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Fowler's approximation for the surface tension and surface energy of Lennard-Jones fluids revisited

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Abstract

We present a detailed study of the validity of Fowler's approximation for calculating the surface tension and the surface energy of Lennard-Jones fluids. To do so, we consider three different explicit analytical expressions for the radial distribution function (RDF), including one proposed by our research group, together with very accurate expressions for the liquid and vapour densities, also proposed by our group. The calculation of the surface tension from the direct correlation function using both the Percus–Yevick and the hypernetted-chain approximations is also considered. Finally, our results are compared with those obtained by other authors by computer simulations or through relevant theoretical approximations. In particular, we consider the analytical expression proposed by Kalikmanov and Hofmans (1994 *J. Phys.: Condens. Matter* **6** 2207–14) for the surface tension. Our results indicate that the values for the surface energy in Fowler's approximation obtained by other authors are adequate, and can be calculated from the RDF models. For the surface tension, however, the values considered as valid in previous works seem to be incorrect. The correct values can be obtained from our model for the RDF or from the Kalikmanov and Hofmans expression with suitable inputs.

1. Introduction

The surface tension in the liquid–vapour interface is one of the most interesting thermophysical properties of fluids, and is related to a great number of natural phenomena as well as to numerous industrial applications. Many attempts have been made to generalize the behaviour of the experimental surface tension of pure substances following diverse empirical or semiempirical approaches (Reid *et al* 1987). Theoretical methods (Croxtton 1980, Rowlinson and Widom 1982) are based on such simple models as the fluid described by the Lennard-Jones (LJ)

intermolecular potential, which is usually accepted as being a good model of certain simple fluids (rare gases, methane, etc).

Using statistical mechanics methods, the surface tension can be obtained from the intermolecular potential and the radial distribution function (RDF) or the direct correlation function (DCF) in the liquid–vapour interface (Lekner and Henderson 1977, Croxton 1980, Rowlinson and Widom 1982). The main difficulty arises in the calculation of those functions, and the problem has usually been solved by considering the RDF or the DCF of the liquid phase for a LJ fluid. In particular, the simplest approximation is that proposed by Fowler (1937), in which a step transition from liquid to vapour phases, with no interfacial zone (and hence with no interfacial thickness), is considered in the calculation of the surface tension and the surface energy. This is a suitable approximation for temperatures near the triple point.

In spite of the great number of theories and computer simulations performed, there is still no clear idea of the range of validity of Fowler's approximation. From a qualitative point of view, it seems obvious that such an approximation should introduce considerable deviations even at the triple-point temperature, since the interfacial thickness is neglected (Lekner and Henderson 1977). A first correction to Fowler's approach was suggested by McLellan (1952) who proposed an expression for the surface tension in which the RDFs of the vapour and liquid phases were somehow weighted by means of square-root functions. Nevertheless, no results calculated using McLellan's (1952) approach have been considered in previous works.

From a quantitative perspective, no systematic study has yet been made of the temperature range over which Fowler's approximation can be taken to be 'valid' or about the deviations of the results in the vicinity of the triple point. Unfortunately, there is no clear reference against which to compare new results. Computer simulations have not always used the same systems or computing methods, and usually the calculation of the contribution of Fowler's approach to the full value of the surface tension or the surface energy is not explicitly considered. Only Freeman and McDonald's (1973) study contains values for the surface tension and the surface energy of LJ fluids computed via Fowler's approximation. Surprisingly, the authors found values for the surface tension which were in good agreement with experimental data for simple fluids near the triple point. On the other hand, their values for the surface energy deviated greatly from experiment. In any case, it is necessary to take into account that the computer simulation results were given in real units by using LJ parameters that are not equal to those used by other authors and that these parameters clearly influence the comparison with experimental data.

Fowler's approximation has been used by several authors. In particular, the RDF of the liquid phase has been obtained from experimental data (Shoemaker *et al* 1970, Berry *et al* 1972), from perturbative methods (Salter and Davis 1975), and from computer simulation techniques (Gray and Gubbins 1975, Haile *et al* 1976, Rao and Berne 1979). Some of these theoretical calculations again showed a certain degree of agreement with the experimental data, although it must be noted that in most cases the LJ parameters used were proposed by the authors themselves. Moreover, a RDF obtained from experimental data cannot be accurate and this must clearly influence the results. Salter and Davis (1975) used a theoretical RDF together with experimental data for the densities and their own LJ parameters. Finally, in none of these cases were the data compared with the computer simulation data for the surface tension or surface energy, so their conclusions about the validity of Fowler's approximation cannot be regarded as fully convincing.

The statistical mechanics calculation of the surface tension and the surface energy was thoroughly reviewed by Lekner and Henderson (1977) from a purely theoretical point of view (i.e. without direct comparison with computer simulations or experimental results). Using the low-density approximation (LDA) for the RDF, they proved that the agreement between

experimental data and results calculated via Fowler's approximation is fortuitous. In fact, it was due to a cancellation between the positive and negative areas in the corresponding integral. Such a cancellation does not exist, however, in the calculation of the surface energy, so there the theoretical values do not reproduce the experimental data. In this sense, one of the goals of the present work is to find out whether such conclusions apply if a more appropriate representation is used for the RDF, such as those given by Xu and Hu (1986), and recently used by Li and Lu (2001) in the calculation of the surface tension of polar fluids, or by Cuadros *et al* (1998).

Lekner and Henderson (1977) also showed that, except at the triple-point temperature, it is necessary to account for the contribution of the vapour density to improve the results obtained via Fowler's approximation. The effect of including that contribution will be studied in this paper.

