

Deviation of the radial distribution function in the Weeks-Chandler-Andersen approximation

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The influence of the attractive part of the potential in the Weeks-Chandler-Andersen perturbation theory is tested in a molecular dynamics calculation. The simulation was carried out at the triple point of a Lennard-Jones system. The differences (not negligible) in the radial distribution function permit the use of perturbation theory, because the thermodynamic properties show the usual linear behavior.

Recently Weeks and Broughton¹ performed computer simulations in two and three dimensions in order to show the accuracy of the van der Waals model in the region of liquid-solid coexistence near the triple point, and also the application of this model to the melting transition of the two-dimensional Lennard-Jones solid. In this model, the structure of a dense fluid or a solid near melting is assumed to be determined by the strong repulsive forces (so-called reference system), so that the attractive forces fix the overall volume of the system. This idea was used by Weeks, Chandler, and Andersen² (WCA) to develop a perturbation theory of liquids in which the attractive part of the potential is treated as a perturbation. This theory was later tested by Verlet and Weis.³ The λ expansion in this theory implies that the radial distribution function (RDF) is replaced by that obtained in the reference system. The intermolecular pair potential can be separated into a strong repulsive short-range part $u_0(r)$ and the weaker long-range attractive part $u(r)$.

The particles repel each other with repulsive Lennard-Jones (LJ) forces corresponding to a WCA potential

$$u_0(r) = \begin{cases} u_{LJ}(r) + \epsilon, & r \leq r_m = 2^{1/6}\sigma, \\ 0, & r > r_m \end{cases} \quad (1a)$$

and the attractive LJ forces are expressed using the λ expansion

$$u(r) = \begin{cases} -\epsilon, & r \leq r_m, \\ u_{LJ}(r), & r > r_m. \end{cases} \quad (1b)$$

The force changes from repulsive to attractive at $r_m \approx 1.12\sigma$.

This separation gives a decomposition of the Helmholtz

TABLE I. Thermodynamic properties obtained from the expressions (6a) and (6b).

λ	T	P	E_{pp}
0.00	0.695 ± 0.001	6.16 ± 0.03	0.693 ± 0.002
0.25	0.700 ± 0.002	4.88 ± 0.03	-0.874 ± 0.002
0.50	0.697 ± 0.003	3.52 ± 0.04	-2.465 ± 0.002
0.75	0.697 ± 0.003	2.12 ± 0.03	-4.063 ± 0.004
1.00	0.696 ± 0.006	0.74 ± 0.04	-5.665 ± 0.005

free energy per particle¹

$$\beta \frac{A}{N} = \beta \frac{A_0}{N} - \beta \rho \alpha(\beta, \rho) \quad (2)$$

Here A_0 is the free energy of the reference system [particles interacting by $u_0(r)$], and $\alpha(\beta, \rho)$ can be written as

$$-\alpha(\beta, \rho) = \frac{1}{2} \int d\vec{r} u(r) g_0(r) + \frac{1}{2} \int_0^1 d\lambda \int d\vec{r} u(r) [g_\lambda(r) - g_0(r)] \quad (3)$$

where $g_\lambda(r)$ is the RDF in a partially coupled system with pair interactions

$$\omega_\lambda(r) = u_0(r) + \lambda u(r) \quad (4)$$

Using Eq. (4) we can calculate directly from the energy equation, the expression⁴

$$\frac{E_\lambda}{N} = \frac{E_0}{N} + \frac{\rho}{2} \int d\vec{r} \lambda u(r) g_0(r) + \frac{\rho}{2} \int d\vec{r} \omega_\lambda(r) [g_\lambda(r) - g_0(r)] \quad (5a)$$

and from the virial equation⁴

$$P_\lambda = P_0 - \frac{\rho^2}{6} \int d\vec{r} r \lambda u'(r) g_0(r) - \frac{\rho^2}{6} \int d\vec{r} r \omega'_\lambda(r) [g_\lambda(r) - g_0(r)] \quad (5b)$$

TABLE II. Values of the integrals corresponding to the expressions (5a) and (5b), where

$$I_1 = (\rho/2) \int d\vec{r} \lambda u(r) g_0(r) \quad ,$$

$$I_2 = (\rho/2) \int d\vec{r} \omega_\lambda(r) [g_\lambda(r) - g_0(r)] \quad ,$$

$$I_3 = (\rho^2/6) \int d\vec{r} r \lambda u'(r) g_0(r) \quad ,$$

and

$$I_4 = (\rho^2/6) \int d\vec{r} r \omega'_\lambda(r) [g_\lambda(r) - g_0(r)] \quad .$$

λ	I_1	I_2	I_3	I_4
0.25	-1.5234	-0.0160	1.1823	0.1099
0.50	-3.0468	-0.0511	2.3645	0.2917
0.75	-4.5703	-0.9049	3.5474	0.5047
1.00	-6.0937	-0.1411	4.7302	0.6699

