamov,[1,2] A.A. Onishchuk,[2] P.A. Purtov,[2,5] S.V. Vosel',[2,3] and A.V. Bolesta[4]

[1]*Novosibirsk State Technical University*
[2]*Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk*
[3]*Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk*
[4]*Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk*
[5]*Novosibirsk State University*

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Systematical calculations of the small droplets' surface tension of the Lennard–Jones liquid have been performed depending on the equimolar radius (R_e) and temperature (T) by the method of molecular dynamics. The surface tension was shown to decrease with decreasing droplet's equimolar radius up to zero for a certain temperature dependent R_0. The ratio of the surface tension of a droplet to the surface tension of a plane liquid–vapor boundary (σ/σ_∞) is a universal function of the ratio of the droplet equimolar radius to R_0. Approximation formulae for functions $\sigma/\sigma_\infty = f(R_e/R_0)$ and $R_0(T)$ are proposed.

Introduction

Surface tension of small droplets plays a decisive part in the classic nucleation theory and its numerous modifications.[1] These theories are permanently used in interpretations of experimental data, but the results obtained are often unsatisfactory. This is associated with the concept of inapplicability of the surface tension concept to small droplets. J.W. Gibbs, who had brought in common use the notion of the tension surface, meant that the concept of surface tension is applicable even to the smallest droplets until the tension surface radius is positive.[2] With decrease of the droplet size, both the radius of the tension surface and the surface tension decrease and vanish simultaneously. Thus, the droplets' surface tension depends on their radius.

Based on thermodynamic considerations, R.C. Tolman has described the surface tension as a function of radius[3]:

$$\frac{\sigma}{\sigma_\infty} = \frac{1}{1 + 2\delta/R_s}, \qquad (1)$$

where σ, σ_∞ are surface tensions of a droplet and of a plane surface "liquid–gas"; R_s is the tension surface radius; $\delta = R_e - R_s$ is the difference between the equimolar radius and R_s. The formula (1) is often used in interpretations of experimental data within the framework of the classical nucleation theory (see, for instance, Ref. 4). However, this formula is applicable only to large droplets, for which δ weakly depends on R_s. In this connection, a problem arises of exact determination of surface tension as a function of the droplet radius.

To solve this problem, the methods of direct numerical simulation, Monte Carlo and molecular dynamics, are most adequate. The method of molecular dynamics is used for a long time in calculations of surface tension of a plane surface "liquid–gas,"[5] as well as in calculations of surface tension of liquid droplets.[5–10] In Refs. 6 and 7, in fact, the foundations of the technique of the molecular-dynamics calculations of the surface tension of small droplets were laid, therefore, they are of particular interest. At the same time, all these calculations can be performed only in a narrow region of the system parameters and fail to determine accurately the dependence of the droplet surface tension on the radius. Besides, these methods do not take into account the applicability of the concept of the surface tension to droplets of a small radius.

In this paper, we present systematic calculations of surface tension of small droplets by the method of molecular dynamics. The calculations were performed in a wide range of the system temperatures and sizes and allowed some generalizations. The limit of applicability of the concept of surface tension to droplets of a small radius has been established.

Computation technique

The surface tension of the plane boundary "liquid–gas" was calculated by the formula

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$$\sigma = \int_{-\infty}^{\infty} (P_N - P_T) dz, \quad (2)$$

where P_T and P_N are the tangential and normal components of the pressure tensor with respect to the interface; the axis z is perpendicular to the surface. The components of the pressure tensor were calculated by the well-known formulae of statistical physics.[5] A plane liquid layer surrounded by vapor and dividing a rectangular cell into two parts was created. The cell contained 4500 molecules.

