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Liquid structure of titanium and vanadium; VMHNC calculations

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Abstract. The first successful calculations for the liquid structure $S(q)$ of the early 3d transition metals are presented; they use effective pair interionic potentials and an integral equation theory of liquids. The effective pair potentials are obtained from a local form that assumes the superposition of the nearly free electron band, described by the empty-core model, and the d-band contribution, which is calculated by using an inverse scattering approach. The liquid state theory used in the calculations is the variational modified hypernetted chain (VMHNC) approximation. The agreement between the calculated $S(q)$ and the available x-ray diffraction data for vanadium is reasonably good, but for titanium is only fair.

1. Introduction

Regnaut (1989) has shown that using the Wills and Harrison (WH) (1983) effective Hamiltonian in conjunction with the WCA-ORPA (see, cf, Andersen *et al* (1976)) liquid state theory has no solution for the liquid structure $S(q)$ of the early 3d transition metals.

Regnaut's findings have been confirmed by Hausleitner *et al* (1991), who have shown that accurate thermodynamically self-consistent integral equation theories of liquids also fail to yield $S(q)$ for the 3d transition metals with half-filled and less than half-filled d bands. In the same work Hausleitner *et al* report that molecular dynamics (MD) simulations, using a modified WH potential, fail to produce reasonable results for the structure of liquids Ti and V. These authors conclude that the root of the problem can be traced to the position and the depth of the first minimum of the WH potential, and suggest that a successful description of the liquid structure of transition metals require a shallower potential well shifted towards larger values of r than those predicted by WH. We note here that the potentials recently developed by Moriarty (1988, 1990) using generalized pseudopotential theory, which have proved very successful in solid state calculations, have potential wells which are even deeper and placed at lower values of r than the WH potentials.

Prompted by the suggestion of Hausleitner *et al*, we have recently developed a new simple effective pair interaction (Bretonnet and Silbert 1992) which appears to have the correct attributes for a good description of the liquid structure for the

transition metals. We derive this pair potential by using a local form that combines the empty-core model to describe the nearly free electron *sp* band, and a *d*-band contribution deduced from an inverse scattering approach. The pair potential contains three parameters: the empty-core radius R_c , a softness parameter a , and the effective *s*-electron occupancy number Z_s , although there are restrictions to the range of values that the ratio R_c/a can take up.

We have recently completed calculations of $S(q)$ for liquid 3d transition metals that combine our potential with a Gibbs–Bogoliubov variational scheme which uses a charge hard sphere reference system (Bretonnet *et al* 1992). These results support the view that this potential is a promising, albeit crude, approach to the study of these systems.

However, as shown by Regnaut (1989) in his study, the use of a reference fluid does not guarantee that when the full potential is used the results will be similarly successful. In the case of the WH potential this appears to be so because its predictions depend critically on the cancellation between two large—one repulsive, one attractive—contributions. Consequently it is appropriate to ask whether our potential, when both contributions are taken into account, is still capable of describing the structure of the 3d liquid transition metals.

In this work we present the results of calculations of $S(q)$ for liquids Ti and V, using our potential in conjunction with the variational modified hypernetted chain (VMHNC) theory of liquids. This theory, originally proposed by Rosenfeld (1986), has been successfully used to study the structure of the liquid alkali metals (Gonzalez *et al* 1991), and has also been extended to the case of multicomponent systems (Gonzalez *et al* 1992). The VMHNC belongs to a new generation of fairly accurate integral equations theories of liquids. It is of comparable accuracy to the thermodynamic self-consistent theory used by Hausleitner *et al* (1991), and our decision for using one rather than the other is discussed by Gonzalez *et al* (1991, 1992).

We have chosen for this study the cases of liquids Ti and V because, as stated above, even MD simulations using the WH potential fail to yield reasonable results. Hence the results presented below are a crucial test for our potential.

