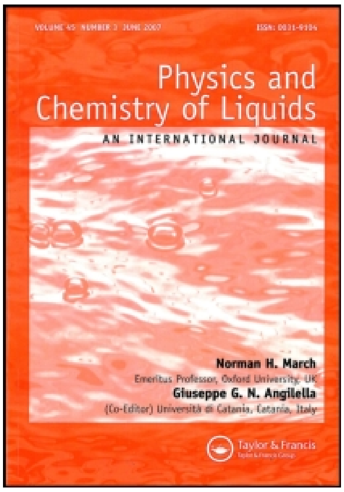

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Structure of Liquid Metals

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Structure of Liquid Metals

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The structure factors and radial distribution functions of liquid sodium and aluminium were calculated using the Hypernetted chain equation and the Machin–Woodhead–Chihara (MWC) integral equation. Various oscillatory potentials suggested for these metals were considered in an attempt to determine the applicability of these integral equations for these potentials. The calculated results are compared with molecular dynamic simulation results. These results indicate that the HNC equation underestimates the main peak in $S(k)$. When the Friedel oscillations are absent then MWC theory gives good results for $S(k)$. But when Friedel oscillations are present then MWC equation reproduces simulation results beyond the main diffraction peak.

I INTRODUCTION

Over the last decade there has been a renewed interest in calculating the structure and thermodynamic properties of liquid metals[1–3] in part due to the determination of effective potentials from the pseudopotential formalism and due to the experimental determination and computer simulation[4–7] of the structure factors of various liquid metals. Liquid metals were chosen because the structure of these fluids is less dominated by steeply repulsive short-ranged forces in contrast to that for the insulating fluids. The effective interionic potential used for liquid metals have long range oscillations and rather soft repulsive cores[8] which differs from the often used hard sphere and Lennard Jones potential functions for insulating fluids. The earlier attempt was by Ashcroft and Lekner[9] who obtained the structure factor from the exact solution[10] to the Percus–Yevick (PY) equation[11] for hard spheres using hard sphere diameter as the one independent parameter to get good fit of the structure factor, $S(k)$. Jones[12] has applied the variational theory of Mansoori

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and Canfield[13] to calculate the equation of state of liquid metals using hard sphere diameter as a variational parameter. Umar and Young[14] used the variational theory to calculate the structure factors. Kumaravadivel and Evans[8] obtained the structure factors of liquid metals using Weeks-Chandler-Andersen[15] (WCA) perturbation theory. Rami Reddy *et al.*[16] applied the optimised cluster theory (OCT) of liquids[17] to calculate the radial distribution function $g(r)$ of liquid metals. All the approaches thus far considered can be classified into four categories: (i) computer simulation, (ii) integral equation approaches, the Percus-Yevick (PY), hypernetted chain[18] (HNC) and the Mean spherical approximation[19] being the most frequently used, (iii) perturbation theories relative to some hard sphere systems and (iv) those based on one component plasma (OCP)[20–22] and charged hard sphere system (CHS).[23]

Blum and Narten[24] applied the Mean spherical approximation and calculated the radial distribution function for liquid aluminium. Recently, Bratkovsky *et al.*[25] made an analysis of the structure factors of liquid metals and concluded that the simple PY approximation appears to be highly accurate in the region of the main peak of $S(k)$ for the simple metals. Rami Reddy[26] on the other hand has shown that the PY and MSA $g(r)$ are in poor agreement with computer simulation results. Ailawadi[3] used the Singwi-Tosi-Land-Sjolander (STLS) scheme[32] to obtain the structure of liquid metals. But the comparison of $S(k)$ for liquid sodium and rubidium indicate that the STLS $S(k)$ oscillates out of phase with the computer simulation results.

In the methods based on the perturbation theory, most of the theories were based on perturbations relative to a chosen hard sphere system. Even though such expansions are accurate for insulating liquids whose repulsive cores mimic the hard repulsions they are not accurate for liquid metals since the repulsive potentials are softer than the Lennard Jones r^{-12} core. The blip function theory[27] which was used to calculate the structure of the repulsive cores has to be carried out to higher terms which involves higher order correlation functions, the information about which is too meagre at this stage. To overcome this difficulty Swamy and Reddy[28] used integral equation perturbation theories[29] and the OCT and obtained good results for $g(r)$ for potentials which have a softer repulsive core. They considered using both the PY and HNC equations. One difficulty with this formalism is that it requires solving twice the integral equation, one for the hard spheres (with the exception for PY for which analytical solutions are available) and the other for the reference part of the potential and thus can be time consuming. Thus calculating $S(k)$ from integral equations is simpler and is the aim of the present work. So far a careful comparison of $S(k)$ obtained from integral equations with computer simulation has not been reported for various oscillatory potentials and this paper attempts to contribute in this direction. In Section II we discuss the HNC and the Machin-Woodhead-Chihara integral equation. Section III presents the various oscillatory potentials used in the present study. Section IV discusses the numerical methods used in solving these integral equations. In Section V we present our results and compare them with the computer simulation results. The conclusions of this study are contained in Section VI.