Surface tension of droplets was calculated by the method of molecular dynamics using a cubic cell containing from 70 to 4500 particles under periodic boundary conditions. The pressure tensor $\mathbf{P}(\mathbf{r})$, radius of the tension surface R_s, and surface tension of droplets σ were calculated by the formulae[5,6]:

$$\mathbf{P}(\mathbf{r}) = \mathbf{e}_r \mathbf{e}_r P_N(r) + (\mathbf{e}_\theta \mathbf{e}_\theta + \mathbf{e}_\varphi \mathbf{e}_\varphi) P_T(r);$$

$$\sigma = \int_0^{\infty} \left(\frac{r}{R_s}\right)^2 [P_N(r) - P_T(r)] dr,$$

$$\sigma = \int_0^{\infty} \left(\frac{r}{R_s}\right)^{-1} [P_N(r) - P_T(r)] dr;$$

$$P_N(r) = kT n(r) - \frac{1}{2} \int d\mathbf{r}_{12} \frac{(\mathbf{r}_{12} \cdot \mathbf{e}_r)^2}{r_{12}} u'(r_{12}) \times$$

$$\times \int_0^1 d\alpha \rho^{(2)}(r_{12}, |\mathbf{r} - \alpha \mathbf{r}_{12}|), \quad (3)$$

$$P_T(r) = kT n(r) - \frac{1}{2} \int d\mathbf{r}_{12} \frac{(\mathbf{r}_{12} \cdot \mathbf{e}_\varphi)^2}{r_{12}} u'(r_{12}) \times$$

$$\times \int_0^1 d\alpha \rho^{(2)}(r_{12}, |\mathbf{r} - \alpha \mathbf{r}_{12}|).$$

The last two formulae correspond to the Irving–Kirkwood pressure tensor. Here $n(r)$ is the concentration of gas or liquid molecules; $\rho^{(2)}(r_{12}, |\mathbf{r} - \alpha \mathbf{r}_{12}|)$ is the paired configuration function of molecules, occurring at the distance r_{12} from each other. The line, which joins these two molecules, goes through the point $\mathbf{r}$ and is divided by it in the ratio $\alpha/(1 - \alpha)$; $u'(r_{12})$ is the derivative of the paired interaction potential of two molecules; $\mathbf{e}_r$, $\mathbf{e}_\theta$, $\mathbf{e}_\varphi$ are the unit vectors in the spherical coordinate system. Temperature T, concentration $n(r)$, and the integrals entering the formulas (3) for the pressure components were computed by the method of molecular dynamics.[5–7]

We used the paired interaction potential, which is the Lennard–Johns potential, "truncated" by a spline[11,12]:

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6} \right], \text{ if } r \le 4.5\sigma_0,$$

$$u(r) = a(r - 5\sigma_0)^2 + b(r - 5\sigma_0)^3, \text{ if } 4.5\sigma_0 \le r \le 5\sigma_0,$$

$$u(r) = 0, \text{ if } r \ge 5\sigma_0. \quad (4)$$

The constants a and b were chosen from the condition of sewing together of the potential and its derivatives at the point $r = 4.5\sigma_0$. All the calculations were performed at average density $\rho = N/V = 0.066143$ in the cell; N is the number of particles in the cell; $V = L_x L_y L_z$ (L_x, L_y, L_z are the cell sizes in σ_0 units).

The initial state of a droplet was formed as follows. The particles were placed in the nodes of a face-centered lattice in the cell center in a deep spherical potential well. Certain velocities were assigned to them in the correspondence with a given temperature. After several thousands of time steps, a spherical droplet was formed in the cell center. Then the potential barrier was removed and the particles gradually occupied the whole volume of the cell at a given temperature. This procedure resulted in an equilibrium system consisting of a liquid droplet in the cell center and vapor, occupying the remaining space. The droplet size depended on the number of particles in the cell and the temperature.

For the produced droplets, the profiles of density, pressure tensor, energy, and temperature were calculated as functions of the distance to the droplet center. The droplet center was sought as the mass center of particles having three or more particles in their nearest neighborhood ($r \le 1.5\sigma_0$). The origin of coordinates was placed in the droplet center, and the whole cell space was divided into 210 spherical layers. In each 20 time steps, the number of particles, energy, and temperature in every layer were calculated, as well as normal and tangential components of pressure at the layer boundaries. The total time of one computation took not less than $1.6 \cdot 10^7$ time steps. P_N was computed by the formulae (3) according to the technique described in Ref. 7. P_T was also computed by the formula (3) in contrast to Ref. 7, where the condition of mechanical equilibrium of a droplet was taken into account.

