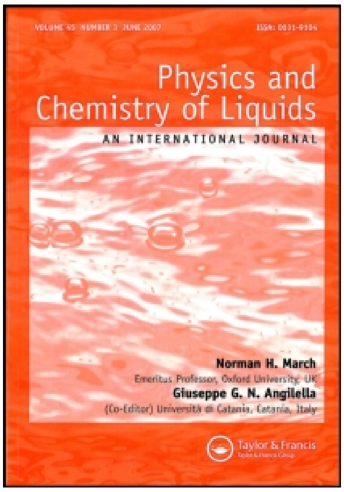

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CALCULATIONS OF $g(r)$ FOR LIQUID Cu AND Ni USING MANY-BODY POTENTIALS

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The pair distribution function, $g(r)$, for Ni and Cu at various temperatures above melting are investigated by using the Finnis-Sinclair (FS) many-body potentials and the thermodynamically self-consistent Variational Modified Hypernetted Chain (VMHNC) theory. The overall agreement with experiment is reasonably good. The calculations indicate that the many-body interactions, precisely taken care of by the FS potentials, are important for the study of $g(r)$ for the liquid transition and noble metals. The results also permit us to examine the applicability of the temperature independent approximation of the FS potentials.

Keywords: Liquid Cu and Ni; many body potentials; variational modified hypernetted chain theory

1. INTRODUCTION

In liquid theories knowledge of the pair distribution function $g(r)$ and the static structure factor $S(q)$ is the essential prerequisite for a complete static description of the structural and thermodynamic properties [1]. The pair distribution function $g(r)$ is related to the structure factor $S(q)$ through a well known Fourier transeformation [2]. On the other hand, $g(r)$ is directly related to the interactions describing the liquid state via some statistical theory. Consequently, interatomic interactions that describe the liquid state ideally can also provide with a better description of $g(r)$.

Now looking at the electronic structures [3], it is noticed that the filled *d* bands in the noble metals lie immediately below the respective Fermi level. On the other hand, the partially filled *d* bands in the transition metals populate around the Fermi level. The occurence of these energy bands in the close vicinity of the Fermi level indicates that any little change in the electron-ion interactions may bring along drastic changes in the pattern of band hybridization and so in the structural aspects of these metals. Since the nature of the electronic structure does not change drastically [4], as the system goes from the solid to the liquid state, we believe that the liquid state is equally sensitive to the details of the interatomic interactions via the electron clouds. Concurrently since the electron mean free paths in these systems are short in comparison with the interatomic separations, a strong scattering situation at all finite temperatures exists in these systems. Consequently the roles of the fine details of non-locality and many-body effects in the interatomic interactions become important [5].

Finnis and Sinclair [6] and Daw and Baskes [7] have proposed independently two models to derive many body potentials. These two models are based on two philosophical ideas. The principal differences between the two approaches lie in the derivation and interpretation of the many body term known as the embedding function [8]. In the Finnis-Sinclair (FS) approach the idea of the many-body term arose from the second moment approximation of the tight binding model. Subsequently there have been many extensions [8 – 12] of the FS approach and it has been observed that the many-body potentials describe properties of the various solid phases more accurately than the pair potential models. Concurrently Holender [13] for the first time applied the FS model to perform molecular dynamics (MD) simulations aiming to study the structural and thermodynamic properties of liquid transition metals. It has been also noted [14] that potentials suitable for MD simulations may not be applicable to the well established integral equation theories; the relevant difficulties primarily lie with non-convergence of the calculations.

In the present calculations we have employed the Ackland *et al.* [8] version of the FS many body potential originally developed to study the noble metals. The reason behind this choice is firstly because that this potential has not been used before to study the liquid structure and thermodynamics and secondly because of its success in the study of fcc noble metals; the latter aspect is expected to have some influence in the structure of Cu and Ni even after melting. This potential is then employed with the thermodynamically self-consistent variational modified hypernetted chain (VMHNC) integral equation theory to perform the liquid state calculations. It is worth noting that the suitability of the VMHNC theory in the calculations of the liquid transition and noble metals have been tested elsewhere [15].

