About applicability of thermodynamic parameters to small drops and clusters

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Abstract. In our paper the results of molecular dynamics calculations of nanodrops are presented. The density profiles, the Irving-Kirkwood pressure tensors, the chemical potentials of the systems, the equimolar radii of the drops and the radii of tension, the mechanical and thermodynamic surface tensions have been calculated. It is shown that both the mechanical and thermodynamic surface tensions decrease with the decrease of the equimolar radius of the drop and reach zero at the same \( R_0 \) depending on temperature. With the further equimolar radius decrease the surface tension becomes negative. It means that such droplet is metastable and that the notion of the macroscopic surface tension cannot be applied to such small drops. The dependence of the ratio of the drop surface tension to the surface tension of the flat liquid-vapor interface on the ratio of the drop equimolar radius to \( R_0 \) is a universal function.

1. Introduction

Thermodynamic description of nanodrops is a very important physical problem. There is a problem of applicability of thermodynamic parameters to small drops and clusters as the parameters are macroscopic thermodynamic notions, but nanodrops are microscopic systems. One of such parameters is the surface tension. J. Gibbs pointed out that the surface tension of a droplet (\( \sigma \)) must decrease with the decrease of the droplet tension surface radius (\( \sigma R \)) so that at \( R = 0 \) the surface tension must be also equal to zero (\( \sigma = 0 \)) [1]. At the same time the equimolar radius of the droplet (\( R_0 \)) is not equal to zero. Consequently, the notion of the surface tension cannot be applied to such droplets.

2. Thermodynamics of drops

The surface tension concept in thermodynamics is propounded by J. Gibbs and is conventional [1]. In accordance with J. Gibbs the additional term \( \sigma dA \) (\( \sigma \) is the surface tension, \( dA \) is a change of a liquid surface area) is introduced in fundamental thermodynamic equations. For example, such equation for the internal energy of the system consisting of a liquid drop and vapor has the usual form

\[
dU = T dS - P_i dV_i - P_v dV_v + \sigma dA + \mu dm .
\]
Here \( dU \), \( dS \), and \( dm \) are changes of the internal energy, entropy, and mass of the whole system, \( dV_l \) and \( dV_v \) are changes of the volumes of the liquid droplet and the vapor, \( dA \) is a change of the drop surface area, \( P_l \), \( P_v \) are the pressures in the drop and in the vapor, \( T \) is the system temperature, \( \mu \) is the chemical potential of the system.

Thus, such surface tension \( \sigma \) determines additional to the thermodynamic potentials energy related to a liquid surface area change and is called the thermodynamic surface tension. In addition to surface tension, J. Gibbs introduced a dividing surface which is termed as a tension surface. It is a mathematical surface, to which the forces of the surface tension are applied. At the thermodynamic description of the systems with flat interfaces of liquid – vapor, the position of the tension surface has no importance, but there is a problem of choice of the tension surface for curved interfaces.

For the system, consisting of a liquid drop surrounded by natural vapor, the value of the surface tension depends on the choice of the tension surface position. J. Gibbs suggested choosing the tension surface so that the surface tension had the minimum value. The Gibbs model assumes that the droplet is a sphere with a radius of the tension surface. Inside the sphere there is a liquid medium with the properties of a bulk liquid. Sometimes this medium is called the comparison phase. The chemical potential of this phase coincides with the chemical potential of the vapor surrounding the sphere. Thus, the pressure, density, and temperature in the droplet are equal to the pressure, density, and temperature in the bulk liquid at the same chemical potential. The tension surface of the drop generally does not coincide with the equimolar surface; therefore the part of the system mass does not belong to any of two phases and is the part of the substance adsorbed on the interface. The difference between the tension surface radius and the equimolar surface radius is determined by the parameter \( \delta = R_e - R_s \) which is called the Tolman length [2]. The difference of the pressures between the comparison phase and the surrounding vapor obeys the Laplace formula

\[
P_l - P_g = 2\sigma/R_s,  \tag{2}
\]

where \( P_l \) and \( P_g \) are the pressures of the liquid in the comparison phase and the vapor respectively. The choice of the pressure and density of the liquid in the comparison phase is arbitrary. The values of \( \sigma \), \( R_s \) and also the equimolar radius \( R_e \) will be changed according to this choice.

On the other hand, there is a mechanical definition of the surface tension [3, 4] connected with the substitution of the continuous droplet pressure profile by the step one. The pressure tensor of a drop has the spherical symmetry

\[
P(r) = e_r s_r P_N(r) + (e_\theta e_\theta + e_\phi e_\phi)P_\theta(r),  \tag{3}
\]

where \( P_N(r) \) and \( P_\theta(r) \) are the normal and tangential pressures.

The mechanical surface tension is obtained from the pressure tensor by [3, 4]

\[
\sigma = \int_0^\infty (r/R_s)^2 (P_N(r) - P_\theta(r)) \, dr.  \tag{4}
\]

Since \( R_s \) is unknown beforehand in this formula, it is necessary to have one more equation determining \( R_s \). In papers [4, 5] it is suggested to use the equation

\[
\sigma = \int_0^\infty (R_s/r)^2 (P_N(r) - P_\theta(r)) \, dr  \tag{5}
\]
which is derived from the Buff’s equations based on the mechanical equilibrium conditions of the system. Using the equations (4) and (5), it is possible to calculate $R_s$ and $\sigma$ if we know the profiles of the pressure tensor components $P_n(r)$ and $P_t(r)$.

It is not obvious in advance that the surface tension calculated by formulae (4) and (5) will coincide with the thermodynamic surface tension used in (1). Here there is a problem of relation of the surface tension determined by formulae (4) and (5) to the Gibbs model of the surface tension.

