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# The slowly varying density 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 the *slowly varying density* approximation to calculate the surface tension and the surface energy of Lennard-Jones fluids. To do so, we consider three explicit analytical expressions for the radial distribution function of the liquid phase, including one proposed by our research group, together with very accurate expressions for the liquid and vapour densities, also proposed by ourselves. The calculation of the surface tension from the direct correlation function using the Percus–Yevick and the hypernetted-chain approximations is also considered. Finally, our results are compared with those obtained by other authors by computer simulation, and also with those estimated via the general expressions (i.e., not in the ambit of the approximation studied here). We demonstrate that although the *slowly varying density* approximation is in good agreement with more complex expressions near the critical point, it is not adequate to calculate the surface energy and the surface tension of Lennard-Jones fluids at every temperature.

## 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 and the surface energy 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. Obviously, this is a suitable approximation for temperatures near the triple point. In a recent work we have carried out a detailed study of the validity of Fowler’s approach to calculate the surface tension and the surface energy of LJ fluids (Mulero *et al* 2003).

Besides Fowler’s approach, other approximations have been proposed to study the surface properties in the liquid–vapour interface. In order to treat the problem more realistically, the existence of an interfacial zone—in which the density of the system varies from that of the liquid coexisting phase to that of the vapour—cannot be neglected. The function describing such a transition is referred to as the density profile. The study of the surface properties in the vicinity of the critical point, at which the thickness of the interfacial zone tends to infinity, is a matter of especial interest. Since a high value of that parameter, compared to the molecular scale, leads to a soft transition in the density (consider that the coexisting liquid and vapour phase densities converge to the same value at the critical point), the approximation at temperatures close to that of the critical point is known as the *slowly varying density* (SVD) *approximation* (Lekner and Henderson 1977).

Mathematically, the SVD approximation corresponds to a series expansion of the integrand in the general expression of the surface energy or the surface tension in terms of the distance  $r$  (Lekner and Henderson 1977), since this integrand includes the RDF and the derivative of the molecular interaction potential which rapidly tend to zero as the interfacial thickness increases (or, in other words, as the system approaches the critical point). This interpretation allows one to simplify quite significantly the analytical expressions involved, which will now include only a parameter related to the interfacial thickness, the coexisting densities at the vapour–liquid equilibrium, and the RDF or the DCF of the liquid phase, as will be shown in detail in section 2.

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). They performed calculations using the so called *low density approximation* for the RDF, and concluded that the SVD approximation can be useful even at temperatures far from that of the critical point. Subsequently, they used this approximation to estimate the thickness of the liquid–vapour interface of real fluids near the triple point (Lekner and Henderson 1978, Henderson and Lekner 1979). In this present work, we check that conclusion by using more appropriate representations for the RDF, such as that given by Xu and Hu (1986), and recently used by Li and Lu (2001) in the calculation of the surface tension of polar fluids, and that of Cuadros *et al* (1998).

We study here the validity of the SVD approximation to calculate the surface tension and the surface energy of Lennard-Jones fluids by comparing new theoretical results with computer simulation values and with those estimated via the general expressions. In section 2 we present all the analytical expressions used. The results from three analytical approximations for the liquid RDF and two for the DCF, as well from two models for the interfacial density profile, are presented in section 3. For the surface energy, section 3.1 compares the results with those of the computer simulation of Freeman and McDonald (1973) and with the experimental values of Stansfield (1958) and of Shih and Uang (1978). For the surface tension, section 3.2 presents

a comparison with the Baidakov *et al* (2000) computer simulation data. Finally, conclusions are presented in section 4.

