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The perturbation approach to the statistical theory of surface tension: new analytical results

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Abstract. A new analytical expression for the surface tension of a planar liquid–vapour interface is obtained. It is based on the Fowler approximation and the statistical-mechanical perturbation approach in the theory of liquids. The expression obtained is explicit in the equilibrium liquid density. Theoretical predictions are shown to be consistent with the results of Monte Carlo and molecular-dynamics simulations of the Lennard-Jones fluid.

1. Introduction

In 1949 Kirkwood and Buff [1] derived (on the basis of the microscopic pressure tensor consideration) an exact expression for the surface tension γ of a planar liquid–vapour interface in a system of pairwise interacting particles (for a review see also [2]):

$$\gamma = \frac{1}{4} \int_{-\infty}^{+\infty} dz_1 \int d\mathbf{r}_{12} \left(r_{12} - \frac{3z_{12}^2}{r_{12}} \right) u'(r_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \rho^{(1)}). \quad (1)$$

Here $u(r_{12})$ is a pair interaction potential of molecules situated at points \mathbf{r}_1 and \mathbf{r}_2 of the inhomogeneous liquid–vapour system, $' = d/dr_{12}$, inhomogeneity is assumed to be along the z direction; $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \rho^{(1)}) = \rho^{(2)}(r_{12}, z_1, z_2; \rho^{(1)})$ is a pair distribution function of the system; $\rho^{(1)}$ is its number density. Application of equation (1) for the calculation of surface tension requires the knowledge of $\rho^{(2)}$ and $\rho^{(1)}$. Unfortunately, no practicable and exact routes exist to determine these functions in the interfacial domain from the knowledge of $u(r)$ only.

Further progress can be achieved in several ways. The first possibility is to perform a *direct* Monte Carlo or molecular-dynamics simulation [3–6]. For this purpose equation (1) can be expressed as

$$\gamma = \frac{1}{A} \left\langle \sum_{i < j} \left(r_{ij} - \frac{3z_{ij}^2}{r_{ij}} \right) u'(r_{ij}) \right\rangle \quad (2)$$

where the summation is taken over all pairs of molecules in a sample of area A , and the angle brackets denote an average over simulation. Another approach consists in determination of $\rho^{(1)}$ and $\rho^{(2)}$ by an iterative procedure using the Yvon–Born–Green hierarchy or the Ornstein–Zernike equation with various approximations (see e.g. [7]). Serious progress in the statistical theory of liquids during the last two decades has been achieved due to

implementation of the perturbation theory in which the attractive part of the interaction potential is treated as a perturbation in the reference system described by the repulsive part of the potential (for a review see [8]). Its extension to liquid–vapour problems was made by Toxvaerd [9] and later on developed by Lee *et al* [10]. In 1979 Evans [11] extended the ideas of the modern density-functional theory (DFT) to the problem of the liquid–vapour interface. Recently Zeng and Oxtoby [12] have calculated the surface tension of a Lennard-Jones fluid using the DFT formalism in combination with the perturbation theory.

All the above-mentioned approaches—direct numerical simulation of γ by means of the Monte Carlo or molecular-dynamics technique, calculation of the density profile and distribution functions by means of iterative procedures—require a considerable amount of computational work. It is the aim of the present paper to propose a simple *analytical* model for the surface tension, which could give qualitatively reasonable results within the range of its validity. This range is limited by the condition that the temperature should not be too close to the critical temperature T_c . The model is formulated in section 2. In section 3 our results for the surface tension are compared with the Monte Carlo and molecular-dynamics data and with the results of the DFT calculations for Lennard-Jones fluids.

2. Model

We assume that the liquid–vapour system has a temperature T not too close to T_c . Then an important simplification of the problem can be achieved if we shrink the physical liquid–vapour transition zone to a mathematical surface of a density discontinuity. The density profile $\rho^{(1)} = \rho(z)$ becomes a step-function: $\rho(z) = \rho_L$ in the liquid phase and $\rho(z) = \rho_V \simeq 0$ in the vapour phase. This approximation, first proposed by Fowler [13], is valid provided that the equilibrium bulk vapour density $\rho_V(T)$ is negligible compared to the equilibrium bulk liquid density $\rho_L(T)$. In this approximation $\rho^{(2)}$ is represented in the form $\rho^{(2)}(r_{12}, z_1, z_2; \rho^{(1)}) = \rho(z_1)\rho(z_2)g(r_{12}; \rho)$ where $g(r_{12}; \rho)$ is the pair correlation function in the bulk. Then equation (1) is converted to [2]:

$$\gamma = \frac{\pi}{8} \rho_L^2 \int_0^\infty dr r^4 u'(r) g(r; \rho_L) \quad (3)$$

where $g(r; \rho_L)$ is a pair correlation function of a homogeneous liquid with the density ρ_L . The function $g(r; \rho_L)$ can be determined experimentally by x-ray or neutron diffraction or numerically with the help of Monte Carlo or molecular dynamics simulations.

