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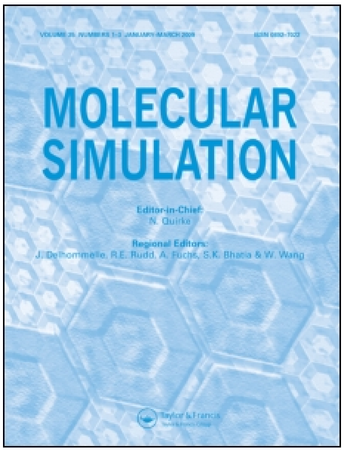

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FITS OF THE THERMODYNAMIC PHASE PLANE

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Using the Weeks-Chandler-Andersen separation of the intermolecular potential we have fitted computer simulation data for Lennard-Jones system for the whole phase plane to the same form expression but in two different ways: locally and globally. We compare the efficacy and the exactness of both methods.

Keywords: Weeks-Chandler-Andersen theory; computer simulation; Lennard-Jones fluids

To investigate the thermodynamics of simple fluids, good models of the equation of state (EOS) constructed on the basis of molecular dynamics (MD) are needed. In many of these models the intermolecular interaction is given by the Lennard-Jones (LJ) potential

$$u_{LJ}(r) = 4((1/r)^{12} - (1/r)^{6}), \tag{1}$$

where r is the interparticle distance.

In [1–5] different three (3D) as well as two-dimensional (2D) EOSs have been published, but they present by themselves two main problems: their large size, making very difficult their mathematical handling and, a more serious handicap the vapour liquid equilibrium (VLE) properties may not be obtained from them [6–7]. In the present work we try to construct a simple and, if possible, accurate EOS using the Weeks-Chandler-Andersen (WCA) perturbation theory [8–11].

In the WCA theory the intermolecular potential forces are separated into repulsive and attractive parts, the latter treated as a perturbation ([8]). Thus the Helmholtz free energy (A) can be written as follows ([12])

$$A = A_0 - \rho\alpha(T,\rho) \tag{2}$$

where A_0 is the free energy of the reference system and $\alpha(T,\rho)$ is the temperature and density function that represents the attractive contribution to A. In the following equations all quantities (including T and ρ) are expressed in the reduced LJ units [7,9–10].

Using standard thermodynamics relations from (2) one can obtain the WCA expressions for the EOS ([13–14])

$$P = (\partial A/\partial\rho)_T = P_0 - \rho^2\alpha(T,\rho) - \rho^3\partial\alpha(T,\rho)/\partial\rho \tag{3}$$

where P and P_0 are the pressures of the perturbed and reference systems respectively. In previous work ([10]), we concluded that, because of the simplicity and relative exactness, the best way to calculate the thermodynamic properties of the reference system is the Carnahan-Starling (CS) formula ([15])

$$\frac{P_0}{\rho T} = (1 + y + y^2 - y^3)(1 - y)^{-3}, \tag{4}$$

where

$$y = \pi\rho d^3/6, \tag{5}$$

and d is the hard sphere (HS) diameter given by the Verlet-Weis criterion ([16])

$$d(T) = \frac{0.3837 + 1.068/T}{0.4293 + 1/T}. \tag{6}$$

To investigate the role of the attractive forces in determining the thermodynamics of simple fluids, we carried out computer simulations for more than 700 states over the complete phase plane (Fig. 1) – perhaps the largest MD computation carried out until now – following the computer procedure described in previous papers ([9,11,13]). From computer simulations we