II HNC AND MACHIN-WOODHEAD-CHIHARA INTEGRAL EQUATIONS

The direct correlation function $c(r)$ is defined in terms of the pair correlation function $g(r)$ by the Ornstein-Zernicke relation

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23})c(r_{13})\,d\mathbf{r}_3 \tag{1}$$

where $h(r) = g(r) - 1$ and $\rho(=N/V)$ is the number density. The HNC equation supplements Eq. (1) with an approximate closure relation by

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r) \tag{2}$$

In Eq. (2)

$$f(r) = e^{-\beta u(r)} - 1 \tag{3}$$

is the Mayer function and $u(r)$ is the interparticle potential function with $\beta = 1/k_B T$ and

$$y(r) = g(r)\,e^{\beta u(r)} \tag{4}$$

Lado[30] and Madden and Fitts[29] have shown that for insulating fluids the effects of long ranged perturbation can be given accurately by approximations based on the HNC theory.

Machin-Woodhead-Chihara integral equation

Using Percus's functional Taylor series expansion Chihara[31] has derived an integral equation and is given by[32]

$$\nabla c(r) = -\nabla[g(r)(e^{\beta w(r)} - 1)] - g(r)\nabla\beta v(r) \tag{5}$$

such that

$$u(r) = w(r) + v(r) \tag{6}$$

Though Chihara offers no prescription for separation of the potential into $w(r)$ and $v(r)$, we made use of the separation proposed for insulating fluids by Weeks *et al.* (WCA).[15] In WCA theory the potential separation is accomplished by setting

$$\begin{aligned} w(r) &= u(r) - u(R_m) \qquad & r \leq R_m \\ &= 0 & r \geq R_m \qquad (7) \\ v(r) &= u(R_m) & r \leq R_m \\ &= u(r) & r \geq R_m \qquad (8) \end{aligned}$$

where R_m is the distance at which the potential is minimum.

The structure factor $S(k)$ can be computed from the direct correlation function through the relation

$$S(k) = 1/[1 - \rho\tilde{c}(k)] \tag{9}$$

where $\tilde{c}(k)$ is the Fourier transform of $c(r)$ defined by

$$\tilde{c}(k) = \int c(r)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \tag{10}$$

III POTENTIAL FUNCTIONS

Calculations were performed for liquid sodium and aluminium for various potential functions. These potentials have different types of repulsive cores. The potentials considered for liquid sodium are:

i) A potential suggested by Schiff with a repulsive core $1/r^7$ intermediate between the Born–Mayer soft core and the Lennard Jones hard core. It has the form

$$V_1(r) = \mathrm{Cos}(2k_{F1}r)\left(\frac{A_1}{r^3} + \frac{B_1}{r^5} + \frac{C_1}{r^7}\right) + \mathrm{Sin}(2k_{F1}r)\left(\frac{D_1}{r^4} + \frac{E_1}{r^6}\right) \tag{11}$$

ii) A potential with a Born–Mayer soft core with large oscillations and has the form

$$\begin{aligned} V_3(r) = {} & \mathrm{Cos}(2k_{F3}r)\left(\frac{A_3}{r^3} + \frac{B_3}{r^5}\right) + \mathrm{Sin}(2k_{F3}r)\left(\frac{C_3}{r^4} + \frac{D_3}{r^6}\right) \\ & + E_3 \exp[F_3 - G_3 r/r_0] \end{aligned} \tag{12}$$

The units of length and energy chosen are $\sigma = 3.24$ Å and $\varepsilon = 599$ K.

In the case of aluminium the following potential functions were considered

i) A potential with a hard $1/r^{12}$ core given by

$$V_5(r) = \mathrm{Cos}(2k_{F5}r)\left(\frac{A_5}{r^3} + \frac{B_5}{r^5} + \frac{C_5}{r^7}\right) + \mathrm{Sin}(2k_{F5}r)\left(\frac{D_5}{r^4} + \frac{E_5}{r^6}\right) + \frac{F_5}{r^{12}} \tag{13}$$

ii) The other three potentials considered for liquid aluminium are all derived from pseudopotential formalism. The first is obtained from Ashcroft pseudopotential and with Geldart-Vosko screening and is designated as AGV. The other two potentials SGT and TGT are obtained from Geldart-Taylor screening. The quasiharmonic phonon dispersion curves for aluminium calculated using these potentials are in good agreement with experiment. Details of computing these potentials is discussed by Ebbsjo *et al.*[6] The TGT potential has been used in investigations of liquid and solid aluminium[33,34] and in a Monte Carlo calculation for liquid aluminium.[35] As seen from Figure 1 the repulsive parts of all these three potentials are similar while the

