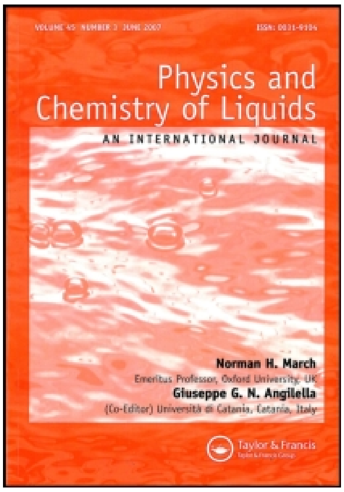

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S. M. Osman[a]; M. Silbert[a]
[a] School of Mathematics and Physics, University of East Ang/ia, Norwich, UK

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Simplified RPA Bhatia–Young Model of the Liquid–Vapour Surface

S. M. OSMAN and M. SILBERT

School of Mathematics and Physics, University of East Anglia,
Norwich NR4 7TJ, UK

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The simplified random phase approximation (RPA) Bhatia–Young model for the bulk properties of liquids has been used in conjunction with the gradient expansion formalism to study the liquid-vapour interface of simple fluids such as argon.

Key Words: Gradient expansion, random phase, pair potential.

1 INTRODUCTION

Bhatia and Young[1] have recently proposed a simple model for the bulk free energy of mixing of a binary fluid using hard sphere as a reference system and a tail interaction between unlike atoms. The latter may be related to the ordering potential whose sign and overall behaviour is known to produce strong effects on the bulk properties of liquid alloys.[2] Moreover there are strong indications that the ordering potential uniquely characterize the behaviour of the concentration-concentration partial structure factor, $S_{cc}(k)$[3]. The approximate relation between $S_{cc}(0)$ and the surface tension in liquid binary alloys[4] suggests that, likewise, there will be strong ordering potential effects on their surface properties.

The simple random phase approximation (RPA) Bhatia-Young model may be used to study the surface properties of liquid binary alloys within the framework of the density functional theory in the gradient expansion formalism.[5] While we acknowledge the limitations of such an approach, we suggest that its simplicity may allow for a systematic study of the effects of the ordering potential on the surfaces properties of liquid mixtures. To our knowledge such a study is not yet available, in spite of the considerable progress made in this field.[6]

The above programme is currently under way. However, in this note we restrict ourselves to the single component case for two main reasons. First, while no new results come out of this study, it affords a didactic presentation of the approach used in the binary case. Second, since the parametrisation is carried out at the level of the pure bulk properties, it is useful to check out how it accounts for the surface properties of the pure liquid.

We assume that the pair potential $v(r)$ is given by

$$v(r) = v_{HS}(r) + v_T(r) \tag{1}$$

where $v_{HS}(r)$ denotes the hard-sphere reference potential with diameter σ.

For didactic purposes we visualize the attractive potential by means of a square-well tail, namely

$$v(r) = \begin{cases} 0 & \text{for } r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma, \\ 0 & \lambda\sigma < r \end{cases} \tag{2}$$

although, as we shall see below, this is not necessary for our description.

In the next section we write down the expressions used in this work with emphasis on the Bhatia-Young results. In Section 3 we present the results of our calculations for both the bulk and surface properties, which are compared with the experimental results for Ar,[7] and computer simulation results for Lennard-Jones fluids.[8] We complete this note with a brief discussion of our results.

2 THEORY

As indicated above the surface properties are to be studied within a van der Waals type of theory, following an approach originally proposed by Yang *et al.*[9] We need not rehearse the arguments leading to the above, except refer the reader to the excellent monograph by Rowlinson and Widom.[10]

The bulk properties of the hard sphere reference systems are those obtained from the Percus-Yevick approximation, and are denoted with the subscript *HS*. For consistency we use the results obtained from the compressibility route to the equation of state.

A Bulk properties

The Helmholtz free energy per atom, f, is given by

$$f = f_{HS} + \tfrac{1}{2}\tilde{v}_T(0) \tag{3}$$

where $\tilde{v}_T(0)$ is the long-wavelength limit of the Fourier transform (FT) of the potential tail,

$$\tilde{v}_T(q) = \rho \int_0^\infty v_T(r) \frac{\sin qr}{qr} 4\pi r^2 \, \mathrm{d}r \tag{4}$$

where ρ is the bulk liquid density.

