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# THERMODYNAMIC PROPERTIES OF NANODROPS. MOLECULAR DYNAMICS SIMULATIONS

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## ABSTRACT

The results of the structural and thermodynamic properties simulations of the nanodrops, which emerge on the first stage of nanoparticle formation process by supersaturated vapor condensation, 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. The radii of tension also reach zero. With the further equimolar radius decrease the surface tension becomes negative, though the drop holds stable in the conditions of the numerical experiment. It means that such droplet is metastable. Apparently, it testifies that the notion of surface tension which is used in macroscopic theory can not be applied to such small drops. The dependence of the ratio of the surface tension of the drop to the surface tension of the flat surface liquid-vapor on the ratio of the equimolar radius of the drop to $R_0$ is a universal function.

## INTRODUCTION

An effective method of nanoparticles production is condensation of the particles from supersaturated vapor. For this purpose some solid material (metal, semiconductor or organic matter) is being evaporated by heating it beyond the melting temperature. Then supersaturated vapor is obtained as a result of quick cooling. The condensation process of the small drops begins in this system. The nanoparticles of various compositions and wide range of sizes can be produced by this method. The first stage of the nanoparticles formation is nucleation – that is the critical nuclei generation. The nanoparticles grow later from the nuclei by joining atoms from supersaturated vapor. The nucleation is not a unique phenomenon and it takes place in gases, solutions, melts and even in solids when a new phase is being formed inside the host phase. There is the so-called Classical Nucleation Theory (CNT), which enables to calculate the nucleation rates depending on the process conditions [1, 2]. This theory is a statistical thermodynamic one really, because it uses the thermodynamic parameters of clusters and small particles, which are the critical nuclei. The critical nuclei at the moment of their occurrence are the liquid clusters or nanodrops and only later they become the solid nanoparticles as a result of cooling. The surface tension of the critical nucleus is an important parameter in the CNT, because it defines the work of the critical nucleus formation [1, 2]. Though this theory often leads to unsatisfactory results, it and its modifications are still being used for interpretation of experimental data [3, 4].

Thermodynamic description of nanodrops is very important physical problem. There is a problem of applicability of thermodynamic parameters to small drop and cluster as these parameters are the macroscopic thermodynamic notions, but nanodrop is a microscopic system. One of the causes of discrepancy between the CNT and experiment can be that the dependence of the surface tension on the critical nucleus radius is ignored often. However J. Gibbs pointed out, that the surface tension of a droplet ($\sigma$) must decrease with the decrease of droplet tension surface radius ($R_s$), so that at $R_s = 0$ the surface tension be also equal to zero ($\sigma = 0$) [5]. At the same time the equimolar radius of the droplet ($R_e$) is not equal to zero. Consequently the notion of the surface tension can not be applied to such droplets.

