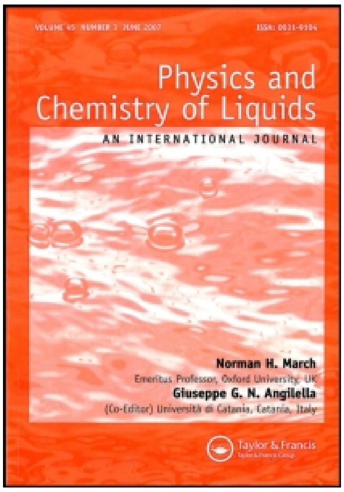

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On the Structure of Liquid Aluminium

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On the Structure of Liquid Aluminium

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The structure of liquid aluminium has been studied by considering the integral equation perturbation theory of Madden and Fitts for the reference part of the pair potential and the optimised cluster theory for the attractive part. Calculations were carried out for various long-range oscillatory potentials for the liquid. The results for the radial distribution functions are compared with the molecular dynamics calculations and with experiment. The agreement is found to be good.

1 INTRODUCTION

Over the past two decades there has been a great deal of interest in calculating the structure and thermodynamic properties of liquid metals. For example Ashcroft and Lekner (AL)[1] used the analytical solution of the Percus–Yevick[2] equation for hard spheres given by Thiele[3] and Wertheim[4] and calculated the structure factor of liquid metals using the packing fraction η, as an adjustable parameter. More recently Umar and Young[5] have calculated the structure factors using the variational theory and Ailawadi *et al.*[6,7] have used a modified version of the Singwi–Tosi–Land–Sjolander[8] (STLS) theory. Badiali *et al.*[9] and Regnaut *et al.*[10] have calculated the structure factor in the optimised random phase approximation of Weeks *et al.*[11] using the repulsive soft potential of Jacobs and Andersen.[12] In all these calculations the soft sphere part of the structure was calculated using the blip function theory of Chandler *et al.*[13] The blip function theory is a zeroth order perturbation theory where one calculates the structure factors for soft spheres using the hard sphere structure factors. To carry out the perturbation theory to higher order one encounters higher order correlation functions, information about which is too meagre. In order to overcome this difficulty Lado[14,15] and Madden and Fitts[16,17] (MF) have formulated perturbation theories in which integral equation approximations are used to obtain the perturbation corrections. In the present paper we have used the MF integral equation perturbation theory approach supplemented by the Percus–Yevick equation for calculating the structure for the reference part of the pair-potential. For calculating the structure for the full potential we have used the optimised cluster theory of Chandler *et al.*[18] Calculations were carried out for Lennard–Jones potential and for liquid aluminium for the following potentials

i) Schiff potential given by

$$V_5(r) = \cos(2K_f r)\left(\frac{A}{r^3} + \frac{B}{r^5} + \frac{C}{r^7}\right) + \sin(2K_f r)\left(\frac{D}{r^4} + \frac{F}{r^6}\right) + \frac{G}{r^{12}}$$

ii) Ashcroft pseudo potential with Geldart–Vosko Screening[19] (AGV) at 975°K.

iii) AGV potential at 1300°K. Molecular dynamics (MD) simulations are available for Schiff potential, $V_5(r)$ from the work of Schiff[20] and for AGV 988°K and AGV 1330°K from the work of Ebbsjo *et al.*[21] In the case of Lennard–Jones potential MD simulations were carried out by Verlet.[22]

Neutron diffraction experiment for liquid aluminium at 976°K was carried out by Stallard *et al.*[23]

2 INTEGRAL EQUATION PERTURBATION THEORY

In a dense fluid the repulsive forces dominate the structure and the effect of the attractive forces are of the mean field type. In applying the perturbation theory the pair potential $u(r)$ is written as

$$u(r) = u_0(r) + \lambda u_1(r) \tag{1}$$

where $u_0(r)$ is the reference part of the potential and $u_1(r)$ is the attractive perturbation; λ is a perturbation parameter. An important aspect in the application of perturbation theory is that a judicious choice has to be made in splitting the potential into a perturbation part and a reference part. In this work following Weeks–Chandler and Andersen (WCA),[11] we take

$$\begin{aligned} u_o(r) &= u(r) + \varepsilon, & r &< r_{\min} \\ &= 0, & r &\geq r_{\min} \end{aligned}$$

and (2)

$$\begin{aligned} u_1(r) &= -\varepsilon, & r &< r_{\min} \\ &= u(r) & r &\geq r_{\min} \end{aligned}$$

Here ε is the depth of the potential well (i.e. the value of $u(r)$ at $r = r_{\min}$). The WCA separation leads to a perturbation series for the Helmholtz free energy which converges more quickly than an earlier separation proposed by Barker and Henderson.[24] A perturbation series for the radial distribution function (RDF), g(r) may be obtained by expanding $g(r)$ in a power series in λ about the known reference system

$$\begin{aligned} g(r;\lambda) &= g_0(r) + \sum_n \frac{\lambda^n}{n!}\left(\frac{\partial^n g(r;\lambda)}{\partial\lambda^n}\right)_{\lambda=0} \\ &= g_0(r) + \sum_n \lambda^n \Delta^n g(r) \end{aligned} \tag{3}$$