In all calculations the reduced variables were used[11]: distance $r = r^*/\sigma_0$, temperature $T = kT^*/\varepsilon$, energy $U = U^*/\varepsilon$, density $\rho = \rho^* \sigma_0^3$, time $t = t^*/\sigma_0 (\varepsilon/m_0)^{1/2}$, pressure $p = p^* \sigma_0^3/\varepsilon$, surface tension $\sigma = \sigma^* \sigma_0^2/\varepsilon$, where ε and σ_0 are parameters of the Lennard–Jones potential, m_0 is the molecular mass.

The variables, marked by the asterisk, are dimensional. The following reduced temperatures T: 0.65; 0.7; 0.75; 0.8; 0.85; 0.9; and 0.95 were used in calculations. The calculation error for surface tension did not exceed 3%.

Results of calculations and discussion

Figure 1*a* presents typical density profiles $\rho(r)$ of a droplet. Equimolar droplet radii were calculated on the base of these profiles by the formula[7]:

$$R_e^3 = \frac{1}{\rho_g - \rho_l} \int_0^{\infty} r^3 \frac{d\rho(r)}{dr} dr, \quad (5)$$

where ρ_l, ρ_g are densities in the droplet center and in gas, respectively.

Figure 1*b* presents components of the pressure tensor as typical functions of the distance from the droplet center. These functions were used to calculate radii of the tension surface and the surface tension of droplets by formulae (3). The results of calculations are presented in Fig. 2.

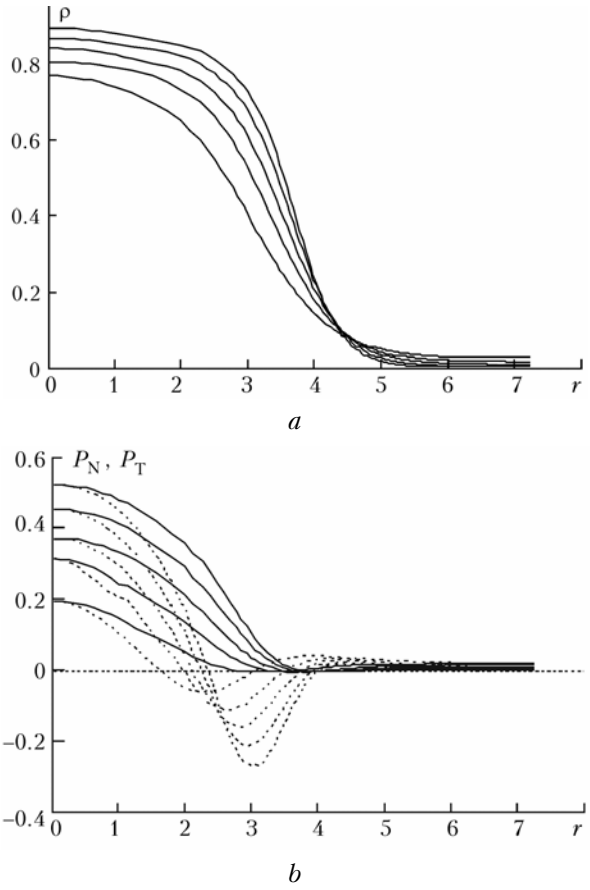

Fig. 1. Profiles of density (*a*) and components of the pressure tensor (*b*) for a system containing $N = 200$ molecules in the cell, $T = 0.65$; 0.7; 0.75; 0.8; 0.85 (from top to bottom). Solid lines correspond to P_N, dashed lines to P_T.

Figure 2*a* presents surface tension as functions of equimolar radius of droplets. With growing radius of droplets the surface tension tends to a limit, corresponding to surface tension of the plane boundary "liquid–vapor" at a given temperature. Surface tension of droplets strongly decreases with the decrease of radius and becomes zero at a certain equimolar radius R_0, whose value depends on the temperature. Note that the radius of the tension surface R_s also becomes zero in correspondence with the Gibbs remark.[2] However, in agreement with Gibbs supposition,[2] the droplet does not vaporize in this case and no qualitative changes can be seen in density profiles and components of the pressure tensor even for droplets characterized by formally negative surface tension. For instance, the curves corresponding to $T = 0.85$ (lower curves in Fig. 1) refer to a droplet with negative surface tension.