More recently, Kalikmanov and Hofmans (1994) have proposed a simple analytical expression for the surface tension of LJ fluids arising from the RDF of a hard-sphere system. They found relatively good agreement with previous computer simulations and with values given by the density functional theory of Zeng and Oxtoby (1991) in which Fowler's approach is not considered. Nevertheless, they did not carry out a comparison with Freeman and McDonald's (1973) computer simulation data, so the validity of their version of Fowler's approach is not at all clear. We note, moreover, that the liquid densities that they used present great deviations with respect to recent computer simulation values, and that their results for the surface tension have not as yet been compared with recent simulation data. In particular, the most recent simulation of the liquid–vapour interface of LJ fluids is that performed by Baidakov *et al* (2000), giving values for the surface tension with very low statistical errors. In this paper we use the Kalikmanov and Hofmans (1994) expression in a more suitable manner and compare the results with both the Freeman and McDonald (1973) and the Baidakov *et al* (2000) data.

More complex approximations than Fowler's have been developed to study the surface properties in the liquid–vapour interface. Nevertheless, the calculations that must be made are generally not easy to perform, as they are based on the general Kirkwood–Buff formula with different models of the interfacial doublet distribution function (Salter and Davis 1975, Bongiorno and Davis 1975), the generalized van der Waals theory (Abbas and Nordholm 1994), the Born–Green–Yvon equation (Toxvaerd 1973, Fischer and Methfessel 1980, Wendland 1997), or density functional theory (Salter and Davis 1975, Ebner *et al* 1976, Zeng and Oxtoby 1991). Moreover, the agreement with computer simulation results for the coexistence densities, the interfacial thickness, and the surface tension is not good in most cases. Hence, the use of the generalized equations given by Lekner and Henderson (1977) represents a good alternative in which the contribution of Fowler's approximation which we will study here is an important part.

In this paper the validity of Fowler's approximation for calculating the surface tension and the surface energy of LJ fluids is studied by comparing new theoretical results with previous theoretical or computer simulation values. In section 2 we present all the analytical expressions used. Results are obtained from three analytical approximations for the liquid RDF and two for the DCF in Fowler's approximation, as well from McLellan's approximation in section 3. For the surface energy, section 3.1, the results are compared with those obtained in the computer simulation of Freeman and McDonald (1973). For the surface tension, section 3.2, comparison is made with the Baidakov *et al* (2000) computer simulation data, and with the theoretical results of Salter and Davis (1975) and of Haile *et al* (1976), based on a previous work of Gray and Gubbins (1975), as well as with the original results of Kalikmanov and Hofmans (1994) and with values obtained using more appropriate inputs in this last approximation. Finally, conclusions are presented in section 4.

2. Analytical expressions

The expressions for the surface energy U and the surface tension γ of LJ fluids according to Fowler's approximation, but also considering the contribution of the vapour density (Lekner and Henderson 1977), are given by (Croxtton 1980, Rowlinson and Widom 1982):

$$U = -\frac{\pi(\rho_L - \rho_V)^2}{2} \int_0^\infty r^3 u(r) g(r) dr \quad (1)$$

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

where r is the intermolecular distance, ρ_L and ρ_V are the coexisting densities of the liquid and vapour phases respectively, $u(r)$ is the LJ intermolecular potential, with $u'(r)$ its derivative, and $g(r)$ is the RDF. We must point out that all the analytical expressions and the results in this paper are in adimensional units, reduced with LJ parameters (lengths reduced with the LJ parameter σ , the distance at which the LJ potential becomes zero, and energies reduced with the LJ parameter ε , the minimum value of the LJ potential (Croxtton 1980)).

If the dependence of the surface tension on the RDF is considered through the DCF (denoted by $c(r)$), equation (2) becomes (Lekner and Henderson 1977):

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2 T}{2} \int_0^\infty r^3 c(r) dr. \quad (3)$$

Equations (1)–(3) represent Fowler's approximation when $\rho_V = 0$ (i.e., when the contribution of the vapour density is neglected).

McLellan (1952) proposed an expression for the surface tension in which the RDFs of the vapour and liquid phases were weighted with square-root functions:

$$\gamma = \frac{\pi}{8} \int_0^\infty r^4 u'(r) \left[\rho_L \sqrt{g_L(r)} - \rho_V \sqrt{g_V(r)} \right]^2 dr. \quad (4)$$

From this, with the same dependence on the RDFs of the liquid and vapour phases, one can straightforwardly derive the corresponding expression for the surface energy:

$$U = -\frac{\pi}{2} \int_0^\infty r^3 u(r) \left[\rho_L \sqrt{g_L(r)} - \rho_V \sqrt{g_V(r)} \right]^2 dr. \quad (5)$$

The validity or accuracy of these expressions has as yet not been tested.

From equation (2) the analytical expression proposed by Kalikmanov and Hofmans (1994) for the surface tension of LJ fluids can be written as

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2 T}{2} \left\{ \int_0^\infty r^3 \left[e^{-\frac{u(r)}{T}} - 1 \right] dr + \left[\frac{4 - 2\Phi(T)}{4(1 - \Phi(T))^3} \right] \int_0^{r_{min}} r^3 \left(e^{-\frac{u(r)+1}{T}} - 1 \right) dr \right\} \quad (6)$$

where $r_{min} = 2^{1/6}$ is the distance that minimizes the LJ interaction potential, and the function $\Phi(T)$ is given by

$$\Phi(T) = \frac{\pi \rho_L [d(T)]^3}{6}, \quad (7)$$

with $d(T)$ being the function that describes the dependence of the effective hard-sphere diameter on temperature. Although in their original work Kalikmanov and Hofmans (1994) neglected the contribution of the vapour density, we take it into account as suggested by Lekner and Henderson (1977). Moreover, Kalikmanov and Hofmans (1994) use the Lu *et al* (1985) (LET) expression for the diameter:

$$d_{LET}(T) = \frac{0.56165T + 0.9718}{0.60899T + 0.92868} \quad (8)$$

and the liquid density given by the Song and Mason (1989) equation of state.

In this work we considered again equations (6) and (7), but now using the diameter expression given by Verlet and Weis (1972) (VW):

$$d_{VW}(T) = \frac{0.3837T + 1.068}{0.4293T + 1} \quad (9)$$

which has also been extensively used by many authors, together with more accurate values for the coexistence densities as will be given below.