From (2) and (4)

$$\begin{aligned} \tilde{v}_T(0) &= -8\varepsilon(\lambda^3 - 1)\eta \\ &\equiv K\eta \end{aligned} \tag{5}$$

where the packing fraction, $\eta = \frac{1}{6}\pi\rho\sigma^3$.

The pressure is given by

$$P = P_{HS} + \tfrac{1}{2}\rho\tilde{v}(0) \tag{6}$$

Using the thermodynamic relation $\rho\mu = \rho f + P$, the chemical potential μ is given by

$$\mu = \mu_{HS} + \tilde{v}_T(0) \tag{7}$$

Within the RPA we may write the FT of the Ornstein-Zernike direct correlation function $c(r)$, as

$$\tilde{c}(q) = \tilde{c}_{HS}(q) - \beta\tilde{v}_T(q) \tag{8}$$

with $\beta \equiv (k_B T)^{-1}$, T the temperature, and k_B the Boltzmann constant.

Actually we only need the small q expansion of Eq. (8), namely

$$\tilde{c}(q) = \tilde{c}(0) + c_2 q^2 + \cdots \tag{9}$$

with

$$c_2 = 4\pi\rho \int_0^\infty r^4 c(r) \, \mathrm{d}r \tag{10}$$

Using Eq. (8),

$$c_2 = c_2^{HS} + c_2^T$$

and from (2) and (10),

$$\begin{aligned} c_2^T &= \tfrac{24}{5}\sigma^2(\lambda^5 - 1)\varepsilon\beta\eta \\ &\equiv R\varepsilon\beta\eta \end{aligned} \tag{11}$$

B Surface properties

Assuming the fluid possesses a planar surface parallel to the xy-plane of area A, the equilibrium density profile, in the absence of an external field, satisfies the Euler–Lagrange equation

$$P_N(z) = \mu\rho_0(z) - f_0(\rho_0(z)) + f_2(\rho_0(z))\left(\frac{d\rho_0(z)}{dz}\right)^2 \tag{12}$$

where z denotes the distance normal to the surface, $P_N(z)$ the pressure normal to the surface, $f_0(\rho_0(z))$ the uniform Helmhotz free energy per atom evaluated at the local density $\rho_0(z)$, and the coefficient f_2 of the non-uniform term is given by

$$f_2(\rho_0(z)) = -\tfrac{1}{2}k_B T c_2 \tag{13}$$

The surface tension γ is given by

$$\gamma = \int_0^\infty dz f_2(\rho_0(z))\left(\frac{d\rho_0(z)}{dz}\right)^2 \tag{14}$$

and the equilibrium density profile by

$$z = \int_{\rho_V}^{\rho_L} d\rho\left[\frac{f_2(\rho(z))}{\bar{P} - \bar{\mu}\rho + \rho f_0(\rho(z))}\right]^{1/2} \tag{15}$$

In Eq. (15) ρ_V, ρ_L denote, respectively, the densities of the vapour and the liquid at the coexistence curve for a given isotherm. $\bar{P}$ and $\bar{\mu}$ are the constant values of the pressure and chemical potential providing the mechanical and chemical equilibrium between the two phases at the same isotherm.

We note that at this level of treatment of the liquid–vapour interface no detailed knowledge of the potential is necessary. The only information required is its zeroth moment, $\tilde{v}_T(0)$, whose knowledge is all the input needed to study the bulk properties of the system, and its second moment which enters the non-uniform term of Eq. (12) through c_2. In other words, provided the assumed pair potential is a function of only the relative distance between two atoms then, once the diameter σ of the hard sphere reference system is chosen, only the knowledge of the constant K, defined by Eq. (5), is needed for the bulk properties, while the additional knowledge of the constant R, defined by Eq. (11), is required for the surface properties. Both K and R are independent of the thermodynamic state of the system. This result is an indication of the simplicity and the shortcomings of the present approach.

3 RESULTS

We have carried out our calculations in reduced units. Thus $\rho^* = \rho\sigma^3$, $T^* = k_B T/\varepsilon$, $\mu^* = \mu/\varepsilon$, $P^* = P\sigma^3/\varepsilon$, and $\gamma^* = \gamma\sigma^2/\varepsilon$ denote, respectively, the reduced density, temperature, chemical potential, pressure, and surface tension. We also denote by $z^* = z/\sigma$ the reduced distance