A further *analytical* calculation of γ , in order to be quantitatively reliable, should take into account a strong density dependence of the correlation function. We write g in the form $g(r; \rho_L) = e^{-\beta u(r)} y(r; \rho_L)$ introducing a cavity function $y(r; \rho_L)$; $\beta = 1/kT$, k is the Boltzmann constant. Then equation(3) can be written as

$$\gamma = \frac{\pi}{8} \rho_L^2 [A_1(T) + A_2(T, \rho_L)] \quad (4)$$

where

$$A_1(T) = \int_0^\infty dr r^4 u'(r) e^{-\beta u(r)} \quad (5)$$

$$A_2(T, \rho_L) = \int_0^\infty dr r^4 u'(r) e^{-\beta u(r)} [y(r; \rho_L) - 1]. \quad (6)$$

Introducing the Mayer function $f(r) = \exp[-\beta u(r)] - 1$ and using its asymptote at $r \rightarrow \infty$ we obtain

$$A_1(T) = 4kT \int_0^\infty dr f(r) r^3 \tag{7}$$

$$A_2(T, \rho_L) = -kT \int_0^\infty dr f'(r) r^4 [y(r; \rho_L) - 1]. \tag{8}$$

Note that A_2 is comparable with A_1 in view of the Fowler approximation, in which ρ_L cannot be considered a small parameter.

We evaluate A_2 with the help of a statistical-mechanical perturbation approach based on the Weeks–Chandler–Andersen (WCA) decomposition [14] of the interaction potential: $u(r) = u_0(r) + u_1(r)$, where

$$u_0(r) = \begin{cases} u(r) + \epsilon & \text{for } r < r_m \\ 0 & \text{for } r > r_m \end{cases} \tag{9}$$

$$u_1(r) = \begin{cases} -\epsilon & \text{for } r < r_m \\ u(r) & \text{for } r > r_m \end{cases}$$

$\epsilon > 0$ is the depth of the potential and r_m its minimum position: $u(r_m) = -\epsilon$. The main idea of the perturbation approach in the theory of liquids [8], which dates back to van der Waals, is that the structure of a dense fluid is determined primarily by the repulsive part of the interaction potential ($u_0(r)$ in the WCA theory). The attractive part, $u_1(r)$, provides a uniform background potential in which molecules move. Therefore attractive forces are treated as a perturbation in the reference system with the repulsive potential $u_0(r)$.

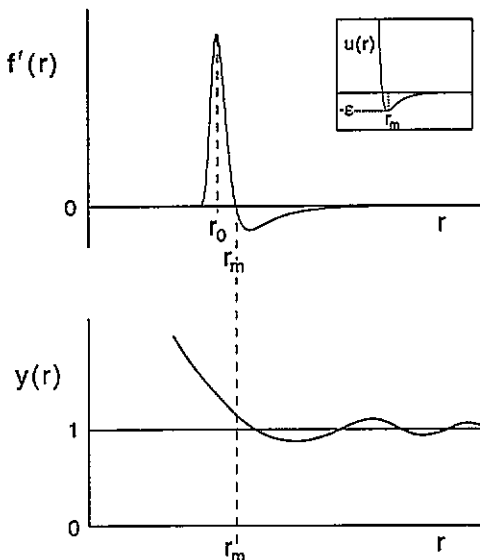


Figure 1. The derivative $f'(r)$ of the Mayer function and the cavity function $y(r)$ for the interaction potential $u(r)$.

