

Disjoining Pressure and Surface Tension of a Small Drop

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The dependence of the surface tension of a small drop on the drop radius is considered to be important for the process of new-phase formation. In this paper it is demonstrated that the Tolman formula is not unique and the size-dependence of the surface tension could be distinct for different systems. The reasoning is based on the relation between the surface tension and the drop disjoining pressure. The theory developed in this paper is applied to the van der Waals and electrostatic interactions. It is shown that the van der Waals interaction does not affect the thermodynamics of new-phase formation since the effects of the disjoining pressure and the size-dependent component of the surface tension cancel each other. However, it is demonstrated that the electrostatic interactions inhibit condensation phenomena.

Introduction

In small systems, many thermodynamic parameters depend on the system size and geometry. The values of these parameters differ from those for large systems, which are usually given in reference books. For instance, when one interface approaches another the transition phase regions overlap. As a result both the surface tension and the pressure in the gap dividing the two surfaces change. This paper focuses on small droplets where the surface tension depends on the drop radius. The description of such a system is important for the theory of nucleation.^{1,2}

Let us consider a globular mass surrounded by a bulk gas phase G , which is sufficiently small that no region of the mass can be regarded as homogeneous or owning bulk properties (see Figure 1). The well-known Tolman formula³ for the effect of drop size on the surface tension² was derived by careful analysis of the Gibbs remarks on the problem.⁴ The relation between the surface tension σ and the drop radius in differential form reads

$$\frac{\partial \sigma}{\partial R_s} = \frac{2x(3 + 3x + x^2)}{3 + 2x(3 + 3x + x^2)} \frac{\sigma}{R_s} \quad (1)$$

where $x = \delta/R_s$, δ is the difference between the radius R_e of the equimolecular dividing surface and the radius R_s of the surface of tension, i.e.

$$\delta = R_e - R_s \quad (2)$$

Assuming δ to be constant, after integration of eq 1, one obtains for small x that

$$\sigma = \sigma_\infty(1 - 2\delta_\infty/R_s) \quad (3)$$

where σ_∞ and δ_∞ refer to the planar liquid–vapor interface. However, the assumption that δ is constant is considered

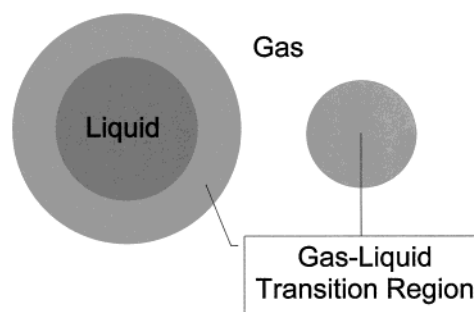


Figure 1. The difference between large drop (left) and small drop (right) is the liquid core inside.

to be questionable⁵ and this is corroborated by the fact that the linear dependence of σ vs R_s^{-1} has not been verified experimentally. Hence, neither the magnitude nor even the sign of the Tolman length δ is obvious. In general, δ depends on the drop size and there is no physical reason it should be constant as required by the derivation of eq 3. Consequently, the size dependence of the surface tension is still an open area of research and several new papers in this field have been published,^{6–13} among them articles with computer simulations.

The problem of the size-dependent surface tension can be considered from an alternative perspective. The thin liquid film is another small system where the two surfaces of discontinuity overlap and no bulk liquid core within the film exists. This fact is quantitatively manifested via the disjoining pressure of the film Π by Derjaguin.¹⁴ The present study aims to calculate the disjoining pressure for a drop and then, using the relation between Π and σ , to obtain the size dependence of the drop surface tension. In the first section of the paper we consider the thermo-

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dynamic description of a small drop and a definition of the disjoining pressure of the drop is derived. In the second section the van der Waals disjoining pressure of the drop is calculated per the method of Hamaker¹⁵ with the equation of London.¹⁶ In addition, the temperature dependence of the liquid–vapor surface tension is discussed here. The last section considers the effect of electrostatics. The paper concludes with a brief discussion on the size dependence of the surface tension of a drop.

