Mendeleev Commun., 2002, 12(3), 97–98

On the surface curvature dependence of the surface energy of a nanoparticle

Anatoly I. Rusanov

Mendeleev Centre, St. Petersburg State University, 199034 St. Petersburg, Russian Federation.
Fax: +7 812 428 6939; e-mail: rusanov@rus.usr.pu.ru

10.1070/MC2002v012n03ABEH001593

The surface curvature dependence of pure dynamic surface energy and surface tension has been derived for a non-polar nanoparticle, the dependence containing no linear term. The effect of entropy and surface structure explains the only slight curvature dependence of real surface tension in the case of non-polar matter.

The surface curvature dependence of surface tension is a central problem in the theory of capillarity. It is especially important for nanoparticles. When relating this problem to the kind of pair interaction,[1] one also touches the problem of surface energy considered earlier only for a flat interface.[2] One of Gibbs' definitions of surface tension treats the quantity σ as the work of formation of unit area of a new surface, say, by cutting a body. Applying this definition to the formation of a curve interface, we can imagine a ball of matter transferred from the interior of a bulk phase to a vacuum. At zero temperature, the work of transfer of the ball from a fixed position in the bulk of a condensed phase to a fixed position in a vacuum is evidently equal to the energy of cohesion of the ball with its surroundings in the bulk phase. Using the molecular pair potential $\varnothing(r_{12})$, the above cohesive energy U_{12} is given by the expression[3]

$$U_{12} = 4\pi^2\rho^2 \int\limits_{r+\delta}^{\infty} y\mathrm{d}y \int\limits_{y-r}^{y+r} \varnothing(r_{12})r_{12}[r^2 - (y - r_{12})^2]\mathrm{d}r_{12}, \tag{1}$$

where ρ is the molecular number density in the bulk phase, r is the ball radius as the distance from the ball centre to the centres of its surface molecules and δ is the minimum intermolecular distance (the molecular size) in the bulk phase (Figure 1). For the particular case of dispersion forces $[\varnothing(r_{12}) = -\lambda r_{12}^6]$ and choosing δ as unit length, equation (1) yields

$$U_{12} = -\frac{\pi^2\rho^2\lambda}{12}\left[4R^2 - 4\ln(2R) - \frac{1}{4R^2}\right], \tag{2}$$

where λ is the London constant and $R \equiv r/\delta + 1/2$ is the dimensionless radius of the equimolecular surface (Figure 1). By dividing (2) by the surface area $4\pi R^2$, we obtain the expression for the cohesive energy u_{12} of a curved interface per unit area

$$u_{12}(R) = -\frac{\pi\rho^2\lambda}{12}\left[1 - \frac{\ln(2R)}{R^2} - \frac{1}{16R^4}\right]. \tag{3}$$

Passing to the limit $R \to \infty$, equation (3) changes to the well-known expression for the dispersion-forces cohesive energy of two half-spaces separated by a flat slit of width δ ($\delta = 1$ this time):[4]

$$u_{12}(\infty) = -\frac{\pi\rho^2\lambda}{12}. \tag{4}$$

Since we integrated from a smallest distance, the question arises about the role of repulsion energy. Using the Lennard–Jones potential $\varnothing(r_{12}) = -\lambda r_{12}^6 + \lambda r_{12}^{12}$, we can calculate the contribution of repulsion energy just in the above way. This contribution depends on R, but is small at large R. In particular, when taking the repulsion energy into account, (4) is replaced by

$$u_{12}(\infty) = -\frac{29\pi\rho^2\lambda}{360}, \tag{5}$$

which shows the repulsion energy to amount only about 3% in the limit $R \to \infty$.