The layout of the paper is as follows. In section 2 we introduce the potential used in this work and outline the essential features of the VMHNC theory. Further details may be found in the references given above. In section 3 we present the results of $S(q)$ for liquids Ti and V, and also analyse the effects on $S(q)$ of a few choices of the parameters of the potential. We complete the paper in section 4 with a brief discussion of our results.

2. Theory

2.1. Effective pair potential

The local pseudopotential is constructed by the superposition of the *sp*- and *d*-band contributions, resulting in the following expression:

$$u(r) = \begin{cases} \sum_{n=1}^2 B_n \exp(\frac{r}{na}) & \text{if } r < R_c \\ -Z_s e^2 / r & \text{if } r > R_c \end{cases} \quad (1)$$

The form inside the core was obtained using an inverse scattering approach, specifically the distorted plane-wave method developed by Swan (1967) and improved

by Oli (1988). It assumes that the potential inside R_c may be expanded as a finite Dirichlet series of which we only keep the first two terms. The coefficients B_1 and B_2 are written in terms of R_c , a , and Z_s as follows:

$$B_1 = (Z_s e^2 / R_c) (1 - 2a/R_c) \exp(R_c/a) \quad (2)$$

$$B_2 = (2Z_s e^2 / R_c) (a/R_c - 1) \exp(R_c/2a). \quad (3)$$

As indicated in the second line of (1), outside R_c we adopt the empty-core model (Ashcroft 1966).

From equation (1), and taking into account (2) and (3), the unscreened form factor $w_0(q)$ is written as

$$w_0(q) = 4\pi\rho a^3 \left[B_1 J_1 / (1 + a^2 q^2)^2 + 8B_2 J_2 / (1 + 4a^2 q^2)^2 \right] - (4\pi Z_s e^2 / q^2) \rho \cos(qR_c) \quad (4)$$

where ρ is the number density, and

$$J_n = 2 - \exp(-R_c/na) \left\{ [(R_c/na)(1 + n^2 a^2 q^2) + (1 - n^2 a^2 q^2)] \sin(qR_c) / naq + [2 + (R_c/na)(1 + n^2 a^2 q^2)] \cos(qR_c) \right\} \quad n = 1, 2. \quad (5)$$

The effective interionic potential may be written, in atomic units, as follows:

$$v(r) = \frac{Z_s^2}{r} \left(1 - \frac{2}{\pi} \int F_N(q) \sin(qr) dq \right) \quad (6)$$

where the normalized energy wave number characteristic, $F_N(q)$, is given by

$$F_N(q) = (q^2 / 4\pi Z_s \rho)^2 w_0(q)^2 [1 - 1/\epsilon(q)] [1/(1 - G(q))] \quad (7)$$

with $\epsilon(q)$ denoting the dielectric function related to the local field function $G(q)$, which is taken from Ichimaru and Utsumi (1981).

We note that, with the above choices, the long-wavelength limit of the screened form factor is preserved, namely

$$\lim_{q \rightarrow 0} \frac{w_0(q)}{\epsilon(q)} \rightarrow -\frac{2}{3} E_F \quad (8)$$

where E_F is the Fermi energy.

2.2. VMHNC liquid theory

The starting point for the VMHNC is the Ornstein–Zernike equation, which relates the pair distribution function $g(r)$ and the direct correlation function $c(r)$,

$$g(r) - 1 = c(r) + \rho \int c(r') [g(|r - r'|) - 1] dr' \quad (9)$$

and the exact closure

$$c(r) = g(r) - 1 - \ln g(r) \exp(\beta v(r) + B(r)). \quad (10)$$

In equation (10) $\beta \equiv (k_B T)^{-1}$, where k_B is the Boltzmann constant and T the temperature, whilst $B(r)$ denotes the bridge function.

We follow Rosenfeld and Ashcroft (1979) in assuming the universality of the bridge function. We further assume that the universal $B(r)$ is adequately described by the Percus–Yevick (PY) hard spheres bridge function $B_{PY}(r, \eta)$ (see, cf, Rosenfeld 1986), namely

$$B(r) = B_{PY}(r, \eta) \quad (11)$$

where $\eta = \eta(\rho, \beta)$, the variational parameter is obtained as follows.