Thermodynamics of a Drop

The two dividing surfaces of interest, i.e., the surface of tension and the equimolecular surface, are defined by the conditions $[\partial\sigma/\partial R] = 0$ at R_s and $[\Gamma] = 0$ at R_e (Γ is the Gibbs adsorption of the one-component drop). The brackets here indicate that the physical state of the considered system remains constant at the virtual operations shown. The mechanical behavior of the drop is determined by its pressure tensor. The normal component P_N of the pressure tensor differs from the pressure P_G in the homogeneous G -phase and the difference is called the capillary pressure

$$P_N - P_G = 2\sigma/R_s \quad (4)$$

The Laplace law (eq 4) holds for the surface of tension² and the surface tension σ is resolved for that position of the spherical dividing surface, where the condition $[\partial\sigma/\partial R] = 0$ is satisfied. Equation 4 holds in any case, no matter if there is a bulk liquid core within the drop with a liquid pressure P_L equal to P_N or the drop is so small that no part is homogeneous. For the latter case, according to the Gibbs consideration,⁴ a hypothetical liquid phase L , having the same temperature and chemical potential as the G -phase, is attributed to the mass, which is conceived as existing within the dividing surface. The pressure P_L in the L -phase differs from P_N and their difference is known as the disjoining pressure¹⁴

$$P_N - P_L = \Pi \quad (5)$$

According to thermodynamics, the characteristic function of a system at constant temperature and chemical potential is the Ω potential. The Ω potential of a liquid drop is given by the expression

$$\Omega = -P_L V + \sigma O \quad (6)$$

where V and O are the drop volume and surface area, respectively. Note that according to the Gibbs–Duhem relation for the L -phase the pressure P_L is constant at constant temperature and chemical potential. On the other hand, the work necessary to change the drop size can be calculated via the relation

$$d\Omega = -P_N dV + \sigma dO \quad (7)$$

Substituting Ω from eq 6 and employing the definition from eq 5 one yields the Gibbs–Duhem relation for a drop at constant temperature and chemical potential

$$\Pi dV = -O d\sigma \quad (8)$$

For the case of a spherical drop eq 8 can be easily transformed to the following expression, relating the

disjoining pressure and the first derivative of the surface tension with respect to the drop radius

$$\Pi = -\partial\sigma/\partial R_s \quad (9)$$

Equation 9 states that the dependence of the surface tension on the drop size indicates excess energy in the small drop compared to the bulk phase. This expression is very similar to the one for foam films,¹⁷ $\Pi = -2\partial\sigma/\partial h$, where h is the film thickness. By integrating eq 9, a useful expression for calculating the surface tension of a drop is obtained

$$\sigma = \sigma_\infty + \int_{R_s}^{\infty} \Pi dR_s \quad (10)$$

It is evident from this equation that the Tolman formula (eq 3) corresponds to a disjoining pressure $\Pi = -2\sigma_\infty\delta_\infty/R_s^2$.

van der Waals Disjoining Pressure Effect

Equation 10 shows that the size dependence of the surface tension is not universal in contrast to the Tolman theory. The surface tension is determined by the specific interactions within the drop, which reflect various components of the disjoining pressure. In the following section, the contribution of the most widespread force, i.e., the van der Waals attraction, is considered. The method of Hamaker¹⁵ is used to calculate the disjoining pressure of the drop. Thus, the van der Waals disjoining pressure is equal to the energy per unit volume of the interaction of a molecule, placed in the center of a bubble with radius R_s , with the surrounding liquid. Using the London equation¹⁶ for the energy of attraction between two molecules, the following expression is obtained

$$\Pi_{vw} = -\frac{1}{v_L^2} \int_{R_s}^{\infty} \frac{\lambda}{r^6} 4\pi r^2 dr = -\frac{4A}{3\pi R_s^3} \quad (11)$$

where λ is the London constant, v_L is volume per molecule of liquid, and $A = \pi^2\lambda/v_L^2$ is the well-known Hamaker constant.

