Radial Distribution Function of Liquid Sodium

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The radial distribution function of liquid sodium has been studied by considering the integral equation Perturbation Theory of Madden and Fitts for the reference part and the optimised cluster theory for the attractive part of the pair potential. Calculations were carried out for the long range oscillatory potential of Schiff. The calculated results are compared with the molecular dynamics calculations HTA, OCT and with experiment. The agreement was found to be satisfactory.

1. Introduction

In recent years, there has been considerable interest in the structure and thermodynamic properties of liquid metals. Many structure factor measurements of simple and non-simple liquid metals [1—6] have been reported. Ashcroft and Lekner (AL) [7] used the Percus-Yevick [8] theory for hard spheres to calculate structure factors for several metals using the packing fraction $\eta = \pi \varrho \sigma^3/6$ as an adjustable parameter, where ϱ is the number density and σ is the hard sphere diameter, and found that the structure factors for various liquid metals upto and including the major diffraction peak are similar to those of a hard sphere fluid with $\eta = 0.45$. Beyond the major peak the agreement with experiment is poor. Umar and Young [9] calculated the hard sphere structure factors using the Gibbs-Bogoliubov inequality. Ailawadi et al. [10—11] used a modified version of the scheme of Singwi et al. [12] for calculating the structure factors of liquid sodium and rubidium. Leribaux and Miller [13] used the PY equation for calculating the structure factors of liquid alkali metals. Badiali et al. [14] and Regnaut et al. [15] have calculated the structure factors by using the repulsive soft potential of Jacobs and Andersen [16] in the optimised random phase approximation of Weeks et al. [17]. In these calculations the soft sphere part of the structure was calculated using the blip function theory of Chandler et al. [18] (WCA).

The blip function theory is a zeroth order perturbation theory and is good for potentials whose repulsive core is hard so that the factors $f(r) - f_{\mathrm{d}}(r)$ behave like a delta function. Here

$$f(r) = \exp(-\beta u(r)) - 1$$

and $f_{\mathrm{d}}(r)$ are those appropriate for a hard sphere system with a diameter "d". Since we are considering metals whose repulsive core is soft the blip function theory is not applicable without taking the theory to higher order terms. Unfortunately higher order terms involve integrals involving higher order distribution functions about which little is known. In order to overcome this difficulty, Lado [19, 20] and Madden and Fitts [21, 22] (MF) formulated perturbation theories in which integral equation approximations are used to obtain the perturbation corrections, and Johnson [23] proposed a new method for choosing a reference pair potential for atomic fluids. He used this method with OCT to calculate pair distribution functions for a number of classical fluids. In this communication we use the MF integral equation perturbation theory supplemented with the Percus-Yevick equation for calculating the radial distribution function for the reference part of the pair potential and the optimised cluster theory of Chandler et al. [24] for the complete potential. The calculations were carried out for the long range oscillatory potential of Schiff [25] for liquid sodium which is given by

$$V_1(r) = \cos(2 K_{\mathrm{f}} r)(A + B/r^2 + C/r^4)/r^3 + \sin(2 K_{\mathrm{f}} r)(E + F/r^2)/r^4 . \quad (1)$$

The parameters in this potential for liquid sodium were taken from Schiff.

The molecular dynamics (MD) simulations were carried out for the above potential by Paskin et al. [26]. Neutron diffraction experiments on liquid sodium at 373° were carried out by Gingrich et al. [27]. Optimised cluster theory calculations and an HTA

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calculation for the above potential at the same density and temperature were carried out by Rami Reddy et al. [28].

In Sect. II the integral equation perturbation theory is discussed. In Sect. III the OCT is discussed. Applications of the methods presented in Sect. II and III and a discusson of the results are given in Sect. IV.

