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A kinetic approach to the calculation of surface tension of a spherical drop

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Abstract. In literature, surface tension has been investigated mainly from a Thermodynamics standpoint, more rarely with kinetic methods. In the present work, surface tension of drops is studied in the framework of kinetic theory, starting from the Sutherland approximation to Van Der Waals interaction between molecules. Surface tension is calculated as a function of drop radius: it is found that it approaches swiftly an asymptotic value, for radii of several times the distance of minimum approach D of the Sutherland potential. This theoretical asymptotic value is compared to experimental values of surface tension in plane surfaces of a few liquids, and is found in reasonable agreement.

PACS. 68.03.Cd Surface tension and related phenomena – 05.70.Np Interface and surface thermodynamics

1 introduction

Droplets in the form of sprays occur in nature, for instance, as clouds, fogs and rain, as well as in numerous technical applications, such as fuel combustion, or spray painting and many, many others. Also for medical applications, the surface tension of biological liquids is important. On the other hand, measuring the surface tension of droplets is very difficult, as witnessed by the lack of experimental data in literature: hence the interest in analytical expressions to calculate it. Deriving one such analytical expression is the aim of this work.

The effect of curvature on surface tension has been investigated widely in the 50's, but mainly within the framework of Thermodynamics (see, e.g., [1,2]). Some studies have taken the point of view of kinetic theory [3,4]. More recent work investigates surface tension, in plane geometry, from the point of view of kinetic theory, making use of the Sutherland potential [5]; still much work is being done taking the Thermodynamics standpoint (see for instance [6–8]). In the present work the problem is studied through kinetic equations derived using the following simplifying assumptions:

1) **Free volume method** [1]. In this approximation, the drop is considered free from the influence of the surrounding, as if it were "in vacuum" or in "free space". That is, the pressure of the external vapor is so low that it can be neglected in the calculation of the surface tension; likewise, all exchanges with the exterior of the drop are neglected as well. This approximation can be bettered including the molecular exchange with the surrounding atmosphere [9]. This effect might form the object of subsequent work.
2) **Uncorrelated molecules**. This assumption is dictated by two considerations: first, the double distribution function (or pair distribution function, as it often referred to) is not well known as it can be calculated exactly only for extremely simplified situations. Albeit it is almost invariably called upon, still the assumptions made to calculate it are often such as to render its benefits very limited; secondly, the importance of correlation can be judged from the ratio γ between the potential energy at the average intermolecular distance and the average kinetic energy of molecules [10,11]:

$$\gamma = \frac{\Phi\left(r_0\right)}{\frac{3}{2}K_B T}. \tag{1}$$

The average intermolecular distance r_0 can be estimated, as usual, from the number density n as $n^{-\frac{1}{3}}$. As will be shown in Section 4, where γ is calculated for several cases, this ratio is of order unity, as might have been expected: therefore, correlation between molecules might play some role. However, it will be neglected here as a first approximation.
3) **Constant density**. The number density will be considered uniform throughout the volume of the drop: this approximation might turn out questionable at the interface, particularly in view of the fact that surface tension is, after all, an interface effect. This assumption will be used as a first approximation, and it will be evaluated in the discussion of the results.

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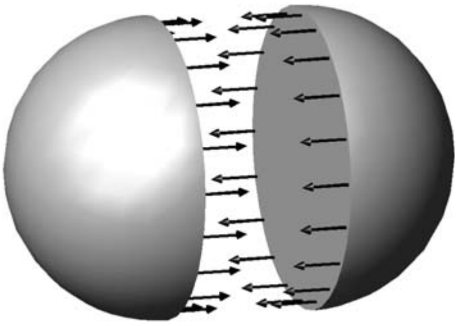

Fig. 1. Schematic representation of surface tension.