In particular, we made calculations using equations (1)–(6) and considering the temperature dependence expressions for the vapour and liquid coexistence densities of LJ fluids given by Okrasinski *et al* (2001a, 2001b) (OPC):

$$\rho_V(T) = 0.3075 + 0.304(1.32 - T) - 0.6027(1.32 - T)^{0.4157} \quad (10)$$

$$\rho_L(T) = 0.3075 + 0.058(1.32 - T) + 0.6027(1.32 - T)^{0.4157} \quad (11)$$

which reproduce computer simulation results (Lotfi *et al* 1992, Baidakov *et al* 2000) quite accurately, and were obtained following a novel method.

For the RDF we used three analytical expressions, including a proposal of our own research group. The first is the so-called LDA:

$$g_{LDA}(r) = e^{-u(r)/T} \quad (12)$$

which was used by Lekner and Henderson (1977) in their landmark theoretical studies. The second is the approximation of Xu and Hu (1986), based on the properties of the well known Dirac delta (δ_D) and Heaviside step functions (θ):

$$g_{XH}(r) = \theta[r - r_2(T)] + \frac{[r_2(T)]^3 - [d_C(T)]^3}{3[r_1(T)]^2} \delta_D[r - r_1(T)], \quad (13)$$

in which $r_1(T)$ and $r_2(T)$ are given by

$$r_1(T) = 1.150d_C(T) \quad (14)$$

$$r_2(T) = 1.575d_C(T) \quad (15)$$

with $d_C(T)$ being the expression of Cotterman *et al* (1986) for the diameter:

$$d_C(T) = \frac{1 + 0.2977T}{1 + 0.3316T + 0.0010477T^2}. \quad (16)$$

The approximation of Xu and Hu (1986) for the RDF has been recently used by Li and Lu (2001) as a first reference term in order to calculate the surface tension of polar fluids. Those authors did not carry out a comparison with other LJ calculations or values for a simple fluid such as argon (in fact, they compared their results only with values for non-polar fluids, considering a suitable interaction potential). Calculations for the surface energy were not performed either. We note that although model XH (equation (13)) must be regarded as a 'caricature' of the real RDF of a liquid, being almost independent of temperature, it was designed in order to give adequate results for the integrals in which it is contained.

Finally, the third expression for the RDF will be that of Cuadros *et al* (1998). They observed that for $r \leq 0.96$ the RDF can be taken to be zero and that for $r \geq 2.5$ it can be approximated as unity. For $r \in (0.96, 2.5)$ they proposed

$$g_{COS}(r) = \sum_{i=0}^{10} C_i r^i, \quad (17)$$

with

$$C_i = D_{i1} + D_{i2}T + D_{i3}T^2 + D_{i4}T^3 + (D_{i5} + D_{i6}T + D_{i7}T^2 + D_{i8}T^3)\rho \quad (18)$$

where D_{ij} are numerical coefficients listed by Cuadros *et al* (1998). Obviously, this is a more complex analytical model, but it is also the closest to the real RDF obtained in computer simulations (Cuadros *et al* 1998). Moreover, it can be used for both liquid and vapour phases, which is not the case for model XH (equation (13)).

In the calculations performed with equation (3) to calculate the surface tension, we used directly the Percus–Yevick (PY) and ‘hypernetted-chain’ (HNC) approximations (Reed and Gubbins 1973):

$$c_{PY}(r) \cong g(r)[1 - e^{u(r)/T}] \quad (19)$$

$$c_{HNC}(r) \cong g(r) - 1 - \ln g(r) - \frac{u(r)}{T} \quad (20)$$

and calculations were performed only with model COS for the RDF, equation (17).

3. Results and discussion

3.1. Surface energy

To test the validity of Fowler’s approximation for the surface energy of LJ fluids we performed calculations using equation (1) and the three proposals for the RDF of the liquid, equations (12), (13), and (17), and also using equation (5) (McLellan approximation) and the COS model for the RDF. The analytical expressions for the vapour and liquid densities given in equations (10) and (11) were used in all cases. The range of temperatures includes values from triple to critical points ($0.7 \leq T < 1.32$). We have found that McLellan’s (1952) approximation gives values surprisingly close to those calculated with equation (1) and the RDF of equation (17) (model COS). Hence, its use is not justified. Results from all calculations (except those with McLellan’s approximation) are compared with the computer simulation results of Freeman and McDonald (1973) in figure 1.

The LDA for the RDF (model LDA) leads to values that become significantly high for low temperatures, being very similar to values obtained with the other approaches only at high temperatures (near the critical point) where densities are higher. This means that the LDA used by Lekner and Henderson (1977) seems not to be appropriate near the triple point, where Fowler’s approximation becomes valid.

As Freeman and McDonald’s (1973) computer simulation data are far from the experimental values, could the LDA model for the RDF (equation (12)) be a better approach for real fluids? Unfortunately, at the triple-point temperature it does not fit the experimental values (no matter what LJ parameters are used to reduce the units), and at higher temperatures it does not reproduce the correct slope of the curve. Hence, we can conclude that the LDA expression for the RDF (equation (12)) used by Lekner and Henderson (1977) leads to values with great deviations with respect to computer simulation results and to some experimental data sets found in the literature (Stansfield 1959, Buff and Lovett 1968, Shih and Uang 1978), no matter what LJ parameters are used to make the units adimensional.