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 corrections. If we approximate the perturbation corrections through integral equations then

$$g(r;\lambda) \simeq g_0(r) + \sum \lambda^n \Delta^n g^{\mathrm{IE}}(r) \tag{4}$$

where $\Delta^n g^{\mathrm{IE}}(r)$ represents the nth order perturbation corrections obtained through the use of integral equations. Defining

$$y(r) = g(r)\exp[\beta u(r)] \tag{5}$$

($\beta = 1/k_B T$, where k_B is the Boltzmann constant and T the absolute temperature) and approximating the perturbations through integral equations we can obtain

$$y_0(r) = y_{\mathrm{HS}}(r;d) + \sum_n \alpha^n \Delta^n y^{\mathrm{IE}}(r). \tag{6}$$

Here $y_0(r)$ is $y(r)$ for a potential $u_0(r)$ and $y_{\mathrm{HS}}(r;d)$ is the hard sphere values of $y(r)$ and $\Delta^n y^{\mathrm{IE}}(r)$ is the nth order perturbation corrections. Madden and Fitts approximated Eq. (6) by writing

$$y_0(r) \simeq y_{\mathrm{HS}}(r;d) + y_0^{\mathrm{IE}}(r) - Y_{\mathrm{HS}}^{\mathrm{IE}}(r;d). \tag{7}$$

In the blip function theory Weeks *et al.* used the approximations

$$y_0(r) = \exp[\beta u_0(r)]g_0(r) \simeq y_{HS}(r;\, d). \tag{6}$$

2.1 OPTIMISED CLUSTER THEORY (OCT)

In the optimized 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 renormalised potential. The OCT has been discussed extensively in the earlier references; we therefore confine ourselves to giving only a brief outline of the theory. Defining

$$\phi(r) = -\beta u_1(r) \tag{9}$$

and its Fourier transform by

$$\phi(k) = \int \phi(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})d\mathbf{r} \tag{10}$$

the normalised potential is given by

$$C_L(r) = \frac{1}{(2\pi)^3}\int d\mathbf{k} \exp(i\mathbf{k}\cdot\mathbf{r})\frac{F_0^2(k)\phi(k)}{[1 - F_0(k)\phi(k)]} \tag{11}$$

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

$$F_0(\mathbf{r}_1, \mathbf{r}_2) = \rho\delta(\mathbf{r}_1, \mathbf{r}_2) + \rho^2 h_0(\mathbf{r}_1, \mathbf{r}_2) \tag{12}$$

where $\delta(\mathbf{r}_1, \mathbf{r}_2)$ is the Dirac-delta function. The RDF is obtained by using

$$g(r) = \exp[-\beta(u_0(r) + u(r))]y_d(r)\exp[C_L(r) - \phi(r)] \tag{13}$$

3 NUMERICAL CALCULATION

In calculating the reference part RDF we have used Eq. (7) together with the Percus–Yevick equation. For $y_{HS}(r;\, d)$ we have used the Verlet–Weis[25] formulations and for $y_{HS}^{IE}(r;\, d)$ we have used the PY solution of Wertheim and Thiele. For $y_0^{IE}(r)$ we have solved the PY equation for the potential $u_0(r)$. The hard sphere diameters were determined and calculated using the WCA[11] criterion. In applying the OCT method the optimization was carried out following the procedure developed by Reddy and Swamy.[26]

RESULTS AND DISCUSSION

Figures 1, 2, 3 are the plots of the calculated radial distribution functions for $V_5(r)$, AGV–975°K and AGV–1300°K for liquid aluminium and Figures 4, 5 are the plots of the calculated radial distribution functions for Lennard-Jones potential at $T^*(=k_BT/\varepsilon) = 0.88$, $\rho(=\rho\sigma^3) = 0.85$ and $T^* = 1.36$, $\rho = 0.5$ respectively. In the figures the MD, HTA (High temperature approximation) and the Neutron diffraction experimental results are also shown for the purposes of comparison. As can be seen from the Figures 1, 2, 3, the calculated distribution functions for liquid Al are in good agreement both with the MD as well as the experimental results. However, for the

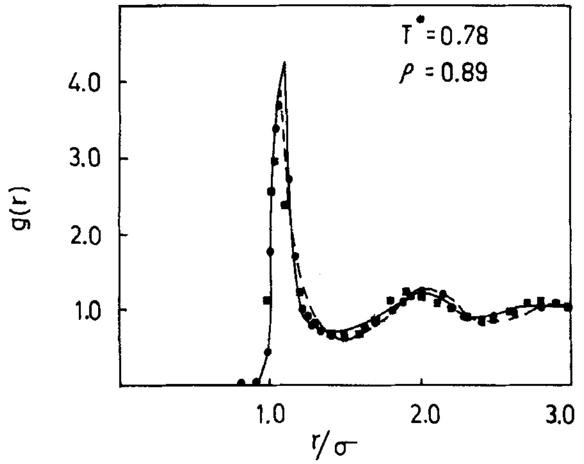

FIGURE 1 Radial distribution function for the $V_5(r)$ at $T^* = 0.78$, $\rho = 0.89$ —— present theory, ■■■ MD, ---- HTA, ●●● neutron difffraction experiment.