4) **Sutherland potential**. The intermolecular Van der Waals forces are modeled with the Sutherland potential. This assumption could be bettered using the full Lennard-Jones potential, however at the cost of greater mathematical difficulties; on the other hand, it can be argued that the error introduced using the Sutherland potential, with suitable parameters, is a reasonable price to pay for the mathematical simplification, which allows solution in closed form. As will be shown in the last section, the results obtained are in very reasonable agreement with experimental data.

In the following sections, a simple method will be derived within the approximations discussed above, to obtain a simple expression for the surface tension as a function of radius. In fact, experimental data on surface tension of droplets are unavailable in literature, and in the present work comparison will be made only with data on plane surfaces, which are abundant and readily available. As the radius becomes larger, the value of surface tension approaches that of a plane surface. Calculations presented for several different liquids, in the large radius limit, are consistent with experimental results for plane surfaces.

2 Governing equations

One useful way to look at surface tension is as follows. Consider a drop (which in the present framework will be perfectly spherical), a plane through the drop center, and the circle intersection of the plane with surface of the drop. This circle divides the spherical surface of the drop into two halves: one can imagine to separate the two halves, with a motion perpendicular to the dividing plane, and measure the force that has to be overcome to achieve the separation. The surface tension can then be calculated as the ratio of this force (which is, in turn, perpendicular to the dividing plane) to the length of the circle. A schematic representation of this concept is shown in Figure 1.

With this picture in mind, the following approach will be taken in the present work: consider the two aforementioned half shells (without loss of generality, one may call them upper and lower half shell, thinking of the dividing plane as being horizontal), and take any one molecule lying on the circle, say in the lower half shell. There is a force acting on this molecule due to the interaction with all the molecules in the upper half drop, and the component of this force that is perpendicular to the dividing plane can be calculated: to give it an easy name, it will be called "tangential force" in the remainder of this paper. Clearly, due to the symmetry of the problem this tangential force will be the same whichever molecule happens to be selected on the circle. If then the number of molecules per unit length of the circle can be estimated, the surface tension can be calculated as the product of this number times the tangential force. The first task is therefore the calculation of the tangential force.

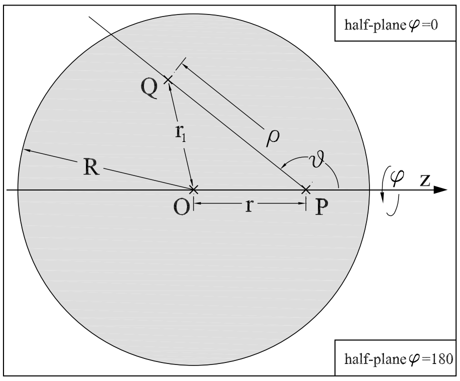

Fig. 2. A section through the drop is represented (that can be chosen arbitrarily as the plane $\varphi = 0$–$\varphi = 180$), to define the geometrical quantities used in the text.

Consider a spherical droplet of radius R centered in the point O, and a point P at a distance r from O, with $r \in [0, R]$. A system of spherical coordinates can be defined, with origin in P and the O–P direction as the polar axis, as depicted in Figure 2. The $\varphi = 0$ half-plane can be chosen arbitrarily, due to the spherical symmetry of the system.

Any point Q within the drop that lies on the $\varphi = 0$ half-plane can then be described uniquely with the pair of coordinates ρ and ϑ (or $\mu = \cos\vartheta$) as defined in Figure 1.

If forces between particles are purely central forces, i.e., depending only on a given power α of the distance, then the force due to the attraction of a particle in Q on the particle at P can be written as

$$\mathbf{F}_{QP} = \frac{G}{\rho^{\alpha}}\hat{\rho} \tag{2}$$

as it is directed from P to Q. In spherical coordinates, the half circle on the $\varphi = 0$ half-plane depicted in Figure 1 is described by the equation

$$\rho = \sqrt{(\mu r)^2 + \left(R^2 - r^2\right)^2} - \mu r \tag{3}$$

or equivalently

$$\mu = \frac{\left(R^2 - r^2\right) - \rho^2}{2r\rho} \tag{4}$$

therefore the domain corresponding to the intersection of the drop with the half-plane is defined as