## 2. Analytical expressions

The expressions for the surface energy  $U$  and the surface tension  $\gamma$  of LJ fluids according to the SVD approximation are given by (Lekner and Henderson 1977)

$$U = 2\pi \int_0^\infty r^2 u(r) g(r) dr \int_{-\infty}^\infty [\rho(z) - \rho_L][\rho(z) - \rho_V] dz \quad (1)$$

$$\gamma = \frac{2\pi}{15} \int_0^\infty r^5 u'(r) g(r) dr \int_{-\infty}^\infty [\rho'(z)]^2 dz \quad (2)$$

where  $r$  is the intermolecular distance,  $\rho_L$  and  $\rho_V$  are the coexisting densities of the liquid and vapour phases respectively,  $u(r)$  is the LJ intermolecular potential, with  $u'(r)$  its derivative,  $g(r)$  is the RDF,  $\rho(z)$  is the density profile in the interfacial zone and  $\rho'(z)$  its derivative, with  $z$  the distance along an axis perpendicular to the interfacial surface. All the analytical expressions and the results in this paper are in adimensional units, reduced with LJ parameters (lengths reduced with the LJ parameter  $\sigma$ , the distance at which the LJ potential becomes zero, and energies reduced with the LJ parameter  $\varepsilon$ , the minimum value of the LJ potential (Croxtton 1980)).

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

$$\gamma = \frac{2\pi}{3} T \int_0^\infty r^4 c(r) dr \int_{-\infty}^\infty [\rho'(z)]^2 dz \quad (3)$$

with  $T$  being the reduced temperature.

Note that in equations (1)–(3) the RDF and the DCF must be calculated at a fixed density for each  $T$ . As Lekner and Henderson (1977) did, we have chosen the density of the liquid phase.

We performed calculations with two expressions for the density profile in the interfacial zone. The first is the exponential model given by Lekner and Henderson (1977)

$$\rho(z) = \begin{cases} \rho_L - \frac{\rho_L - \rho_V}{2} e^{z/\lambda} & z < 0 \\ \rho_V + \frac{\rho_L - \rho_V}{2} e^{-z/\lambda} & z > 0, \end{cases} \quad (4)$$

where  $\lambda = (2 \ln 5)^{-1} t$ ,  $t$  being the so-called ‘10-90’ interfacial thickness whose values have been taken from the computer simulation of Baidakov *et al* (2000). Lekner and Henderson (1978) specifically recommend the use of the parameter  $t$  because it is relatively insensitive to different choices of density profile. The second is Fermi’s hyperbolic tangent model (Croxtton 1980):

$$\rho(z) = \frac{\rho_L + \rho_V}{2} - \frac{\rho_L - \rho_V}{2} \tanh\left(\frac{z}{2\delta}\right) \quad (5)$$

in which  $\delta = (2 \ln 9)^{-1} t$ .

The use of the exponential density profile (equation (4)) in equations (1)–(3) gives the following expressions for the surface energy and surface tension in the SVD approximation (Lekner and Henderson 1977):

$$U = -\frac{3\pi(\rho_L - \rho_V)^2 \lambda}{2} \int_0^\infty r^2 u(r) g(r) dr \quad (6)$$

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2}{30\lambda} \int_0^\infty r^5 u'(r) g(r) dr \quad (7)$$

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2}{6\lambda} T \int_0^\infty r^4 c(r) dr. \quad (8)$$

On the other hand, if Fermi's density profile (equation (5)) is used, the expressions obtained in the SVD approximation are (Lekner and Henderson 1977)

$$U = -2\pi(\rho_L - \rho_V)^2 \delta \int_0^\infty r^2 u(r) g(r) dr \quad (9)$$

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2}{45\delta} \int_0^\infty r^5 u'(r) g(r) dr \quad (10)$$

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2}{9\delta} T \int_0^\infty r^4 c(r) dr. \quad (11)$$

As was noted in section 1, the expressions in the SVD approximation arise from the general ones through a series expansion in terms of the distance  $r$ . The general expressions for the surface energy and for the surface tension of LJ fluids (with either direct dependence on the RDF or through the DCF) when the exponential (equation (4)) or hyperbolic tangent (equation (5)) density profiles are considered can be found in the paper of Lekner and Henderson (1977).