So far as the temperature independence of the potentials is concerned, there is evidence [13] that the same potential may be suitable for both the solid and liquid phases. However the question of transferability of potentials should be treated with caution.

The layout of the paper is as follows: In section 2 we briefly present the theory for the effective interionic interactions. Results of the calculations for $g(r)$ at various temperatures in the liquid state are presented in section 3. Some concluding remarks are presented in section 4.

2. THEORY

1. Effective pair potential

The total energy of an atom in a system can be written as [13]

$$U = \frac{1}{2}\sum_i \sum_j{}' V(r_{ij}) - \sum_i f(\rho_i) \tag{1}$$

where $V(R)$ is a central pair potential and $f(\rho_i)$ an embedding function describing the many body interactions. The argument ρ_i, identified with the second moment of the density of states [6], is expressed as

$$\rho_i = \sum_j{}' \o(r_{ij}) \tag{2}$$

where $\phi(r_{ij})$ is a function relevant to the many body interactions.

The effective interatomic pair interaction may be approximated [8] from eq. (1) if the second and higher order derivatives of f are neglected as

$$V_{\rm eff} = V(r) - 2{\rm f}'(\rho)\o(r) \tag{3}$$

The function $V(r)$ and $\phi(r)$ are given by

$$\begin{aligned} V(r) &= \sum_k a_k(r_k - r)^3 H(r_k - r) \qquad (a) \\ \o(r) &= \sum_k A_k(r_k - r)^3 H(R_k - r) \qquad (b) \end{aligned} \tag{4}$$

where r_k and R_k are chosen knot points of cubical spline such that $r_1 > r_2 > r_3 > r_4 > r_5 < r_6$, and $R_1 > R_2$. In eqs. (4)

$$\begin{aligned} H(X) &= 1 \quad X < 0 \\ &= 0 \quad X < 0 \end{aligned} \tag{5}$$

Hence r_1 and R_1 represent the cutoff radii of V and ϕ respectively. The coefficients $a_1, a_2, \ldots a_5$, A_1 and A_2 have been determined by fitting exactly to the equilibrium lattice parameter, cohesive energy; elastic constants, vacancy formation energy and stacking fault energy; a_6 has been adjusted to fit the pressure volume relation [8].

2. The VMHNC Theory of Liquid

The variational modified hypernetted chain (VMHNC) theory of liquids pertains to a new generation of fairly accurate integral equation theories. The starting point for this theory is the Ornstein-Zernike (OZ) equation which relates the pair distribution function, $g(r)$, and the direct correlation function $c(r)$ as follows:

$$g(r) - 1 = c(r) + \rho \int c(r')[g(|\mathbf{r} - \mathbf{r}'|) - 1]\, d\mathbf{r}' \tag{6}$$

and the exact closure

$$c(r) = g(r) - 1 - \ln g(r) - \exp(\beta V(r) + B(r)) \tag{7}$$

In eq. (6), ρ is the average number density and in eq. (7) $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant, T the temperature, and $B(r)$ is the so called bridge function. Here we follow Rosenfeld and Ashcroft [16] in assuming the universality of the bridge function. We further assume that $B(r)$ is adequately described by the Percus-Yevick (PY) hard sphere bridge function, namely

$$B(r) = B_{PY}(r,\eta) \tag{8}$$

where $\eta = \eta(\rho,\beta)$ is the variational parameter. This parameter is determined by minimizing the reduced Helmholtz free energy functional $f^{\mathrm{VMHNC}}(\beta,\rho;\eta) = (F^{\mathrm{VMHNC}}/Nk_BT)$ with respect to the parameter, symbolically

$$(\partial f^{\mathrm{VMHNC}}/\partial\eta)_{\beta,\rho} = 0 \tag{9}$$

here f^{VMHNC} may be written as

$$f^{\mathrm{VMHNC}} = F^{\mathrm{MHNC}} - \Delta_V(\eta) \tag{10}$$

Here f^{MHNC} is the MHNC free energy functional [17] and Δ_V is given by

$$\Delta_V(\eta) = \frac{\rho}{2}\int d\eta' \int \mathbf{dr}\ \ g_{PY}(r,\eta')(\partial B_{PY}(r,\eta')/\partial\eta') - \delta_V(\eta) \tag{11}$$