## NOMENCLATURE

| | | |
|---|---|---|
| $\sigma$ | [N/m] | Surface tension |
| $\sigma_\infty$ | [N/m] | Surface tension of a flat interface of liquid - vapor |
| $R_s$ | [m] | Droplet tension surface radius |
| $R_e$ | [m] | Equimolar radius of a droplet |
| $U$ | [J] | Internal energy of thermodynamic system |
| $V_l$ | [m$^3$] | Volume of a liquid drop |
| $V_v$ | [m$^3$] | Volume of vapor |
| $A$ | [m$^2$] | Surface area of liquid |
| $T$ | [K] | Temperature |
| $S$ | [J/K] | Entropy of a system |
| $P_l$ | [Pa] | Pressure in a drop |
| $P_v$ | [Pa] | Pressure in vapor |
| $\mu$ | [J/kg] | Chemical potential of a system |
| $m$ | [kg] | Mass of a system |
| $\delta$ | [m] | The Tolman length |
| $r$ | [m] | Distance from the centre of a drop |
| $P(r)$ | [Pa] | Pressure tensor |
| $P_N(r)$ | [Pa] | Pressure tensor normal component |
| $P_T(r)$ | [Pa] | Pressure tensor tangential component |
| $\mathrm{e}_r, \mathrm{e}_\theta, \mathrm{e}_\phi$ | [-] | Unit vectors corresponding to spherical coordinate system |
| r,<br>$\theta$,<br>$\phi$ | [m],<br>[rad],<br>[rad] | Spherical coordinates |
| $r_{12}$ | [m] | Distance between molecules 1 and 2 |
| $\mathbf{r}_{12}$ | [m] | Vector directed from molecule 1 to molecule 2 |
| $n(r)$ | [m$^{-3}$] | Concentration of molecules |
| $\rho(r)$ | [kg/m$^3$] | Density |
| $\rho_l, \rho_g$ | [kg/m$^3$] | Densities of liquid and vapor |
| $\rho^{(2)}\left(r_{12}, \lvert\mathbf{r} - \alpha\, \mathbf{r}_{12}\rvert\right)$ | [m$^{-6}$] | Pair correlation function of molecules 1 and 2 |
| $\varepsilon$ | [J] | Lennard-Jones potential parameter |
| $r_0$ | [m] | Lennard-Jones potential parameter |
| $m_0$ | [kg] | molecule mass |
| $\mu_l$ | [J/kg] | Chemical potential of liquid |
| $\mu_g$ | [J/kg] | Chemical potential of vapor |
| $\mu_0$ | [J/kg] | Chemical potential of classical ideal gas |
| $R_0$ | [m] | Equimolar radius of a droplet at which the surface tension becomes equal to zero |

Usually reduced variables are used in computational simulations. In that case the basic units are $r_0$, $r_0\left(\varepsilon/m_0\right)^{-1/2}$ and $m_0$ for distance, time and mass respectively.

## TERMODYNAMICS OF DROPS

The surface tension concept is proved by J. Gibbs [5] in thermodynamics and it is conventional. This concept provides introduction of additional term $\sigma\, dA$ ($\sigma$ is the surface tension, $dA$ is a change of the surface area of a liquid) in fundamental thermodynamic equations. Such equation for the internal energy of the system consisting of a liquid drop and vapor surrounding it, has the usual form

$$dU = T\,dS - P_l\,dV_l - P_v\,dV_v + \sigma\,dA + \mu\,dm. \qquad (1)$$

Here $dU$, $dS$ and $dm$ are changes of the internal energy, of entropy and of mass of all system, $dV_l$, $dV_v$ and $dA$ are changes of volumes of the liquid drop, of the vapor and of the drop surface area, $P_l$, $P_v$ and $T$ are pressures in the drop and in the vapor and system temperature, $\mu$ is chemical potential of the system.

Thus, such surface tension $\sigma$ determines additional energy to the thermodynamic potentials, related to change of a surface area of a liquid and it 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 of a zero thickness to which the forces of surface tension are applied. At the thermodynamic description of systems with flat interfaces of liquid – vapor the position of the tension surface has no importance. For curved interfaces there is a problem of a choice of the tension surface.

For the system consisting of a liquid drop surrounded by natural vapor, the value of surface tension depends on the choice of the tension surface position. J. Gibbs has suggested choosing the tension surface so that the surface tension had the minimum value. Thus the model of Gibbs assumes that in sphere with radius of the tension surface there is a medium with properties of a bulk liquid which is called sometimes comparison phase. The chemical potential of this phase coincides with the chemical potential of the vapor surrounding the sphere. Thus, pressure, density and temperature in the drop are equal to the values of pressure, density and temperature in the bulk liquid at the same chemical potential. The tension surface of the drop generally does not coincide with equimolar surface, therefore the part of mass of the system does not belong to any of two phases and it is the part of 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.

The difference of the pressures between the comparison phase and the surrounding vapor obeys the Laplace formula

$$P_l - P_g = 2\sigma/R_s\,, \qquad (2)$$

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. According to this choice values of $\sigma$, $R_s$, and also the equimolar radius $R_e$ will be changed.