By introducing eq 11 into eq 10 and integrating the result one yields

$$\sigma = \sigma_\infty(1 - a^2/R_s^2) \quad (12)$$

where $a = \sqrt{2A/3\pi\sigma_\infty}$. The values of the Hamaker constant and surface tension are usually in the ranges of 10^{-19} – 10^{-20} J and 10^{-2} – 10^{-1} N/m², respectively. Thus, the length a is of the order of 1.5–15 Å. It is evident that the size-dependent surface tension from eq 12 is inversely proportional to the square of the drop radius, and, consequently, differs from the Tolman formula (eq 3). This suggests that the Tolman length δ is not a constant and questions the applicability of the Tolman approximation to the van der Waals liquid drops. The dependence of δ on the radius R_s can be obtained by introducing eq 12 into eq 1, viz.

$$\delta = \frac{R_s}{\sqrt[3]{1 - 3a^2/R_s^2}} - R_s \quad (13)$$

From this equation it would appear that δ exhibits strange behavior. For instance, it predicts negative values

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of the radius R_e if $R_s^2 < 3a^2$. However, this is an artifact arising from insufficient extrapolation to too small droplet radii. Equation 11 describing the van der Waals disjoining pressure implies a relatively large drop since integration is reasonable for this case only. Hence, the following theory is valid for small values of the ratio a/R_s , where eq 13 reduces to $\delta = a^2/R_s$. Note that the continuous theory developed by the authors in a previous paper¹⁸ predicts also $\delta_\infty = 0$. This is a consequence of the fact that in simple liquids the molecular force field follows the molecule density profile. Hence, the peak of interfacial excess energy is located at the region with the largest density gradient, i.e., the surface of tension appears to be the equimolecular surface, too.

By replacing the surface tension in eq 4 with eq 12 and subtracting eq 5 from the result, one obtains the following relation

$$P_L - P_G = 2\sigma_\infty/R_s \quad (14)$$

This expression holds either for relatively large drops, where $P_L = P_N$, or for very small drops, where $P_L \neq P_N$. In both cases the generalized Laplace law (eq 14) involves the surface tension σ_∞ of the plane interface. The authors are of the opinion that eq 14 is in fact expressed by the Gibbs statement: "With this understanding with regard to the phase of the fictitious interior mass, there will be no ambiguity in the meaning of any of the symbols which we have employed, when applied to cases in which the surface of discontinuity is spherical, however small the radius may be".⁴

By combining eq 4, eq 5 and eq 14 the following equation can be obtained

$$2\sigma_\infty/R_s + \Pi_{VW} = 2\sigma/R_s \quad (15)$$

This equation can also be derived by the force balance method, in which a spherical drop with radius R_s is cut in two equal parts and one of these parts is "solidified" (the Steven method). The liquid part of the drop is characterized by σ and P_N , while the solidified part of the drop is represented by σ_∞ and P_L . Hence, at mechanical equilibrium the force balance $\pi R_s^2 P_N - 2\pi R_s \sigma = \pi R_s^2 P_L - 2\pi R_s \sigma_\infty$ is applicable, which also results in eq 15. A similar situation exists in the mechanical description of the transition zone between a plane-parallel liquid film and a bulk liquid meniscus. In this case, the Derjaguin approach¹⁹ with constant surface tension and disjoining pressure and the de Feijter approach²⁰ with size-dependent surface tension without disjoining pressure are found to be equivalent.²¹ However, eq 15 only holds for the van der Waals interaction. It will be shown later in this paper that both these approaches are inappropriate for drops with electrostatic forces and the correct solution requires either size-dependent surface tension or disjoining pressure.

At equilibrium, the chemical potentials in the G - and L -phases are equal and at constant temperature the corresponding Gibbs–Duhem relations are

$$v_G dP_G = d\mu_G = d\mu_L = v_L dP_L = v_L d(P_G + 2\sigma_\infty/R_s) \quad (16)$$

Equation 14 was used in obtaining the last relation. Equation 16 can be conveniently presented in an integral

form

$$P_\infty - P - \int_P^{P_\infty} (v_G/v_L) dP_G = 2\sigma_\infty/R \quad (17)$$

The pressure P_∞ represents the gas pressure at the planar liquid–vapor interface. A useful simplification is to consider the liquid as incompressible, i.e., $\partial v_L/\partial P_G = 0$. By assuming ideal gas behavior with the equation of state $P_G v_G = kT$, eq 17 can be integrated to obtain the Thomson–Gibbs relationship

$$P_\infty - P + (kT/v_L) \ln(P/P_\infty) = 2\sigma_\infty/R \quad (18)$$

Equation 18 enables the temperature dependence of the surface tension σ_∞ to be calculated. Consider the case where the gas pressure is so high that the vapor density nearly equals to the liquid one, $v_G(P_0) = v_L$. Since the drop shrinks with increasing pressure, the equilibrium drop at the pressure $P_0 = kT/v_L$ has the smallest possible radius $R_0 = \sqrt[3]{3v_L/4\pi}$. Hence, introducing P_0 and R_0 in eq 18 the surface tension of the liquid–vapor interface acquires the following form

$$\sigma_\infty = \sqrt[3]{3/32\pi v_L^2} [P_\infty v_L - kT + kT \ln(kT/P_\infty v_L)] \quad (19)$$