In eq. (11) $\delta_V(\eta)$ is chosen so as to obtain as close as possible a virial compressibility, but without enforcing it. In practice

$$\delta_V(\eta) = \mathrm{f}_{cs}(\eta) - \mathrm{f}_{PY} \tag{12}$$

where f_{PY} and f_{cs} are respectively the hard sphere expressions for PY and Carnahan-Starling reduced free energies. The value of the variational parameter, η, obtained at a given thermodynamic state is used to evaluate B_{PY} which, in turn is used in eq. (6) to solve for $g(r)$ in conjunction with eq. (7).

3. RESULTS AND DISCUSSIONS

We have presented results of calculations for the pair distribution function $g(r)$, for Ni and Cu at various temperatures. The input temperatures and corresponding number densities are taken from Waseda [18].

For numerical solution of the OZ equation (6) and the closure relation (7), Gillan's algorithm [19] have been used: in all cases we find that 1024 points with step size $\delta r = 0.06\,\mathring{A}$ are adequate for our calculations. For the minimization of the configurational energy, a linear search procedure [20] has been applied.

Figure 1 shows the results for, $g(r)$, for Ni at temperatures. 1773, 1873, 1923, and 2023 K. These are compared with the experimental values, derived from the X-ray diffraction data [18]. The comparison in

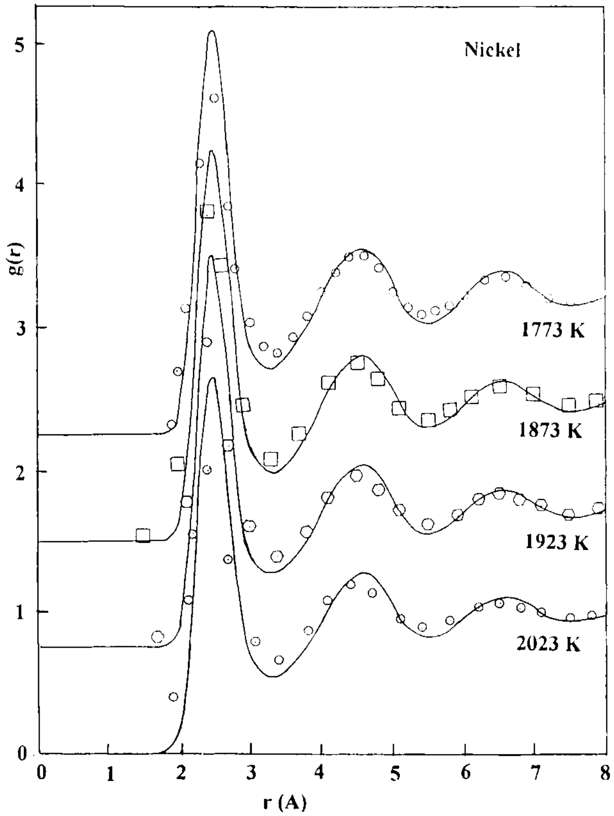

FIGURE 1 The pair distribution function $g(r)$ for Ni at temperatures 1773, 1873, 1923, 2023 K. Solid lines denote the present theoretical results and the other notations denote the experimental values[18]. The input temperatures and corresponding number densities are taken from Waseda[18].

general is very good except that in the principal peak values of $g(r)$; here the theoretical results are somewhat over estimated. A closer look at the principal peaks, however, reveals that the differences between the calculated and experimental values are low at temperatures near melting, and high at relatively high temperatures. Figure 2 illustrates $g(r)$ for liquid Cu at temperatures 1423, 1523, 1773 and 1873 K. In this case values of $g(r)$ at the principal peak positions are very consistent with experiments; in particular the comparison is remarkably good at temperatures near melting.