For the temperature dependence of the coexisting vapour and liquid densities of LJ fluids, we used the expressions given by Okrasinski *et al* (2001a, 2001b) (OPC):

$$\rho_V(T) = 0.3075 + 0.304(1.32 - T) - 0.6027(1.32 - T)^{0.4157} \quad (12)$$

$$\rho_L(T) = 0.3075 + 0.058(1.32 - T) + 0.6027(1.32 - T)^{0.4157} \quad (13)$$

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 considered three analytical expressions, including a proposal of our own research group. The first is the so-called *low density approximation* (LDA):

$$g_{LDA}(r) = e^{-u(r)/T} \quad (14)$$

which was used by Lekner and Henderson (1977) in their landmark theoretical studies. The second is the approximation of Xu and Hu (1986) for the RDF in the liquid state, based on the properties of the well known Dirac delta ( $\delta_D$ ) and Heaviside step ( $\theta$ ) functions:

$$g_{XH}(r) = \theta[r - r_2(T)] + \frac{[r_2(T)]^3 - [d_C(T)]^3}{3[r_1(T)]^2} \delta_D[r - r_1(T)], \quad (15)$$

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

$$r_1(T) = 1.150d_C(T) \quad (16)$$

$$r_2(T) = 1.575d_C(T) \quad (17)$$

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

$$d_C(T) = \frac{1 + 0.2977T}{1 + 0.3316T + 0.0010477T^2}. \quad (18)$$

The approximation of Xu and Hu (1986) for the RDF has recently been 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 polar fluids, considering a suitable interaction potential). Calculations for the surface energy were not performed either. We note that although the XH model (equation (15)) should 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) (COS). 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 to unity. For  $r \in (0.96, 2.5)$  they proposed

$$g_{\text{COS}}(r) = \sum_{i=0}^{10} C_i r^i, \quad (19)$$

with coefficients

$$C_i = D_{i1} + D_{i2}T + D_{i3}T^2 + D_{i4}T^3 + (D_{i5} + D_{i6}T + D_{i7}T^2 + D_{i8}T^3)\rho \quad (20)$$

where  $D_{ij}$  are numerical values listed by Cuadros *et al* (1998). Obviously, this is a more complex analytical model, but it is also the closest to the 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 the XH model (equation (15)).

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

$$c_{\text{PY}}(r) \approx g(r)[1 - e^{u(r)/T}] \quad (21)$$

$$c_{\text{HNC}}(r) \approx g(r) - 1 - \ln g(r) - \frac{u(r)}{T} \quad (22)$$

and calculations were performed only with the COS model for the RDF, equation (19).

### 3. Results and discussion

#### 3.1. Surface energy

To test the validity of the SVD approximation for the surface energy of LJ fluids we performed calculations using equations (6) and (9) with the three proposals for the RDF of the liquid phase, equations (14), (15), and (19). The analytical expressions for the vapour and liquid densities given in equations (12) and (13) were used in all cases. The range of temperatures includes values from the triple to the critical points ( $0.7 < T < 1.32$ ). The results of all the calculations are given in table 1 and are compared with the computer simulation data of Freeman and McDonald (1973) in figure 1, as well as with the experimental values of Stansfield (1958) and of Shih and Uang (1978).

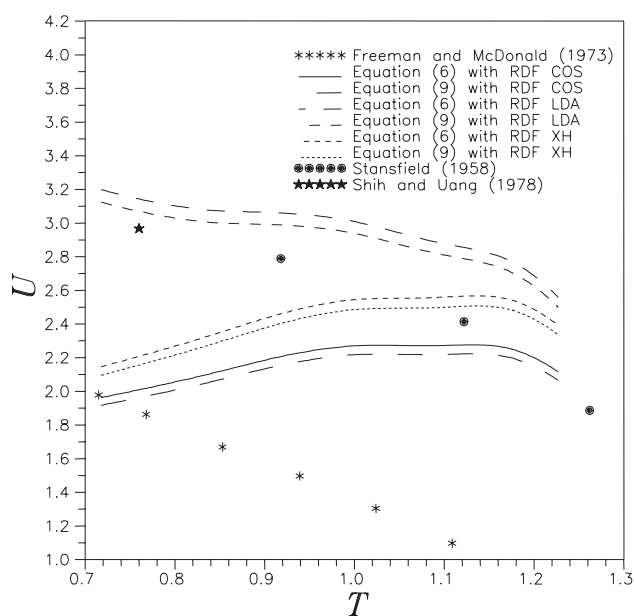
A direct inspection of equations (6) and (9) shows that the results calculated with the two expressions would coincide if the parameters related to the interfacial thickness  $\lambda$  and  $\delta$  satisfied the following ratio:

