

# The Effect of Microdroplet Size on the Surface Tension and Tolman Length

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A monomolecular layer model of the surface phase of microdroplets was proposed, and the exact expression for Tolman length was derived in this paper. The Tolman lengths of water, *n*-pentane, and *n*-heptane were calculated by the expression, and the values are quite in agreement with the experimental values. By use of the Gibbs–Tolman–Kening–Buff equation, the exact relationship between the microdroplet surface tension and the radius is obtained, and the predicted values agree well with the simulated values. The results show that there is an obvious effect of the size of microdroplets (or nanoparticles) on the surface tension, and the surface tension decreases with decreasing droplet size. For the microdroplets of general liquid, only if their radius approaches or reaches  $10^{-9}$  m does the effect become significant.

## 1. Introduction

Surface tension, a fundamental property of liquid droplets and gas–liquid interface,<sup>1–4</sup> plays an important role in a variety of scientific and industrial fields.<sup>5</sup> It influences unit operations, for instance, distillation, condensation, gas absorption, and extraction.<sup>6</sup> It is also an important basic data of many fields, such as oil industry, chemical industry, metallurgy, environmental protection, and so on.<sup>7</sup> For the surface tension of a plane fluid, the experimental determination is very easy. However, when the droplet radius becomes very small, its surface tension is different from that of a large droplet and it is difficult to determine the surface tension by experiment. Therefore, it is currently calculated by the approximative relationships.

Early in the 19th century, Gibbs had concluded that surface tension would be subject to the curvature when the droplet size is very small. In 1949, Tolman<sup>8</sup> found that the surface tension decreases with decreasing droplet size in a wide range and obtained the formula of surface tension, which proved Gibbs's conclusion. However, the Tolman length is a constant in the formula ( $\delta_\infty$ , the Tolman length of a flat interface), and the estimated value of argon's Tolman length is approximately taken as the constant in the actual calculations.<sup>9,10</sup> When the droplet sizes are less than 30–50 nm, the calculated values of surface tension show a major warp, and the Tolman formula cannot be applied to calculate the surface tension.<sup>11</sup> In 1960, Rusanov et al.<sup>12</sup> deduced the approximate linear relationship between the surface tension of a small droplet and its size, that is,  $\gamma = KR_s$ , where  $K$  is a proportionality coefficient depending on the temperature and the pressure,<sup>13</sup>  $\gamma$  and  $R_s$  are the surface tension and the radius of the surface of tension, respectively. However, the experimental data of the coefficient  $K$  in the relationship is meager. In 1963, Dufour and Defay obtained the relationship between surface tension and droplet size,<sup>14</sup> that is,  $\sigma_{l/v}/\sigma_{l/v}^0 = 1 + 2\Gamma M/R(\rho_l - \rho_v)$ , where  $\Gamma$  is Gibbs absorption at the surface of tension,  $\sigma_{l/v}$  is the surface tension when the droplet radius is  $R$ , and  $\sigma_{l/v}^0$  is the surface tension at zero curvature;  $M$ ,  $\rho_l$ , and  $\rho_v$  are the molecular weight, liquid density, and vapor density,

respectively. However, it is still an approximate relationship. Here, the surface adsorption  $\Gamma$  in the relationship was estimated to be approximate to the order of one-half the concentration of a completely filled monolayer. In 1999, Samsonov et al.<sup>11</sup> calculated the surface tension values of a simple Lennard-Jones solution, polymers, and molten metal with different droplet sizes by the thermodynamic perturbation theory, which proved that Rusanov's linear equation is credible. However, it is still difficult to obtain the proportional coefficient  $K$  in the equation; thus, this formula is seldom used in practical calculations. In 2004, Samsonov et al.<sup>15</sup> concluded that the Gibbs thermodynamics may be extended to nanosystem if the effective surface tension (the specific excess free energy) is interpreted as a function of the particle radius. In recent years, computer simulation is used to study the effect of size on surface tension.<sup>16,17</sup> However, the process of simulation is complex, the amount of calculation is very great, and a concrete relationship between surface tension and droplet size cannot be obtained by the simulation. Therefore, computer simulation cannot be widely used in practice to calculate the surface tension.