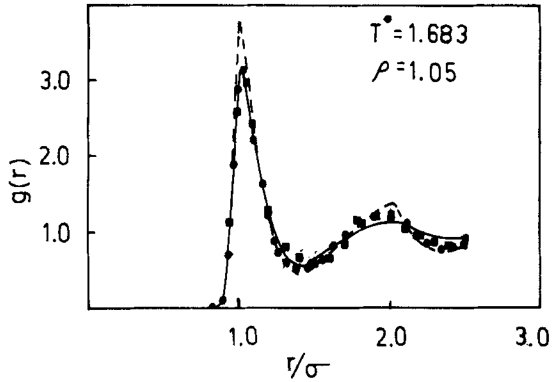

FIGURE 2 Same as Figure 1 but for AGV–975 K; $T^* = 1.683$, $\rho = 1.05$.

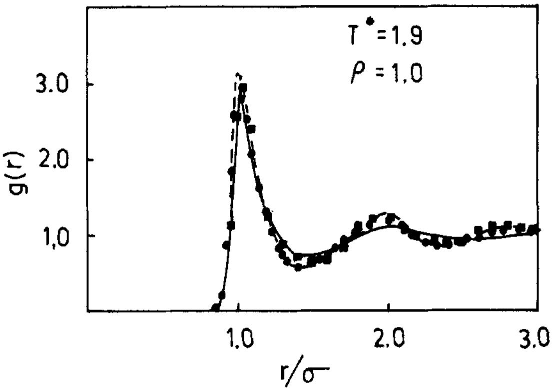

FIGURE 3 Same as Figure 1 but for AGV–1300 K; $T^* = 1.9$, $\rho = 1.0$.

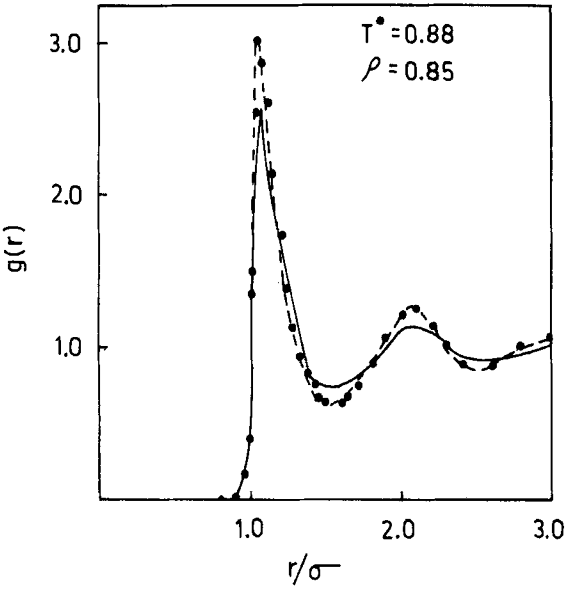

FIGURE 4 Radial distribution function for Lennard–Jones potential at $T^* = 0.88$, $\rho = 0.85$ ——— present theory, · · · MD, ---- HTA.

Lennard–Jones potential (see Figure 4) the agreement of the present results with the MD values is less satisfactory. This would appear to suggest that the integral equation perturbation theory with OCT generates the structure of long range oscillatory potentials with a fair accuracy.

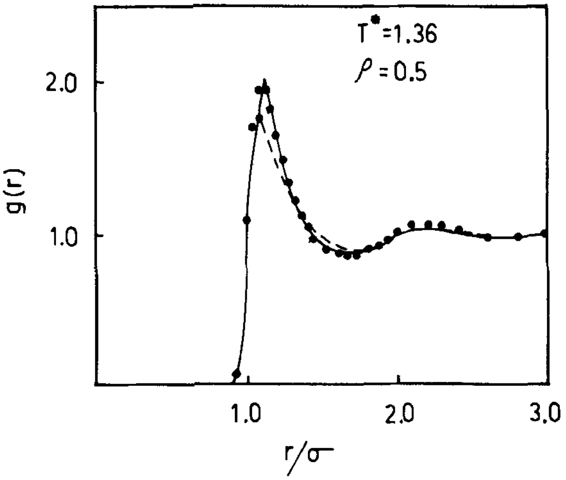

FIGURE 5 Same as Figure 4 but at $T^* = 1.36$, $\rho = 0.5$.

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