USE OF THE YUKAWA FLUID AS THE REFERENCE SYSTEM IN PERTURBATION THEORY

P.J. CUMMINGS, J.R. SMITH, and C.C. WRIGHT
Department of Mathematics, University of Melbourne, Parkville, Victoria 3052, Australia

Received 10 May 1979; in final form 18 June 1979

The Weeks-Chandler-Anderson (WCA) perturbation theory is studied utilizing recent results for the Yukawa model fluid. Replacing the attractive tail of the Lennard-Jones potential with a Yukawa tail, where the Yukawa parameters are chosen using a least squares fit, it is shown that accurate radial distribution functions can be generated via the F-XP approximation of the WCA optimized cluster theory. The comparative ease and accuracy with which the correlation functions for the Yukawa fluid can be computed render this a very useful method for studying the equilibrium properties of simple liquids.

1. Introduction

There has been much recent study [1-4] of the properties of the Yukawa fluid, a model fluid which is described by the Ornstein-Zernike relation between the total correlation function $h(r)$ and the direct correlation function $c(r)$.

$$h(r) = c(r) + \rho \int d\sigma \left| s \right| h(|r - s|).$$

(1)

where $\rho$ is the number density; the hard core condition

$$h(r) = -1, \quad r < d.$$  

(2)

where $d$ is the diameter of the impenetrable core; and the Yukawa closure for $c(r)$,

$$c(r) = K_0 \exp \left[ -\gamma (r - d) \right] r, \quad r > d.$$  

(3)

Considerable study has been made [3,4] of the case in which eqs. (1) to (3) are regarded as the mean spherical approximation (MSA) [5] conditions for a fluid of hard spheres with attractive Yukawa interaction. That is, the direct correlation function is approximated as $c(r) = -\beta \delta(r)$ for $r > d$, where

$$c(r) = -\gamma \delta(r - d)$$

is an attractive Yukawa pair interaction potential. The results of this study which are particularly relevant to the discussion in this letter are:

(i) the existence of a liquid-gas phase-transition within the MSA for temperatures below a critical value $T_c$;

(ii) the availability of analytic expressions for energy and virial pressures; and

(iii) the ease of computation of radial distribution functions for the model fluid.

The Yukawa fluid has been used in a number of model settings, including adsorption studies [6], a model for phase separation [3,7] and a model for configurationally disordered spin systems [8]. In this paper we show how the Yukawa fluid may be used within the context of the successful perturbation theory of Weeks, Chandler and Anderson (WCA) [9] to generate the equilibrium properties of simple fluids. In this paper we will confine our discussion to describing a system of particles interacting via the Lennard-Jones potential, given by

$$u(r) = 4\varepsilon [(a/r)^{12} - (a/r)^6].$$  

(4)

The WCA perturbation theory begins with the separation of the potential $u(r)$ into two parts, $u_0(r)$ and $u_1(r)$, given by
\[ u_0(r) = u(r) + c, \quad r < 2^{1/6}a, \]  
\[ = 0, \quad r > 2^{1/6}a; \]  
\[ u_1(r) = e, \quad r < 2^{1/6}a, \]  
\[ = u(r), \quad r > 2^{1/6}a. \]  

The reference potential \( u_0(r) \) contains all the rapidly varying repulsive forces whilst the perturbation \( u_1(r) \) contains the smoother attractive tail. This is a fortuitous choice of reference potential since at high densities the liquid structure is dominated by excluded volume effects. The reference potential \( u_0(r) \) may be replaced by an effective hard sphere potential \( u_d(r) \) with density and temperature dependent hard sphere diameter \( d \) given by

\[ \int B(r) d^3r = 0. \]  
where

\[ B(r) = \nu_d(r) \{ \exp[-\beta u_0(r)] - \exp[-\beta u_d(r)] \}. \]  
and \( \beta = 1/kT; k \) being the Boltzmann constant and \( T \) the absolute temperature. The subscript \( d \) refers to hard sphere quantities where the hard sphere diameter is \( d \). The Helmholtz free energy \( A_0 \) of the reference system is then given by

\[ A_0 \approx A_d \]  
and the reference system radial distribution function is given by

\[ g_0(r) \approx g_d(r) \exp[-\beta u_0(r)]. \]  
The free energy of the full system is then given by

\[ A \approx A_d + \int u_1(r) g_0(r) dr. \]  

Eq. (12) shows that the ideas of van der Waals concerning the dominance of excluded volume effects can be rigorously derived in the context of perturbation theory [9].

In the high density regime eqs. (10), (11) and (12) prove to be quite accurate due to the dominance of repulsive forces, and comparison of \( g_0(r) \) given by eq. (11) with computer simulation radial distribution functions (rdf's) for the Lennard-Jones fluid shows excellent agreement. However, for lower densities in the liquid regime near the coexistence curve for which attractions become important eq. (11) does not adequately describe the particle–particle correlations.