As can be seen in figure 1, equation (1) with $\rho_V = 0$ and the COS model for the RDF reproduces very accurately the computer simulation values of Freeman and McDonald (1973), with an averaged absolute percentage deviation (APD) of 1.2% (in the range $0.700 \leq T \leq 1.109$), with the highest individual APD 2.2% at $T = 0.715$. When the contribution of the vapour density is taken into account (i.e., using the expression as it appears in equation (1)), lower values for the surface tension are found as the temperature increases, approaching zero near the critical point. The use of the expression XH (equation (13)) for the RDF gives results quite similar to those calculated with the RDF of equation (17), especially as the temperature increases. The APDs with respect to Freeman and McDonald’s (1973) computer simulation

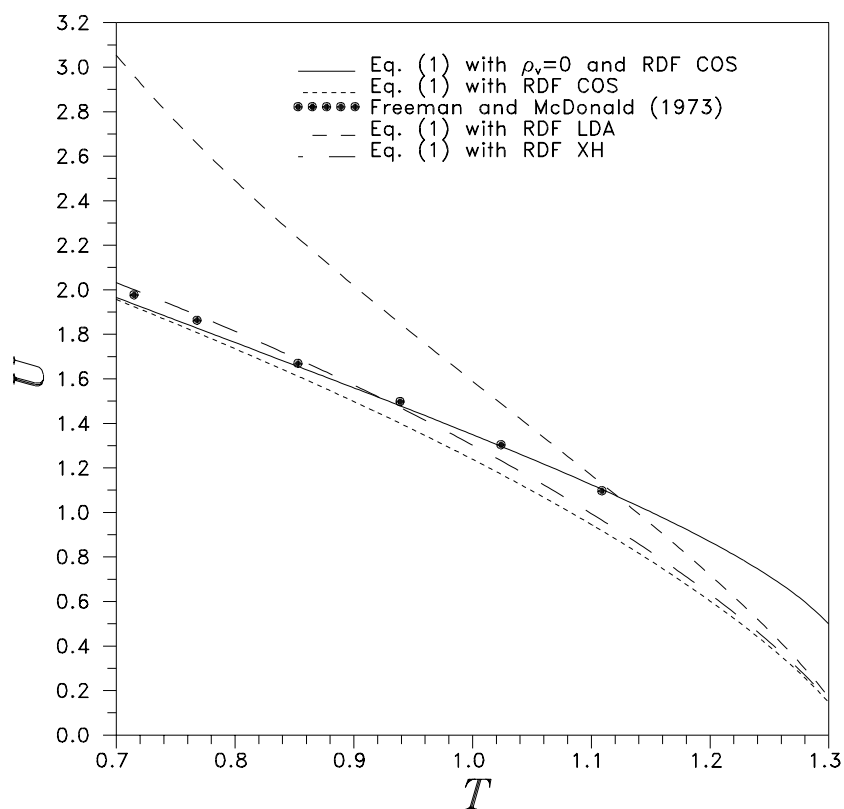


Figure 1. Surface energy for LJ fluids calculated via equation (1) with the RDF approximated to be that of the liquid phase. The three models for the RDF labelled LDA, XH, and COS correspond to equations (12), (13), and (17) respectively. Computer simulation data of Freeman and McDonald (1973) are also shown. Triple and critical points are approximately located at $T = 0.7$ and 1.32 respectively.

data at temperatures close to the triple point ($T < 0.9$) are all below 1.5%. Near the critical point, all the approximations converge to the same value, with the simple LDA model then being accurate enough.

Our results prove the validity of Fowler's approach in the calculation of the surface energy when an adequate model for the RDF and the coexistence densities are used. As Lekner and Henderson (1977) stated (and we have proved for ourselves), no cancellation between positive and negative contributions in the integral of the surface energy (equation (1)) takes place, and the corresponding results show major discrepancies with respect to experimental data.

Unfortunately, there are no more theoretical or computer simulation results to compare with. Although Shoemaker *et al* (1970) used experimental values as a reference, they show discrepancies (when they are reduced using the LJ parameters given by those same authors) with those used by other authors and reduced with other LJ parameters.

From a theoretical point of view we must note that, according to our first estimates, the contribution of Fowler's approximation to the value of the surface energy of a LJ fluid at the triple-point temperature has a weight of 70%. Assuming that the deviation at that temperature between the values given by the Freeman and McDonald (1973) computer simulation and by experiment (the value reduced with classical LJ parameters) is approximately 24%, we

conclude that our results (i.e. using the COS model for the RDF, equation (17), the OPC model for the liquid density (equation (11))), and setting $\rho_V = 0$) can be taken as the most accurate theoretical representation of the contribution of Fowler's approximation in the calculation of LJ fluid surface energy.

When the LDA approximation (equation (12)) for the RDF at the triple point is used, the surface energy is overestimated with a deviation of only 11% with respect to the value obtained with a general expression containing a density profile. Nevertheless, we have proved in this work that the LDA approximation fails to reproduce the contribution of Fowler's approximation in the calculation of the surface energy.

Finally, our results show that XH model (equation (13)) for the RDF gives correct values for the integrals used for the calculation of the surface energy following Fowler's approach, even though the integrand is not correct from a strict physical point of view.

3.2. Surface tension

Calculations of the surface tension of LJ fluids were performed with the three proposals for the RDF, equations (12), (13), and (17), using both Fowler's approximation (equation (2)) with $\rho_V = 0$) and the Lekner–Henderson–Fowler expression (equation (2)). McLellan's (1952) approximation (equation (4)) together with the COS expression (equation (17)) for the RDF was also used. Results are given in table 1. As can be seen, the approximation of McLellan (1952) has a very similar behaviour to that of Lekner and Henderson's (1977) expression (equation (2)) which is simpler. For that reason, McLellan's approach will not be considered further.

The LDA approximation (equation (12)) for the RDF appears to overestimate the surface tension if it is compared to the values calculated with the other two expressions, especially near the triple point. The use of this approach by Lekner and Henderson (1977) must then be taken merely as a rough estimate of the contribution of Fowler's equation to the full surface tension at the triple point. As is seen in table 1, the best agreement between the LDA approximation and the other results is found at the highest temperatures, i.e. near the critical point.

Table 1 also includes values obtained with the XH model (equation (13)) for the RDF, both considering and neglecting the contribution of the vapour coexistence density given by equation (10). As can be observed, when the vapour density is not neglected, the results are closer to those calculated with the COS expression (equation (17)) for the RDF as the temperature increases. Nevertheless, at the triple point the difference is 22% with respect to the value obtained with the COS model, and around 40% with respect to Freeman and McDonald's (1973) or Baidakov *et al*'s (2000) computer simulation data. Values obtained by neglecting the vapour density contribution have recently been used by Li and Lu (2001) as a reference in a more complex calculation. We compared the integrals given by the XH and the COS model in equation (2), and observed that the differences between them near the triple point are due to the contribution of the Dirac delta for the XH model, i.e. it seems to be that the Dirac delta does not give an adequate contribution to the calculation of the surface tension.