The opposite limit $R \to 1/2$ (when the ball includes only one molecule) requires a separate calculation in the point-force approach since equation (3), which is based on the integration over the ball volume, yields $u_{12} = 0$ when the ball degenerates into a point. The result is easily obtained as

$$U_{12}(1/2) = 4\pi\rho\int\limits_{1}^{\infty}\varnothing(r_{12})r_{12}^2\,\mathrm{d}r_{12} \tag{6}$$

or, using the Lennard–Jones potential,

$$U_{12}(1/2) = 4\pi\rho\lambda\left(\frac{1}{9} - \frac{1}{3}\right) = -\frac{8}{9}\pi\rho\lambda, \tag{7}$$

where the contribution of repulsion is shown to amount 1/3 of that of attraction. In the dimensionless units used, the volume of a spherical molecule is $\pi/6$ and its surface area is π, so that the cohesive energy per unit surface area for a single molecule is

$$u_{12}(1/2) = U_{12}(1/2)/\pi = -\frac{8}{9}\rho\lambda. \tag{8}$$

Assuming the structure of matter unchanged (as a consequence, *e.g.*, of non-compressibility and zero temperature), the work of disjoining of the ball and its surroundings is just equal to the reverse cohesive energy. Then surface energy ε (coinciding with surface tension at zero temperature) is defined as half of reverse cohesive energy per unit surface area. Thus, we have from (3) (neglecting the contribution of repulsion)

$$\varepsilon(R) = \frac{\pi\rho^2\lambda}{24}\left[1 - \frac{\ln(2R)}{R^2} - \frac{1}{16R^4}\right], \tag{9}$$

which exhibits a monotonic increase of the surface energy of a nanoparticle with the particle size. Expanding (9) into a series with respect to $1/R$ ($b = \ln 2 + 1/2 \approx 1.193$)

$$\varepsilon(R) = \frac{\pi\rho^2\lambda}{24}\left[1 - \frac{b}{R^2} + \ldots\right], \tag{10}$$

we discover the absence of a linear term typical of the curvature dependence of surface tension.[5,6] This effect is predictable. The cohesion energy equally belongs to convex and concave surfaces in touch with each other if they possess identical structures (coinciding with the structure of the bulk phase). As a result, the surface energies of both of the surfaces are the same and, therefore, are independent of the curvature sign, which is possible only in the absence of a linear term from (10). Thus, we can conclude that a linear term can appear due to the effects of entropy (at temperatures above zero) and specific surface structure (different for a convex surface and a concave one) as a consequence of non-zero compressibility.

In two opposite limiting cases $R = \infty$ and $R = 1/2$, we have from (5) and (8) (exact results accounting for repulsion)

$$\varepsilon_\infty = -\frac{29\pi\rho^2\lambda}{720}; \tag{11}$$

$$\varepsilon_1 = -\frac{4}{9}\rho\lambda \tag{12}$$

for a macroscopic body and a single molecule in a vacuum, respectively. From (11) and (12) we obtain

$$\varepsilon_1/\varepsilon_\infty = 4{\times}720/29{\times}9{\times}\pi\rho \approx 3.5/\rho. \tag{13}$$

The result is not surprising: it is much more difficult to extract a molecule from the bulk than to transfer the molecule to the surface. The particular value of $\varepsilon_1/\varepsilon_\infty$ depends on the value of ρ ($1 \le \rho < 2$), which, in turn, depends on the type of packing;

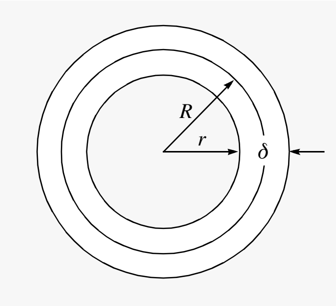

Figure 1 The interaction of the ball of matter with its surroundings.

$\rho = 1$ and $\varepsilon_1/\varepsilon_\infty \approx 3.5$ for the cubic packing. The most compact packing of hard spheres requires $\rho = 1.4$ and $\varepsilon_1/\varepsilon_\infty \approx 2.5$.