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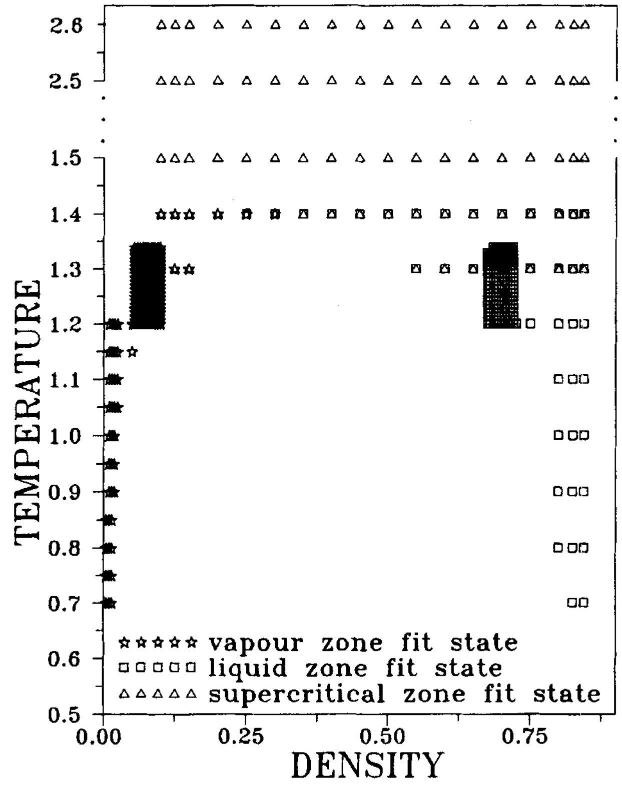

FIGURE 1 All simulated states.

have obtained $\Delta P = P - P_0$ and α. We have analysed quantitively the temperature and density dependence of the $\alpha(T, \rho)$ function. This analysis shows that α is approximately linear with respect to density and cubic with respect to temperature. Therefore we have tried to fit ourresults with the expressions ([11, 13])

$$\alpha_{\text{cal}}(T, \rho) = C_1(T) + C_2(T)\rho, \tag{7}$$

where $C_1(T)$ and $C_2(T)$ are the following functions:

$$C_1(T) = B_1 + B_2T + B_3T^2 + B_4T^3,$$

$$C_2(T) = B_5 + B_6T + B_7T^2 + B_8T^3. \tag{8}$$

We have divided the phase plane into three parts: vapour, fluid and supercritical in such manner that the parts have common points at the borders (see Fig.1). Using a regresion method we have made the fit of α to the expression (7) in the three parts. The coefficients $B_i (i = 1,\ldots,8)$ have the values given in Table I. The absolute percentage mean deviation (APMD) between α and α_{cal} for three considered parts is given in Table II. The greatest deviation between the α_{cal} and α is around 2.5%. Using α_{cal} we can calculate

$$\Delta P_{\text{cal}} = -C_1(T)\rho^2 - 2C_2(T)\rho^3 \tag{9}$$

The APMD between ΔP and ΔP_{cal} in the considered parts is given by Table III. If we consider states from vapour or liquid zones for temperature T between 1.3 and 1.4 then we can also use the supercritical fit because in this part of the phase plane the APMDs for α and ΔP are much more better that those presented in Tables II and III.

We have tried to apply the same method of the fitting to find the global fit for all three parts having the form (7) – (8). But the APMD between α_{cal} and α is greatest than 15% and for ΔP is much more great. Because of this we have changed a little the method of the fit. We have tried to fit directly the numbers C_i $(i = 1,2)$ which appear in (7) and (9) in the following manner. For every simulated state (ρ, T) we have calculated the numbers

$$C_1 = (\Delta P + 2\alpha\rho^2)/\rho^2$$

$$C_2 = -(\Delta P + \alpha\rho^2)/\rho^3. \tag{10}$$

We have fitted these numbers with the expressions (8). In the case of C_1 we have obtained a satisfactory fit. But the fit for C_2 has been impossible because of very great errors especially for low densities. To avoid this problem we have decided to consider the numbers $C_2\rho$ instead of C_2. We

TABLE I The coefficients for the fit presented by formulas (7) and (8) in the local and global cases

	Vapour	*Liquid*	*Supercritical*	*Global*
B_1	10.2104	8.7743	5.7087	−1.0096
B_2	−15.8483	−4.6752	0.3602	10.5792
B_3	16.0398	2.3882	−0.1578	−5.1610
B_4	−5.1508	−0.3910	0.0249	0.8252
B_5	43.1370	−1.7254	2.3475	7.3662
B_6	123.2895	5.3521	−0.1787	−10.4382
B_7	−255.2906	−2.7952	−0.0017	5.4165
B_8	104.8465	0.4582	0.0037	−0.9304