Using the Gibbs thermodynamic method to study the microdroplet size dependence of surface tension, the Tolman length is very important. For the tiny droplets, the Tolman length is the function of droplet size,<sup>2,9,18,19</sup> and so far there is not a precise relationship. In addition, the precise relationship between the surface tension and droplet size has not been reported.

Therefore, we will propose a monomolecular layer model of the surface phase of a microdroplet, and deduce the relationship between the Tolman length and droplet radius, thus obtain the precise relationship between surface tension and droplet radius by use of the Gibbs–Tolman–Kening–Buff equation, and then take the sodium as an example to discuss the effect of tiny droplet size on surface tension.

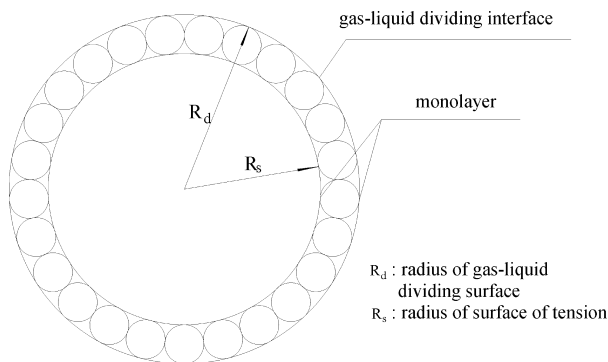
## 2. Model

In this paper, the object of study is a thermodynamic system which is composed of a microdroplet and the vapor phase. The temperature is a constant and the system is in thermodynamic equilibrium.<sup>20</sup> For such a system, according to the Gibbs thermodynamic theory, the differential relationship of surface

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**Figure 1.** The schematic diagram of the monolayer model.

tension and tiny droplet radius can be obtained, that is, the Gibbs–Tolman–Kening–Buff equation:<sup>9</sup>

$$\frac{d\sigma_s}{\sigma_s} = -\frac{2(\delta(R_s) + c\delta^2(R_s) + c^2\delta^3(R_s)/3)}{1 + \frac{2(\delta(R_s) + c\delta^2(R_s) + c^2\delta^3(R_s)/3)}{R_s}} d\left(\frac{1}{R_s}\right) \quad (1)$$

where  $c$  denotes the curvature of the surface of tension (and  $c = 1/R_s$ ) and  $R_s$  is the radius of the surface of tension;  $\delta$  is the Tolman length, and it is the function of the radius of the surface of tension, that is,  $\delta = R_e - R_s$ .<sup>21</sup> Here,  $R_e$  is the radius of the equimolecular dividing surface on which Gibbs absorption is equal to zero. Many researchers considered the magnitude of the Tolman length to be the order of molecular dimension. However, the experimental determination of the Tolman length is very difficult. Until now, the sign of the Tolman length is still controversial.<sup>2,4,22,23</sup> It is general to assume that  $\delta > 0$  for spherical droplets and  $\delta < 0$  for bubbles in liquid.<sup>2</sup> It can be seen from eq 1 that, to obtain the precise relationship between surface tension and droplet size, the relationship between Tolman length and droplet size must be obtained first. Therefore, the monomolecular layer model of the surface phase of a microdroplet is proposed, and several basic assumptions for the monolayer model are as follows:

- (1) The surface phase is monolayer where atoms (or molecules) arrange tightly and regularly.
- (2) The atoms (or molecules) in the surface phase are spherical.
- (3) The outer surface of the monolayer is the gas–liquid interface, and the radius is  $R_d$ ; when we calculate the surface density, this surface is chosen to calculate the surface area of the surface phase; the inner surface of the monolayer is the surface of tension, and its radius is  $R_s$ . The schematic of the monolayer model is shown in Figure 1.

### 3. The Size Dependence of the Tolman Length

Tolman obtained the precise relationship between Tolman length and surface density when he studied the effect of droplet size on surface tension by the thermodynamic method, and the expression<sup>8</sup> is as follows:

$$\frac{\Gamma}{\Delta\rho} = \delta + c\delta^2 + \frac{1}{3}c^2\delta^3 \quad (2)$$

where  $\Delta\rho$  is the difference of the two-phases density (mol/m<sup>3</sup>),  $\Gamma$  is the surface density (mol/m<sup>2</sup>), and  $\Gamma = n_s/A_s$ . Here,  $n_s$  is the amount of substance of the monolayer and  $A_s$  is the surface area of the surface phase. According to the definition of surface density, and combining with the above model, the relationship between the surface density and the radius of the surface of tension can be obtained.