$$\frac{\lambda}{\delta} = \frac{4}{3} = 1.\widehat{3}. \quad (23)$$

However the ratio those parameters actually satisfy (see their definitions in section 2) is not that of equation (23), but

$$\frac{\lambda}{\delta} = \frac{\ln 9}{\ln 5} \approx 1.365. \quad (24)$$

From this it follows that the values obtained with equation (6) are higher than those calculated with equation (9) (as will be seen in section 3.2, the opposite is the case for the surface tension). In particular, the differences between the values of the surface energy calculated via equations (6) and (9) must be almost constant and approximately 2% (the percentage difference



**Figure 1.** Surface energy for LJ fluids calculated in the SVD approximation. The three models for the RDF labelled LDA, XH, and COS correspond to equations (14), (15), and (19) respectively. Computer simulation data of Freeman and McDonald (1973) are also shown. The experimental values of Stansfield (1958) and of Shih and Uang (1978) have been reduced to adimensional units using the LJ parameters proposed by Cuadros *et al* (1995) for argon ( $\varepsilon/k = 111.84$  K,  $\sigma = 0.3623$  nm).

**Table 1.** Surface energy of LJ fluids calculated in the SVD approximation using the models for the RDF given in equations (14), (15), and (19). The values for the interfacial thickness to obtain the parameters  $\lambda$  and  $\delta$  of the density profile were taken from the computer simulation of Baidakov *et al* (2000).

$T$	$U$ (equation (6))			$U$ (equation (9))		
	COS RDF	LDA RDF	XH RDF	COS RDF	LDA RDF	XH RDF
0.718	1.963	3.199	2.146	1.917	3.124	2.096
0.831	2.093	3.080	2.318	2.045	3.008	2.263
0.921	2.210	3.059	2.465	2.158	2.988	2.407
0.996	2.269	3.013	2.543	2.216	2.943	2.484
1.091	2.271	2.887	2.558	2.218	2.820	2.498
1.171	2.257	2.782	2.548	2.204	2.717	2.489
1.227	2.115	2.558	2.392	2.066	2.498	2.336

between the ratios  $\lambda/\delta$  shown in equations (23) and (24)). This can be directly observed from table 1 as well as in figure 1.

The values for the interfacial thickness used to perform the calculations listed in table 1 were taken from the computer simulation of Baidakov *et al* (2000). As can be seen, the choice of a given model to represent the RDF of the system leads to clearly different results. In particular, the LDA model (equation (14)) gives the highest values for the surface energy, whereas the lowest ones are found using the COS expression (equation (19)). In the vicinity

of the triple point, the LDA model (equation (14)) leads to values 63% and 49% higher than those obtained with the COS (equation (19)) and XH (equation (15)) expressions, respectively. However these differences decrease to 21% and 7% at temperatures close to that of the critical point.

According to Lekner and Henderson (1977), who used the LDA approximation in equation (6) with  $\lambda = 1$ , the SVD approximation can be taken as valid in the calculation of the surface energy even at temperatures far from the critical point. In order to analyse the validity of this statement, we compared the results calculated in this work with those estimated by using more general expressions for the surface energy (i.e., not in the ambit of the SVD approximation) (Lekner and Henderson 1977). In particular, when the COS model is used for the RDF, the deviation in the surface energy calculated in the SVD approximation with respect to that obtained through the general expression is approximately 30% at temperatures close to the triple point. Deviations are found to be below 10% only at  $T > 1$ . Hence we conclude that the SVD approximation for the surface energy can be taken as valid only at temperatures in the vicinity of the critical point. Our results permit us to quantify in detail the conclusion of Lekner and Henderson (1977) about the limit of applicability of the SVD approximation, since those authors used in their calculation the LDA model, which is a rough expression to represent the RDF of the system (at least in comparison with the COS expression). Also, we found that the use of the SVD approximation in the calculation of the surface energy at temperatures close to the triple point leads to values which do not agree with those obtained via the general expressions. This result could invalidate the values obtained by Lekner and Henderson (1978), Henderson and Lekner (1979) for the interfacial thickness of real fluids near the triple point.