Tolman [6] has derived dependence of the surface tension on the radius of the tension surface in the form

$$\ln\frac{\sigma}{\sigma_\infty}=\int_{\infty}^{R_s}\frac{\left(2\delta/r^2\right)\left[1+\left(\delta/r\right)+\frac{1}{3}\left(\delta^2/r^2\right)\right]}{1+\left(2\delta/r\right)\left[1+\left(\delta/r\right)+\frac{1}{3}\left(\delta^2/r^2\right)\right]}dr\,. \tag{3}$$

Here $\sigma_\infty$ is the surface tension of a flat interface of liquid - vapor. If we assume that $\delta=\delta_\infty=const$ and $\delta/r<<1$ we obtain the approximate formula which is true for big drops

$$\sigma/\sigma_\infty=1/\left(1+2\delta/R_s\right). \tag{4}$$

## THE MECHANICAL SURFACE TENSION

On the other hand, there is a mechanical definition of surface tension [7, 8] related to the change of continuous profiles of density and pressure by the step ones. The pressure tensor of drop has a spherical symmetry

$$P(r)=\mathrm{e_r e_r}P_N(r)+(\mathrm{e_\theta e_\theta}+\mathrm{e}_\phi\mathrm{e}_\phi)P_T(r) \tag{5}$$

The mechanical surface tension is expressed through the pressure tensor [7, 8]:

$$\sigma=\int_0^\infty(r/R_s)^2(P_N(r)-P_T(r))dr\,. \tag{6}$$

Since in this formula $R_s$ is unknown beforehand, it is necessary to have one more equation determining $R_s$. In papers [8, 9] it is suggested to use the equation

$$\sigma=\int_0^\infty(R_s/r)(P_N(r)-P_T(r))dr\,, \tag{7}$$

which is derived from the equations of Buff based on the mechanical equilibrium conditions of the system of drop – vapor. Using the equations (6) and (7), it is possible to calculate $R_s$ and $\sigma$, if we know the profiles of the pressure tensor components.

In advance it is not obvious that the surface tension calculated by formulae (6) and (7), will coincide with the thermodynamic surface tension used in (1). Here there is a problem of relation of the surface tension determined by formulae (6) and (7) to Gibbs model of surface tension.

## METHODS OF SIMULATION

The molecular dynamics method has been long used to calculate the surface tension for the flat division surface between liquid and gas [10]. It was also used many times to calculate the surface tension of the liquid drops [9, 11 - 15]. From this point of view the most interesting papers are [9, 11], in which the basic methods of molecular dynamics calculations of small drops surface tension are developed. At the same time all these calculations have been done in a narrow range of system parameters and give no possibility of precise determination of the dependence of the drops surface tension on their radii. Besides, these papers do not concern the problem of applicability of the surface tension concept to the droplets of small radii.

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 molecules was specified by the Lennard-Jones potential

$$u(r_{12})=4\varepsilon\left[\left(\frac{r_0}{r_{12}}\right)^{12}-\left(\frac{r_0}{r_{12}}\right)^{6}\right],\ \text{if}\ r_{12}\le 4.5r_0$$

$$u(r_{12})=a(r_{12}-5r_0)^2+b(r_{12}-5r_0)^3,\ \text{if}\ 4.5r_0\le r_{12}\le 5r_0$$

$$u(r_{12})=0,\ \text{if}\ r_{12}\ge 5r_0$$

(8)