We require the reduced Helmholtz free energy functional $f^{\text{VMHNC}}(\beta, \rho; \eta) = F^{\text{VMHNC}}(\beta, \rho; \eta)/Nk_B T$ to be stationary with respect to variations of the variational parameter, namely

$$(\partial f^{\text{VMHNC}}(\beta, \rho; \eta)/\partial \eta)_{\beta, \rho} = 0. \quad (12)$$

f^{VMHNC} may be written as

$$f^{\text{VMHNC}}(\beta, \rho; \eta) = f^{\text{MHNC}}(\beta, \rho; \eta) - \Delta_v(\eta) \quad (13)$$

where $f^{\text{MHNC}}(\beta, \rho; \eta)$ is the MHNC free energy functional (Rosenfeld, 1986) and $\Delta_v(\eta)$ is given by

$$\Delta_v(\eta) = \frac{\rho}{2} \int d\eta' \int dr g_{PY}(r; \eta') \frac{\partial B_{PY}(r; \eta')}{\partial \eta'} - \delta_v(\eta) \quad (14)$$

In equation (14) $\delta_v(\eta)$ is chosen so as to obtain as close as possible a virial-compressibility thermodynamic consistency, but without enforcing it. In practice we follow Rosenfeld and use

$$\delta_v(\eta) = f_{\text{CS}}(\eta) - f_{\text{PYV}}(\eta) \quad (15)$$

where f_{PYV} and f_{CS} are the hard-sphere expressions from the PY virial and Carnahan–Starling reduced free energies, respectively.

The value of the variational parameter $\eta(\rho, \beta)$, obtained at a given thermodynamic state, is used to evaluate $B_{PY}(r; \eta)$ which, in turn, is used in (10) to solve for $g(r)$, in conjunction with (9). With the calculated pair distribution function we then evaluate $S(q)$.

3. Results

We have calculated the liquid structure of titanium and vanadium near the triple point, using as input densities and temperature the values given by Waseda (1981), namely $\rho = 0.0522 \text{ \AA}^{-3}$, $T = 1973 \text{ K}$ for Ti, and $\rho = 0.0633 \text{ \AA}^{-3}$, $T = 2173 \text{ K}$ for V.

For the numerical solution of the Ornstein–Zernike equation (9) and closure relation (10) we have used Gillan's (1979) algorithm; in all cases we find that 1024 points with a step size $\Delta r = 0.06 \text{ \AA}$ are sufficient for our calculations. For the minimization of the free energy, equation (12), we have used the linear search procedure discussed by Aviram and Tildesley (1978).

The potentials used in the calculations have been constructed using the following parametrization. The core radii R_c have been fitted following a procedure similar to that discussed by Regnaut (1989) and Hausleitner *et al* (1991), giving $R_c = 2.01 \text{ au}$ for Ti and $R_c = 1.656 \text{ au}$ for V.

The self-consistent calculations by Moriarty (1990) showed that for 3d and 4d transition metals at normal densities, Z_s takes on values in the narrow range $1.1 < Z_s < 1.7$, with a typical value of 1.4. In this work we use this typical value for V and one close to it, $Z_s = 1.3$, for Ti. This choice follows a search as to which value of Z_s , within the above range, is likely to predict the best results for $g(r)$ *vis à vis* experiment. The main effect is that, a larger value of Z_s , increases the height of the peaks of $g(r)$ without altering their positions. We illustrate this effect for the case of V, in figures 4(a) and 4(b) where we have changed Z_s from 1.4 to 1.3.

The value of the softness parameter a is restricted in order that $4 < R_c/a < 5$. It is only within this range of values that the d-band contribution to the potential results in a short-ranged repulsive part and an attractive tail; otherwise it is purely repulsive. A larger value of a will both shift the position of the peaks in $g(r)$ towards smaller values of r and damp the oscillations. A larger a results in a softer repulsive potential, although the positions of both the first zero and minimum are not affected by changes in a . These features are illustrated in figures 2(a) and 2(b) for Ti and figures 5(a) and 6(b) for V.

