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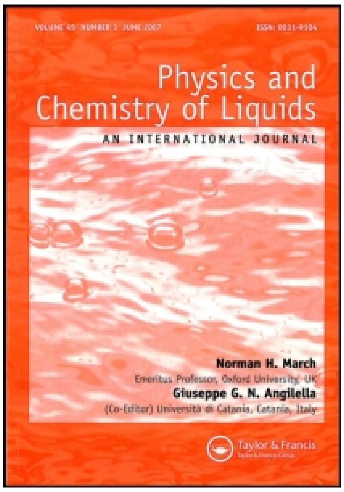

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INTERIONIC INTERACTIONS IN TRANSITION METALS. APPLICATION TO VANADIUM

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A new model is proposed for transition metals to obtain effective interionic pair potentials. The local form factor combines the empty-core model, which accounts for the nearly free electron band, and a contribution giving all the features associated with the *d* band obtained by an inverse scattering approach.

The effective interionic pair potentials depends on two parameters. The first is the core radius; the second is a measure of the softness of the repulsive potential. The influence of the parametrisation on the pair potential for vanadium is studied, and the results are compared with other potentials available in the literature.

KEY WORDS: Interaction in transition metals.

1 INTRODUCTION

The combination of pseudopotential theory and liquid state theories has led to a good understanding of, at least, the structural and thermodynamic properties of simple, s–p bonded, liquid metals. In comparison the study of similar properties of liquid transition metals has been slow to come, although a few tentative attempts have been put forward recently, some on the thermodynamic properties[1,2], others on the structure[3–6].

In the pseudopotential theory for simple metals the electrons are assumed to be free in between the pseudoatoms with their scattering completely described by the pseudoatom itself. Transition metals, with their broad *d* bands straddling the Fermi energy, are much more complicated. In this case, an incoming plane wave with the atomic *d* state gives rise to a resonance in the $l = 2$ phase shift which, for a given energy E, is

$$\tan \eta_2 = \frac{\Gamma}{2(E_d - E)} \tag{1}$$

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The d resonance is completely specified by the resonance energy E_d which characterises the position of the d band, and by the width Γ which is related to the virtual bound d state at a given ion site. The expansion in $\Gamma/(E_d - E)$ should, in principle, allow the incorporation of the effects due to the d resonance into a perturbation theory and thus extend pseudopotential theory to transition metals[7]. There is mounting evidence that, for transition metals, a successful theory not only should express the pair potential in terms of appropriate non local pseudopotentials, but it must also take account of multi-ion terms resulting, at best, in non-negligible three body contributions[8,9], a point we return to in the final section of this paper.

When it comes to liquid transition metals only the local form proposed by Wills and Harrison[10] has been used to probe the structure. These results show that, even with suitably adjusted core radii, integral equation theories of liquids of the WCA-ORPA[5] and HMSA[6] variety, while leading to reasonable $S(q)$'s for those systems with neary full d bands, they fail to produce results for those with a half and less than half-filled bands. Preliminary VMHNC calculations lend support to these conclusions[11]. While bearing in mind the remarks made at the end of the preceeding paragraph, there is a case to search for pair interactions for liquid transition metals which, at least, are capable of predicting their structure.

The purpose of this paper is to present a new local form factor for transition metals, leading to an effective interionic pair potential. In Section 2 we present the formalism and the results for Vanadium; in Section 3 we discuss our results in the context of recent developments.

2 THEORY AND RESULTS

We assume it is possible to separate the contribution due to the nearly free electron band formed by the s and p states from that obtained from Eq. (1) by using an inverse scattering approach giving all the features associated with the d band. For the former we assume the empty-core model potential[12]. The latter, which takes account of the s–d mixing, is based on the distorted plane-wave method for deducing potential interactions from elastic scattering phase shifts[13–15].

It has been shown by Swan[14] that an approximate potential may be obtained—with reasonable accuracy—from the knowledge of the d-phase shift by just using the first two terms of a Dirichlet series sum of short range exponential functions, namely

$$u_c(r) = \sum_{n=1}^{2} B_n \exp\left[-\frac{r}{na}\right]. \tag{2}$$

The above potential may be either purely attractive or attractive with a repulsive core depending on the values taken up by the three parameters B_1, B_2 and a.

Since the s–d mixing effect is written as the sum of individual atomic terms, just as the pseudopotential, we may spatially superpose the empty-core potential to the

s–d mixing potential to obtain the following bare potential

$$w(r) = \begin{cases} \sum_{n=1}^{2} B_n \exp\left[-\dfrac{r}{na}\right] & r < R_c \\ -\dfrac{Z_s e^2}{r} & r > R_c \end{cases} \tag{3}$$

where R_c stands for the empty-core radius and Z_s for the effective number of valence electrons per atom.