The expression of Lekner and Henderson (1977) used to obtain the surface tension from the DCF (equation (3)) was used with both PY and HNC approximations (equations (19) and (20), respectively), using the COS model for the RDF (equation (17)). As is shown in figure 2, equation (3) significantly overestimates the simulation data, and also those calculated with equation (2), near the triple point. Nevertheless they all present similar converging behaviour as the temperature approaches the critical point (except equation (2) with $\rho_V = 0$, for the reason explained above). In any case, the PY approximation seems to give more accurate results than the HNC one.

Table 1. Surface tension of LJ fluids calculated with the expression of Lekner and Henderson (1977), equation (2), and with that of McLellan (1952), equation (4). Three proposals have been used for the RDF in equation (2): LDA (equation (12)), XH (equation (13)), and COS (equation (17)).

T	Equation (2) ($\rho_V = 0$)		Equation (4)	Equation (2)		
	$g_{COS}(r)$	$g_{XH}(r)$		$g_{COS}(r)$	$g_{LDA}(r)$	$g_{XH}(r)$
0.700	1.166	1.421	1.161	1.161	2.072	1.415
0.725	1.135	1.378	1.126	1.127	1.988	1.369
0.750	1.104	1.336	1.093	1.094	1.908	1.324
0.775	1.074	1.293	1.059	1.061	1.829	1.277
0.800	1.044	1.251	1.025	1.027	1.753	1.231
0.825	1.015	1.208	0.9910	0.9942	1.678	1.184
0.850	0.9863	1.166	0.9567	0.9609	1.605	1.136
0.875	0.9580	1.124	0.9221	0.9273	1.532	1.088
0.900	0.9299	1.082	0.8869	0.8933	1.460	1.040
0.925	0.9020	1.040	0.8511	0.8589	1.388	0.9907
0.950	0.8742	0.9986	0.8145	0.8237	1.316	0.9409
0.975	0.8463	0.9565	0.7770	0.7878	1.244	0.8904
1.000	0.8182	0.9144	0.7384	0.7509	1.172	0.8392
1.025	0.7897	0.8720	0.6985	0.7128	1.099	0.7871
1.050	0.7608	0.8294	0.6573	0.6733	1.025	0.7340
1.075	0.7312	0.7863	0.6145	0.6323	0.9497	0.6799
1.100	0.7008	0.7426	0.5698	0.5894	0.8731	0.6245
1.125	0.6693	0.6982	0.5231	0.5443	0.7947	0.5678
1.150	0.6363	0.6528	0.4740	0.4966	0.7140	0.5095
1.175	0.6014	0.6061	0.4221	0.4458	0.6306	0.4492
1.200	0.5641	0.5575	0.3670	0.3912	0.5438	0.3866
1.225	0.5233	0.5062	0.3079	0.3319	0.4526	0.3211
1.250	0.4773	0.4508	0.2438	0.2664	0.3555	0.2516
1.275	0.4230	0.3883	0.1728	0.1923	0.2501	0.1765
1.300	0.3506	0.3102	0.0906	0.1035	0.1302	0.0916

Let us now consider the differences between the results calculated with equation (2) (in both cases: $\rho_V = 0$ and $\rho_V \neq 0$) and the COS model (equation (17) for the RDF, and those of Freeman and McDonald's (1973) computer simulation (see figure 2). At the triple-point temperature both approximations have APD = 15% with respect to the simulation data. Also, equation (2) with $\rho_V = 0$ does not converge to zero as the temperature approaches the critical point, but does tend to the simulation value of Freeman and McDonald at the highest temperature. As is well known, the vapour density (equation (10)) increases with temperature, and thus its contribution to the surface tension in equation (2) becomes more significant as T approaches the critical point. In any case, equation (2) does not reproduce the computer simulation results, except perhaps for reduced temperatures close to 1.

A comparison of our results with other theoretical approaches (as well as with computer simulation data) is shown in figures 3 and 4. Figure 3 shows results obtained using the approximations given by Salter and Davis (1975), by Haile *et al* (1976), and by Kalikmanov and Hofmans (1994), together with computer simulation data from Freeman and McDonald (1973) and Baidakov *et al* (2000). The results of Salter and Davis (1975) are in good agreement with Freeman and McDonald's (1973) computer simulation, with a maximum APD of 3.5% at the triple-point temperature (no such comparison was made by Salter and Davis). Also, for that concrete temperature, that theory reproduces very accurately the computer simulation