3. Simulation and results

In this work, the thermodynamic properties of droplets were calculated by the molecular dynamics method. The calculations were made for the system containing 60 – 4500 molecules in a cubic cell with periodic boundary conditions. Interaction between the molecules was specified by the Lennard-Jones potential. A special procedure was used to obtain an equilibrium system composed of a liquid drop in the center of the cell and vapor occupying the remaining space. The size of the drop depended on the number of particles in the cell and the mean density of the system. The Irving-Kirkwood pressure tensor was calculated by the formulae of statistical mechanics [4]. The density profiles, chemical potential of the system, equimolar and surface tension radii of drops, mechanical and thermodynamic surface tensions, and Tolman length, $\delta$, were calculated.

Reduced variables were used: distance $r = r^*/r_0$, temperature $T = kT^*/\varepsilon$, energy $U = U^*/\varepsilon$, density $\rho = \rho^*/\rho_0$, time $t = t^*/(\varepsilon/m_0)^{1/2}$, pressure $p = p^*/\varepsilon$, surface tension $\sigma = \sigma^*/\varepsilon$, and chemical potential $\mu = \mu^*/\varepsilon$. Here $\varepsilon$ and $r_0$ are the Lennard-Jones potential parameters, $m_0$ is the molecule mass. The variables labeled by an asterisk are dimensional. The calculations methods of the mechanical and thermodynamic surface tensions were discussed in our papers [6 – 8].

*Figure 1.* The dependence of the mechanical (□) and thermodynamic (+) surface tensions on the equimolar radius $R_s$ at the temperature $T = 0.65$

*Figure 2.* The dependence of $R_0$ on the temperature. The solid line is the dependence (7)

Figure 1 presents the mechanical and thermodynamic surface tension dependences on the drop equimolar radius. Significant decrease of both mechanical and thermodynamic surface tension can be observed with $R_s$ decrease. Both surface tensions equal zero at a certain equimolar radius $R_0$. This radius corresponds to the drop containing about 50 molecules. The radius of the tension surface $R_s$ also equals zero. The surface tension becomes negative at the further equimolar radius decrease though the drop holds stability in the conditions of the numerical experiment. Figure 1 shows that the thermodynamic surface tension coincides with the mechanical one for relatively big drops containing
2000 and more molecules. For the drops containing smaller quantity of molecules, the thermodynamic surface tension exceeds the mechanical one up to their disappearance at $R_e = R_0$.

It has been established in our papers [6 - 8] that the dependence of the nanodrops mechanical surface tension on the equimolar radius is a universal function relative to the temperature, at which the numerical experiment is conducted. It has been found that approximation of this dependence by the polynomial of the ratio $R_e/R_0$ can be expressed as follows

$$\sigma(R_e) = \sigma_\infty \left[1 - 0.519 \cdot (R_e/R_0) + 0.426 \cdot \left((R_e/R_0)^2\right) - 0.907 \cdot \left((R_e/R_0)^3\right)\right].$$

(6)

In addition, the drop equimolar radius $R_0$, at which $\sigma = 0$, greatly depends on the temperature and becomes infinite in the point equal 1.199 (see figure 2). The approximation of the dependence of $R_0$ on the temperature can be expressed by the fit

$$R_0 = 0.768 + \frac{0.963}{1.199 - T}.$$  

(7)

The surface tension of the flat dividing surface of liquid – vapor $\sigma_\infty$ also depends on the temperature and becomes zero in the same point.

The thermodynamic surface tension dependence on the equimolar radius $R_e$ is similar in its quality to that of the mechanical surface tension though it differs a little in its quantity. For relatively large drops, the surface tension approaches the value of the surface tension of the flat dividing surface. For quite small drops, the surface tension becomes zero or even negative. But the drop does not evaporate at these conditions. If the number of molecules in the simulation cell is increased at the same pressure, the drop will evaporate after all. It leads to the increase of fluctuations of the force acting on the nanodrop from the vapor. That’s why the state of a nanodrop with a negative surface tension can be considered as a metastable one in respect of small fluctuations.

On the other hand, the negative surface tension and negative radius of tension surface $R_e$ have no physical meaning and become formal mathematical parameters of the model. Apparently, it testifies that the notion of surface tension, which is used in macroscopic theory, cannot be applied to such small drops. The limit of applicability of the surface tension concept to the droplets changes from about 50 molecules at $T = 0.65$ to about 300 molecules at $T = 0.95$.

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References

[1] Gibbs J W 1928 Thermodynamics. The Collected Works Vol. I. (Longmans, Green. New York)

[2] Tolman R C 1949 J. Chem. Phys. 17 333.

[3] Ono S, Kondo S 1960 Molecular Theory of Surface Tension in Liquids (Springer – Verlag, Berlin – Gottingen – Heidelberg)

[4] Rowlinson J S, Widom B 1982 Molecular theory of capillarity (Clarendon Press, Oxford)

[5] Thompson S M, Gubbins K E, Walton J P R B, Chantry R A R, Rowlinson J S 1984 J. Chem. Phys. 81 530.

[6] Kharlamov G V, Onischuk A A, Purtov P A, Vosel S V, Bolesta A V 2008 Atmospheric and Oceanic Optics, 21 679 (in Russian).

[7] Kharlamov G V, Onischuk A A, Purtov P A, Vosel S V, Bolesta A V 2010 e-Journal of Surface Science and Nanotechnology, 8 197.

[8] Kharlamov G V, Onischuk A A, Vosel S V, Purtov P A 2011 Colloids and Surfaces A379 10.