Figure 2*b* presents droplet surface tension as functions of temperature at constant equimolar radii. The upper boundary refers to surface tension of the plane boundary "liquid–vapor" calculated by formula (2) for a plane layer of a liquid. This function can be well approximated in a given range of temperatures by the straight line $\sigma_\infty = 2.5421 - 2.1202T$. Droplets of large equimolar radius show the similar temperature dependence, but the straight lines lay somewhat lower. There exists such a temperature for small droplets, at which the surface tension becomes negative. This temperature is much lower than the critical temperature of the system.

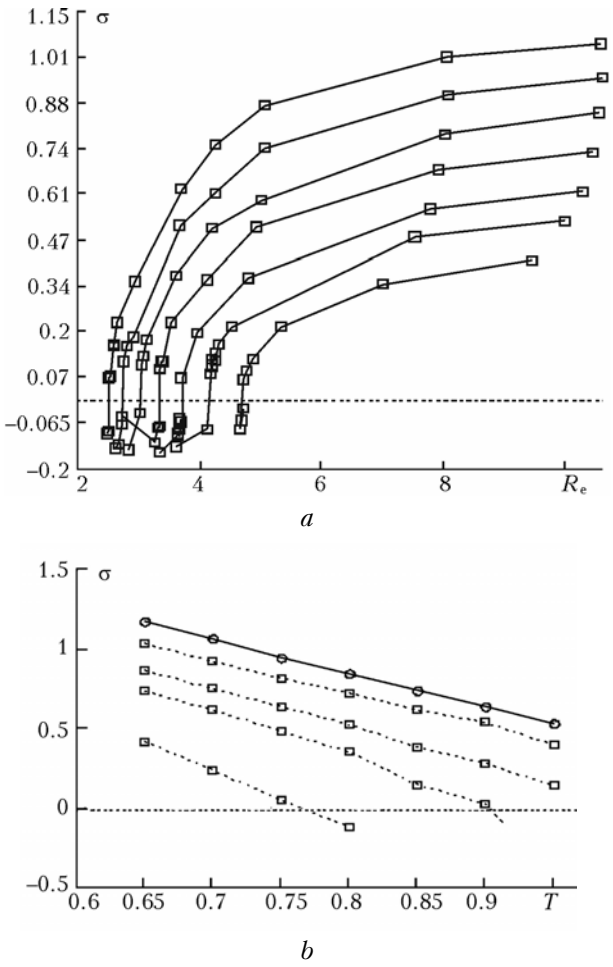

Fig. 2. Surface tension of droplets (σ) as a function of equimolar radius (R_e) at constant temperature ($T = 0.65$; 0.7; 0.75; 0.8; 0.85; 0.9; 0.95 from top to bottom) (*a*) and of temperature (T) at constant equimolar radius ($R_e = \infty$; 10; 5; 4; 3 from top to bottom) (*b*).

The presented results allow some generalization. For instance, if to assume σ/σ_∞ as a function of the R_e/R_0, then the points, corresponding to different temperatures, lay onto the same curve (Fig. 3*a*).

This means that the relation between surface tension and equimolar radius of a droplet is of universal character.

Approximation of this function by the polynomial of third degree R_0/R_e has the form

$$\frac{\sigma(R_e)}{\sigma_\infty} = 1 - 0.519\frac{R_0}{R_e} + 0.426\left(\frac{R_0}{R_e}\right)^2 - 0.907\left(\frac{R_0}{R_e}\right)^3. \quad (6)$$

Figure 3*b* presents R_0 as a function of temperature, which is well approximated by the expression