We note that the effective total potential is weak and without explicit reference to the d band width. It simply modifies the core of the empty-core model and can be treated as a perturbation. Besides the requirement that $w(r)$ be continuous at the core, $r = R_c$, we impose the weak condition that its first derivative be also continuous at the core. The reason for appealing to this condition is that, physically, the repulsive part of $u_c(r)$ should not affect drastically the behaviour of the s electrons, while the attractive part should only slightly deepen the interaction potential so as to contract the s states making the transition metals more compact and more tightly bound. Although d states extend further away from the nucleus than typical core electrons, we physically expect d electrons to be fairly well localised on their own atoms with the ability to hop to others through the s–d mixing. Hence, B_1 and B_2 may be deduced from the values of the parameters a, R_c, and Z_s through the expressions

$$\begin{aligned} B_1 &= \frac{Z_s e^2}{R_c}\left(1 - \frac{2a}{R_c}\right)\exp\left(\frac{R_c}{a}\right) \\ B_2 &= \frac{2Z_s e^2}{R_c}\left(\frac{a}{R_c} - 1\right)\exp\left(\frac{R_c}{2a}\right). \end{aligned} \tag{4}$$

From Eq. (3), and taking into account (4), the unscreened form factor $w_0(q)$ is written as

$$w_0(q) = 4\pi \frac{N}{V} a^3 \left[\frac{B_1 J_1}{(1 + a^2q^2)^2} + \frac{8B_2 J_2}{(1 + 4a^2q^2)^2}\right] - \frac{4\pi Z_s e^2}{q^2}\frac{N}{V}\cos(qR_c) \tag{5}$$

where the J_n are defined by

$$J_n = 2 - \exp\left(-\frac{R_c}{na}\right)\left\{\left[\frac{R_c}{na}(1 + n^2a^2q^2) + (1 - n^2a^2q^2)\right]\frac{\sin qR_c}{naq} + \left[2 + \frac{R_c}{na}(1 + n^2a^2q^2)\right]\cos qR_c\right\}. \tag{6}$$

It is worth noting that, owing to its particular form, the term corresponding to the s–d mixing effects tends to zero when q tends to zero, and the long-wavelength limit of the screened form factor $w(q)$ is preserved,

$$\lim_{q \to 0} \frac{w_0(q)}{\varepsilon(q)} \to -\frac{2}{3} E_F. \tag{7}$$

It is also useful to point at the similarity, inside the core, between this model potential and the more elaborated norm-conserving pseudopotential of Bachelet *et al*[16].

We apply this formalism to the case of vanadium. This has been a much studied system and, as a result, useful comparisons can be made. Using standard transformations the effective interionic pair potential is given by

$$u(r) = \frac{Z_s^2 e^2}{r} \left[1 - \frac{2}{\pi} \int F_N(q) \frac{\sin qr}{q} \, dq \right] \tag{8}$$

where $F_N(q)$ is the normalised energy-wavenumber characteristic

$$F_N(q) = \left(\frac{q^2}{4\pi e^2 Z_s} \frac{V}{N} \right)^2 w_0^2(q) \left[1 - \frac{1}{\varepsilon(q)} \right] \left[\frac{1}{1 - G(q)} \right] \tag{9}$$

and $\varepsilon(q)$ is the dielectric function related to the local-field function $G(q)$.

We choose for the number of valence electrons per atom the value $Z_s = 1.425$, taken from the self-consistent pseudopotential theory for vanadium of Moriarty[8]. For the electron–electron interaction we use the local-field function $G(q)$ of Ichimaru and Utsumi[17]. The model parameters R_c and a should, in principle, be chosen so as to give the correct phase shift or fit some experimental quantities. However, in this study we choose values of R_c close to that used by Wills and Harrison[10], and values for a such that $4 < (R_c/a) < 5$ for which $u_c(r)$ is guaranteed to have a repulsive short range and an attractive tail.

We now turn to the results of our calculations. In Figure 1 we show our effective pair interionic potential for vanadium with $R_c = 0.87$ Å and $(R_c/a) = 4.5$. This is compared with the effective potentials of Wills and Harrison[10] (WH), Finnis and Sinclair[18] (FS), and Moriarty[8] (M); for the last two we are only considering their pairwise contribution to the total potential.