In an earlier work (Bretonnet *et al* 1992) we used a different parametrization which, combined with the Gibbs–Bogoliubov variational scheme, led to a reasonable description of the liquid structure. In that work the choice of $R_c = r_0/2$, where r_0 denotes the Wigner–Seitz radius, and the fitting of the softness parameter a to the small- q behaviour of $S(q)$, gives a value of $R_c/a > 5$ for both titanium and vanadium. This results in a soft repulsive potential which is all what is needed for a good description of the structure within the variational scheme. In the present work, only the imposed constraint $4 < R_c/a < 5$ allows the necessary interplay between the repulsive and attractive contributions to the potential which does justice to both the equilibrium pressure and the bulk modulus for the systems of interest. This constraint calls, in turn, for the more precise prescription of R_c which has been used in this work (see also the discussions by Regnaut (1989) and Hausleitner *et al* (1991)). Nevertheless we note that, regardless of the parametrization used, the VMHNC theory in conjunction with our potential always converges to a solution. Our results contrast sharply with the calculations carried out by Regnaut (1989) and Hausleitner *et al* (1991) using the full WH potential, where the integral equation theories fail to converge to a solution for $S(q)$, except for systems with a nearly full d band.

In figure 1 we have plotted the potentials used in the work, and have also included

the corresponding WH potentials for comparison. We note that the first minima in our potentials are shallower than those of WH. The energies of the potential wells are about four to five times smaller than the corresponding WH energies. Also the positions of the wells are displaced towards slightly larger values of r . The combination of these two features makes possible the convergence of the solutions of the integral equation theory of liquids, in accordance with the suggestion of Hausleitner et al (1991).

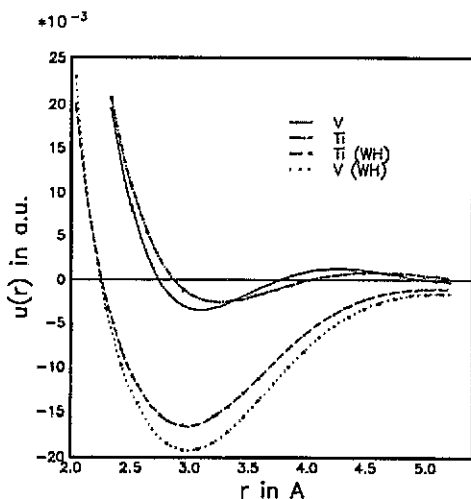


Figure 1. Effective interionic pair potentials for liquids Ti (dash-dotted line) and V (full line), obtained from the local form given by equation (4) using the following parametrization. Ti: $R_c = 2.01$ au, $Z_s = 1.3$, $a = 0.4771$ au; V: $R_c = 1.656$ au, $Z_s = 1.4$, $a = 0.368$ au (see text). The corresponding Wills-Harrison potentials are included for comparison: Ti (broken line), V (dotted line).

We now turn to the comparison of our calculated $S(q)$ s with the experimental data of Waseda (1981). In his book, Waseda states that, of all the 3d liquid transition metals, the x-ray diffraction data of Ti and V are the least accurate. The ensuing discussion disregards the uncertainties which may result from this, and considers the experimental data as listed by Waseda.

For Ti we have not been able to find a set of parameters, within the self-imposed constraints by which we carried out the parameter search, which does full justice to both positions and peak heights of $S(q)$. The positions of the peaks in the calculated $S(q)$ are always shifted to the right of the experimental data. Moreover any attempt to fit the position of the principal peak always result in a poorer fitting of the subsidiary peaks of $S(q)$. We also find that the oscillations in the calculated $S(q)$ die out more rapidly than in the experimental data, suggesting too soft a repulsive potential. Slightly increasing the value of a does not improve the agreement. We show in figures 2(b) and 3(b) the calculated $S(q)$ as they compare to the experimental data. The agreement is only fair, with the results obtained by using $a = 0.477$ au only marginally better.