In order to complete our study it would be desirable to compare our results with computer simulation data of LJ fluids or with experimental values for simple fluids. Since such results are not available using the SVD approximation, the computer simulation data of Freeman and McDonald (1973) obtained via Fowler's approximation (Fowler 1937) as well as the experimental values of Stansfield (1958) and of Shih and Uang (1978) for argon were taken as references. These values, together with those of table 1, are shown in figure 1. It can be observed that the dependence of the simulation data of Freeman and McDonald on the temperature is very similar to that of the experimental results (even though the values of the two data sets are markedly different), and that in any case this dependence is reproduced satisfactorily by equations (6) or (9) (as was the case in Fowler's approximation (see Mulero *et al* 2003)). While the computer simulation and experimental values present a constant decrease as  $T$  increases, the results obtained using equations (6) or (9), with the XH (equation (15)) or COS (equation (19)) models for the RDF, present a positive slope up to a maximum somewhere in  $1.1 < T < 1.2$ , and only have a negative slope in a small range for  $T > 1.2$  (see figure 1).

Figure 1 also shows the coincidence between the result for the surface energy obtained from the COS expression for the RDF and the computer simulation value of Freeman and McDonald (1973) in the vicinity of the triple point, as well with Fowler's approximation at that temperature (Mulero *et al* 2003). This proves that at temperatures close to that of the triple point, Fowler's and the SVD approximations lead to very similar values of the surface energy if the COS model is used for the RDF. Obviously, this conclusion does not apply in other temperature ranges. At  $T \cong 1.22$  the COS model in the SVD approximation roughly reproduces the experimental values expressed in reduced units by using the LJ parameters given by Cuadros *et al* (1995).

It can also be observed that the values of the surface energy calculated from the LDA expression (equation (14)) for the RDF have a negative slope, although its value is less than that of the experimental results. They agree with experiment in the vicinity of the triple point,



**Table 2.** Surface tension of LJ fluids calculated in the SVD approximation using the models for the RDF given in equations (14), (15), and (19), and the approximations for the DCF given in equations (21) and (22). The values for the interfacial thickness to obtain the parameters  $\lambda$  and  $\delta$  of the density profile were taken from the computer simulation of Baidakov *et al* (2000).

$T$	$\gamma_{\text{simul.}}$	Calculations using the RDF						Calculations using the DCF			
		$\gamma$ (equation (7))			$\gamma$ (equation (10))			$\gamma$ (equation (8))		$\gamma$ (equation (11))	
		COS	LDA	XH	COS	LDA	XH	PY	HNC	PY	HNC
0.718	0.935	2.071	2.709	2.125	1.716	2.466	1.934	2.095	2.560	1.907	2.330
0.831	0.679	1.466	1.857	1.489	1.214	1.690	1.355	1.496	1.783	1.362	1.623
0.921	0.511	1.053	1.305	1.057	0.872	1.187	0.962	1.078	1.258	0.981	1.145
0.996	0.375	0.769	0.937	0.763	0.637	0.852	0.695	0.787	0.904	0.717	0.822
1.091	0.210	0.470	0.560	0.459	0.390	0.510	0.418	0.480	0.539	0.437	0.490
1.171	0.098	0.253	0.295	0.242	0.210	0.269	0.221	0.256	0.282	0.233	0.257
1.227	0.040	0.133	0.153	0.125	0.110	0.139	0.114	0.134	0.145	0.122	0.132