In the region $r < r_m$ the function $f'(r)$ has a sharp positive peak and the cavity function $y(r; \rho_L)$ monotonically decreases [14]. In the region $r > r_m$, $f'(r)$ is negative and asymptotically tends to zero, whereas $[y(r; \rho_L) - 1]$ oscillates about zero (figure 1). In view of these oscillations we can set the upper limit of the integral in equation (8) equal to r_m . For $r < r_m$, $f'(r) = f'_0(r) \exp(\beta\epsilon)$, where $f_0(r) = \exp[-\beta u_0(r)] - 1$ is the Mayer function corresponding to the reference interaction. In the framework of the perturbation approach we expand $f'(r) \simeq f'_0(r)(1 + \beta\epsilon)$. In the same domain $r < r_m$ one can replace the function $y(r; \rho_L)$ by its repulsive part $y_0(r; \rho_L) = e^{\beta u_0(r)} g_0(r; \rho_L)$ ($g_0(r; \rho_L)$ is the reference system correlation function) because $y(r; \rho_L)$ and $y_0(r; \rho_L)$ are quite similar [15]. Thus A_2 can be approximated as

$$A_2(T, \rho_L) = -kT \int_0^{r_m} dr f'_0(r) (1 + \beta\epsilon) r^4 [y(r; \rho_L) - 1]. \quad (10)$$

In order to evaluate the integral on the right-hand side we follow the arguments of Song and Mason (SM) [16] who have recently used similar considerations to obtain an analytical representation of the compressibility equation for liquids explicit in density. Function $f'_0(r)$ has a sharp peak at some $r_0 < r_m$, therefore the major contribution to the integral in equation (10) originates from the vicinity of r_0 , where y_0 behaves to first order as a straight line:

$$y_0(r; \rho_L) = y_0(R; \rho_L) + \left(\frac{dy_0}{dr} \right)_R (r - R) + \dots \quad (11)$$

with a negative slope $(dy_0/dr)_R$; R is a point near r_0 . Substitution of this expansion into equation (10) gives

$$A_2 = -kT(J_0 + J_+ + J_- + \dots) \quad (12)$$

where

$$J_0 = [y_0(R; \rho_L) - 1] \int_0^{r_m} dr f'_0(r) r^4 \quad (13)$$

$$J_+ = \beta\epsilon [y_0(R; \rho_L) - 1] \int_0^{r_m} dr f'_0(r) r^4 \quad (14)$$

$$J_- = \left(\frac{dy_0}{dr} \right)_R \int_0^{r_m} dr f'_0(r) r^4 (r - R). \quad (15)$$

At intermediate to high temperatures the integrals J_+ and J_- are negligible compared to J_0 . At low temperatures they tend to compensate each other: J_+ is positive and J_- is negative for all temperatures. So

$$A_2 \simeq -kT J_0 = 4kT [y_0(R; \rho_L) - 1] \int_0^{r_m} dr f_0(r) r^3. \quad (16)$$

Physically, function $y_0(r; \rho_L)$ gives the correlations that exist in the reference system beyond the range of the reference interaction $u_0(r)$, $y_0(r)$ is a more slowly varying function of r than $g_0(r)$. Since the reference interaction is harshly repulsive, y_0 is fairly insensitive to any

particular form of the repulsive potential and therefore can be approximated by the similar function appropriate to a hard-sphere system of some effective diameter d [14]:

$$\gamma_0(R; \rho_L) \simeq \gamma_d(d; \rho_L) = g_d(d^+; \rho_L) \quad (17)$$

where $g_d(d^+; \rho_L) = \lim_{r \rightarrow d+0} g(r; \rho_L)$ is the hard-sphere correlation function at contact. For $g_d(d^+; \rho_L)$ we use the Carnahan–Starling formula [17] which is known to give accurate results up to the freezing density;

$$g_d(d^+; \rho_L) = \frac{4 - 2\phi_d}{4(1 - \phi_d)^3} \quad (18)$$

where $\phi_d = (\pi/6)d^3\rho_L$ is the hard-sphere packing fraction. Substitution of equations (7), (16) and (17) into equation (4) gives the final analytical expression for the surface tension, which is explicit in density;

$$\gamma = \frac{\pi}{2} \rho_L^2 kT \left[\int_0^\infty dr f(r) r^3 + (g_d(d^+; \rho_L) - 1) \int_0^{r_m} dr f_0(r) r^3 \right]. \quad (19)$$