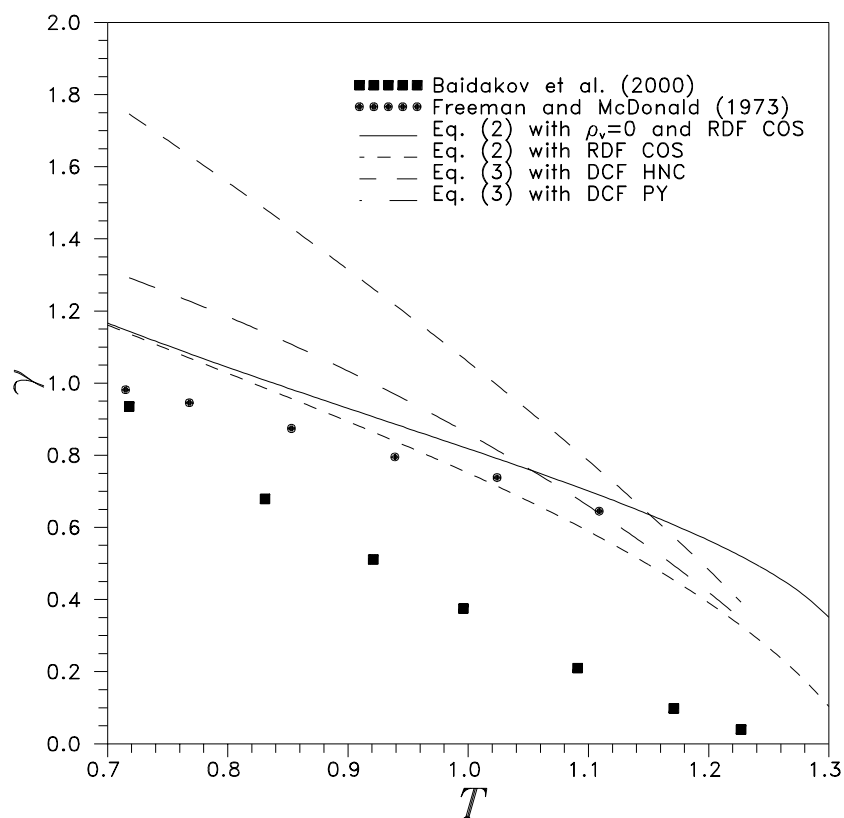


Figure 2. Surface tension for LJ fluids calculated in this work together with computer simulation data of Freeman and McDonald (1973) and of Baidakov *et al* (2000). In equations (2) and (3) the RDF is approximated as that of the liquid phase. The COS model for the RDF is given in equation (17), and the PY and HNC approximations for the DCF are in equations (19) and (20) respectively.

value obtained by Baidakov *et al* (2000) (see figure 3), where Fowler's approximation is not used. We would note however that this result is not consistent. The RDF used by Salter and Davis was designed under theoretical considerations, whereas they use experimental values for the liquid density and do not consider the interfacial thickness. This means that although their approximation gives good values for the surface tension near the triple point (not at higher temperatures), those values would not be in agreement with the 'full' value (i.e. that obtained with a non-zero interfacial thickness) if they represented adequately the contribution of Fowler's approximation.

The theoretical development of Haile *et al* (1976), based on a previous work of Gray and Gubbins (1975), is founded on the use of the RDF obtained by computer simulation (Verlet 1968). We obtained the values that appear in figure 3 by using the coexisting densities given by equation (11), together with the analytical expression proposed by those authors. It can be observed that these values are very close to Salter and Davis (1975), and hence to Freeman and McDonald's (1973) computer simulation data.

Figure 3 also includes Kalikmanov and Hofmans's (1994) results as they were obtained originally, i.e. from equations (6) and (7) with the LET expression (equation (8)) for the diameter, and the liquid coexistence densities of the Song and Mason (1989) equation of state (which do not reproduce successfully recent computer simulation values), and hence

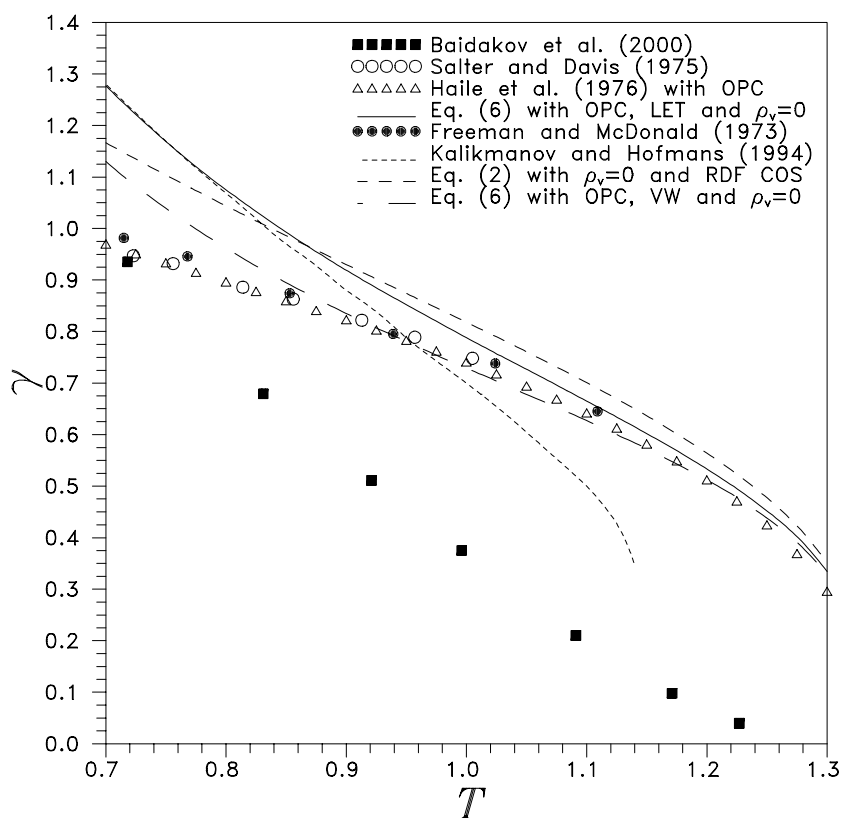


Figure 3. Values for the surface tension of LJ fluids obtained from equations (2) and (6), compared with the theoretical approaches of Salter and Davis (1975), Haile *et al* (1976), and Kalikmanov and Hofmans (1994), together with computer simulation data of Freeman and McDonald (1973) and Baidakov *et al* (2000). In equation (6) the effective hard-sphere diameters of Lu *et al* (1985) (LET, equation (8)) and of Verlet and Weis (1972) (VW, equation (9)), as well as the liquid phase density OPC (equation (11)), have been used. In all cases the contribution of the vapour phase density has been neglected.

with $\rho_v = 0$. As can be seen, although Kalikmanov and Hofmans (1994) found relatively good agreement with other old computer simulation results as well as with the theory of Zeng and Oxtoby (1991), their values for the surface tension following Fowler's approximation are clearly far from both Freeman and McDonald's (1973) (based on that same approach) and Baidakov *et al*'s (2000) computer simulation data, the latter being more accurate values for LJ fluid surface tension.