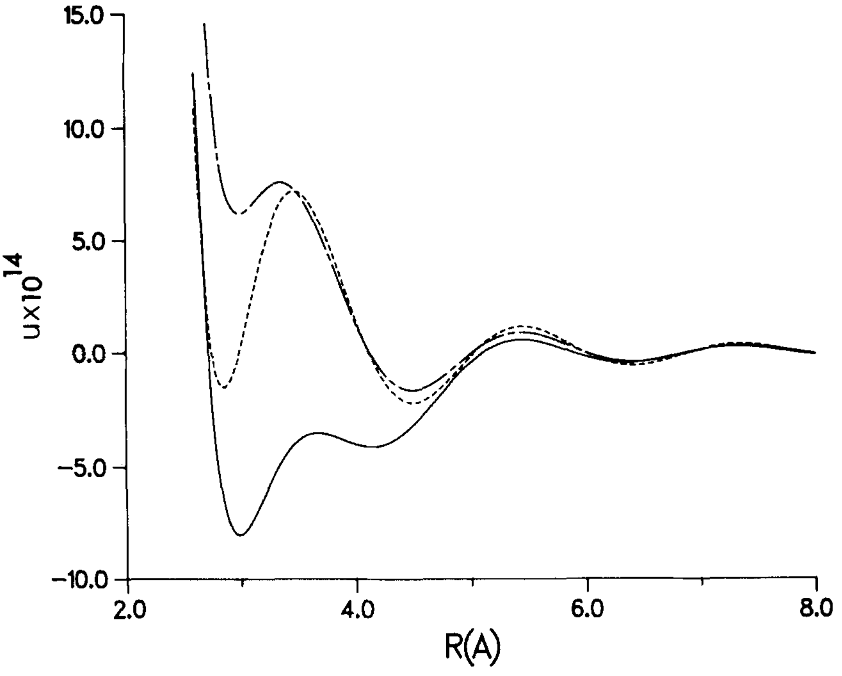

FIGURE 1 AGV, SGT and TGT potentials: ———— AGV, ------------ SGT, ——— TGT. The energy is in units of erg and distance in A.

parts outside the core are different. The units of length and energy chosen are $\sigma = 2.56$ Å and $\varepsilon = 1198$ K. The potential parameters for V_1, V_3 and V_5 are taken from Schiff.[7]

In the case of V_1, V_3 and V_5 the molecular dynamic simulations were carried out by Schiff. For AGV, SGT and TGT potentials molecular dynamic simulations were carried out by Ebbsjo *et al.*[6]

IV NUMERICAL COMPUTATIONS

The HNC and Machin–Woodhead–Chihara integral equations were solved in the r-space by transforming Eq. (1) into bipolar coordinates. In the case of V_1, V_3 and V_5 a step size of 0.05 σ was used whereas for AGV, SGT and TGT a step size of 0.039 σ was used. All the integrals were evaluated using Simpsons rule. The iterations were truncated when

$$|y_{\text{in}}^{n}(r) - y_{\text{out}}^{n+1}(r)| \leq 0.001 \tag{14}$$

Convergence was enhanced by using Broyles mixing technique. All the Fourier transforms were evaluated using Filon's method.

RESULTS

In Figure 2 we compare the results of the radial distribution functions obtained from the Machin–Woodhead–Chihara and the HNC equations for liquid sodium for the potentials V_1 and V_3 and compare them with the molecular dynamic simulation results of Schiff. A similar comparison is made in Figures 3–5 for the structure factor $S(k)$. The wave number k in these figures is given as a dimensionless variable in units of σ. These comparisons clearly indicate that when the Friedel oscillations are absent the MWC integral equation is in excellent agreement with the computer simulation results. When the Friedel oscillations are present then except near the main diffraction peak the MWC results are in good agreement with MD results. The HNC results in both cases are not in such good agreement with MD as those for MWC results.

In Figure 6, a comparison of $g(r)$ from MWC and HNC integral equations for liquid aluminium for $V_5(r)$ is made with available MD simulation results and Figures 7 and 8 make a similar comparison for the $S(k)$. A similar trend found for sodium is observed in the case of aluminium also.

The results for $g(r)$ obtained from the MWC and HNC for AGV, SGT and TGT potentials for liquid aluminium are compared with MD results in Figures 9–11. In Figures 12–14 a similar comparison is made for $S(k)$. These