whereas for states close to the critical point they have greater deviations (and are closer to the values calculated with the XH expression (equation (15)) for the RDF). Nevertheless, it must be taken into account that the experimental results shown in figure 1 have been reduced to adimensional units using the LJ parameters given by Cuadros *et al* (1995) ( $\epsilon/k = 111.84$  K,  $\sigma = 0.3623$  nm), which clearly differ from those used by Lekner and Henderson (1978) when the SVD approximation is used in the vicinity of the triple point for simple fluids such as argon. When classical LJ parameters are used ( $\epsilon/k = 119.8$  K,  $\sigma = 0.3405$  nm) (Croxtton 1980, Reid *et al* 1987), the reduced values of the surface energy are significantly less than those shown in figure 1, and thus at temperatures close to that of the triple point they are closer to the values obtained using more recent expressions for the RDF.

### 3.2. Surface tension

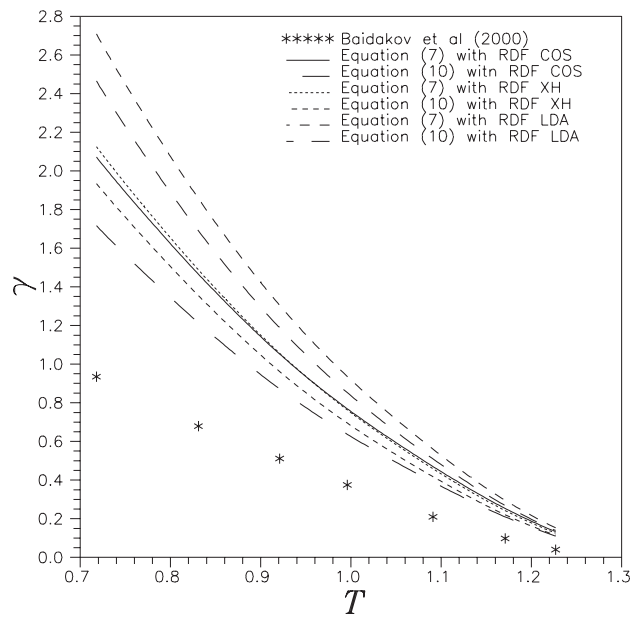
Calculations of the surface tension of LJ fluids in the SVD approximation were performed with the three proposals for the RDF (equations (14), (15), and (19)) of the liquid phase. Some of the expressions which were used include a direct dependence on the RDF (equations (7) and (10)), and in others this dependence is included in the DCF (equations (8) and (11)). The results are given in table 2 and shown in figures 2 and 3, including the computer simulation data of Baidakov *et al* (2000) as a reference.

A direct comparison between the expressions for the surface tension (equations (7) and (10)) in the SVD approximation leads to a ratio analogous to equation (23):

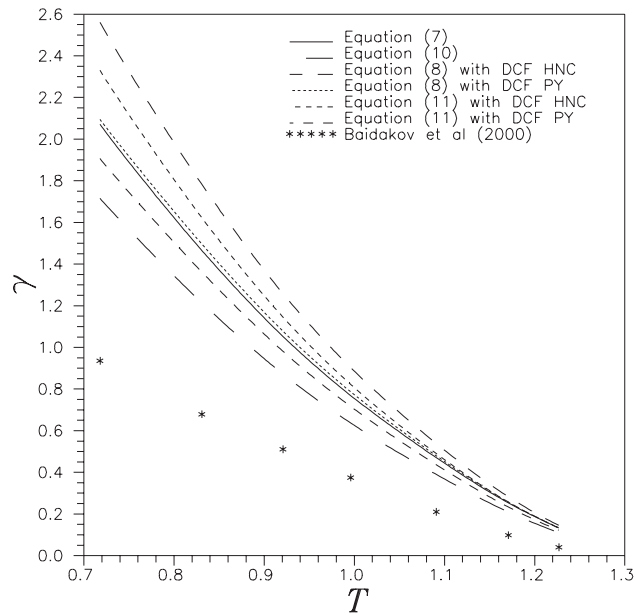
$$\frac{\lambda}{\delta} = \frac{3}{2} = 1.5. \quad (25)$$

As was noted in section 3.1, the ratio those parameters satisfy is given by equation (24). It is thus expected that the values of the surface tension calculated using Fermi's hyperbolic tangent density profile (equation (5)) via equation (10) would be less than those obtained with the exponential profile (equation (4)) in equation (7), since the parameter  $\delta$  is greater than it would have to be to obtain the same result for the surface tension with both density profiles. Note that this is opposite to the case of the surface energy. As can be seen in figures 2 and 3, this will make the values of the surface tension calculated with Fermi's density profile (equation (5)) closer to the computer simulation data of Baidakov *et al* (2000).