In this work we performed calculations to see whether the expression of Kalikmanov and Hofmans (1994), equation (6), can lead to adequate values if appropriate diameter and coexistence density expressions are considered. In this sense, we think it is interesting to consider the Verlet and Weis (1972) (VW) diameter (equation (9)) instead of Lu *et al*'s (1985) (equation (8)) for two reasons:

- (i) it has been widely used in the development of the perturbation theory of Weeks, Chandler, and Andersen (Weeks *et al* 1971); and
- (ii) it was used to develop the OPC model for the densities in the liquid–vapour equilibrium, equations (10) and (11).

Results are shown in figure 3.

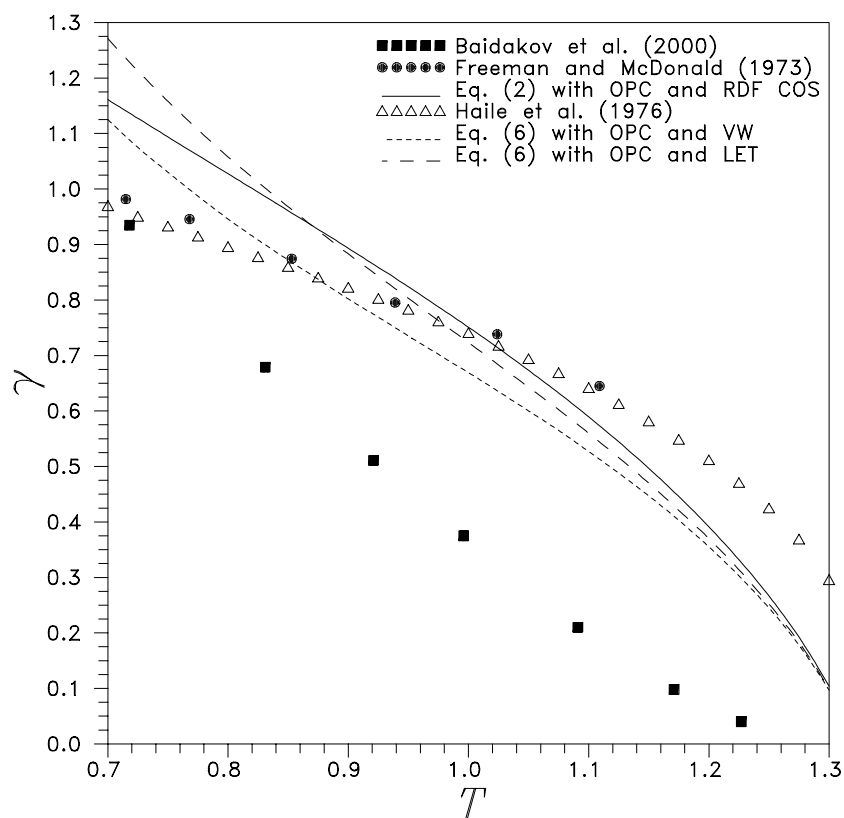


Figure 4. Values for the surface tension of LJ fluids. Calculations for equation (6) have been performed with the effective hard-sphere diameters of Lu *et al* (1985) (LET, equation (8)) and of Verlet and Weis (1972) (VW, equation (9)). In equations (2) and (6) the contribution of the vapour density was taken into account, and the OPC model for the vapour and liquid densities (equations (10) and (11) respectively) was used. Other theoretical and simulation results are shown for reference (see the caption of figure 3 for details).

In the vicinity of the triple point, none of the calculations performed with the Kalikmanov and Hofmans (1994) approximation (equation (6)) fit computer simulation data (see figure 3). For high temperatures ($T > 0.8$), equation (6) with $\rho_V = 0$ and the liquid densities of the OPC model (equation (11)) and the VW diameter (equation (9)) reproduces Freeman and McDonald's (1973) simulation data and Haile *et al*'s (1976) theoretical values quite successfully. It can also be seen in figure 3 that the effect of introducing Verlet and Weis's (1972) diameter instead of Lu *et al*'s (1985) in the expression of Kalikmanov and Hofmans (1994) for the surface tension has no relevance near the critical point, but a great discrepancy is found at temperatures near the triple point. When the contribution of the vapour density is not neglected in equation (6), the values obtained have great deviations from those of Freeman and McDonald (1973), Haile *et al* (1976), and Salter and Davis (1975) for temperatures close to the critical and triple points (see figure 4).

Our results show that the values obtained with equation (6), coexisting OPC densities (equations (10) and (11)), and the VW diameter (equation (9)) are the best approximation to Fowler's contribution to the surface tension of LJ fluids that can be obtained from Kalikmanov and Hofmans' theory. As shown in figure 4, at temperatures close to the triple and critical

points these values are in good agreement with those calculated with equation (2) using the COS model (equation (17)) for the RDF. In particular, the deviation at the triple-point temperature ($T = 0.7$) is around 3%. For intermediate temperatures the results calculated with equation (6) are slightly closer to those of Baidakov *et al*'s (2000) computer simulation, although the curves that describe the temperature dependence of the surface tension are not similar (see figure 4).

As Lekner and Henderson (1977) pointed out, we think that the accordance between experimental or recent computer simulation data and results calculated from Fowler's approximation is fortuitous. In fact, at the triple-point temperature the interfacial thickness is not strictly zero, and hence the surface tension obtained assuming Fowler's approximation should not be the same as that calculated by more general methods or by computer simulation methods in which this approximation is not used. In other words, the accordance between the results of Salter and Davis (1975), Haile *et al* (1976), and Freeman and McDonald (1973) may be due to the quality of the data involved and to a fortuitous cancellation of deviations. In the case of the results of Salter and Davis (1975) it must be taken into account that the RDF given by the Weeks–Chandler–Andersen perturbation theory (Weeks *et al* 1971) is too drastic an approximation, as the authors themselves admitted. Also, the LJ parameters used to compare with real data were calculated specifically for that purpose. With respect to Haile *et al*'s (1976) results, it must be borne in mind that the computer simulation data used for the RDF were given by Verlet (1968), when the statistical mechanics tools needed to improve the computer simulation techniques were not completely developed. Moreover, such simulation data were integrated numerically (Gray and Gubbins 1975) and fitted to certain analytical expressions afterwards. For these reasons, the final values for the surface tension have implicit deviations that lead to the fortuitous agreement with Freeman and McDonald's (1973) computer simulation data.