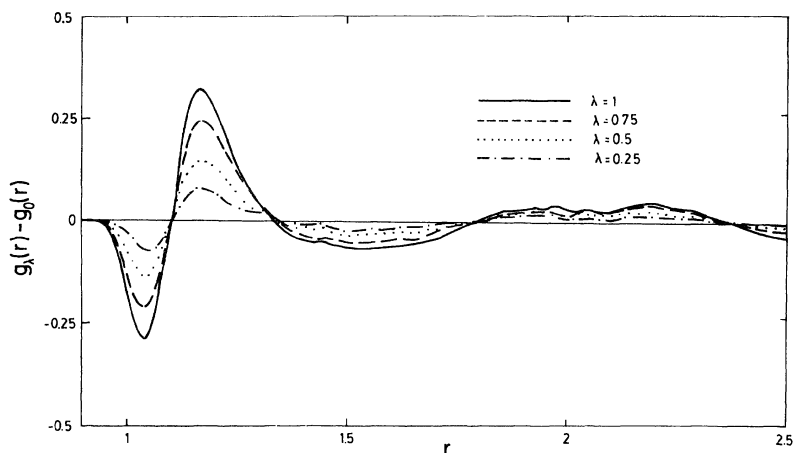


FIG. 1. Differences between the RDF's (in reduced LJ units).

In the WCA theory, the last terms in Eqs. (3) and (5) can be ignored because $g_\lambda(r) - g_0(r)$ is considered zero. This permits calculation of the thermodynamic properties only knowing the RDF of the reference system, and it is found that E_λ and P_λ are linear in λ . The goal of this Brief Report is to check this assumption in perturbation theory for dense fluids. We have followed the same technique that has recently been used in simulations of the solid-fluid interface at the triple point (or close to the triple point).⁵ These calculations were carried out for different strengths of the pair interaction by gradually bringing in the attractive forces. By using this technique, one approaches the triple point asymptotically, and at the same time, obtains information about the influence of the forces on the structure and thermodynamics of the fluid close to the triple point; therefore, one circumvents the difficulties of determining the exact triple point.

We have performed molecular dynamic simulations in three dimensions for different values of λ ($\lambda = 0, 0.25, 0.50, 0.75, 1$). Our computer experiments were carried out near the triple point⁶ ($\rho = 0.844$, $T = 0.7$, in reduced LJ units), running 10 000 time steps for $\lambda = 0.25, 0.50$, and 0.75 , and

20 000 time steps for $\lambda = 0$, and 1 . The number of particles was $N = 504$ and the range of the potential $r_c = 2.5\sigma$.

Every 1000 times steps the RDF, temperature, pressure, and potential energy per particle were obtained in order to calculate the root-mean-square (rms) deviation with respect to the time average, using the expressions

$$P = \frac{N}{V} \left\langle kT = \frac{1}{6N} \left\langle \sum_j \sum_{i \neq j} r_{ij} \frac{\partial \omega_{ij}}{\partial r_{ij}} \right\rangle \right\}. \quad (6a)$$

$$\frac{E}{N} = \frac{1}{2N} \left\langle \sum_j \sum_{i \neq j} \omega_{ij} \right\rangle. \quad (6b)$$

The thermodynamic data (pressure and energy per particle) are shown in the Table I (all are expressed in reduced LJ units).

As one can see, the behavior is linear, in agreement with perturbation theory, and one can conclude that, in Eqs. (5a) and (5b), the terms which include the differences between the RDF's can be ignored.

We have also calculated the second term of Eq. (2) with $\Delta r = 0.02$ using Eq. (3). In the Eq. (3) we have two terms

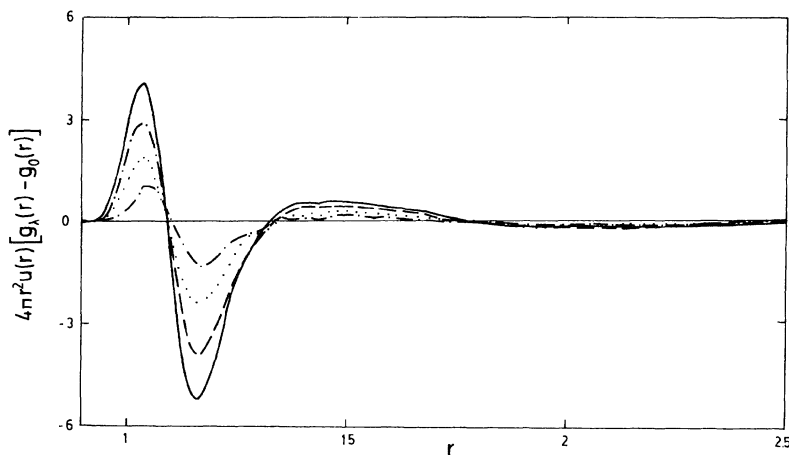


FIG. 2. Integrand of the integral of the last term in (3), $4\pi r^2 u(r)[g_\lambda(r) - g_0(r)]$, as function of r (in reduced LJ units).

