Optimised Cluster Theory for the Triangular Well Potential

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The optimised cluster theory of Andersen and Chandler has been applied to calculate the radial distribution functions of a triangular well fluid with the width σ the hard sphere diameter. The results agree well with Monte Carlo Calculations of Card and Walkley.

Introduction

This paper deals with the application of the optimised cluster theory (OCT) of liquids proposed by Andersen and Chandler [1] for the triangular well potential given by

$$u(r) = \infty, \quad r < \sigma,$$
$$= \frac{n \varepsilon}{n-1}\left(\frac{r}{n \sigma} - 1\right), \quad \sigma < r < n \sigma,$$
$$= 0 \qquad r > n \sigma, \tag{1}$$

where σ is the hard sphere diameter. We consider the case $n = 2$ in the present paper since Card and Walkley [2] report the Monte Carlo (MC) calculations for such a system. In earlier papers [3, 4] we have obtained analytical expressions for the Helmholtz free energy of a triangular well fluid in the Barker-Henderson perturbation theory [5]. Smith et al. [6] have calculated the pair correlation functions and other thermodynamic properties of the triangular well fluid in the Barker-Henderson perturbation theory. Since in a dense fluid, the repulsive forces dominate the structure, various perturbation theories were developed [5, 7, 8]. Recently, Andersen and Chandler proposed an approximation known as the optimised cluster theory of liquids in which a computationally convenient method for calculating the thermodynamic properties and pair correlation functions were presented. The Mayer cluster series for the Helmholtz free energy and the pair correlation functions are transformed using topological reductions suggested

by Morita and Hiroike [8] to more compact forms involving a renormalised potential. In such an application the potential is divided into

$$u(r) = u_H(r) + u_1(r), \tag{2}$$

where $u_H(r)$ is the repulsive part of the potential given by

$$u_H(r) = \infty, \quad r < \sigma,$$
$$= 0, \quad r > \sigma \quad \text{and} \tag{3}$$

$u_1(r)$ is the attractive perturbation given by

$$u_1(r) = \frac{n \varepsilon}{(n-1)}\left(\frac{r}{n \sigma} - 1\right), \quad \sigma < r < n \sigma$$
$$= 0, \quad r > n \sigma. \tag{4}$$

Defining

$$\Phi(r) = -u_1(r)/kT \tag{5}$$

and its former transform

$$\Phi(k) = \int d\mathbf{r} \exp[-i \mathbf{k} \cdot \mathbf{r}] \Phi(\mathbf{r}), \tag{6}$$

the renormalised potential $C(r)$ is given by

$$p^2 C(r) = \frac{1}{(2\pi)^3} \int dk \exp[i \mathbf{k} \cdot \mathbf{r}] \frac{\hat{F}_0^2(k) \hat{\Phi}(k)}{[1 - \hat{F}_0(k) \hat{\Phi}(k)]}, \tag{7}$$

where the hypervertex $F_0(\mathbf{r}_1, \mathbf{r}_2)$ is defined by

$$F_0(\mathbf{r}_1, \mathbf{r}_2) = \varrho \delta(\mathbf{r}_1, \mathbf{r}_2) + \varrho^2 h_0(\mathbf{r}_1, \mathbf{r}_2), \tag{8}$$

where $\delta(\mathbf{r}_1, \mathbf{r}_2)$ is the Dirac delta function and $h_0(\mathbf{r}_1, \mathbf{r}_2) = g_0(\mathbf{r}_1, \mathbf{r}_2) - 1$ is the total correlation function for the reference system. Andersen et al. proposed the Exponential approximation (EXP)

$$g(r) = g_0(r) \exp[C(r)] \tag{9}$$

and the linearised exponential approximation (LEXP)

$$g(r) = g_0(r)[1 + C(r)], \qquad (10)$$

where $g(r)$ is the radial distribution function for the potential (2).

Results

Since the properties of the fluid of molecules interacting through the potential (2) must be independent of the value of the perturbation $u_1(r)$ for the physically impossible inter particle separations $r < \sigma$, it is equally clear that the EXP and LEXP for the free energy and the pair distribution functions depend on the value of the perturbation inside the hard core, since the renormalised potential is a functional of $\Phi(r)$. This unphysical behaviour was eliminated by choosing $u_1(r)$ in such a way that

$$C(r) = 0, \quad r < \sigma. \qquad (11)$$

This implies that

$$\frac{\delta V a_{\text{ring}}}{\delta \Phi(r)} = 1/2 \varrho^2 C(r) = 0, \quad r < \sigma, \qquad (12)$$

where a_{ring} is the ring contribution to the free energy and is given by

$$a_{\text{ring}} = \qquad (13)$$
$$-\frac{1}{2(2\pi)^3} \int d\boldsymbol{k} [\hat{F}_0(k)\hat{\Phi}(k) + \ln\{1 - \hat{F}_0(k)\hat{\Phi}(k)\}].$$
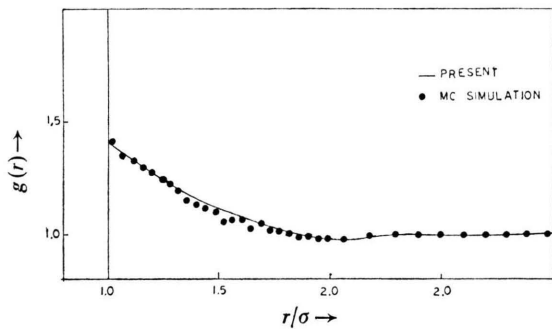