In addition, the densities of the liquid and the vapor coincide at the critical temperature T_c . Using the approximation $P_\infty v_L = kT_c$ the temperature dependence of the surface tension can be derived from eq 19

$$\sigma_\infty = \sqrt[3]{3/32\pi v_L^2} kT_c [1 - T/T_c + (T/T_c) \ln(T/T_c)] \quad (20)$$

It is clear from this equation that the surface tension vanishes at the critical point. Equation 20 shows that, apart from the well-known linear dependence of the surface tension on the ratio T/T_c , there is an additional logarithmic term. The origin of the latter is clearly entropic, since it is evident from this derivation that the logarithmic term corresponds to the ideal gas contribution only. Moreover, the surface tension from eq 20 is inversely proportional to the 2/3-power of v_L , as found by Eötvös.

Electrostatic Disjoining Pressure Effect

Consider the case of an electroneutral drop of liquid as an electrolyte solution. According to electrostatic theory the electrical potential in the drop obeys the Poisson–Boltzmann equation. For relatively small potential φ the charge density is linearly proportional to φ and the Poisson–Boltzmann equation acquires the form

$$\partial^2 \varphi / \partial r^2 + (2/r) \partial \varphi / \partial r = \kappa^2 \varphi \quad (21)$$

where κ^{-1} is the Debye length. The solution of eq 21 for a drop is

$$\varphi/\varphi_s = (R_s/r) \sinh(\kappa r) / \sinh(\kappa R_s) \quad (22)$$

where φ_s is the potential at the surface of tension. Note that pure water is also an electrolyte with a surface potential of about -35 mV.²² The surface charge density can be obtained using eq 22

$$q = \epsilon_0 \epsilon (\partial \varphi / \partial r)_{R_s} = \epsilon_0 \epsilon \varphi_s [\kappa \coth(\kappa R_s) - 1/R_s] \quad (23)$$

The surface tension of the drop can be calculated from the

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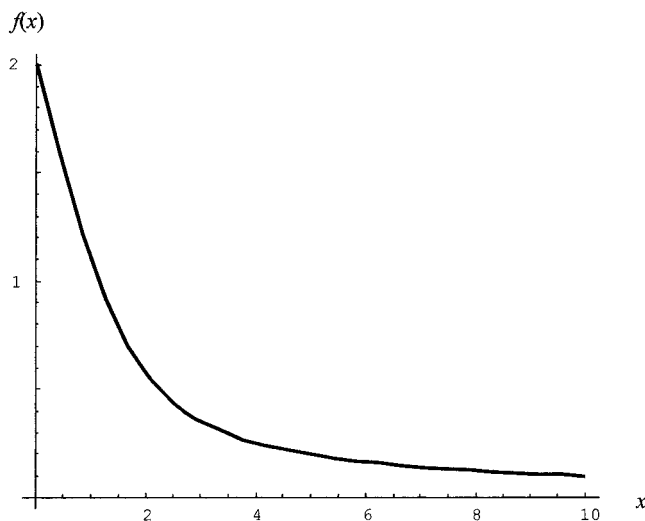


Figure 2. The plot of the function $f(x) = 2 - 2 \coth(x) + 1/x + x/\sinh^2(x)$.