We can conclude that the surface tension values calculated at the triple point through Fowler's approximation using suitable input properties (in particular, those proposed here) in the Kalikmanov and Hofmans (1994) approximate equation or in the Lekner and Henderson (1977) expression are more correct than those given by:

- (i) the computer simulation of Freeman and McDonald (1973);
- (ii) other theoretical approximations such as those of Salter and Davis (1975) or Haile *et al* (1976); and
- (iii) the expression of Lekner and Henderson (1977) including the LDA or the XH approximations for the RDF.

These values, which have been taken as a reference so far, seem not to be valid to represent Fowler's approximation.

Hence, our results prove that at the triple-point temperature ($T = 0.7$) the correct contribution to the full surface tension of a LJ fluid is somewhere between 1.12 and 1.17, in reduced LJ units—more than 15% higher than the aforementioned values. According to our estimates, at the triple-point temperature the deviation of the value given by Fowler's approximation with respect to that calculated with a more general expression (taking into account the form of the density profile in the interfacial zone) including the COS model (equation (17)) for the RDF, is approximately 20%. In other words, the deviation is similar to that of Fowler's approximation, as calculated here, with respect to the value given by Baidakov *et al* (2000). This confirms the validity of the present results. Also, near the critical point all the theoretical results and computer simulation data based on Fowler's approach are very similar. In this case, the final value depends mainly on the consideration of the contribution of the vapour density.

It may be interesting to have a rough idea of the validity of Fowler's approximation when values are compared with more general theoretical approximations. In any case, one must consider that the coexisting densities used or obtained in those theories do not always fit the computer simulation results, and that the interfacial thickness values do not coincide with those of Baidakov *et al*'s (2000) simulation either.

There exist some general theories whose values for the surface tension near the triple-point temperature have higher deviations with respect to computer simulation than those obtained from Fowler's approximation. In particular, results from Toxvaerd (1973), Bongiorno and Davis (1975), Ebner *et al* (1976), and Zeng and Oxtoby (1991), among others, present deviations over 20%. Of course, other theories give more accurate results at the triple-point temperature, with deviations below those corresponding to Fowler's approximation. In this sense, the theories of Abbas and Nordholm (1994) and Wendland (1997) give deviations below 7%. Nevertheless, these theoretical approximations require more complex calculations than those of Fowler.

4. Conclusions

Our results for the surface energy of LJ fluids, considering only the liquid density contribution (i.e. neglecting that of the vapour phase density) and using an appropriate model for the RDF of the liquid phase, are in good agreement with Freeman and McDonald's (1973) computer simulation data, and hence do not reproduce the experimental values for argon or other simple fluids, mainly due to the influence of the interfacial density profile and interfacial thickness. The method that we propose in this work, using an explicit analytical model for the distance, density, and temperature dependence of the RDF of the LJ liquid (Cuadros *et al* 1998), was found to be the best theoretical representation obtained so far for the contribution of Fowler's approximation in the calculation of surface energy, which represents about 70% of the 'full' value. The results can also be reproduced with simpler models for the RDF, such as that of Xu and Hu (1986). If Fowler's approximation is used near the critical point, the contribution of the vapour density must be taken into account, and even a very simple model for the RDF, such as that denoted as 'LDA', will be accurate enough to give adequate values.

We compared the theoretical calculations to obtain the contribution of Fowler's approximation to the 'full' value of the surface tension of LJ fluids. Our results confirm (as Lekner and Henderson (1977) pointed out) that the accordance between surface tension values obtained through Fowler's approximation by Salter and Davis (1975) and by Haile *et al* (1976), and the computer simulation values of Freeman and McDonald (1973) (or even experimental values or recent computer simulation values at temperatures close to that of the triple point) is strictly fortuitous. This is in agreement with the influence of a non-zero interfacial thickness at the triple-point temperature, and we can hence conclude that these data do not properly represent the contribution of Fowler's approximation.

The results obtained by Kalikmanov and Hofmans (1994) disagree with all the other theoretical or simulated values. Nevertheless, this does not mean that their theoretical approach was invalid. We showed that adequate values can be obtained by using more accurate coexistence densities (this becomes more relevant at high temperatures) and by using a suitable expression for the effective hard-sphere diameter (with relevance mainly near the triple-point temperature).

We also tested the validity of the expression of Lekner and Henderson (1977) that relates the surface tension to the DCF. Our results showed that the PY or HNC approximations in that expression do not successfully represent the contribution of Fowler's method to the calculation of the surface tension of LJ fluids.

Calculations considering three different models for the RDF and the influence of the vapour density were performed at high temperatures. The 'LDA' model for the RDF previously used by Lekner and Henderson (1977), and the model of Xu and Hu (1986) used by Li and Lu (2001), lead to very high values when compared with computer simulation data and with values obtained here through a properly modified Kalikmanov and Hofmans (1994) theoretical expression or from the COS model for the RDF (the only one that accounts for the true form of the RDF). These last two theoretical values coincide near both the triple-point and the critical temperatures, and show a clear discrepancy with respect to Baidakov *et al*'s (2000) computer simulation values of LJ fluid surface tension. Nevertheless, we estimated that at the triple-point temperature the contribution of the 'non-Fowler' part in the calculation of the surface tension is of the same order as the difference between our values and those simulation results (20% approximately). This is further clear proof of the validity of the new values calculated in this present work for Fowler's contribution, in contrast to those given in previous works.

Finally, our results allow one to quantify the contribution of the vapour phase density when Fowler's approximation is used at high temperatures. A review of the use of the 'slowly varying density approximation' near the critical point, and the calculation of the surface tension with more general expressions will be developed in future work.

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