The surface energy and surface tension coincide at zero temperature. However, they can be different at room temperature. The surface tension is equal to the specific free surface energy of pure liquids. The common mechanical definition of surface tension is scarcely applicable to a free single molecule, but we can operate with free surface energy σ to characterise this case. Using the Dupré rule

$$w = A\Delta\sigma, \qquad (14)$$

we can easily calculate the specific free surface energy σ of a single molecule from the work w of transfer of the molecule from a fixed position in a condensed phase to a fixed position in a vacuum (A is the surface area). Since the free surface energy of a molecule inside a bulk phase is zero, the specific free surface energy of the molecule in a vacuum can be estimated as

$$\sigma = w/A. \qquad (15)$$

In turn, the work of transfer of a molecule from a condensed phase α to a gaseous phase β can be found from the standard relationship

$$w = kT\ln(\rho^\alpha/\rho^\beta), \qquad (16)$$

where k is Boltzmann's constant, T is temperature, and the equilibrium phase concentration ratio stands under the logarithm sign.

Here, we present the calculation for carbon tetrachloride at 20 °C. The reference data for CCl_4 are as follows: molecular mass $M = 153.81$, density $d = 1595$ kg m^{-3}, surface tension $\sigma = 25.68$ mJ m^{-2}, and vapour pressure $p^\beta = 91.28$ Torr.[7] Assuming the ideal behaviour of a gaseous phase, we find $\rho^\beta = p^\beta/kT = 3.01\times10^{24}$ m^{-3}. Further calculations gave: $\rho^\alpha = N_A(d/M) = 6.25\times10^{27}$ m^{-3} (N_A is Avogadro's number) and $\rho^\alpha/\rho^\beta = 2075$. Equation (16) yields $w = 3.09\times10^{-20}$ J.

The volume per molecule of CCl_4 in the liquid phase is $v^\alpha = 1/\rho^\alpha = 160.1\times10^{-30}$ m^3. Choosing the location of the dividing surface of a single spherical molecule of CCl_4 as to occupy the same volume in a vacuum, we calculate the molecular diameter as $\delta = (6v^\alpha/\pi)^{1/3} = 6.76\times10^{-10}$ m. Correspondingly, the dividing surface area is $A_1 = \pi\delta^2 = 142.6\times10^{-20}$ m^2 and the specific free surface energy (surface tension) attributed to this dividing surface is $\sigma_1 = w/A_1 = 21.66$ mJ m$^{-2} \approx 0.84\sigma$. In contrast with surface energy, the free surface energy of a single molecule is relatively close to the macroscopic surface tension. This quite different behaviour of surface energy and free surface energy gives evidence for a great role of entropy. The extraction of a molecule from the depth of a bulk phase requires much more energy but is accompanied by a much greater release of entropy as compared with the transfer of the molecule to the surface. The compensation effect of entropy explains the slight dependence of the surface tension of non-polar liquids on the surface curvature.

This work was supported by the Russian Foundation for Basic Research (grant no. 98-03-32009a).

References

1 R. Tsekov, K. W. Stöckelhuber and B. V. Toshev, *Langmuir*, 2000, **16**, 3502.

2 A. I. Rusanov, *J. Colloid Interface Sci.*, 1982, **90**, 143.

3 A. I. Rusanov, *Micellization in Surfactant Solutions, Chemistry Reviews*, ed. M. E. Vol'pin, Harwood Academic Publ., 1997, vol. 22, part 1.

4 J. Mahanty and B. W. Ninham, *Dispersion Forces*, Academic Press, London, 1976.

5 J. C. Melrose, *Ind. Eng. Chem.*, 1968, **60** (3), 53.

6 A. I. Rusanov, *Phasengleichgewichte und Grenzflaechenerscheinungen*, Akademie-Verlag, Berlin, 1978.

7 *Spravochnik khimika* (*Reference Book of a Chemist*), Gosudarstvennoe Nauchno-tekhnicheskoe Izdatel'stvo Khimicheskoi Literatury, Leningrad, 1963, vol. 1.

Received: 19th April 2002; Com. 02/1919