$$\mu \in [-1, 1]\,; \quad \rho \in \left[0, \sqrt{(\mu r)^2 + \left(R^2 - r^2\right)^2} - \mu r\right] \tag{5}$$

or equivalently

$$\rho \in [0, R+r]\,; \quad \mu \in \left[-1, \min\left\{1, \frac{\left(R^2-r^2\right)-\rho^2}{2r\rho}\right\}\right]. \tag{6}$$

If there are $n\left(r_1\right)$ particles per unit volume (due to the spherical symmetry the density can only depend on the radial position r_1, and this can be expressed in terms of r, ρ and μ), in a volume element dV (expressed in spherical coordinates) at location (ρ, μ, φ) there are a number of particles given by

$$ndV = n\left(r_1\left[r, \rho, \mu\right]\right)\rho^2 d\rho d\mu d\varphi \tag{7}$$

exerting on the particle at P a force $d\mathcal{F}$

$$d\mathcal{F} = \frac{G}{\rho^{\alpha}} ndV = Gn\left(r_1\right)\rho^{2-\alpha} d\rho d\mu d\varphi. \tag{8}$$

The component of $d\mathcal{F}$ perpendicular to z is:

$$d\mathcal{F}_{\perp} = d\mathcal{F}\sin\vartheta = Gn\left(r_1\right)\rho^{2-\alpha}\sqrt{1-\mu^2}\, d\rho d\mu d\varphi. \tag{9}$$

Consider now a molecule that is lying right on the edge of one half drop, say at the intersection of the polar axis with the drop surface. In keeping with the geometry defned in Figure 2, the horizontal plane corresponds to $\varphi = \pm\frac{\pi}{2}$, and the tangential force on a molecule on the edge of the lower half shell is along the $\varphi = 0$ direction. The tangential force dF_T acting on this molecule due to all elements in the upper half shell with coordinates (ρ,ϑ), is given by the integral over φ of $d\mathcal{F}_{\perp}\cos\varphi$ in the upper half of the drop, i.e., for $\varphi \in \left[-\frac{\pi}{2}, \frac{\pi}{2}\right]$:

$$\begin{aligned} dF_T &= \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \left[Gn\left(r_1\right)\rho^{2-\alpha}\sqrt{1-\mu^2}\, d\rho d\mu\right]\cos\varphi d\varphi \\ &= 2Gn\left(r_1\right)\rho^{2-\alpha}\sqrt{1-\mu^2}\, d\rho d\mu. \end{aligned} \tag{10}$$

To calculate the total tangential force on the molecule, the above expression is to be integrated over ρ and μ. In the following the density will be considered constant, as discussed in point 3) in the introduction. Recalling the expression for the domain in equation (6), noted that in this case $r = R$, the following integral is obtained:

$$\begin{aligned} \frac{F_T}{2nG} &= \int_D^{2R} \rho^{2-\alpha} d\rho \int_{-1}^{\frac{-\rho}{2R}} \sqrt{1-\mu^2}\, d\mu \\ &= \frac{1}{2}\int_D^{2R} \rho^{2-\alpha}\left\{\arcsin\left(\frac{-\rho}{2R}\right)\right. \\ &\qquad \left. -\frac{\rho}{2R}\sqrt{1-\left(\frac{\rho}{2R}\right)^2} + \frac{\pi}{2}\right\} d\rho. \end{aligned} \tag{11}$$

Here D is the distance of minimum approach, as will be discussed in the next section.