From Figures 1 and 2, it is noticed that the value for $r_{\min}$, for which $g(r)$ is non-zero decreases with increasing temperature. For example,

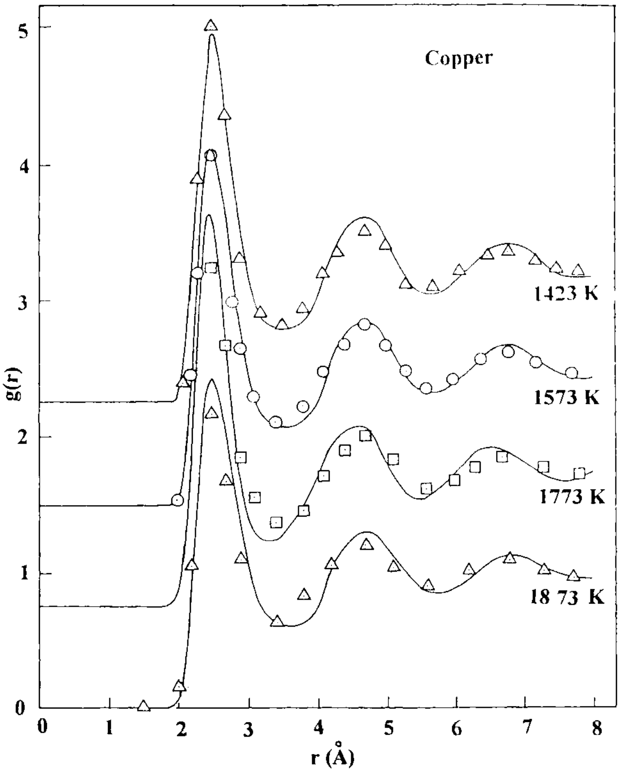

FIGURE 2 The pair distribution function $g(r)$ for Cu at 1423, 1523, 1773 and 1873 K. The labelling of curves and other details follow those of FIGURE 1.

for Cu, $r_{\min} = 1.426$, 1.364 and 1.302 Å at temperatures 1423, 1573 and 1773 K respectively. This trend is a manifestation of the aspect that with increasing temperature ions gain increased kinetic energy and are more probable to penetrate smaller interionic distances.

The principal peak values of $g(r)$ as a function of temperature for Ni and Cu are illustrated in Figure 3. It is noticed that the peak values decrease with the increase of temperature. For example, the height of the principal peaks for Cu are 2.72, 2.61 and 2.47 at temperatures 1423, 1573 and 1773 K respectively. The reason is presumably that near melting, liquids still have a remnant of the crystalline structure of the parent solids. In other words, liquids still maintain a short range order manifested by the higher peak values of $g(r)$. As the temperature increases, the kinetic energy increases too and the liquid becomes more disordered. Consequently, the heights of the peak values of oscillations of $g(r)$ becomes lower and more flatened. When we compare the

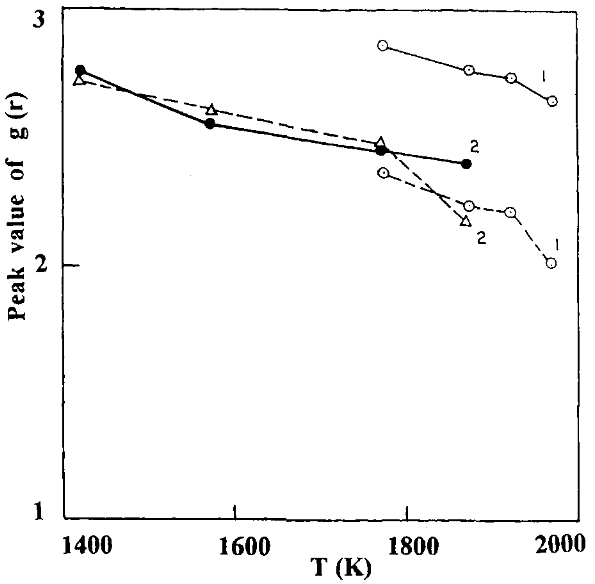

FIGURE 3 The principal peak values of $g(r)$ as a function of temperature of Ni and Cu. Curves 1 and 2 represent results for Ni and Cu respectively. The notations on the solid lines denote the theoretical results while those on the broken lines denote the experimental values.