The WH potential is the sum of three distinct contributions: (i) an s-electron like term; (ii) an attractive potential proportional to the d-band width; and (iii) a repulsive potential arising from the shift of the centre of gravity of the d band. The last two terms are responsible for the fairly hard repulsive behaviour of $u(r)$ and for the rather flat bottom in the first minimum. We note that this potential has exactly the same contribution of s electrons as ours, given the same choice for R_c. The pairwise contribution to the N-body potential proposed by FS is approximated by a polynomial (in their original paper) cut-off at short range, and its parameters are adjusted

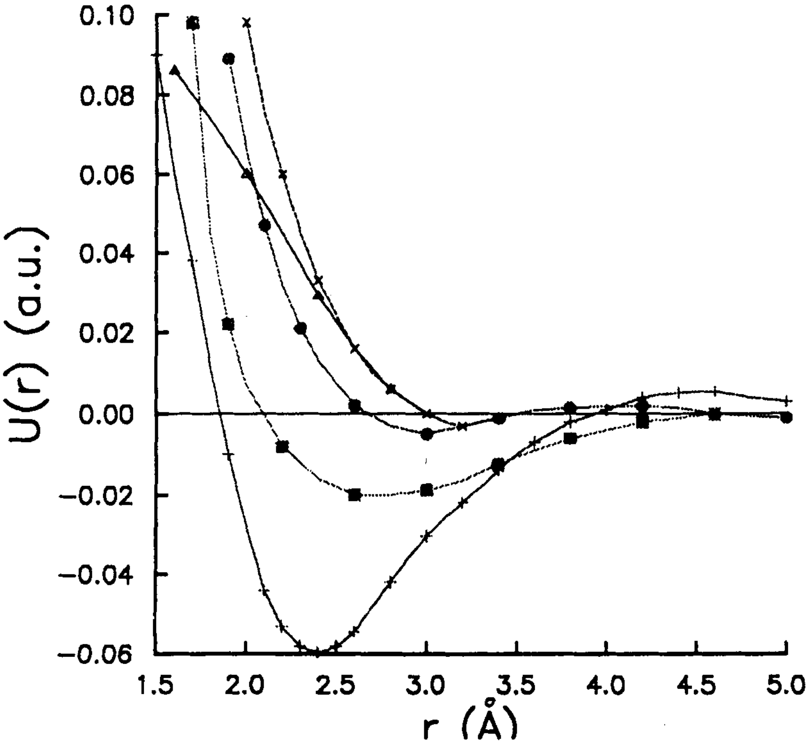

Figure 1 Effective interionic pair potentials for vanadium.

—●—●—: this work ($R_c = 0.87$ Å; $R_c/a = 4.5$)
—■—■—: Wills and Harrison (1983)
—▲—▲—: Finnis and Sinclair (1984)
—+—+—: Moriarty (1988)

Ashcroft's empty-core model, which completely ignores the *d*-electrons, is included for comparison: -- × -- × -- ($R_c = 0.87$ Å).

so as to reproduce exactly the values of the elastic constants. The agreement with experiment basically requires that the slopes of $u(r)$ at the nearest and next-nearest neighbour positions have the correct value. Over this range the FS potential overlaps with that obtained from the empty-core model, which is also included in the figure for comparison. Moreover the FS potential is purely repulsive, with a very soft core; this probably restricts its use to problems where only a small part of the repulsive potential and/or its derivatives are actually probed. The more recent *M* potential was obtained using the density-functional formulation of a generalised pseudopotential theory. The non-negligible contribution due to three-body forces which, according to Moriarty, is strongly angular dependent and strongly repulsive for near-neighbour interactions, has not been included in our Figure 1.

The potential proposed in this work has some promising features. The difficulties encountered with WH potential lies in the nature of its attractive forces, in particular the very deep potential well. Some improvements were made[5,6] by increasing the value of R_c, thus shifting the position of the well and making it shallower. This procedure works well for the very late liquid transition metals but not for those with half and less than half-filled *d* bands. Our potential possesses these two features; the potential well is both shallower and its position is displaced towards larger values of *r*, as shown in Figure 1. The potential well of the pair contribution to the *M* potential is even deeper and at a lower value of *r* than WH, suggesting greater difficulties. Even if use is made of a procedure borrowed from the classical theory of fluids[19] to construct an effective pair potential which incorporates the three-body forces—whose feasibility we are currently checking—it is unlikely that this will correct the problem, given that the contribution of the latter is about one order of magnitude smaller than the pairwise term depicted in Figure 1.

Figure 2 illustrates the role of R_c and *a* in the pair potential. The most striking feature is the stability of the position of the first zero of the potential, which is rather insensitive to the variation of either or both parameters. A decrease in R_c results in a slightly softer repulsive part, whereas the long range Friedel oscillations are damped with a splitting of the first maximum. These two changes are even more marked when *a* is decreased. In particular, the hardness of the repulsive part of $u(r)$ is very sensitive to variations of *a*. On the other hand, the positions of the first zero and the minimum of the attractive well—which correspond to the first and second nearest neighbour distances, 2.63 Å and 3.04 Å respectively—are unaffected by the changes in *a*. Our effective pair potential for vanadium exhibits a repulsive part clearly dominated by the presence of *d* states, and also a distortion in the Friedel oscillations which could be related to the non-spherical nature of the Fermi surface in transition metals.