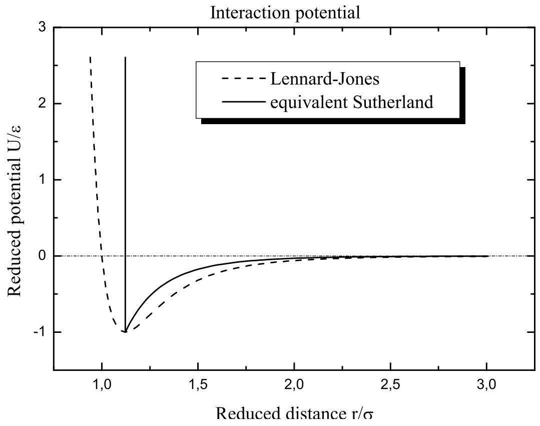

Fig. 3. Schematized Sutherland potential.

3 Solution with Van der Waals type forces

Van der Waals interactions are usually represented as a Lennard-Jones potential [12]

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{12}$$

This last can be approximated by a Sutherland potential [12], usually written as

$$U_S(r) = \begin{cases} \infty & r < D \\ -A\left(\frac{D}{r}\right)^{\omega} & r \geq D \end{cases} \tag{13}$$

with suitable choice of the (positive) constants ω, A and D. A condition typically imposed is to conserve the asymptotic behavior of ULJ, which entails $\omega = 6$ and $A{\cdot}D^6 = 4\varepsilon{\cdot}\sigma^6$; a second condition can be chosen as follows: the rest position of a particle in the field of another particle is the bottom of the potential well, therefore it seems reasonable to choose the constants so that this position is the same in the two cases. Therefore, $D = \sigma \cdot 2^{\frac{1}{6}}$. With the above positions the Sutherland potential becomes

$$U_S(r) = \begin{cases} \infty & r < D = \sigma \cdot 2^{\frac{1}{6}} \\ -\varepsilon\left(\frac{D}{r}\right)^{6} & r \geq D = \sigma \cdot 2^{\frac{1}{6}}. \end{cases} \tag{14}$$

This potential is depicted in Figure 3. This corresponds to the present model for the force equation (2), with $\alpha = 7$ and

$$G = 6\varepsilon D^6. \tag{15}$$

It is worth pointing out that the length D in the Sutherland approximation is the minimum possible distance between two molecules: this is not to be confused with the average distance r_0 between molecules, which is always larger due to thermal motion. Since D is the distance of minimum approach, it serves as the lower limit of the integral in equation (11). Calculating that integral, and recalling the expression for G in equation (15), the following expression is obtained for the tangential force

Table 1. Comparison of calculated and experimental values of surface tension.

	Density $[\mathrm{m}^{-3}]$	Lennard-Jone parameters [13] σ [Å]	$\varepsilon/K_{\mathrm{B}}$ [K]	$\gamma = \frac{\Phi(r_0)}{\frac{3}{2}\mathrm{KT}}$	Calculated value [N/m]	Experimental value [N/m]
Water, 20 °C	3.34×10^{28}	2.641	809.1	1.4	248×10^{-3}	72.75×10^{-3} [14]
Ethanol, 20 °C	1.01×10^{28}	4.530	362.6	1.5	66.5×10^{-3}	22.75×10^{-3} [14]
Acetone, 20 °C	0.671×10^{28}	4.600	560.2	0.57	61.5×10^{-3}	23.70×10^{-3} [14]
Benzene, 20 °C	0.677×10^{28}	5.349	412.3	2.01	62.0×10^{-3}	28.88×10^{-3} [13]
Liquid Oxigen, −183 °C	2.14×10^{28}	3.467	106.7	1.26	31.2×10^{-3}	13.2×10^{-3} [14]
Liquid Nitrogen, −183 °C	1.72×10^{28}	3.798	71.4	0.94	18.8×10^{-3}	6.6×10^{-3} [14]

acting on a molecule:

$$F_T = \frac{3}{2} n \varepsilon D^2 \left\{ \arcsin\left(\frac{-D}{2R}\right) + \frac{D}{2R}\sqrt{1-\left(\frac{D}{2R}\right)^2}\left[1-2\left(\frac{D}{2R}\right)^2\right] + \frac{\pi}{2} \right\}. \quad (16)$$