This result should be completed by the equation of state for determination of $\rho_L(T)$ and by the algorithm of determination of the effective hard-sphere diameter d . A perturbation technique similar to that described above can be applied to the compressibility equation resulting in the SM equation of state [16]

$$\frac{P}{\rho kT} = 1 + B_2 \rho + \alpha \rho [g_d(d^+; \rho_L) - 1] \quad (20)$$

where p is the pressure, ρ the number density,

$$B_2(T) = 2\pi \int_0^\infty dr r^2 [1 - e^{-\beta u(r)}] \quad (21)$$

the second virial coefficient of the original system and

$$\alpha(T) = 2\pi \int_0^{r_m} dr r^2 [1 - e^{-\beta u_0(r)}] \quad (22)$$

the second virial coefficient of the reference system. The equilibrium liquid density can be found from equation (20) by imposing the conditions of phase equilibrium: $p(\rho_L, T) = p(\rho_V, T)$, $\mu(\rho_L, T) = \mu(\rho_V, T)$ (μ is a chemical potential). In view of the Fowler approximation we can treat the vapour phase as an ideal gas with a vanishingly small density. Therefore $\rho_L(T)$ becomes a solution of the fourth-order algebraic equation

$$\alpha(T)\rho_L [g_d(d^+; \rho_L) - 1] = -B_2(T)\rho_L - 1. \quad (23)$$

The choice of an effective hard-sphere diameter d represents a separate problem. In the WCA theory d is found by equating the compressibility of the reference system to that of the hard spheres. It depends on temperature and density and is calculated by *iteration* using

the Percus–Yevick approximation for a hard-sphere fluid. In the Barker and Henderson theory [8] d is a function of T only and is given by a closed form *analytical* expression: $d = \int_0^\infty dr [1 - \exp(-\beta u_0)]$. For the case of a Lennard-Jones fluid Lu *et al* [18] found an algebraic approximation for the Barker–Henderson diameter by fitting to the Monte Carlo simulations of the Lennard-Jones coexistence curve [19], [20]:

$$d(T) = \frac{a_1 T + b}{a_2 T + a_3} \sigma \quad (24)$$

where $a_1 = 0.56165k/\epsilon$, $a_2 = 0.60899k/\epsilon$, $a_3 = 0.92868$ and $b = 0.9718$; σ is a ‘molecular diameter’ in the Lennard-Jones potential.

An alternative general expression for $d(T)$, which describes correctly the low- and high-temperature limits and behaves smoothly in between, was proposed by SM:

$$d^3(T) = 3 \int_0^{r_m} dr r^2 [1 - (1 + \beta u_0(r)) e^{-\beta u_0(r)}]. \quad (25)$$

3. Results and discussion

We calculate the surface tension (equation (19) with ρ_L given by equation (23)) for the Lennard-Jones system with the potential $u(r) = u_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. In figure 2 the reduced surface tension $\gamma\sigma^2/\epsilon$ is shown as a function of reduced temperature kT/ϵ . Two curves—the solid one and the dashed one—correspond to the two different algorithms for $d(T)$: equation (24) and equation (25), respectively. Also shown in figure 2 are the results of direct Monte Carlo and molecular dynamics simulations of surface tension by Chapela *et al* [3], Miyazaki *et al* [4], Salomons and Mareschal [5], and Holcomb *et al* [6]. In the computer simulations the Lennard-Jones potential was truncated at some distance r_c . The surface tension calculated for the truncated potential was extrapolated to the full potential value using a tail correction. In figure 2 the results taking into account tail corrections are shown. From the results displayed one can see that the simulation data are situated somewhat lower than the theoretical curves. The reason for this is that even when the tail correction is used one obtains underestimated values of surface tension, as analysed by Holcomb *et al* [6].

In order to evaluate how our model works in comparison with more sophisticated theories, we refer to the results of recent calculations of Zeng and Oxtoby [12] based on the DFT. In the approach of [12] the grand potential functional $\Omega[\hat{\rho}]$ of an unknown density profile of the inhomogeneous liquid–vapour system is related to the intrinsic Helmholtz free-energy functional. Using the WCA decomposition of the interaction potential equation (10), the local-density approximation for the free energy of the reference system, and the random-phase approximation for the perturbation of the free energy, the equilibrium density profile $\rho(\mathbf{r})$ is found from the variational condition $\delta\Omega/\delta\hat{\rho}(\mathbf{r})|_{\rho(\mathbf{r})} = 0$. The integral equation for $\rho(z)$ is then solved by iteration; the surface tension of the planar interface is found from the relation $\gamma = (\Omega[\rho] + pV)/A$, where p is the equilibrium (saturation) pressure at temperature T , V is the volume of the system and A the interfacial area; $\Omega[\rho]$ is evaluated at the equilibrium density profile $\rho(z)$.