2. Integral Equation Perturbation Theory

In the application of the statistical mechanical perturbation theory, one writes for the potential:

$$u(r) = u_0(r) + \lambda u_1(r), \tag{2}$$

where λ is the perturbative parameter. For $\lambda = 1$, (2) gives the potential of the system of interest ($u(r)$) and for $\lambda = 0$, (2) gives the potential for the reference system ($u_0(r)$). An important aspect in the application of the perturbation theory is that a judicious choice has to be made in spliting the potential into a perturbation part and a reference part. In this work we followed the division of the potential due to WCA.

$$\begin{aligned} u_0(r) &= u(r) + \varepsilon, & r &< r_{\min}, \\ &= 0, & r &\geqq r_{\min}, \\ u_1(r) &= -\varepsilon, & r &< r_{\min}, \\ &= u(r), & r &\geqq r_{\min}, \end{aligned} \tag{3}$$

where ε is the depth of the potential well. The WCA separation (3) leads to a perturbation series for the Helmholtz free energy which converges much faster than an earlier separation proposed by Barker and Henderson [29].

A perturbation series for the radial distribution function may be obtained by expanding $g(r)$ in a powers of λ about the known reference system.

$$\begin{aligned} g(r;\lambda) &= g_0(r) + \sum_n \frac{\Delta^n}{n!}\left(\frac{\partial^n g(r;\lambda)}{\partial \lambda^n}\right)_\lambda = 0 \\ &= g_0(r) + \sum_n \lambda^n \Delta^n g(r), \end{aligned} \tag{4}$$

where $g_0(r)$ is the RDF for the reference system with pair potential $u_0(r)$, and $\Delta^n g(r)$ is the nth order perturbation correction. If we approximate the perturbation correction through integral equations, then

$$g(r;\lambda) = g_0(r) + \sum_n \lambda^n \Delta^n g^{\mathrm{IE}}(r), \tag{5}$$

where the superscript IE emphasizes that an integral equation is used to obtain the desired quantity and $\Delta^n g^{\mathrm{IE}}(r)$ represents the n-th order perturbation correction obtained through the use of integral equations.

Defining

$$y(r) = g(r)\exp[\beta u(r)], \tag{6}$$

where $\beta = 1/K_{\mathrm{B}}T$, and approximating the perturbations through integral equations we obtain

$$y_0(r) = y_{\mathrm{HS}}(r;d) + \sum_n \alpha^n \Delta^n y^{\mathrm{IE}}(r). \tag{7}$$

The function $y(r)$ is used because it is continuous everywhere. Here $y_0(r)$ is $y(r)$ for a potential $u_0(r)$ and $y_{\mathrm{HS}}(r;d)$ is the hard sphere value of $y(r)$. Madden and Fitts approximated (7) by writing

$$y_0(r) = y_{\mathrm{HS}}(r;d) + y_0{}^{\mathrm{IE}}(r) - y_{\mathrm{HS}}^{\mathrm{IE}}(r;d). \tag{8}$$

In the blip function theory of Weeks et al., $y_0(r)$ was approximated by

$$y_0(r) = \exp[\beta u_0(r)] g_0(r) \approx y_{\mathrm{HS}}(r;d). \tag{9}$$

3. Optimised Cluster Theory (OCT)

In the optimised cluster theory the Mayer cluster series for the Helmholtz free energy and the pair correlation functions are transformed using topological reductions to a compact form involving a renormalized potential. Since the method has been discussed in detail in the earlier references, we give a brief outline of the theory. In this application the potential is divided into

$$u(r) = u_0(r) + u_1(r), \tag{10}$$

where $u_0(r)$ is the hard sphere part given by

$$\begin{aligned} u_0(r) &= \infty, & r &< d, \\ &= 0, & r &> d, \end{aligned} \tag{11}$$

and $u_1(r)$ is the attractive perturbation. Defining

$$\Phi(r) = -\beta u_1(r) \tag{12}$$

and its fourier transform

$$\Phi(k) = \int \mathrm{d}\boldsymbol{r} \exp(-i\boldsymbol{k}\cdot\boldsymbol{r})\Phi(\boldsymbol{r}), \tag{13}$$

the renormalized potential is given by

$$\varrho^2 C_{\mathrm{L}}(r) = \frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k} \cdot \exp(i\boldsymbol{k}\cdot\boldsymbol{r})\frac{\hat{F}_0{}^2(k)\hat{\Phi}(k)}{[1-\hat{F}_0(k)\hat{\Phi}(k)]}, \tag{14}$$

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

$$F_0(\boldsymbol{r}_1, \boldsymbol{r}_2) = \varrho\, \partial(\boldsymbol{r}_1, \boldsymbol{r}_2) + \varrho^2 h_0(\boldsymbol{r}_1, \boldsymbol{r}_2), \quad (15)$$

where $\partial(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the Dirac-delta function and $h_0(r) = g_0(r) - 1$ is the total correlation function.