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. We call such drop obtained in numerical experiment real. 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 formulae of statistical mechanics [8]

$$P_N(r)=kT\,n(r)-\frac{1}{2}\int d\,\mathrm{r}_{12}\frac{(\mathrm{r}_{12}\cdot\mathrm{e_r})^2}{r_{12}}u'(r_{12})\times$$
$$\times\int_0^1 d\alpha\,\rho^{(2)}\left(r_{12},|\mathrm{r}-\alpha\,\mathrm{r}_{12}|\right)$$
$$P_T(r)=kT\,n(r)-\frac{1}{2}\int d\,\mathrm{r}_{12}\frac{(\mathrm{r}_{12}\cdot\mathrm{e}_\phi)^2}{r_{12}}u'(r_{12})\times$$
$$\times\int_0^1 d\alpha\,\rho^{(2)}\left(r_{12},|\mathrm{r}-\alpha\,\mathrm{r}_{12}|\right) \tag{9}$$

Density profiles, chemical potential of the system, equimolar radii 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 - $\rho=\rho^*r_0^3$, time - $t=t^*/r_0\left(\varepsilon/m_0\right)^{1/2}$, pressure - $p=p^*r_0^3/\varepsilon$, surface tension - $\sigma=\sigma^*r_0^2/\varepsilon$, and chemical potential - $\mu=\mu^*m_0/\varepsilon$. Here $\varepsilon$ and $r_0$ are the Lennard-Jones potential parameters, $m_0$ is the molecule mass. Variables labeled by an asterisk are dimensional.

## RESULTS OF THE SIMULATIONS

Figure 1 presents typical profiles of drop density $\rho(r)$. The equimolar radii of the drops were calculated according to these dependences by the formula [9]

$$R_e^3 = \frac{1}{\rho_g - \rho_l} \int_0^{\infty} r^3 \frac{d\,\rho(r)}{d\,r}\, d\,r\,. \tag{10}$$

Here $\rho_l, \rho_g$ are the comparison phase and gas densities respectively.

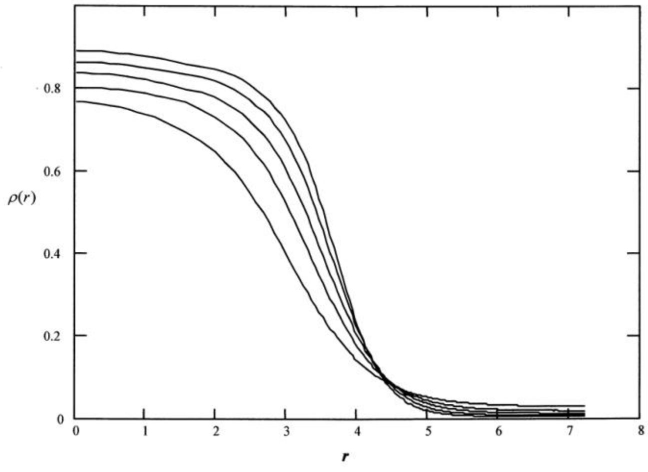

**Figure 1** The density profiles for the system, containing $N$ = 200 molecules in the cell at the temperatures $T$ = 0.65; 0.7; 0.75; 0.8; 0.85 (from the top)

Figure 2 presents typical profiles of the pressure tensor components $P_N(r)$ and $P_T(r)$ used for calculations of the tension surface radius $R_s$ and the surface tension $\sigma$.

Figure 3 presents the nanodrops mechanical surface tension dependences on the equimolar radius $R_e$ for various temperatures. One can see, that the mechanical surface tension decreases greatly with the $R_e$ decrease and becomes equal to zero at a certain $R_e = R_0$, which depends on temperature. The mechanical surface tension approaches the value of the surface tension of liquid – vapor flat surface with $R_e$ increase.

To calculate surface tension of drops according to J. Gibbs definition, first, one should know the dependence of chemical potential of bulk liquid phase on pressure, and, second, chemical potential of vapor. To solve the first problem, we have made special series of bulk liquid phase chemical potential calculations by molecular dynamics method at the temperature $T$ = 0.65. First, we obtained the equilibrium system consisting of flat liquid phase layer surrounded by vapor from two sides. The layer thickness exceeded the molecules interaction radius three times. The computations have shown that vapor far from the flat separating surface is an ideal gas, i.e. the ideal gas equations $p = nT$ ($n$ is vapor concentration) holds accurate to 1%. Chemical potential of vapor, and, therefore, liquid layer was calculated by formula $\mu_0 = -(5/2)T\ln(T) + T\ln(p)$ suitable for classical ideal gas.