As explained earlier, to obtain the surface tension this tangential force on a single molecule must be multiplied by the average number of molecules per unit length of the circle dividing the two half shells, or in other words, the inverse of the average distance between molecules along the circle. This last quantity is estimated in this work as the average distance between molecules considering a uniform density n, in keeping with approximation number 3), given by $n^{-\frac{1}{3}}$. Therefore, in this approximation the number of moleules per unit length can be estimated as $n^{\frac{1}{3}}$, and the surface tension calculated as

$$T_{sur}(R) = \frac{3}{2} n^{\frac{4}{3}} \varepsilon D^2 \left\{ \arcsin\left(\frac{-D}{2R}\right) + \frac{D}{2R}\sqrt{1-\left(\frac{D}{2R}\right)^2}\left[1-2\left(\frac{D}{2R}\right)^2\right] + \frac{\pi}{2} \right\}. \quad (17)$$

The graph of the reduced surface tension $\frac{T_{sur}}{\frac{3}{2} n^{\frac{4}{3}} \varepsilon D^2}$ as a function of $\frac{2R}{D}$, the drop diameter in units of D, is shown in Figure 4.

As can be gathered from the graph, the surface tension approaches rapidly the asymptotic value as the drop diameter grows to only a few tens of times D.

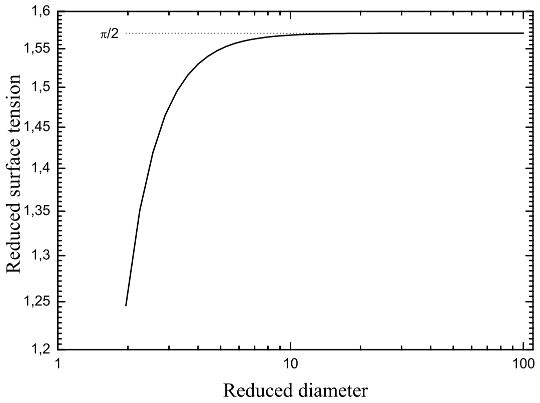

Fig. 4. Reduced surface tension vs. drop diameter in units of D.

4 Comparison with experimental data

Limiting values of surface tension for large radii have been calculated from equation (17) for several liquids, and compared with known experimental values for plane surfaces. The results are shown in Table 1. As can be gathered from the data reported, the agreement is quite good for such a qualitative approach, being always within a factor of 2 to 3 (3.4 for water). As the results depend on the parameters of the Sutherland potential, agreement might be improved by a different choice, the one choice made here being somewhat arbitrary albeit reasonable. In [15], for instance, detailed calculation and comparison with Lennard-Jones parameters is reported for several inert gases.

On the other hand, the density is indeed essentially constant throughout the drop except near the boundary, where it is generally found to decrease [1,5,16–20]. As the layers close to the boundary give the main contribution to the integral in equation (14), the actual density profile should be considered in the integration. This will form the object of a subsequent work, for the present the following view will be taken: in the literature, the density is always shown to decrease rather abruptly near the interface, taking a relative value at the interface of roughly one half the bulk value. Therefore, introducing the actual density in the integral will decrease this latter by a factor that is between 0.5 and 1. On the other hand, in calculating the number of molecules per unit length at the surface, the value of density at the surface must be considered; altogether then, adding the two effects, the result changes by a factor of between 0.4 and 0.8, which has the right magnitude to provide the correction needed for reconciling calculated values with those found experimentally.

5 Conclusions

As anticipated in the introduction, aim of this work was to propose a simple equation for calculating surface tension in drops as a function of radius. The asymptotic behaviour for large radii is in very reasonable agreement with experimental data on plane surfaces. This result was obtained in the simplifying assumptions discussed in the introduction. Accurate description of the density profile is needed to improve confidence in the results yielded by the method proposed.

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