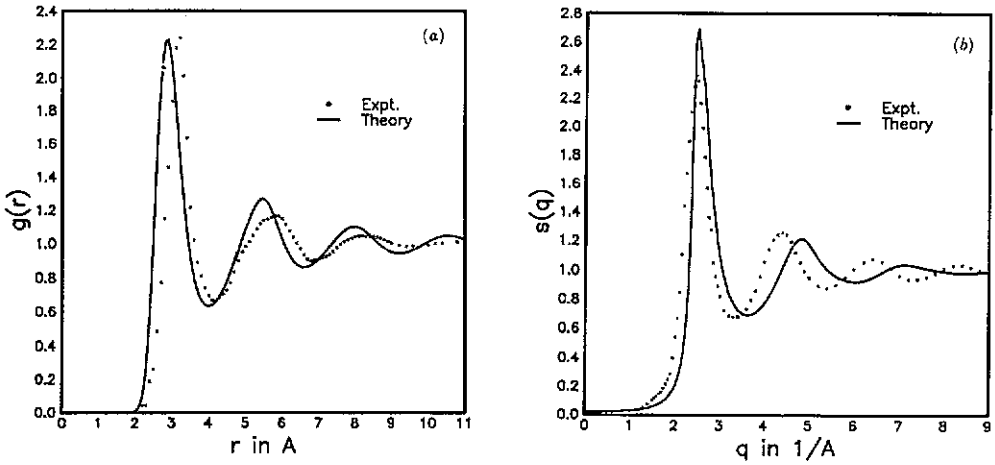


Figure 2. Structure of liquid Ti at density $\rho = 0.0522 \text{ \AA}^{-3}$ and temperature $T = 1973 \text{ K}$ using the following parametrization (see text): $R_c = 2.01 \text{ au}$, $Z_s = 1.3$, $a = 0.466 \text{ au}$, (a) pair distribution function $g(r)$: theory (full line); experiment (dotted line) (b) structure factor $S(q)$: theory (full line); experiment (dotted line).

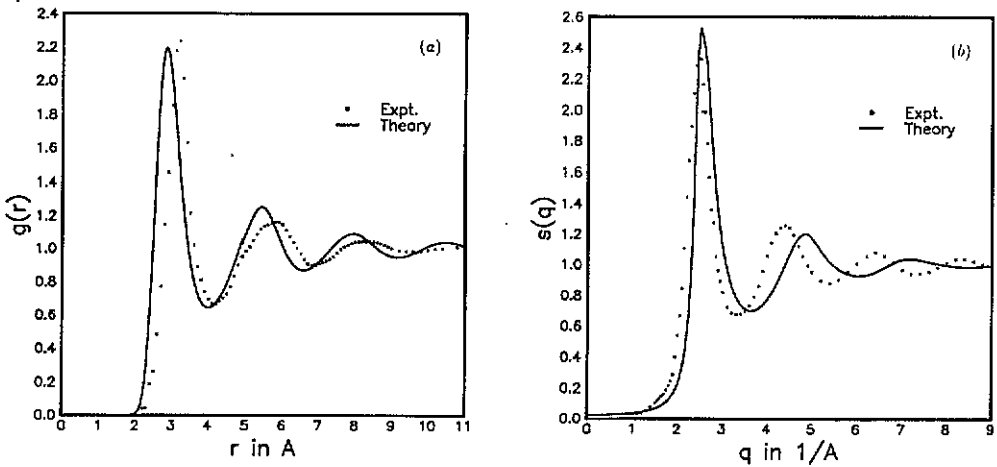


Figure 3. Structure of liquid Ti at density $\rho = 0.0522 \text{ \AA}^{-3}$ and temperature $T = 1973 \text{ K}$ using the following parametrization (see text): $R_c = 2.01 \text{ au}$, $Z_s = 1.3$, $a = 0.477 \text{ au}$, (a) pair distribution function $g(r)$: theory (full line); experiment (dotted line) (b) structure factor $S(q)$: theory (full line); experiment (dotted line).