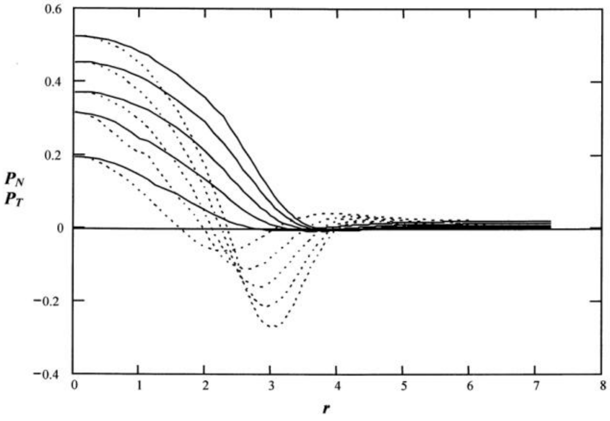

**Figure 2** The profiles of the pressure tensor components for system, containing $N$ = 200 molecules in cell at temperatures $T$ = 0.65; 0.7; 0.75; 0.8; 0.85 (from the top). (solid lines are $P_N$, dashed lines are $P_T$)

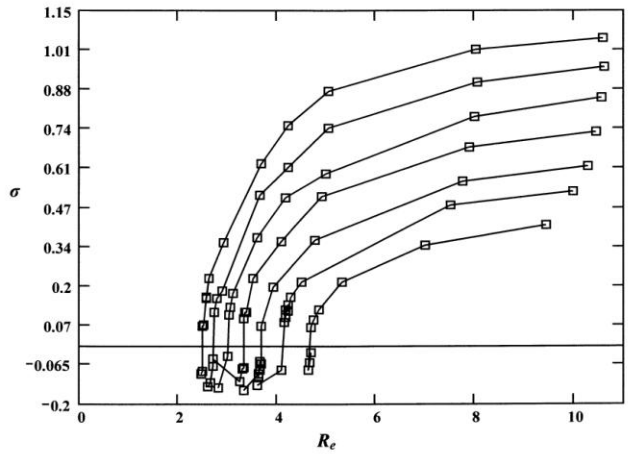

**Figure 3** The drop mechanical surface tension dependences ($\sigma$) on the equimolar radius ($R_e$) for various temperatures ($T$ = 0.65; 0.7; 0.75; 0.8; 0.85; 0.9; 0.95 from the top).

Then calculations were made of a similar system with two repulsing walls on the opposite sides of the cell that served as plungers compressing the flat liquid layer. Reducing the cell volume, we obtained liquid phases at different pressures. Thus the equation of liquid state at a given temperature has been obtained. Chemical potential of the liquid phase was calculated by the formula

$$\mu_l = \mu_0 + \int_{P_0}^{P_l} d\,p/\rho\,. \tag{11}$$

Approximation curve of dependences $P_l$ and $\rho_l$ on $\mu_l$ was established.

Chemical potential of vapor has also been calculated by formula (11) with $\mu_l$ replaced by $\mu_g$ and $P_l$ – by $P_g$. Equation of vapor state has been obtained from molecular dynamics data for equilibrium systems containing liquid drop surrounded by its own vapor, i.e., from the calculations of surface tension of drops. Vapor pressure and density were taken far away from the drop at the distance exceeding the interaction radius of molecules. After estimation of the chemical potential of the vapor around the drop we equated it to the comparison phase chemical potential and got $P_l$ and $\rho_l$ of the comparison phase. We used approximation curve of the dependence of these values on liquid chemical potential. Further, using formula (2) and the first equation (6), we calculated $\sigma$ and $R_s$ for thermodynamic surface tension.