For a microdroplet whose space utilization of atoms (or molecules) of the monolayer is  $U$  (approximately using the crystal space utilization in the concrete calculations), the amount of substance of surface monolayer is as follows:

$$n_s = U \cdot \frac{\frac{4}{3}\pi R_d^3 - \frac{4}{3}\pi(R_d - 2r_a)^3}{\frac{4}{3}\pi r_a^3 N_A} \quad (3)$$

where  $N_A$  is the Avogadro constant and  $r_a$  is the atom (or molecule) radius of the droplet.

According to the assumptions, the surface area of the surface phase is as follows:

$$A_s = 4\pi R_d^2 \quad (4)$$

According to the definition of surface density, and combining eqs 3 and 4, the expression of surface density is as follows:

$$\Gamma = \frac{U \cdot [R_d^3 - (R_d - 2r_a)^3]}{4\pi r_a^3 \cdot N_A \cdot R_d^2} \quad (5)$$

Equation 5 can be rearranged into

$$\Gamma = \frac{3U}{2\pi r_a^2 \cdot N_A} \left(1 - \frac{2r_a}{R_d} + \left(\frac{2r_a}{R_d}\right)^2\right) \quad (6)$$

Applying  $R_s = R_d - 2r_a$  (from Figure 1) to eq 6, we derived

$$\Gamma = \frac{3U}{2\pi r_a^2 \cdot N_A} \left(\frac{R_s}{R_s + 2r_a} + \left(\frac{2r_a}{R_s + 2r_a}\right)^2\right) \quad (7)$$

Combining eq 7 with eq 2, one has

$$\frac{3U}{2\pi r_a^2 \cdot \Delta\rho \cdot N_A} \left(\frac{R_s}{R_s + 2r_a} + \left(\frac{2r_a}{R_s + 2r_a}\right)^2\right) = \delta(R_s) + c\delta^2(R_s) + \frac{1}{3}c^2\delta^3(R_s) \quad (8)$$

The solution of eq 8 can be written out in the form

$$\frac{\delta}{r_a} = -\frac{R_s}{r_a} + \frac{R_s}{r_a} \sqrt[3]{1 + \frac{9U}{2\pi \cdot r_a^3 \Delta\rho \cdot N_A} \left(\frac{1}{R_s/r_a + 2} + \frac{r_a}{R_s} \left(\frac{2}{R_s/r_a + 2}\right)^2\right)} \quad (9)$$

**TABLE 1: The Calculated Values and the Experimental Values of Tolman Length for Several Substances<sup>a</sup>**

		$\delta/\text{nm}$			$\text{expt}^{24}$	$T/\text{K}$
		calcd				
substance	$R_s/\text{nm}$	$r_{a,\text{max}}$	$r_{a,\text{min}}$	$r_{\text{av}}$		
<i>n</i> -pentane	0.74	0.30	1.28	0.24	1.00	263
<i>n</i> -heptane	0.52	0.21	1.17	0.24	0.72	293
H <sub>2</sub> O	0.53			0.14	0.11	300

<sup>a</sup> Note: Assuming the molecules are spherical, the average molecular radius  $r_{\text{av}}$  in Table 1 was obtained by use of the liquid density. For the molecules of *n*-pentane and *n*-heptane, their structures depart from spherical; thus, two radii are opted to calculate the Tolman length also; one is parallel to the carbon chain direction, and the other is perpendicular to the carbon chain direction. Half of the length of a straight chain is taken as the maximum radius  $r_{a,\text{max}}$ , and half of the maximum diameter which is perpendicular to the carbon chain direction is taken as the smallest radius  $r_{a,\text{min}}$ . The C–C bond length  $L$  is 0.154 nm, and the C–H bond length  $L_0$  is 0.11 nm.<sup>25</sup> For a straight-chain alkane molecule with different numbers of carbon atoms,  $r_{a,\text{min}} = (L + 2L_0)(\cos 54.44)/2$ ,  $r_{a,\text{max}} = (2/3)^{1/2}(n_0 - 1)L/2 + (2/3)^{1/2}L_0$ , where  $n_0$  is the number of carbon atoms. For the space utilization of molecules of *n*-pentane, *n*-heptane, and water, it is approximately equal to the space utilization of covalent molecular crystals with the most close-packed structure, that is,  $U = 0.7406$ .