Anderson and Chandler [10], using graph theoretical techniques \(^\dagger\), were able to effect a topological reduction of the Mayer cluster series for the Helmholtz free energy and the pair correlation functions in terms of a renormalized potential \( \Theta_L(r) \). This formalism allows the effect of attraction to be more adequately accounted for than in the perturbation scheme outlined above. In terms of the renormalized potential, eq. (11) now becomes

\[ g(r) = \nu_d(r) \exp\{-\beta [u_0(r) + u_1(r)] \} \times \exp[\Theta_L(r) - \Phi(r)]. \]  
where

\[ \Phi(r) = -\exp\{-\beta u_d(r)\} \nu_1(r) \]  
and the hard sphere diameter is now chosen according to the condition

\[ \int \nu_d(r) \{ \exp[-\beta u_0(r)] - \exp[-\beta u_d(r)] \} \times \exp[\Theta_L(r) - \Phi(r)] dr = 0. \]  

When the Percus–Yevick approximation is used to generate the hard sphere quantities for input to eqs. (13), (14) and (15), the renormalised potential \( \Theta_L(r) \) is given by its Percus–Yevick (PY) approximation [10]

\[ \Theta_L^{(PY)}(r) = h_d^{(MSA)}(r) - h_d^{(PY)}(r), \]  
where the quantity \( h_d^{(MSA)}(r) \) is the total correlation function obtained from the solution of the MSA for the following potential:

\[ \phi(r) = \infty, \quad r < d, \]  
\[ = u_1(r), \quad r > d. \]  

For the Lennard-Jones potential, the solution of the MSA for \( \phi(r) \) given by eq. (17) is not available. Therefore we propose that the potential in eq. (17) be

\(^\dagger\) An excellent review of graph theoretical techniques and their relation to perturbation theories is given in ref. [11].
approximated by a Yukawa potential, as first suggested by Hyne and Stell [12]. For potentials with slowly varying attraction, eq. (15) may be replaced by its simpler version, eq. (7), with no appreciable change in hard sphere diameter $d$ [9]. Hence the outline of our method for calculating Lennard-Jones rdf's is as follows:

(i) Calculate the hard sphere diameter $d$ using eq. (7) and the Percus-Yevick approximation for hard sphere quantities.

(ii) Calculate the Yukawa parameters by least squares, minimising the squared error

$$Z = \sum_{i=1}^{N} [\phi_y(r_i) - \phi(r_i)]^2.$$  

where $\phi_y(r)$ is the Yukawa approximate form for $\phi(r)$ given by eq. (17). In all calculations reported here, the value of $N$ (the number of points in the fitting procedure) was 60 and the fit was over four hard sphere diameters ($d < r_i < 5d$).

(iii) Using eqs. (16), (14) and (13), and the methods for solution of the MSA for the Yukawa fluid [3,4], approximate radial distribution functions may be obtained.

We note that since $d$ is temperature and density dependent, $K$ and $z$ [eq. (3)] will also be temperature and density dependent.

2. Results and discussion

The procedure given in outline above was used to calculate Lennard-Jones rdf's over a range of densities and temperature representative of states in both the liquid and gaseous regimes. In figs. 1 to 6 they are compared to the molecular dynamics rdf results of Verlet [13] for the Lennard-Jones potential given by eq. (4). The units used are the reduced units, $T^* = kT/e$ and $\rho^* = \rho\sigma^3$. At high densities the height is overestimated and tends to be a little narrower than the machine results, although the position of the first peak is in the correct place. This latter feature is desirable from the point of view of calculating any thermodynamic properties using the approximate rdf.

In figs. 4 and 5, the states are relevant to the Lennard-Jones fluid in the moderate density liquid regime close to its critical point. Again we see the

---

Fig. 1. Comparison of the Lennard-Jones radial distribution functions, calculated using the Yukawa fluid in eq. (13) ——— The circles are the computer simulation results of Verlet [13]. The interparticle separation $R$ is in units of $d$. The Yukawa parameters are $d = 1.019 a$, $K = 1.332 d$, $zd = 1.849$, $\eta = \pi\rho d^3/6 = 0.36$. The Lennard-Jones parameters are given on the graph.

Fig. 2. As for fig. 1, with Yukawa parameters $d = 1.012 a$, $K = 1.17 d$, $zd = 1.803$, $\eta = 0.407$. 

280
The correct position of the first peak. At these states the peak heights are much closer to the machine values and in fact the quantitative accuracy is comparable to that obtained using the optimized cluster theory (OCT) [10]. In the OCT, the MSA for a fluid with potential given by eq. (17) is solved numerically, and involves significantly more complicated numerical techniques than the simple scheme we have used in this work. At high temperature in the gaseous state (fig. 6) accurate results are again obtained.

An interesting feature of the perturbation scheme used in this work is that the resulting state of the reference Yukawa fluid, as characterized by the values of $K$, $z$, and $\eta$, is in approximately the same state in relation to the coexistence curve [4] as the Lennard-Jones fluid. This suggests that more detailed analysis will locate the coexistence curve of the reference state in approximately the same place as the Lennard-Jones fluid.
The results obtained for the rdf's suggest that the method will be very useful, both in theoretical and practical terms, for the calculation of the equilibrium properties of simple fluids. Work is currently in progress for determining the thermodynamic properties of the Lennard-Jones fluid using this perturbation scheme. Also a means of choosing a single density- and temperature-independent value of \( \gamma \) is under consideration, based on the observation that \( \gamma \) remains fairly constant around 1.75 \( \sigma \), and for constant \( \rho, K \) varies approximately as \( 1/T^* \).

References