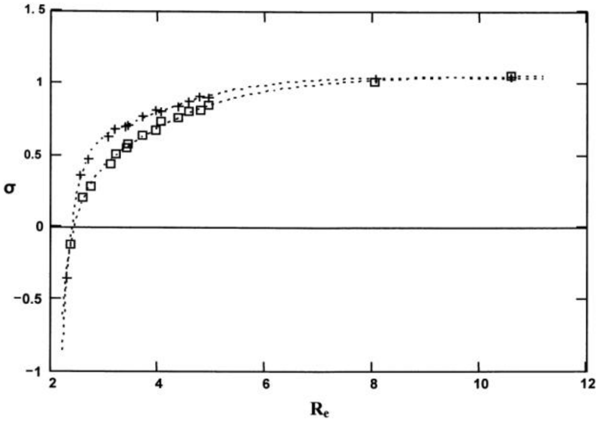

**Figure 4** The dependence of mechanical (□) and thermodynamic (+) surface tensions on the equimolar radius $R_e$ at the temperature $T = 0.65$

Figure 4 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 $R_e$ decrease. At a certain equimolar radius $R_0$ both surface tensions go to zero. This radius corresponds to the drop, containing about 50 molecules. The radius of the surface of tension $R_s$ also goes to zero. With the further equimolar radius decrease the surface tension becomes negative, though the drop holds stable in the conditions of the numerical experiment. Figure 4 shows that the thermodynamic surface tension coincides with the mechanical one for relatively big drops containing 2000 and more molecules. For drops containing smaller quantity of molecules the thermodynamic surface tension exceeds the mechanical one up to their disappearance at $R_e = R_0$.

## DISCUSSION OF RESULTS

It has been established in our papers [16-18] 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 (see Figure 5). It has been found that approximation of this dependence by the polynomial of the ratio $R_0/R_e$ can be expressed as follows:

$$\begin{aligned}\sigma(R_e) = \sigma_\infty\big[&1-0.519\cdot R_0/R_e+0.426\cdot(R_0/R_e)^2-\\&-0.907\cdot(R_0/R_e)^3\big]\end{aligned}. \quad (12)$$

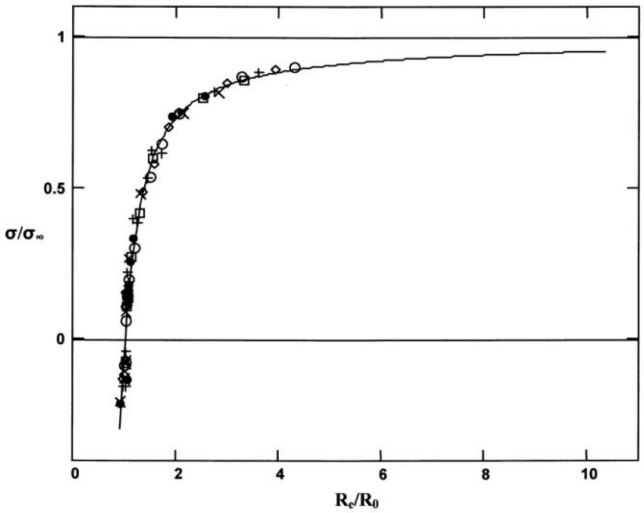

**Figure 5** The dependence of the ratio of the mechanical surface tension of the drop to the surface tension of the flat surface liquid-vapour (*σ/σ*∞) on the ratio of the equimolar radius of the drop to *R0* for various temperatures (*T* = 0.65(◦); 0.7(◊); 0.75(+); 0.8(□); 0.85(×); 0.9(•); 0.95(+)). Solid line is the dependence (12).