heights of the principal peaks with experimental data, it is noticed that at temperatures near melting, the theoretical results are closer to experiments, but for temperatures away from the melting point the discrepency becomes more visible; this trend is more apparent in Ni. The discrepencies between the theoretical and experimental data may arise either due to the underlying liquid state theory or, due to the effective pair potentials used or both. To examine this point, the calculated results of $g(r)$ for Cu are compared with the available molecular dynamics (MD) simulation results [13] (Fig. 4) obtained from the same potential and a good agreement is found. This comparison suggestes that the accuracy of the VMHNC liquid state theory is well established in the case of noble and transition metals.

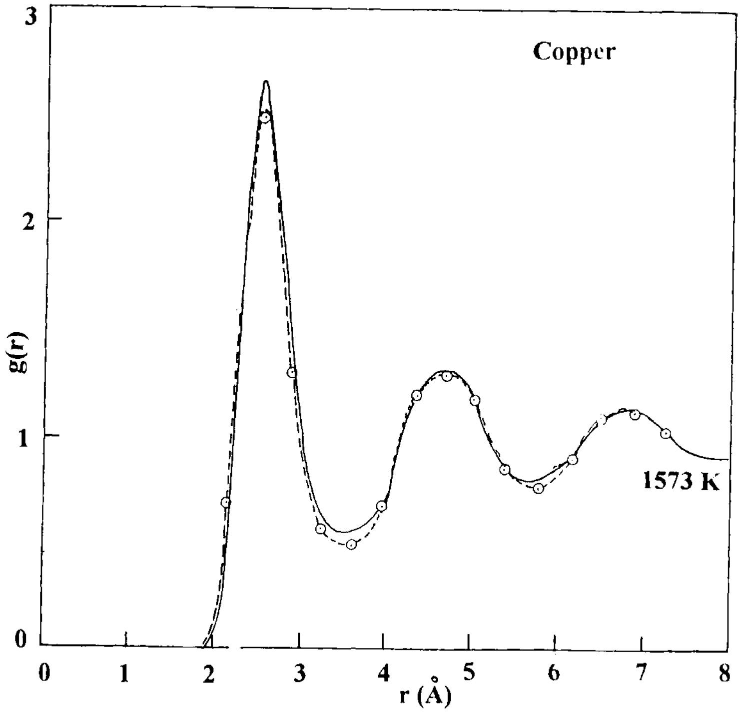

FIGURE 4 The pair distribution function $g(r)$ for Cu corresponding to 1527 K. The solid curve denotes the theoretical results while the broken curve denotes the molecular dynamics (MD) calculations[13].

Thus the remnant of any visible discrepencies in the limit of higher temperature may arise from any probable imbalance between the repulsive and attractive contributions to the effective pair potential; this is simply because the height and position of the principal peak are attributed by a delicate balance between these two contributions.

4. CONCLUSIONS

In this paper we have presented the pair distribution function, $g(r)$, for liquid Ni and Cu at different temperatures above their melting points. We have found good agreement with experimental data and MD results. The calculated results suggest that the accuracy of the VMHNC theory is comparable to that of the MD simulations of the liquid noble and transition metals. We would, however, like to make the following critical remarks on the state of art of the present approach:

1. In the present calculations we have assumed a temperature independent potential. However, the transferability of potentials is not beyond question. In reality, all interionic interactions are temperature dependent; this is simply because the mode of dynamics at all finite temperatures control these interactions in any metallic system. This aspect becomes more relevant in the limit of higher temperatures.
2. In any effective many-body or pair potential, the balance between the repulsive and attractive contributions is extremely important for all structural and thermodynamic purposes. Any imbalance between these two contributions may lead to unphysical results.

Work considering the fine details of temperature independence and the global profile of the many-body interactions within the Finnis-Sinclair (FS) frame-work is in progress.

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