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TABLE II The comparison of the APMD for α in three phases with that obtained from the global fit

	Vapour	*Liquid*	*Supercritical*
Local fit	1.11%	0.12%	0.77%
Global fit	5.05%	6.84%	4.67%

TABLE III The comparison of the APMD for ΔP in three phases with that obtained from the global fit

	Vapour	*Liquid*	*Supercritical*
Local fit	2.29%	5.43%	7.52%
Global fit	2.31%	6.09%	5.21%

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have fitted successfully these numbers with the expression $C_2(T)\rho$, where $C_2(T)$ is given by (8). The coefficients B_i $(i = 1,\ldots,8)$ have values given in the Table I. With this fit we have calculated that the APMD between α and α_{cal} is about 5.58% and APMD between ΔP and ΔP_{cal} is about 4.49%. The greatest deviation between α and α_{cal} is about 10.5% for some of low densities. With this global fit we have also made suitable calculations of errors for three parts considered in the case of local fits. The Tables II and III give these results. We can observe that for every phase the APMD for α is much more better for the local fit than for the global one. It is because in the subcritical zone for a given temperature the vapour and liquid phases have different linear local fits for α whereas the linear global fit is the same for both phases (Fig. 2). Also for the vapour and liquid phase the APMD for ΔP is better for the local fit than for the global one. However in the supercritical zone the APMD for ΔP is better for the global fit. Our calculations confirm also that the APMD for P in vapour and liquid phases for the local fit is better than for the global one, but in the supercritical zone we have the inverse relation between APMDs of the considered fits.

We must emphasize that in the case of the local fit we use the more simple method and apply the fitting procedure only to α. By checking we see that this fit is also good for ΔP obtained from numerical simulations. But in the case of the supercritical case the APMD for ΔP is better for the global fit. Why? Because the local fit works well enough in the case when the number of simulated state is not so large. But in our case the supercritical zone contains much more states that the vapour or liquid ones. We

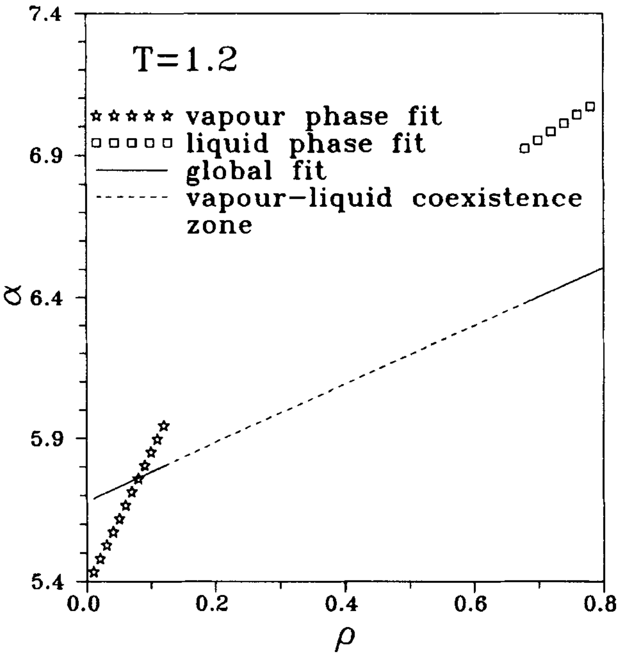

FIGURE 2 Local and global fits of $\alpha(T,\rho)$ at $T = 1.2$.

must also say that the procedure of the global fit, as we have seen, takes simultaneously into account both α and ΔP obtained from simulations and because of it seems to be better to fit a large number of states. Sumarizing we can say that the local fit is more appropriate to study quantitative behavior of the vapour-liquid equilibrium (VLE) as the determination of the VLE curve ([13–14]) whereas the global fit is more convenient to observe the qualitative behaviour of the VLE as, for example, van der Waals loops.

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