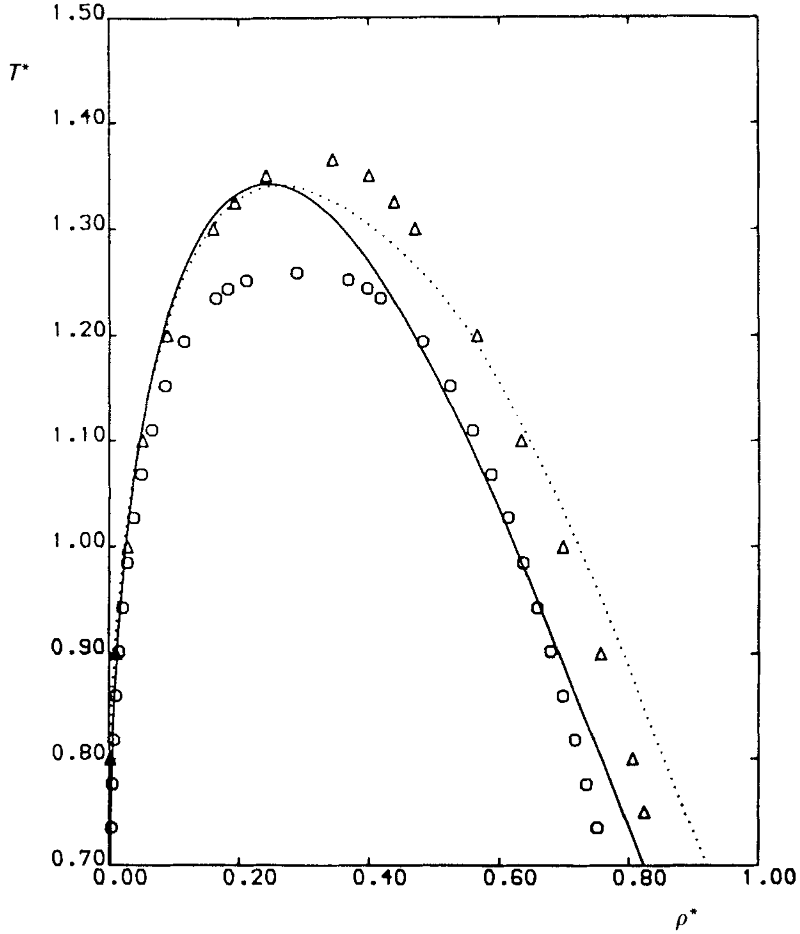

Figure 1 Liquid–vapour coexistence curve for a simple fluid with parameters appropriate for argon. *Theoretical*: —— this work; ······ results of Evans and Telo da Gama[14] for a Lennard-Jones potential. *Computer simulation*: △ Monte Carlo results of Hansen and Verlet[13] for a Lennard-Jones potential. *Experimental*: ○ experimental results for argon (Ref. 12).

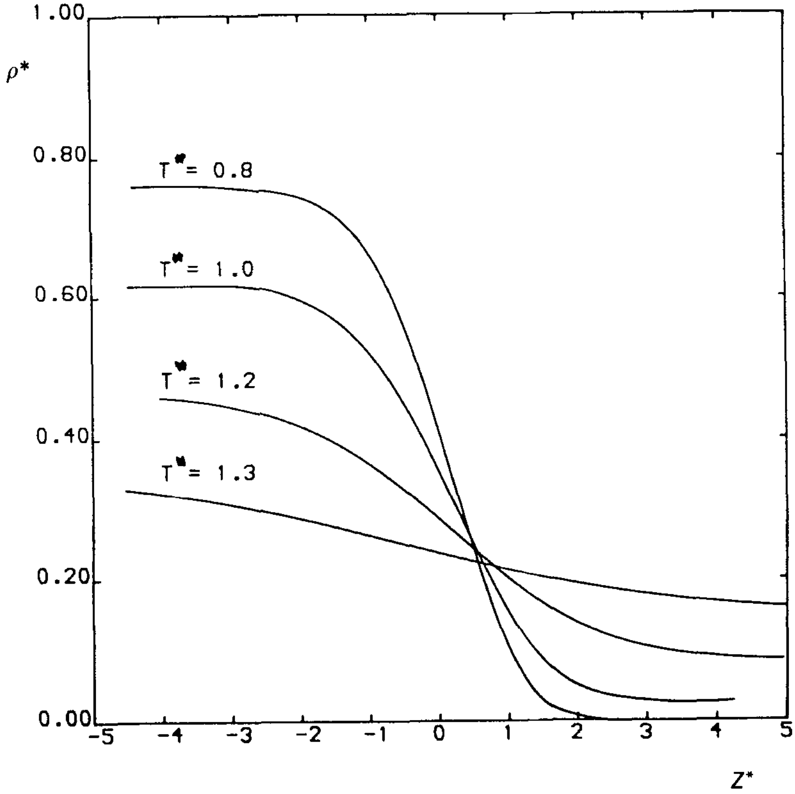

Figure 2 Equilibrium density profile of the liquid-vapour interface at temperatures $T^* = 0.8$, 1.0, 1.2, and 1.3 (this work).

normal to the surface, and by $d^* = d/\sigma$ the reduced surface thickness.