Equation 9 is the precise relationship between the Tolman length and the radius of the surface of tension. It is obvious that  $\delta/r_a$  depends only on  $R_s/r_a$ ,  $r_a^3\Delta\rho$ , and  $U$ . Substituting  $\delta = R_e - R_s$  into eq 9, the expression for the radius of equimolecular dividing surface can be obtained, that is,

$$R_e = R_s \sqrt[3]{1 + \frac{9U}{2\pi r_a^3 \Delta\rho N_A} \left( \frac{1}{R_s/r_a + 2} + \frac{r_a}{R_s} \left( \frac{2}{R_s/r_a + 2} \right)^2 \right)} \quad (10)$$

where  $9U/(2\pi r_a^3 \Delta\rho N_A)$  for the general liquid is on the order of  $10^0$ . Thus, for  $R_s = 10^{-8}$  m,  $[2/(R_s/r_a + 2)]^2$  is on the order of  $10^{-4}$  and the second term under the radical sign in eq 10 is on the order of  $10^{-2}$ . According to the approximate formula,  $(1 + x)^{1/3} \approx 1 + x/3$ , eq 9 can be reduced to

$$\delta = \frac{\delta_\infty}{1 + 2r_a/R_s} \quad (11)$$

where

$$\delta_\infty = \frac{3U}{2\pi r_a^2 \Delta\rho N_A} \quad (12)$$

Equation 11 and the formula  $\delta = \delta_\infty/(1 + a/R_s)$  which was obtained by Schmelzer et al.<sup>20</sup> have the same form. By comparison,  $a$  in the formula is equal to  $2r_a$  in eq 11. It can be seen from eq 11 that, when  $R_s \gg 2r_a$ , the effect of droplet size on the Tolman length can be neglected, and it becomes significant only when the droplet radius is comparable with that of atoms (or molecules).

The precise calculated values by using eq 9 and the experimental values of the Tolman length of several substances are shown in Table 1.

It is obvious from Table 1 that the experimental values of *n*-pentane and *n*-heptane are between the two calculated values corresponding to  $r_{a,\text{max}}$  and  $r_{a,\text{min}}$ , respectively. However, the calculated values of *n*-pentane and *n*-heptane given by the average molecular radius exhibit high deviation from the experimental values, and the calculated value of water is close to the experimental value. In the above monolayer model, we assumed that the atoms (or molecules) in the surface phase are spherical. For the water, its molecule is near-spherical, so the calculated value is close to the experimental value. The molecules of *n*-pentane and *n*-heptane depart largely from spherical, so their calculated values show a major warp, and it may be that the arrangement of the linear molecules on the droplet surface is quite different from that of nondirectional close-packed spherical molecules. It is obvious that applying eq 9 to calculate the Tolman length of spherical or near-spherical molecules is reliable. At the same time, it can be seen from Table 1 that the calculated values of Tolman length are greater than zero. It is consistent with the general assumption,<sup>2</sup> that is,  $\delta > 0$  for spherical droplets.

#### 4. The Effect of Droplet Size on Surface Tension

Substituting eq 9 into eq 1, the exact integral relationship between the surface tension and the radius of the surface of tension can be expressed as

$$\int_{\sigma_\infty}^{\sigma} \frac{d\sigma}{\sigma} = \int_{R_s}^{\infty} \frac{2 \frac{\delta_\infty}{r_a} \left( \frac{1}{1 + 2r_a/R_s} + \left( \frac{2}{R_s/r_a + 2} \right)^2 \right)}{\left( \frac{R_s}{r_a} \right)^2 + 2 \frac{\delta_\infty R_s}{r_a} \left( \frac{1}{1 + 2r_a/R_s} + \left( \frac{2}{R_s/r_a + 2} \right)^2 \right)} d\left( \frac{R_s}{r_a} \right) \quad (13)$$

where  $\sigma_\infty$  denotes the surface tension of the planar interface ( $R_s \rightarrow \infty$ ) and  $\sigma$  is the surface tension corresponding to  $R_s$ .