The calculations of $S(q)$ for V show a much better agreement between theory and experiment. The results of $S(q)$ for different parametrizations are shown in figures 4(b), 5(b) and 6(b), with the $S(q)$ shown in the first of these figures probably in better agreement with experiment, except for the difference in height at the principal maximum of $S(q)$.

4. Conclusions

In the preceding section we have presented the first successful calculations of the

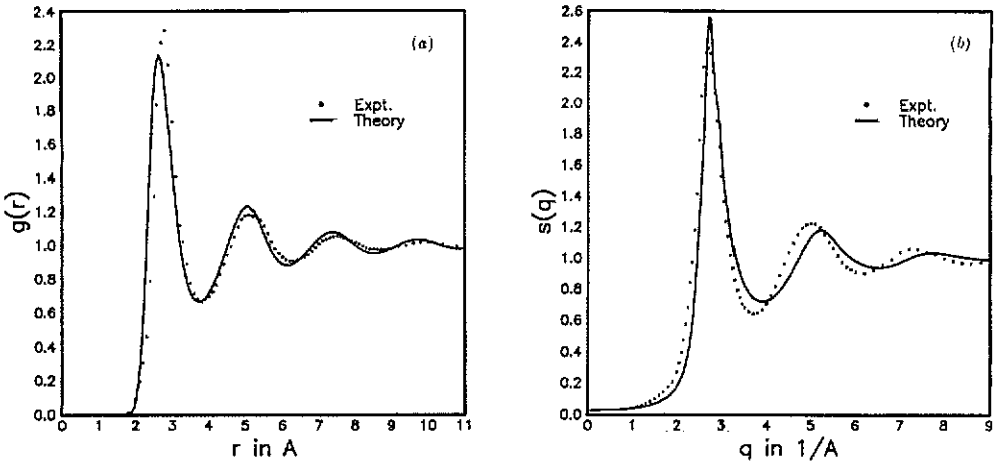


Figure 4. Structure of liquid V at density $\rho = 0.0633 \text{ \AA}^{-3}$ and temperature $T = 2173 \text{ K}$ using the following parametrization (see text): $R_c = 1.656 \text{ au}$, $Z_s = 1.3$, $a = 0.376 \text{ au}$, (a) pair distribution function $g(r)$: theory (full line); experiment (dotted line) (b) structure factor $S(q)$: theory (full line); experiment (dotted line).

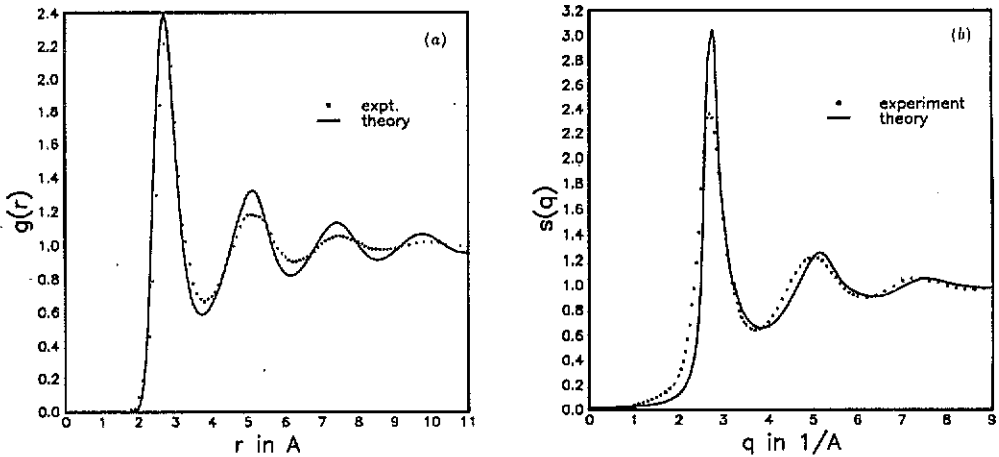


Figure 5. Structure of liquid V at density $\rho = 0.0633 \text{ \AA}^{-3}$ and temperature $T = 2173 \text{ K}$ using the following parametrization (see text): $R_c = 1.656 \text{ au}$, $Z_s = 1.4$, $a = 0.368 \text{ au}$, (a) pair distribution function $g(r)$: theory (full line); experiment (dotted line) (b) structure factor $S(q)$: theory (full line); experiment (dotted line).