Figures 2 and 3 show as a general feature that results obtained with all the configurations considered (choice of the model for the RDF, of the density profile, and of either the direct



**Figure 2.** Surface tension for LJ fluids calculated in the SVD approximation via equations (7) and (10). The three models for the RDF labelled LDA, XH, and COS correspond to equations (14), (15), and (19) respectively. Computer simulation data of Baidakov *et al* (2000) are also shown.



**Figure 3.** Surface tension for LJ fluids calculated in the SVD approximation through the DCF (using the PY and HNC models, equations (21) and (22)). Results obtained directly from the RDF using equations (7) and (10) are also shown. The COS model (equation (19)) for the RDF was used in all cases. Computer simulation data of Baidakov *et al* (2000) are included as a reference.

dependence on the RDF or via the DCF) converge approximately to the same value as the system approaches the critical point. This does not apply in the vicinity of the triple point, where differences between all the results become significantly greater. As one could expect from the arguments given above, the values are closer to the computer simulation data when Fermi's hyperbolic tangent density profile (equation (5)) is used instead of the exponential form (equation (4)), both for the expression containing the RDF as well for that in which the dependence is included via the DCF.

At  $T \cong 1$ , the deviations of the values calculated with equations (7) or (10), and the COS model for the RDF, with respect to the computer simulation data are approximately 100% and 70% respectively. If the LDA expression for the RDF is used, as in Lekner and Henderson (1977), the deviations remain greater than 127% for  $T > 0.99$  and reach 190% and 160% (for equations (7) and (10)) at the temperature closest to that of the triple point ( $T = 0.718$ ). This contradicts the statement of Lekner and Henderson (1977) that the SVD approximation for the surface tension can be taken as valid not only in the vicinity of the critical point, but also for lower temperatures.

At  $T = 1.227$  (the highest temperature considered in the computer simulation of Baidakov *et al* (2000)) the results for the surface tension are up to three times greater in value than the corresponding computer simulation value. In particular, the lowest deviation (175%) is obtained with the COS model for the RDF and (as was expected for the reason given above) Fermi's hyperbolic tangent density profile. At this concrete temperature ( $T = 1.227$ ) other more complex theories—those proposed by Bongiorno and Davis (1975), by Nordholm and Gibson (1981), by Hooper and Nordholm (1984), by Wendland (1997), and one of those proposed by Abbas and Nordholm (1994)—lead to values for the surface tension with similar or even greater deviations with respect to the computer simulation value of Baidakov *et al* (2000). Moreover, the density functional theory of Ebner *et al* (1976) gives a deviation of almost 140% with respect to computer simulation, i.e. a value which is close to that obtained by us. In all these theories large deviations arise because the critical point predicted by the mean-field theories is not located as estimated by computer simulation or experimental methods.

At high temperatures the results calculated with the COS and XH models are not very different, whereas the LDA expression leads to higher values for the surface tension, which hence present greater deviations with respect to the computer simulation data (see figure 2). The use of this expression for the RDF at  $T = 1.227$  in equations (7) and (10) gives results 3.8 and 3.5 times larger (respectively) than the corresponding computer simulation value. The deviations of the results with respect to the values calculated using the COS expression for the RDF are 15% and 26%. A detailed study of the form of the integrands that appear in the surface tension expression (for each of the three models of the RDF) shows that, even though their negative parts do not present great differences, their positive contributions are significantly different, that of the LDA model being greater than the other two.