The parameterisation is discussed below, with particular reference to liquid argon.

We choose for the hard-sphere diameter the value $\sigma = 3.3$ Å. The values of the constants $K^* = K/\varepsilon$ and $R^* = R/\sigma^2$ are determined by optimising the fitting to the experimental coexistence curve at low and intermediate temperatures. Comparison between the results of calculations of our model and those obtained from computer simulations for the bulk properties of a square-well fluid[11] shows that the agreement is better for a range of temperatures between the triple point to about half-way to the critical point. This comparison, not included here, guided us in the choice of the best strategy of parameterisation. The values thus obtained are $K^* = -28.6$ and $R^* = 55.7$ which we have used in all subsequent calculations.

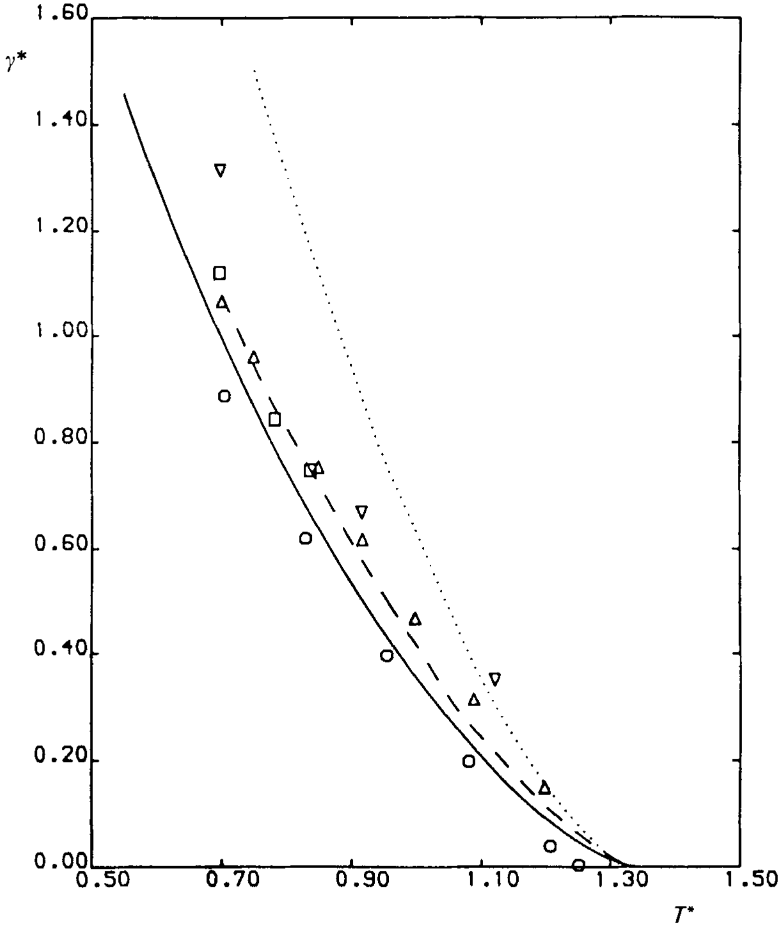

Figure 3 Surface tension as a function of temperature, with parameters appropriate for argon. *Theoretical*: —— this work; ······ results of Evans and Telo da Gama,[14] and - - - of Ebner *et al.*[15] for a Lennard-Jones potential. *Computer simulation*: Monte Carlo results for a Lennard-Jones potential: △ Lee *et al.*,[8] and ▽ Chapela *et al.*[8] Molecular Dynamics results for a (shifted) Lennard-Jones potential: □ Chapela *et al.*[8] *Experimental*: ○ experimental results for argon (Ref. 7).

Figure 1 shows the the coexistence curve obtained from our model. We have also included, for comparison, the experimental results for Ar[12], Monte Carlo (MC) results for a Lennard-Jones fluid,[13] and the theoretical results of Evans and Telo da Gama.[14] The last two use for the Lennard-Jones parameters the values $\varepsilon/k_B = 119.8$ K and $\sigma = 3.405$ Å.