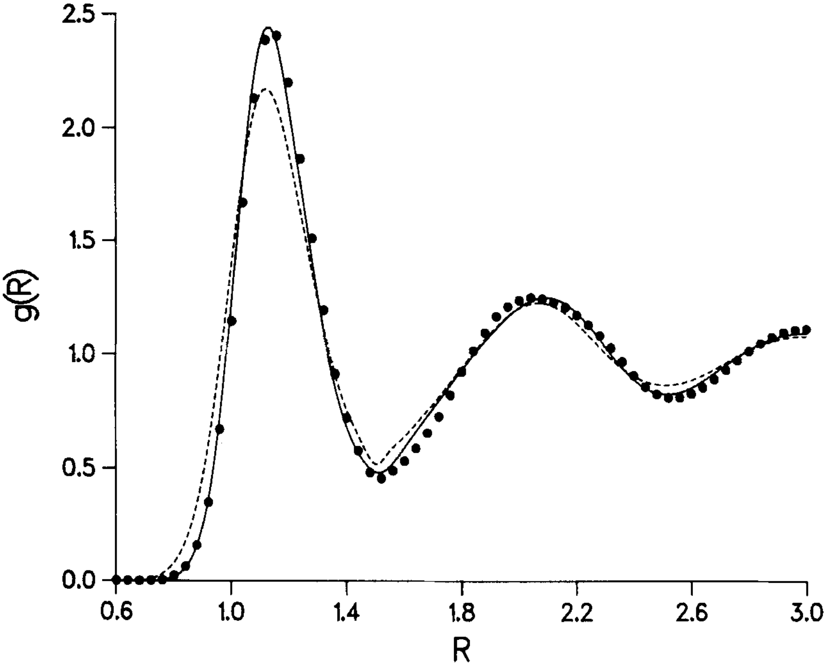

FIGURE 2 $g(r)$ for $V_3(r)$ cut at $r = 1.5$: ••• MD, ———— MWC and ------------ HNC.

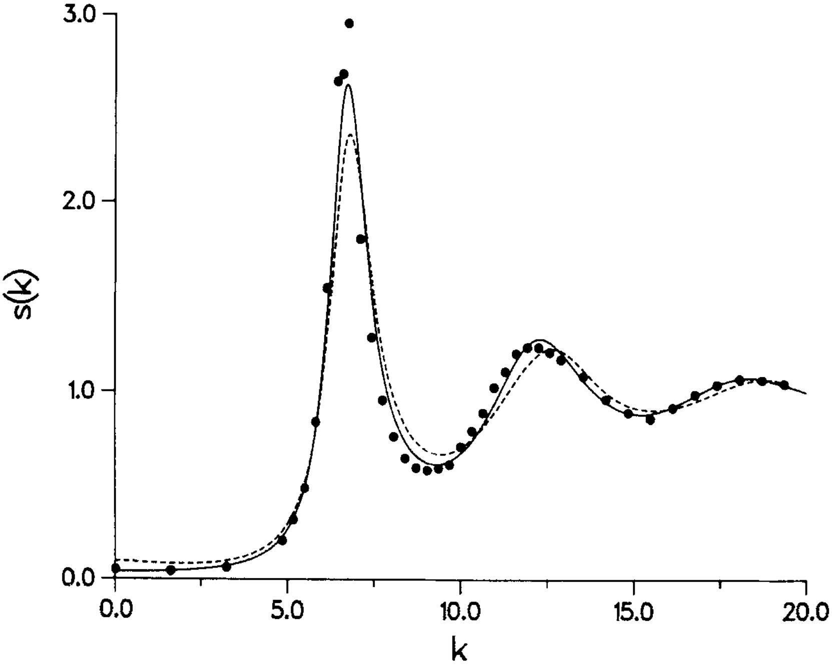

FIGURE 3 $S(k)$ for $V_1(r)$ cut at $r = 1.53$: ••• MD, ———— MWC and ------------ HNC.