If results of the surface tension calculated with equation (10) and the model COS for the RDF are compared with those estimated via the general expression (i.e., not in the ambit of the SVD approximation), one finds a great degree of coincidence (deviation of 6.8% at  $T = 1.227$ ). The deviations increase as the temperature decreases, reaching 80% at  $T = 0.718$ . If equation (7) is used instead of equation (10) (also using the COS model for the RDF), the deviations vary from 23% to 119%.

According to the results shown in figure 3, the use of the PY (equation (21)) or HNC (equation (22)) approximations for the DCF in the SVD expressions for the surface tension seems not to be justified on the basis of any criterion of analytical simplicity. It can be seen that equation (10) with the COS model for the RDF leads to values of the surface tension which

are closer to the computer simulation data than any of the possible configurations that include the dependence by way of the DCF.

#### 4. Conclusions

In the determination of the surface energy of LJ fluids, the differences between the values calculated by using either the exponential or the hyperbolic tangent models for the density profile are found to be almost constant over the whole range of temperatures. Nevertheless, the results are strongly conditioned by the choice of a model for the RDF of the system. In particular, the LDA approximation gives the highest values, while the lowest ones correspond to the COS model, with the differences being smaller as the temperature approaches that of the critical point.

Lekner and Henderson (1977) stated that the SVD approximation could be taken as valid even at temperatures far from the critical point. We have proved however that deviations with respect to values estimated by using a general expression with the exponential density profile (Lekner and Henderson 1977) are less than 10% only at temperatures  $T > 1$ .

Hence we conclude that the SVD approximation seems not to be adequate to calculate the surface energy of LJ fluids, except for a small range of temperatures in the vicinity of the critical point where the results approach those obtained with a general expression. In particular, the values which best reproduce the experimental ones for argon in that temperature range (reduced with the LJ parameters of Cuadros *et al* (1995)) are those calculated with the COS model for the RDF. With respect to the choice of a suitable expression for the density profile, it is not clear which of the two possible ones should be used since they lead to results which are proportional to each other and there is no clear reference for comparison. It is clear that at temperatures close to that of the triple point the use of an appropriate model for the RDF influences the results for the interfacial thickness of real fluids obtained by Lekner and Henderson (1978), Henderson and Lekner (1979).

The detailed analysis of the calculated values for the surface tension of LJ fluids in the SVD approximation showed that the different configurations in the expressions proposed by Lekner and Henderson (1977, 1978), containing the RDF explicitly or implicitly in the DCF, converge to approximately the same value as the system approaches the critical point. This is an expected result since it is at that state (i.e., the critical point) that the SVD approximation becomes valid, as was noted in section 1. In contrast, greater differences are found as the temperature decreases towards that of the triple point.

Even though the SVD approximation leads to similar results to those estimated by using more general expressions (i.e., not in the ambit of the SVD approximation) in the vicinity of the critical point, they present a clear discrepancy with the computer simulation data of Baidakov *et al* (2000). For that reason, the use of a liquid phase RDF to calculate the surface tension of LJ fluids instead of the interfacial zone RDF does not lead to reliable results at temperatures close to that of the critical point, even if a general expression for the surface tension is used. Obviously, it must be noted that this statement is highly influenced by the fact that the locations of the critical point predicted by theories do not meet the computer simulation or experimental values. Nevertheless, equation (10) is significantly simpler than other theoretical analytical expressions, and even has smaller deviations with respect to the computer simulation data of Baidakov *et al* (2000) near the critical point.

In practice, either of the models, COS or XH, can be chosen for the RDF in the SVD approximation, since they lead to very similar values of the surface tension of LJ fluids. One should note, however, that the former is a better representation of the RDF, whereas the latter must be regarded rather as a convenient analytical design. The values calculated with the LDA

expression for the RDF, as used by Lekner and Henderson (1977), present greater deviations with respect to the computer simulation data of Baidakov *et al* (2000).

A review of the use of the general expressions proposed by Lekner and Henderson (1977) for the surface energy and the surface tension of LJ fluids will be the subject of future work.

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