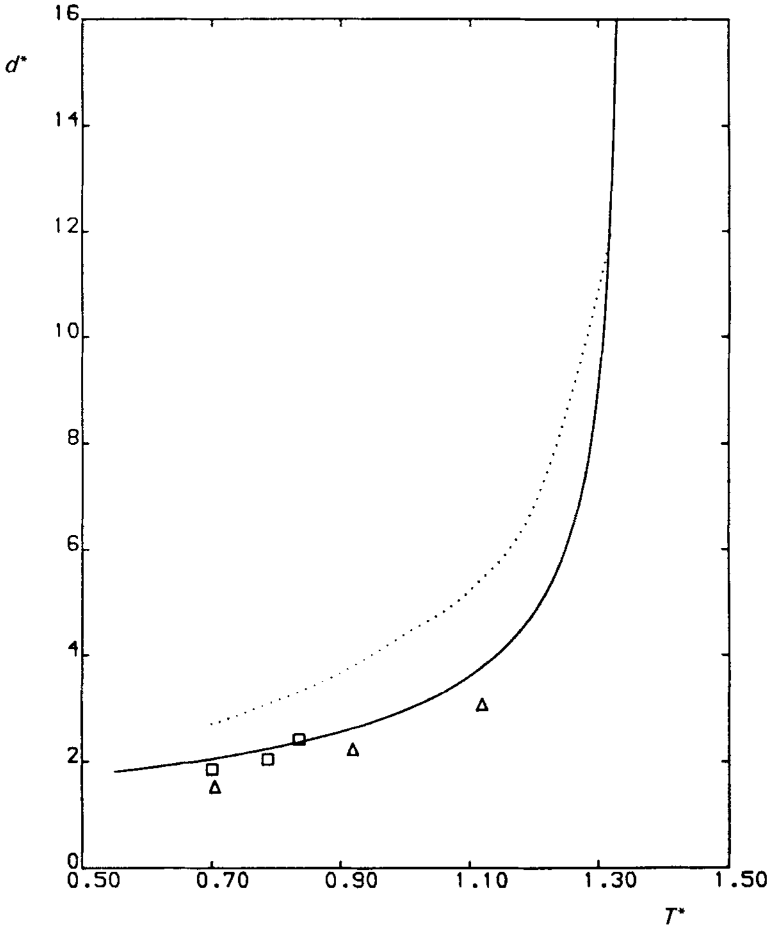

Figure 4 Surface thickness (as defined in the text) as a function of temperature, with parameters appropriate to argon. *Theoretical*: —— this work; ······ results of Evans and Telo da Gama[14] for a Lennard-Jones potential. *Computer Simulation*: △ Monte Carlo results of Chapela *et al.*[8] for a Lennard-Jones potential. ☐ Molecular Dynamics results of Chapela *et al.*[8] for a (shifted) Lennard-Jones potential.

We now turn to the surface properties. In Figure 2 we present the results of our model for the equilibrium density profile, Eq. (15), at different temperatures.

In Figure 3 we present the results of our calculations for the surface tension as a function of temperature. We have also included in this figure the experimental results for Ar,[7] MC and MD (Molecular Dynamics) results for a Lennard-Jones fluid,[8] as well as the theoretical results of Evans and Telo da Gama (loc. cit.) and Ebner *et al.*[15] We note that our results compare well with the others, following closely the experimental data.

Finally, Figure 4 shows our results for the surface thickness. Here we have used the conventional "10–90" criterion, namely we define the surface thickness as the distance over which the density changes from 0.9 ρ_L to 0.1 ρ_L. We have also included, for comparison, MC and MD results as well as the theoretical results of Ref. 14.

To conclude the following observations are in order. At this level of description of the liquid-vapour interface, the details of the potential are not important. Therefore whenever the assumed effective pair interactions in a simple liquid depend only on the relative distance between two atoms, the theory presented in this work is applicable. As discussed above the parameters are fitted to bulk properties. A similar parameterisation is being carried out for liquid mixtures. However, in this case there is an additional parameter, associated to the non-additivity of the potentials tails, which probes directly the ordering potential. It is the effects of this parameter on the surface properties of liquid mixtures which we are investigating at present.

The satisfactory agreement obtained in this paper between theory and experiment of pure, simple, liquids suggests that we may undertake with some degree of confidence the more probing calculations of the surface properties of liquid mixtures.

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