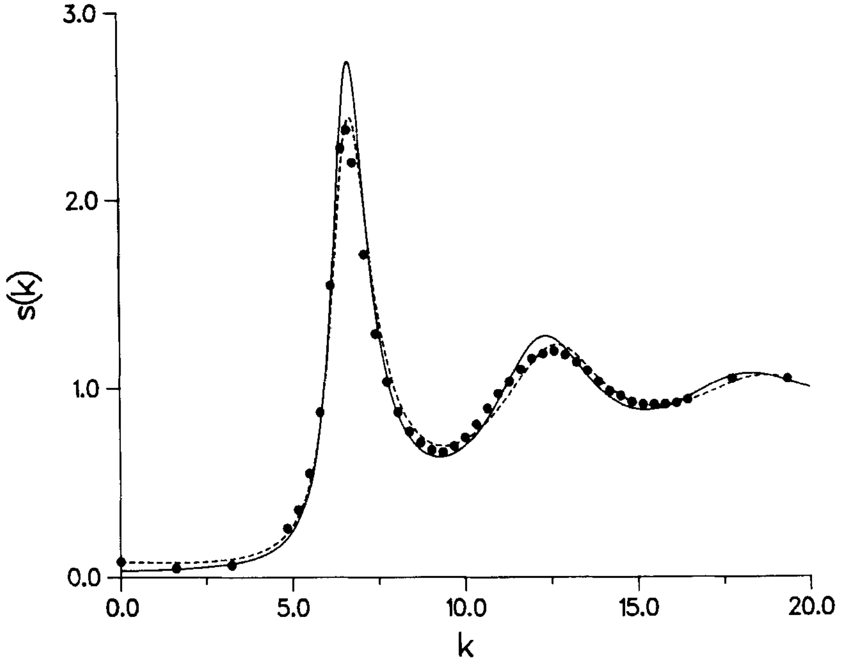

FIGURE 4 Same as Figure 3 but cut at $r = 3.2$

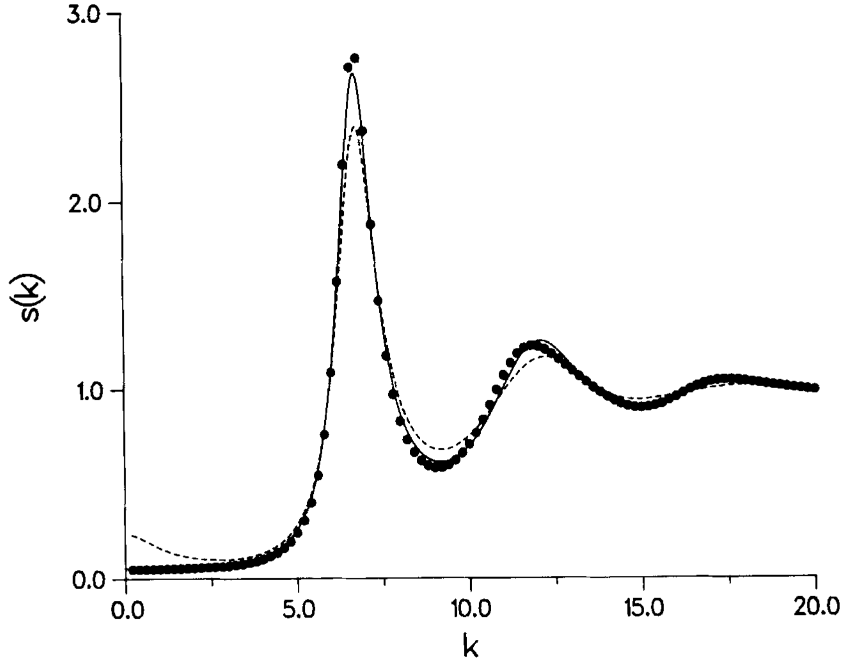

FIGURE 5 $S(k)$ for $V_3(r)$ cut at $r = 1.2$. See Figure 3 for other symbols.

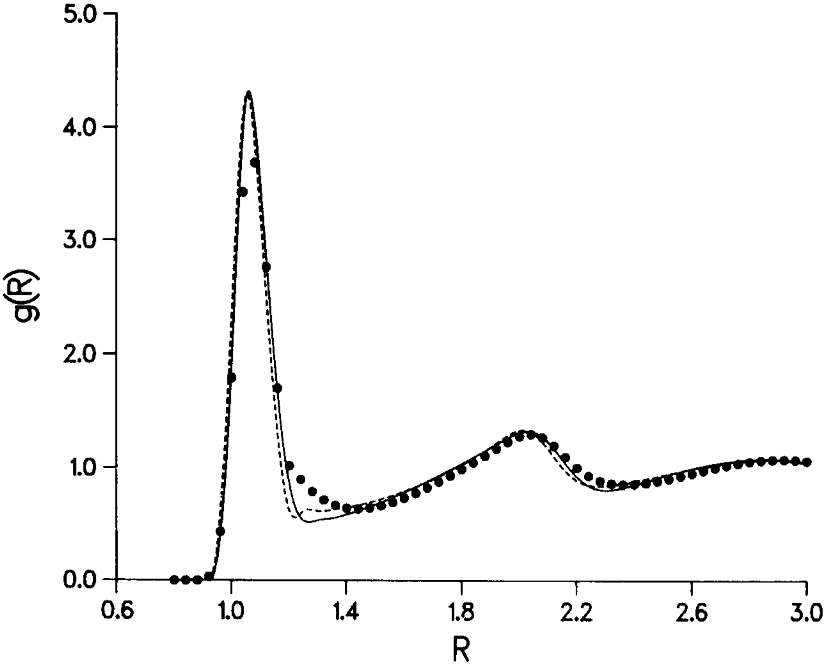

FIGURE 6 $g(r)$ for $V_5(r)$ cut at $r = 1.2$. See Figure 2 for other symbols.

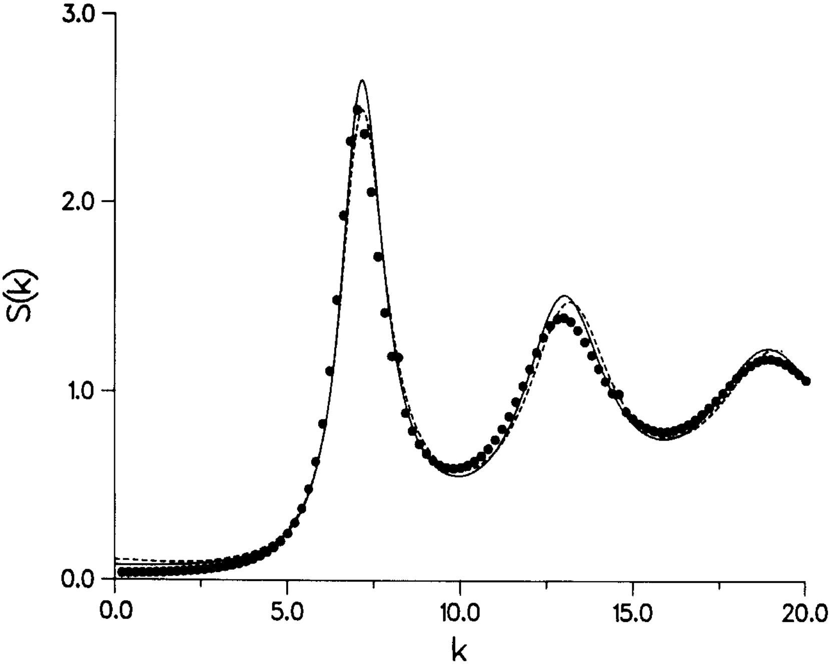

FIGURE 7 $S(k)$ for $V_5(r)$ cut at $r = 1.2$. See Figure 3 for the symbols.