In addition, the drop equimolar radius $R_0$, at which $\sigma$ = 0, greatly depends on the temperature and becomes infinite in the point is equal 1.199 (see Figure 6). The approximation of the dependence of $R_0$ on the temperature can be expressed by the fit

$$R_0 = 0.768 + \frac{0.963}{1.199 - T}. \quad (13)$$

The surface tension of the flat dividing surface 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 the same in its quality as that for 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 liquid – vapor. For quite small drops the surface tension becomes zero or even negative. But the drop does not evaporate at that time. Though the drop will evaporate after all, if we increase the number of molecules in the simulation cell at the same pressure, because that 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.

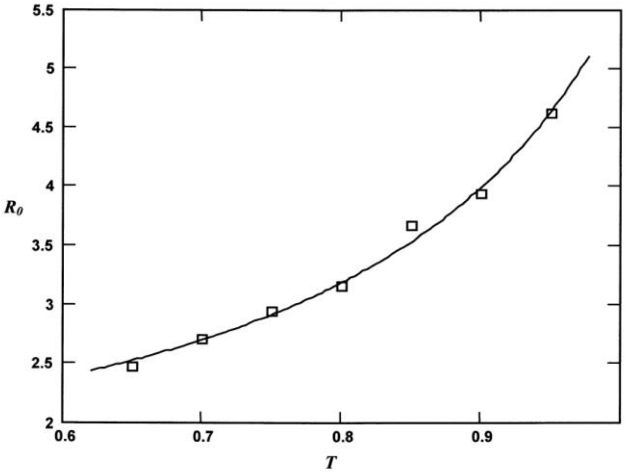

**Figure 6** The dependence of $R_0$ on the temperature. Solid line is the dependence (13)

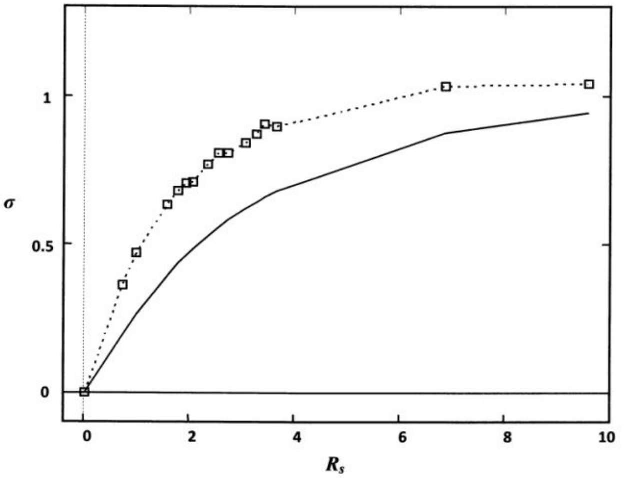

**Figure 7** The thermodynamic surface tension (□) and surface tension calculated by Tolman formula (3) (solid line) as a function of the $R_s$ at the temperature $T = 0.65$.

On the other hand, the negative surface tension and the negative radius of tension surface $R_s$ 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 can not 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 $T = 0.95$.

Figure 7 shows disagreement between the thermodynamic surface tension calculated by molecular dynamics method and surface tension calculated by Tolman formula (3). It is possibly that the Tolman equation does not adequate for the small droplets.

## CONCLUSION

Thus, it has been established that both mechanical and thermodynamic surface tensions decrease greatly with the decrease of tension surface radius $R_s$ and become equal to zero at a certain $R_e = R_0$. A universal dependence of mechanical surface tension is observed, i.e., the dependence of $\sigma$ on the temperature is expressed by the dependence of parameters $\sigma_\infty$ and $R_0$ on the temperature. The value of the thermodynamic surface tension coincides with value of the mechanical surface tension for relatively large nanodrops (> 2000 molecules) and exceeds it for relatively small nanodrops (< 2000 molecules).

The notion of surface tension which is used in macroscopic theory can not be applied to small droplets with equimolar radius less then $R_0$.

## ACKNOWLEDGMENTS

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