3 DISCUSSION

A simple model potential has been derived to partially include the *d* **state effects and has been illustrated for Vanadium, which is one case for which the WH potential is unable to predict the liquid structure even using Molecular Dynamics simulations**[6]. A number of properties need to be studied in order to have a full picture of the flexibility of this model potential, and we also have to produce a precise prescription for the choice of parameters. Work on these problems for all the transition metals is in progress and will be reported on completion.

Admittedly a pair potential description is more difficult to justify for transition metals than for simple metals, and many studies have been devoted to this question, though mainly addressed to problems in the solid state. As our interest lies in the study of the properties of liquid transition metals, it is extremely useful—and probably necessary on computational grounds—to consider the proposition that *effective* pair potentials are developed which, coupled with volume terms that incorporate the effects of the many-body forces, lead to a better understanding of the properties of these systems. If such a proposition is valid, then we submit that the effective pair potential proposed in this work is a promising starting point.

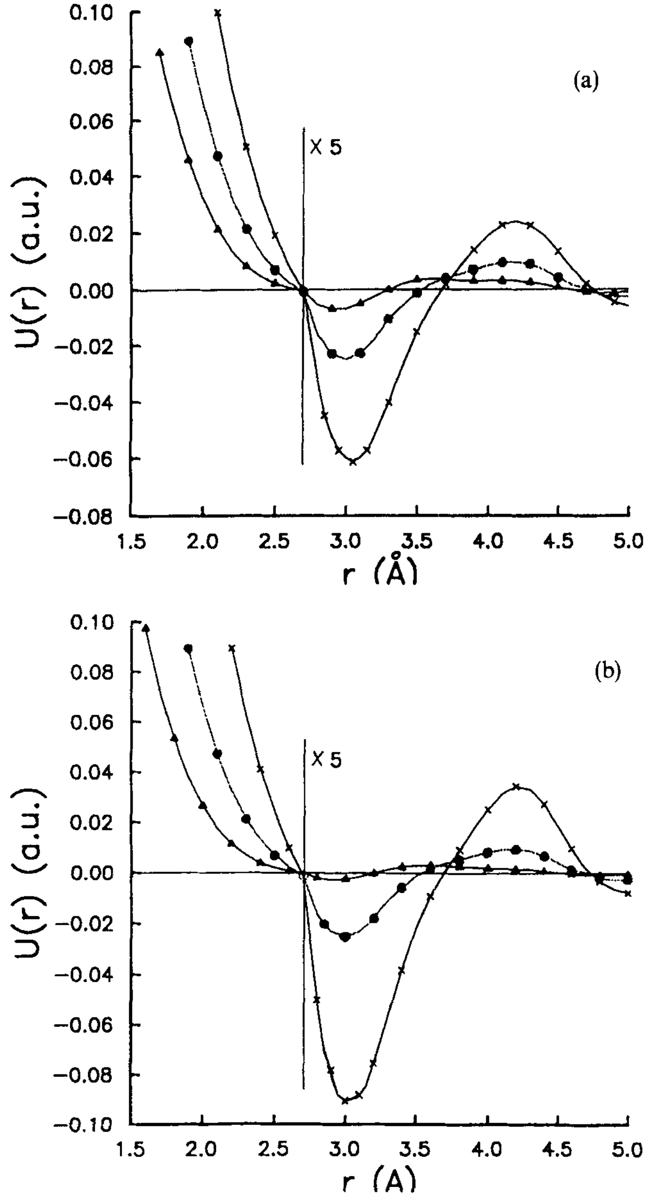

Figure 2 The effects of parametrisation on the effective pair potential of this work. Note that the scale s amplified by a factor of 5 for values of r larger than the position of the first zero of the potential $r > 2.63$ Å)

a) the effect of R_c ($a = 0.193$ Å): —×—×—, $R_c = 0.92$ Å; $R_c/a = 4.77$
: —●—●—, $R_c = 0.87$ Å; $R_c/a = 4.50$
: —▲—▲—, $R_c = 0.82$ Å; $R_c/a = 4.25$
b) the effect of a ($R_c = 0.87$ Å): —×—×—, $R_c/a = 5.0$
: —●—●—, $R_c/a = 4.5$
: —▲—▲—, $R_c/a = 4.0$

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