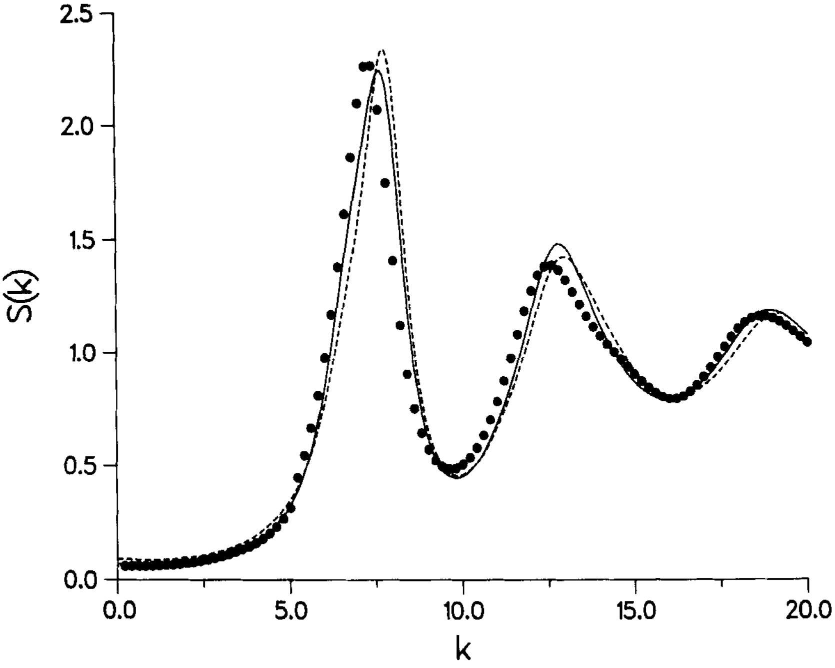

FIGURE 8 Same as Figure 7 but cut at $r = 3.3$.

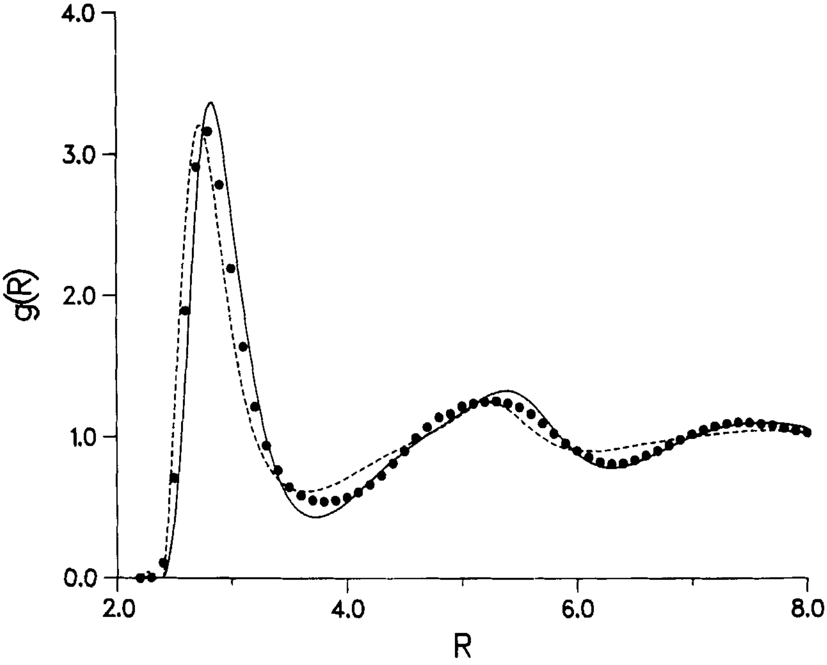

FIGURE 9 $g(r)$ for AGV at 988 K. See Figure 2 for the symbols used.