liquid structure of the early transition metals titanium and vanadium using effective pair interionic potentials which we have developed for these systems, and an integral equation theory of liquids, the VMHNC.

The good accuracy in describing the structure of liquid V is tempered by the fair description of $S(q)$ achieved for liquid Ti, suggesting that there is still a need to improve on the potentials.

We believe the present work is an important step forward in the understanding of the liquid structure of transition metals. As noted in the introduction, previous calculations using the WH potentials in conjunction with integral equation theories of

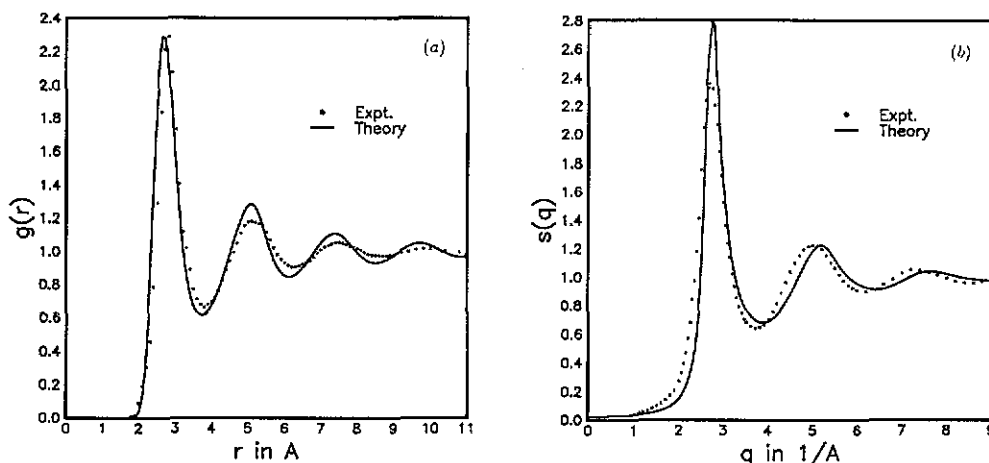


Figure 6. Structure of liquid V at density $\rho = 0.0633 \text{ \AA}^{-3}$ and temperature $T = 2173 \text{ K}$ using the following parametrization (see text): $R_c = 1.656 \text{ au}$, $Z_s = 1.4$, $a = 0.376 \text{ au}$, (a) pair distribution function $g(r)$: theory (full line); experiment (dotted line) (b) structure factor $S(q)$: theory (full line); experiment (dotted line).

liquids of the WCA-ORPA and HMSA variety, have failed to converge for the early 3d transition metals. We have found similar difficulties using the VMHNC (Bhuiyan *et al* (1991), unpublished results). Hence the problems of convergence may be attributed to the use of the WH potentials in liquid state calculations, for the reasons clearly discussed in some detail by Hausleitner *et al* (1991), who have also reported the failure of this potential to produce a reasonable structure of liquids V and Ti using MD simulations. Also, Adams and Foiles (1990), in their recent study of vanadium using an embedded-atom potential, report that whereas MD simulations yield the correct liquid density they produce a structure resembling an amorphous solid rather than a liquid.

The fact that we can now produce reasonable $S(q)$ s for the early 3d transition metals gives us the confidence to study the trends in both the liquid structure and the thermodynamic properties along the 3d series; even though the use of a local potential is, admittedly, an important limitation. Liquid transition metals have, so far, proved very difficult systems to study. Hence the present work may be regarded as a promising beginning, which will we hope lead to more exacting developments.

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