The results of these calculations [12] are shown in figure 2 by the dashed-dotted line. One can see that they are close to the predictions of our theory (solid line) when the same

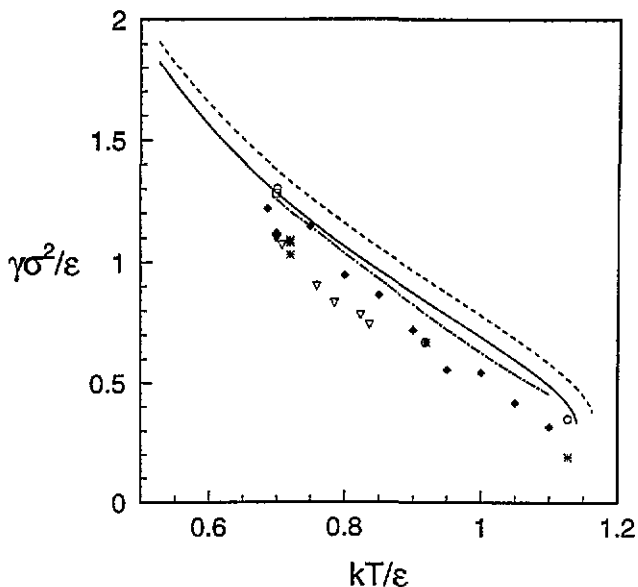


Figure 2. The surface tension of a Lennard-Jones fluid: solid line, $d(T)$ calculated from equation (24); dashed line, $d(T)$ calculated from equation (25); dashed-dotted line, density-functional results of Zeng and Oxtoby [12]; triangles, molecular-dynamics results of Chapela *et al* [3]; asterisks, molecular-dynamics results of Holcomb *et al* [6]; square, Monte Carlo result of Miyazaki *et al* [4]; diamonds, Monte Carlo results of Salomons and Mareschal [5]; circles, Monte Carlo results of Chapela *et al* [3].

expression for the effective hard-sphere diameter (equation (24)) is chosen in both theories. Note that the theory presented is of the mean-field type and therefore all fluctuations, such as capillary waves, are entirely suppressed [2].

In conclusion, a new analytical expression for the surface tension of a planar liquid-vapour interface is obtained. It is based on the Fowler approximation and statistical-mechanical perturbation approach in the theory of liquids. The expression obtained is explicit in the equilibrium liquid density. It is this feature that is responsible for a good agreement of our theoretical predictions with the results of Monte Carlo and molecular-dynamics simulations and with the DFT calculations of the Lennard-Jones fluid.

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References

- [1] Kirkwood J G and Buff F P 1949 *J. Chem. Phys.* **17** 338
- [2] Rowlinson J S and Widom B 1982 *Molecular theory of capillarity* (Oxford: Clarendon Press)
- [3] Chapela A G, Saville G, Thompson S M and Rowlinson J S 1977 *J. Chem. Soc. Faraday Trans. II* **73** 1133

- [4] Miyazaki J, Barker J A and Pound J M 1976 *J. Chem. Phys.* **64** 3364
- [5] Salomons E and Mareschal M 1991 *J. Phys.: Condens. Matter* **3** 3645
- [6] Holcomb C D, Clancy P and Zollweg J A 1993 *Mol. Phys.* **78** 437
- [7] Toxvaerd S J 1976 *J. Chem. Phys.* **64** 2863
- [8] Barker J A and Henderson D 1976 *Rev. Mod. Phys.* **48** 587
- [9] Toxvaerd S J 1971 *J. Chem. Phys.* **55** 3116
- [10] Lee J K, Barker J A and Pound G M 1974 *J. Chem. Phys.* **60** 1976
- [11] Evans R 1979 *Adv. Phys.* **28** 143
- [12] Zeng X C and Oxtoby D W 1991 *J. Chem. Phys.* **94** 4472
- [13] Fowler R H 1937 *Proc. R. Soc. A* **159** 229
- [14] Weeks D, Chandler D and Andersen H C 1971 *J. Chem. Phys.* **54** 5237
- [15] Verlet L 1968 *Phys. Rev.* **165** 201
- [16] Song Y and Mason E A 1989 *J. Chem. Phys.* **91** 7840
- [17] Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
- [18] Lu B Q, Evans R and Telo da Gama M M 1985 *Mol. Phys.* **55** 1319
- [19] Adams D J 1976 *Mol. Phys.* **32** 647
- [20] Hansen J P and Verlet L 1969 *Phys. Rev.* **184** 151