Lippmann relation $\partial\sigma/\partial\varphi_s = -q$. Substituting q with eq 23 and integrating the following expression is derived

$$\sigma = \sigma_\infty [1 + b/R_s + \kappa b - \kappa b \coth(\kappa R_s)] \quad (24)$$

where $b = \epsilon_0 \epsilon \varphi_s^2 / 2\sigma_\infty$. In water, for instance, b is equal to 2 Å at $\varphi_s = 200$ mV. The electrostatic disjoining pressure can now be obtained according to eq 9 from the R_s -derivative of eq 24

$$\Pi_{\text{EL}} = (\epsilon_0 \epsilon \varphi_s^2 / 2) [1/R_s^2 - \kappa^2 / \sinh^2(\kappa R_s)] \quad (25)$$

It is clear from this eq 24 that electrostatic interactions increase the surface tension. This effect is due to the electrostatic attraction between the surface and bulk ions. Thus, an additional force appears which tries to decrease the drop energy by decreasing the surface area. If $\kappa R_s \geq 2$ equation 24 can be well approximated by

$$\sigma = \sigma_\infty (1 + b/R_s) \quad (26)$$

This expression formally coincides with the Tolman formula (eq 3) and suggests that the Tolman length is negative, $\delta_\infty = -b/2$. This can be explained by the electrostatic repulsion of the ions in the drop. The positive Π_{EL} applied on the surface of tension is trying to increase R_s as compared to the radius R_e of the equimolecular surface given by the mass balance of the noncharged solvent.

Using eq 24 and eq 25 the difference between the pressures in the G - and L -phases can be calculated to obtain

$$P_L - P_G = [2 + \kappa b f(\kappa R_s)] \sigma_\infty / R_s \quad (27)$$

The function $f(x) = 2 - 2 \coth(x) + 1/x + x/\sinh^2(x)$ is shown in Figure 2. It is clear from eq 27 that the generalized Laplace law (eq 14) does not hold for the case of electrostatic interactions. By repeating the derivation of the Thomson–Gibbs relation (eq 18) for the present

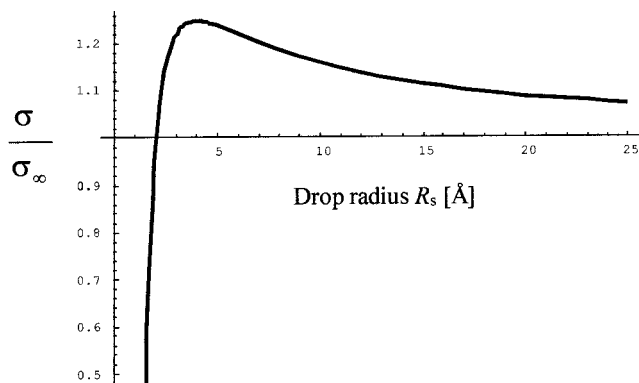


Figure 3. The dependence of the surface tension on the drop radius at $a = b = 2$ Å.

case one yields the following result

$$P_\infty - P + (kT/v_L) \ln(P/P_\infty) = [2 + \kappa b f(\kappa R)] \sigma_\infty / R \quad (28)$$

For larger drops $\kappa R \geq 2$, eq 28 reduces to

$$P_\infty - P + (kT/v_L) \ln(P/P_\infty) = (2 + b/R) \sigma_\infty / R \quad (29)$$

Since the function $f(x)$ is positive, the existence of electrolyte in the drops will inhibit condensation. This should not be confused with the favorite effect of a sole charge on the new-phase formation.²³

Discussion

The research presented in this paper shows that there is a general relationship between the surface tension of a drop and the disjoining pressure. Since the latter reflects many different types of interactions, e.g., van der Waals, electrostatic, hydrophobic, structural, etc., the dependence of the surface tension on the drop radius is not universal. It is an integral effect of all the interactions in the drop and, consequently, is system specific. For instance, the van der Waals effect is inversely proportional to the square of the drop radius, while the electrostatic contribution is inversely proportional to the drop radius to the power of unity. Combining eq 12 and eq 26, the surface tension of the drop equals

$$\sigma = \sigma_\infty (1 + b/R_s - a^2/R_s^2) \quad (30)$$

It is obvious from eq 30 that σ exhibits a maximum at $R_s = 2a^2/b$ (see Figure 3). Since the values of the lengths a and b are usually on the order of angstroms (cf. the previous sections), the results presented in this paper are meaningful for very small droplets (radius smaller than 50 Å where the surface tension changes exceed 5%). Hence, the practical usage of the present theory is its application to condensation phenomena. It has been demonstrated in this paper that the van der Waals interactions do not affect the equations describing the thermodynamics of new-phase formation. In contrast, the electrostatic interactions increase the work for nuclei creation and, consequently, inhibit the phase transition.

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