For a droplet of a substance which is composed of atoms or small molecules, if  $R_s > 10$  nm,  $(2/(R_s/r_a + 2))^2$  is on the order of  $10^{-4}$ , and therefore this term can be neglected in eq 13. An approximate relationship can be obtained after integral of eq 13, that is,

$$\frac{\sigma}{\sigma_\infty} = \left( \frac{1}{1 + 2\delta_\infty/R_s + 2r_a/R_s} \right)^{\delta_\infty/(\delta_\infty + r_a)} \quad (14)$$

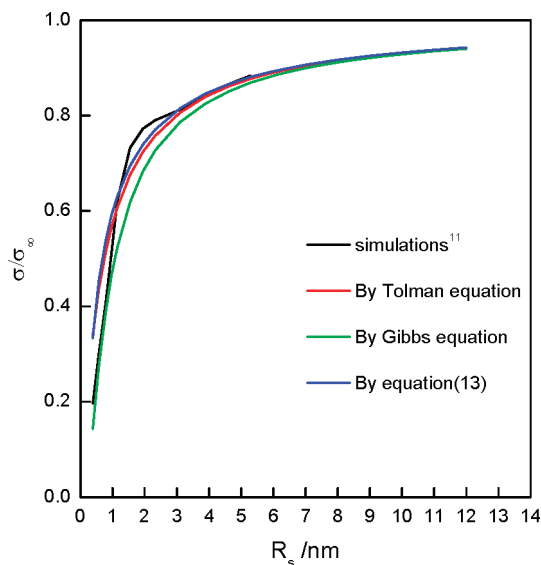
If  $\delta_\infty \gg r_a$ , the well-known Tolman equation<sup>11</sup> will be obtained after further simplifying eq 14, and the equation is

$$\frac{\sigma}{\sigma_\infty} = \frac{1}{1 + 2\delta_\infty/R_s} \quad (15)$$

It can be concluded from the above that the conditions of applying the Tolman equation are  $R_s > 10$  nm and  $\delta_\infty \gg r_a$ .

The surface tension values of sodium microdroplets with different radii were calculated by eq 13, the Gibbs equation<sup>20</sup> ( $\sigma/\sigma_\infty = \exp(-2\delta_\infty/R_s)$ ), and the Tolman equation at melting temperature (taking  $\delta_\infty = 0.372^2$ ), respectively. The calculated results and the computer simulations<sup>11</sup> are shown in Figure 2.

From Figure 2, it is observed that the surface tension of a sodium droplet decreases with decreasing radius. For  $R_s > 7$



**Figure 2.** The relationship between the surface tension and the radius of a sodium droplet at the melting temperature.

nm, the surface tension calculated by eq 13 almost coincides with that calculated by the Gibbs equation and the Tolman equation, respectively. For  $R_s$  from 1.5 to 6 nm, the calculated values by eq 13 are close to the simulations.<sup>11</sup> It can also be found from Figure 2 that the effect of droplet size on surface tension becomes significant only when the droplet size approaches or reaches the order of  $10^{-9}$  m.

In theory, the monomolecular layer model is also applicable to small crystals. Therefore, the above relationships can also be used to calculate the surface tension of nanoparticles.

## 5. Conclusions

The following conclusions can be reached through the above studies and discussions.

The exact relationship between the Tolman length and the droplet radius can be derived on the basis of the monomolecular layer model of the surface phase of a microdroplet. The Tolman length of tiny droplets is dependent not only on their size but also on the atom (or molecule) radius, the difference of the two-phase density, and the space utilization of atoms (or molecules). When the droplet radius  $R_s$  is much greater than  $2r_a$ , the effect of droplet size on the Tolman length can be neglected. If the shape of the atoms (or molecules) is closer to spherical, the calculated values are closer to the experimental values.

The exact expression for surface tension as a function of droplet size can be derived on the basis of the monomolecular layer model. The effect of droplet size on the surface tension of microdroplets (or nanoparticles) is obvious, and the surface tension decreases with decreasing droplet size. Only if the radius of the microdroplets (or nanoparticles) approaches or reaches the order of  $10^{-9}$  m does the effect become significant.

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