Fig. 1. The radial distribution function for the triangular well fluid for $n = 2$. The curve is calculated with the OCT using the LEXP approximation, and the points are the results of the MC simulation. $T^* = 5.0$ and $V/V_0 = 8.0$ ($V_0 = N\sigma^3/\sqrt{2}$ is the close packed volume).
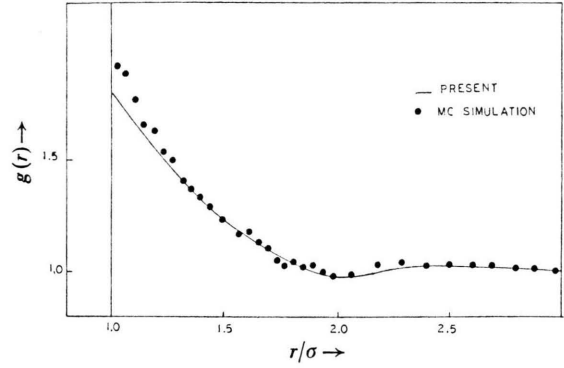

Fig. 2. Same as Fig. 1, but for $T^* = 1.5$ and $V/V_0 = 8.0$.
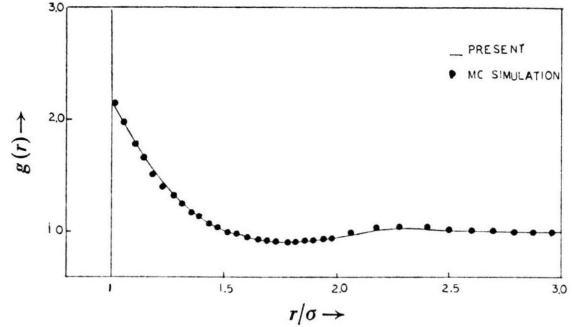

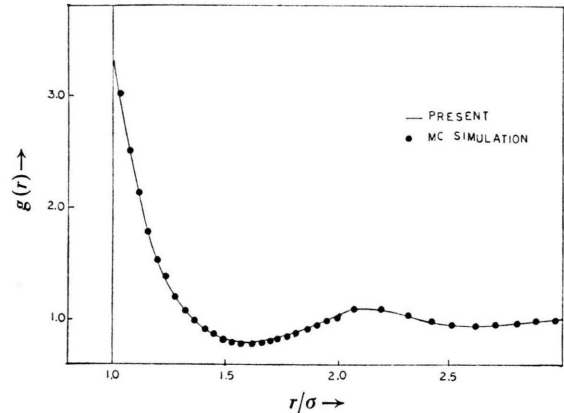Fig. 3. Same as Fig. 1, but for $T^* = 1.5$ and $V/V_0 = 3.0$.

Fig. 4. Same as Fig. 1, but for $T^* = 1.5$ and $V/V_0 = 2.0$.

In order to solve the variational problem given by (12), we assumed a trial solution of the form

$$\Phi(r) = \sum_{n=0}^{3} a_n (1 - r/\sigma)^n, \quad r < \sigma,$$
$$= \Phi(r), \quad r > \sigma, \qquad (14)$$

and minimised $V a_{\text{ring}}$ with respect to the coefficients a_0, a_1, a_2 and a_3 by a Newton-Raphson

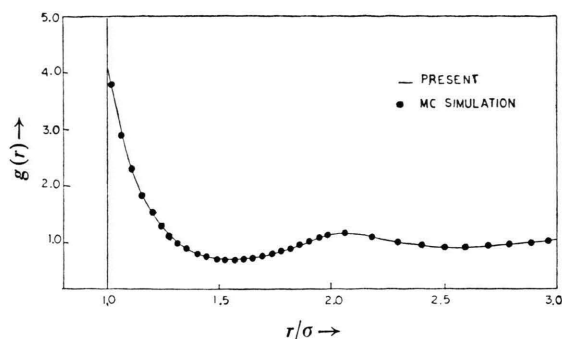Fig. 5. Same as Fig. 1, but for $T^* = 1.5$ and $V/V_0 = 1.75$.

Fig. 6. Same as Fig. 1, but for $T^* = 0.8$ and $V/V_0 = 1.75$.

method. The hard sphere radial distribution functions were calculated using the Verlet-Weis [9] method. The renormalised potential was calculated using (7), and the radial distribution functions were calculated in both the EXP and LEXP approximations. The temperatures and densities were chosen to agree with the available MC data for the radial distribution functions. In Figs. 1−6 the radial distribution functions calculated from LEXP are compared with the (MC-)simulations of Card and Walkley.
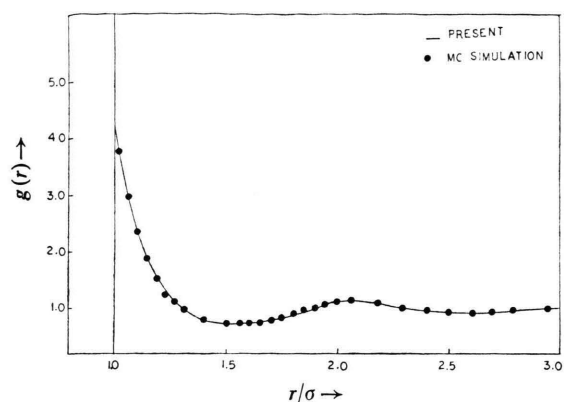
Discussion

From Figs. 1−6 it is evident that the present calculations based on the LEXP approximation are in good agreement with the MC simulation data except for $T^* = 1.5$ and $V/V_0 = 8.0$. The results based on the EXP approximation are not distinguishable from the LEXP approximation on the graph and hence were not included. This suggests that the Optimised Cluster theory generates the structure and thermodynamic properties of the triangular well fluid accurately.

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