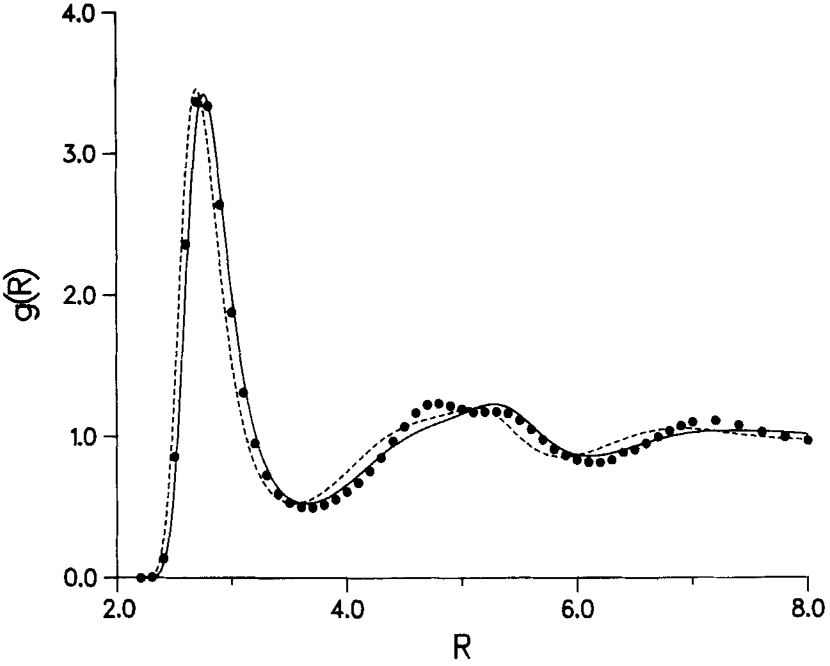

FIGURE 10 Same as Figure 9 but for SGT at 970 K.

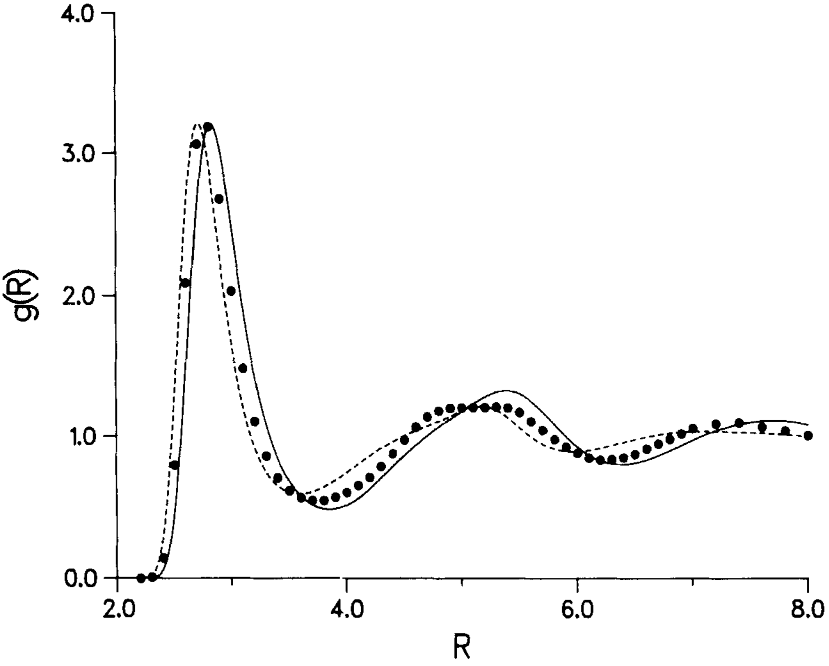

FIGURE 11 Same as Figure 9 but for TGT at 984 K.

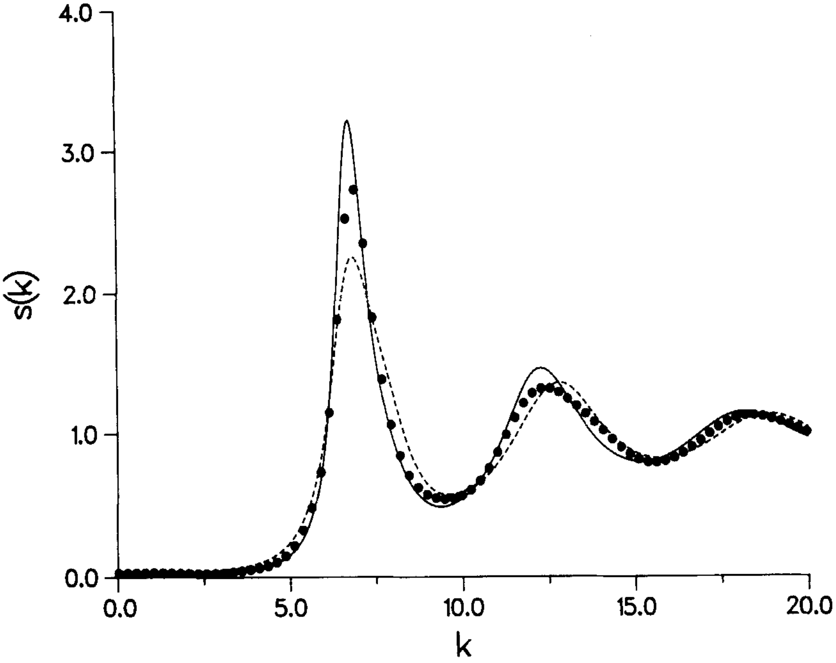

FIGURE 12 *S*(*k*) for AGV at 988 K. See Figure 3 for other symbols.