The properties of the fluid of molecules interacting through the potential (10) must be independent of the perturbation $u_1(r)$ for the physically impossible interparticle separations $r < d$. This unphysical behaviour was eliminated by choosing $u_1(r)$ in such a way that

$$C_L(r) = 0, \quad r < d. \quad (16)$$

This implies that

$$\frac{\partial V a_{\text{ring}}}{\partial \Phi(r)} = \tfrac{1}{2}\varrho^2 C_L(r) = 0, \quad r < d. \quad (17)$$

Here a_{ring} is the ring contribution to the Helmholtz free energy and is given in the OCT by

$$a_{\text{ring}} = -\frac{1}{2(2\pi)^3} \cdot \int \mathrm{d}\boldsymbol{k}[\tilde{F}_0(k)\tilde{\Phi}(k) + \ln[1 - \tilde{F}_0(k)\tilde{\Phi}(k)]]. \quad (18)$$

The variational problem defined by (17) was solved by the method of Reddy and Swamy [30]. The hard sphere RDF was calculated using the Verlet-Weiss [31] method. The renormalized potential was calculated using (14). The RDF is obtained by using

$$g(r) = \exp[-\beta[u_0(r) + u_1(r)]]\, y_d(r) \cdot \exp[C_L(r) - \Phi(r)], \quad (19)$$

where

$$y_d(r) = g_d(r)\exp[\beta u_d(r)], \quad (20)$$

$y_d(r)$ being the radial distribution function for a system of hard spheres of diameter d.

Results and Discussion

The potential $V_1(r)$ of Schiff is shown in Figure 1. In Fig. 2 the radial distribution function for liquid soidum at $T^*(K_B T/\varepsilon) = 0.97$, and $\varrho\sigma^3 = 0.83$, obtained from the present work is compared with the molecular dynamics simulations (MD), the high temperature approximation (HTA) and with experiment. The OCT results in which the reference part RDF was obtained from the zeroth order blip function theory and denoted by OCT is also shown. Figure 2 shows that the integral equation perturbation theory with OCT generates the structure of long range oscillatory potentials satisfactorily.

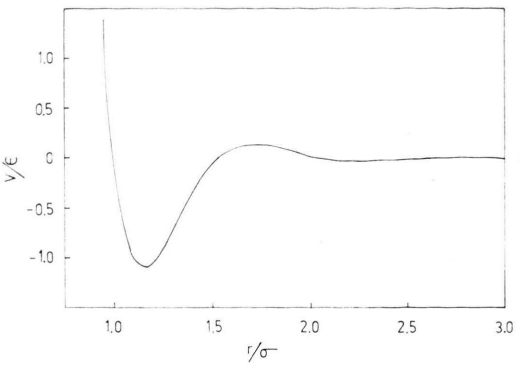

Fig. 1. $V_1(r)$.

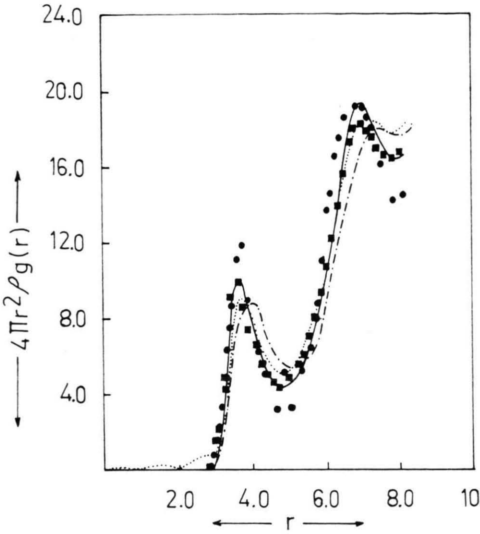

Fig. 2. $4\pi r^2 \varrho g(r)$ for liquid sodium for $V_1(r)$ at $T^* = 0.97$, $\varrho\sigma^3 = 0.83$. -·-·-·- present theory, ——— OCT, ●●●● MD, ■■■■ HTA, ... Neutran difraction experiment.

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