$$R_0 = 0.768 + \frac{0.963}{1.199 - T}. \quad (7)$$

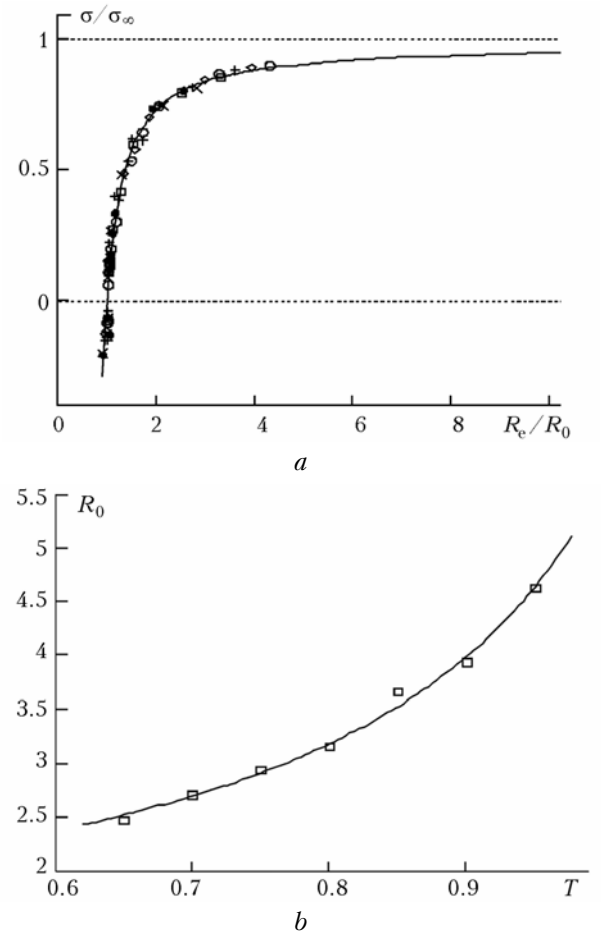

Fig. 3. The ratio of surface tension of a droplet to surface tension of a plane surface (σ/σ_∞) as a function of the ratio of equimolar radius to R_0 (*a*); and R_0 as a function of temperature (*b*). *a*: $T = 0.65$(°); 0.7(◊); 0.75(+); 0.8(□); 0.85(×); 0.9(•); 0.95(+); the solid line is the function (6); *b*: □ denotes the results of MD calculations, the solid curve is the function (7).

This approximation was selected so that R_0 become infinite at a critical temperature $T_c \approx 1.199$, because even the plane boundary "liquid–vapor" disappears at this temperature.

Recently, an experimental work on measuring nucleation rate of argon in a pulse cryogenic chamber at a temperature from 42 to 58 K appeared,[13] in which the critical nucleus size was estimated by the Gibbs–Thomson formula

$$n_{GT} = \frac{32\pi}{3}\frac{v_l^2\sigma^{*3}}{(kT^*\ln S)^3}. \quad (8)$$

Here n_{GT} is the number of molecules in the critical nucleus; v_l is the volume of a molecule; $S = p^*/p_e^*$ is the vapor supersaturation; σ^* is the surface tension of the critical nucleus; it was taken equal to surface tension of the volume liquid phase. Variables in formula (8) are dimensional. The following values of n_{GT} were obtained: 80 at $T^* = 58$ K; 40 at $T^* = 42$ K. The estimates made by formula (7) demonstrate that values of R_0 for argon ($\varepsilon/k = 120$ K) are 2.33 and 1.9, respectively, at these temperatures. By our estimates, the density of the liquid in the droplet center under these conditions is 0.82. If R_{GT} is defined in correspondence with the formula $n_{GT} = 4/3\pi(R_{GT})^3\rho_l$, then values of R_0 for these temperatures is 2.86 and 2.27, respectively. Using Eq. 6, we obtained 0.368 and 0.33 for σ/σ_∞. Evidently, that the application of formula (8) is incorrect in estimations of the critical nucleus size. The decrease of the surface tension of the critical nucleus as compared to σ_∞ should be taken into account.

In Ref. 14, nucleation of argon was studied by the method of molecular dynamics. The size of critical nuclei was estimated by models, which include the concept of the surface tension. It was found that the size of the critical nucleus varied from 11 to 28 atoms in the temperature range from 45 to 70 K. These values lead to "negative" surface tension of the critical nucleus. Thus, the concept of surface tension in this case is inapplicable to estimation of the critical nucleus size.

Although the concept of surface tension can be used in building the nucleation theory in some cases, it is necessary to be careful in its application. The calculation methods dealing with formation of critical nuclei in the process of nucleation should be developed, which do not use the droplet model.

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