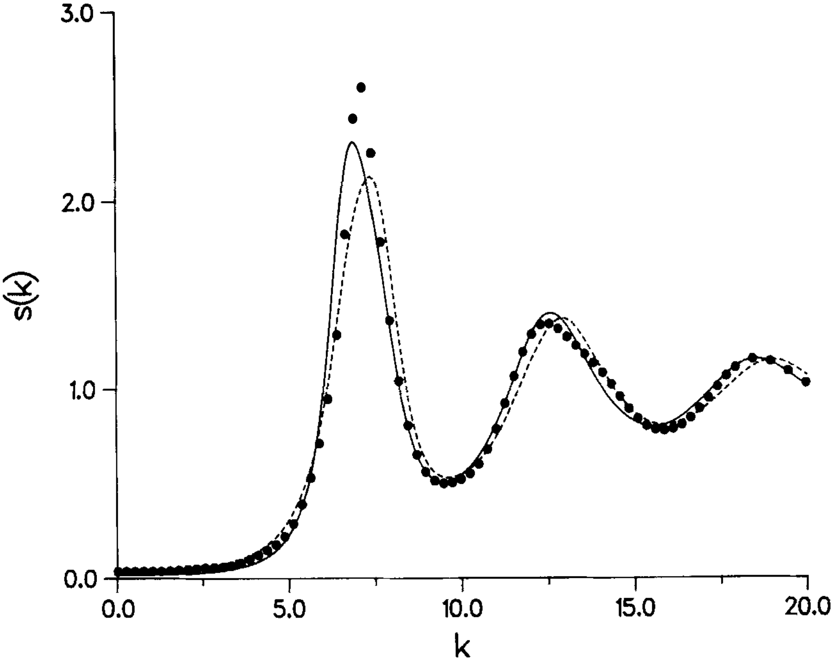

FIGURE 13 Same as Figure 12 but for SGT at 970 K.

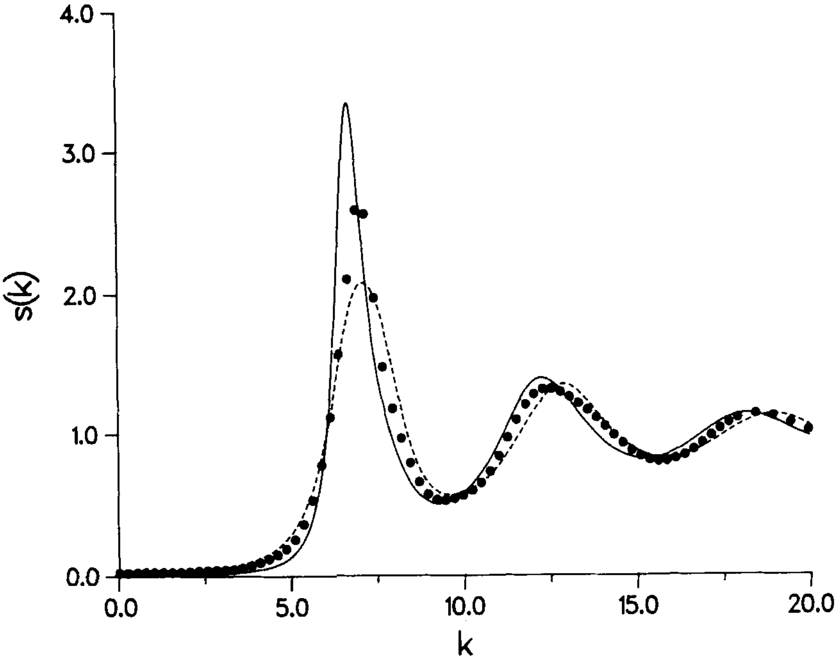

FIGURE 14 Same as Figure 12 but for TGT at 984 K.

comparisons clearly indicate that neither the MWC nor the HNC give quantitative agreement with simulation results for these potentials.

In Table I we collect the $S(0)$ values for the various potentials obtained from MWC and HNC equations. The compressibility κ, is related to $S(0)$ through the compressibility sum rule

$$S(0) = \rho k_B T \kappa \tag{15}$$

TABLE I

Potential	$S(0)$ MWC	$S(0)$ HNC	$S(0)$ MD
V_3 cut at 1.2	0.055	0.239	0.050
V_5 cut at 3.3	0.070	0.091	0.060
V_5 cut at 1.2	0.078	0.105	0.030
AGV	0.014	0.037	0.038
SGT	0.018	0.038	0.041
TGT	0.008	0.026	0.024

CONCLUSIONS

The main conclusion of this work is that the MWC integral equation gives good results for the radial distribution function and $S(k)$ for the liquid metals considered when the Friedel oscillations are suppressed. When the Friedel oscillations are present except in the vicinity of the main diffraction peak the MWC results are in good agreement with MD results. The results obtained from HNC are not in quantitative agreement with the simulation results.

The above conclusions were drawn when the potential separation was accomplished using WCA criterion. One could try a potential separation such that the Mayer function $(e^{-\beta w(r)} - 1)$ very closely resembles that of a hard sphere system. It has been shown earlier by Swamy and Reddy that such a separation is not going to improve the results any better.

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