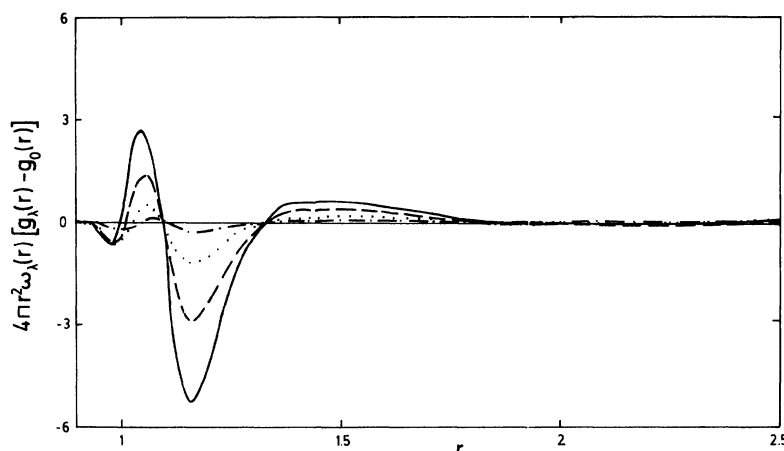


FIG. 3. Integrand of the integral of the last term in (5a), $4\pi r^2 \omega_\lambda(r) [g_\lambda(r) - g_0(r)]$, as function of r (in reduced LJ units).

for $\alpha(\beta, \rho)$. The first is calculated using the RDF of the reference system; the value obtained is 7.220. The second is obtained from the differences of the RDF's, obtaining a value of 0.033, being of the same order as the fluctuations (rms) in the thermodynamic functions.

However, from the microscopic point of view, we think there are slight differences. The RDF's for the different values of λ are different from the RDF of the reference system, and so we then calculated the influence of these differences on the integrals (3), (5a), and (5b).

In Fig. 1, one sees that these differences in all cases are much larger than the fluctuations in the time-averaged RDF. The statistical error in the RDF is estimated to be of the order of 0.01.

These differences play a role that cannot be ignored. The values of the integrals for the different values of λ of Eqs. (5a) and (5b) are given in Table II. There the integrals corresponding to the last terms of Eqs. (5a) and (5b) are larger in all cases than fluctuations of the energy and pressure, but fortunately they preserve its linearity.

We show in Figs. 2, 3, and 4 the integrands of the integrals of the last terms in (3), (5a), and (5b), respectively, as a function of r .

But the linearity of the thermodynamic functions in λ re-

quires only that in Eq. (3), the second term must cancel. One can see in Fig. 2 that in the integrands $4\pi r^2 u(r) \times [g_\lambda(r) - g_0(r)]$ the positive part is canceled by the negative part.

Furthermore, we have calculated the structure factor for all values of λ :

$$S(k) = 1 + \rho \tilde{h}(k) ,$$

where $\tilde{h}(k)$ is the Fourier transform of $h(r) = g(r) - 1$.

The results show peaks for same value of k , but with different values of $S(k)$, so as λ increases, the first peak increases linearly from $S_{\max}(k)_{\lambda=0} = 2.0586$ to $S_{\max}(k)_{\lambda=1} = 2.1630$.

Our computations lend further support to Weeks and Broughton's use of perturbation theory for the melting transition,¹ because the linearity of the thermodynamic properties is maintained without needing to assume that the RDF's are equal. As they conclude, "In 2D as well 3D the van der Waals picture should aid our understanding of the melting transition, and of the structure of the fluid and solid phases." This model has recently been used to study the order of the transition.⁷

The data of RDF's and the structure factor can be obtained from the authors.

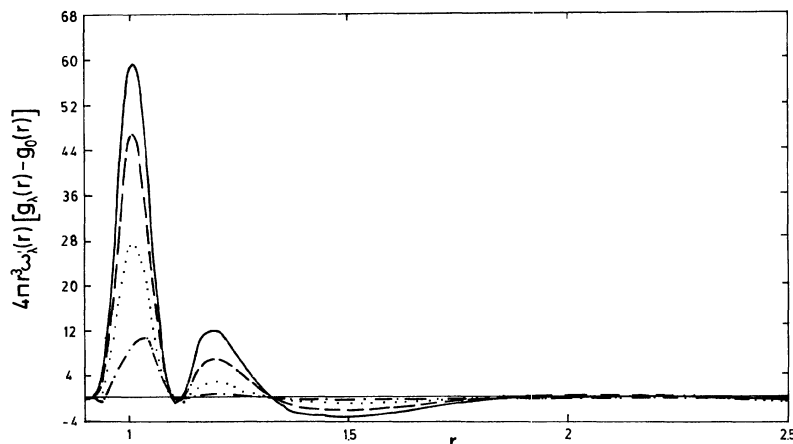


FIG. 4. Integrand of the integral of the last term in (5b), $4\pi r^3 \omega'_\lambda(r) [g_\lambda(r) - g_0(r)]$, as function of r (in reduced LJ units).

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