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Liquid structure of transition metals: investigations using molecular dynamics and perturbation- and integral-equation techniques

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Abstract. We present investigations of the structure of liquid 3d and 4d transition metals using molecular dynamics simulations, thermodynamic perturbation theories, and integral-equation techniques. The effective pair interactions are calculated within a hybridized nearly-free-electron-tight-binding theory. The parameters determining the d electron contribution to the potential are deduced from the known electronic properties of the crystalline metals, the core radius of the pseudopotential specifying the s-electron contribution is determined by a molecular-dynamics fit of the liquid structure. The resulting pair interactions are used to test the applicability of liquid state perturbation techniques and integral equations to liquid transition metals.

1. Introduction

Recently we have presented quite successful *ab initio* calculations of the structure and thermodynamic properties of liquid transition metals, based on effective pair interactions calculated within a hybridized nearly-free-electron-tight-binding (NFE-TB) theory [1] and on a thermodynamic variation method with a soft-sphere (hard-sphere Yukawa HSY) reference system [2]. The results show that despite their relatively crude form the pair potentials describe the interplay of s and d electrons in transition-metal bonding quite well. It is also found that a soft-sphere reference system is sufficient to account for most of the differences in the structure of molten transition metals and of molten simple metals: transition metals are considerably softer. This might seem surprising, but is readily understood in terms of competing s and d electron interactions. It is quite surprising, however, that the rather strong attractive interactions arising from covalent d electron bonding (they are up to ten times stronger than the attractive interactions in simple metals) should have only a rather small influence on the structure of the melt. A first attempt to solve this problem was made by Regnaut [3] using the optimized random-phase approximation (ORPA). At the level of the Weeks–Chandler–Anderson (WCA) perturbation theory, which considers only the short-range repulsive forces, the results are very similar to those obtained using the soft-sphere variational approach. Including the attractive forces via the OPRA leads to rather different results: for liquid Ni one finds a pronounced increase of the structure factor in the region of the first peak and at low momentum transfer (indicating the existence of strong density fluctuations), for liquid Co and Fe the attractive forces induce a divergence of the structure factor in the long-wavelength limit, the ORPA has no solution for the elements

from the middle of the transition metal series. Regnaut showed that a slight modification of the *s* electron contribution to the effective pair interaction (increasing the pseudopotential radius) allows one to achieve reasonable results for metals with nearly full (Co, Ni) or nearly empty (Sc) *d* bands, but does not solve the problem for the metals with a half-filled *d* band (and hence with the strongest covalent bonding effects). It is not immediately clear whether this difficulty arises from the limited validity of the thermodynamic perturbation theory or from the breakdown of the NFE-TB approach to the interatomic forces. In this work we continue the search for reliable pair interactions for liquid transition metals. We re-examine the dependence of the pair potentials on the pseudopotential- and tight-binding parameters, in particular on the pseudopotential core radius R_c . We use molecular dynamics simulations to test the validity of the potentials for calculating the liquid structure. We find that except for the lightest 3d metals (Ti, V) we can achieve a very accurate description of the liquid structure for all 3d and 4d elements with potential parameters that are consistent with the known electronic properties. Finally we discuss the application of liquid state integral equations to transition metals. We confirm Regnaut's result that the ORPA describes liquid Fe, Co and Ni quite well, but fails completely for the *d* elements with half-filled bands and stronger covalent interaction. Similarly we show that the modern thermodynamically self consistent integral equations lead to realistic structures for liquid Ni, Fe, Co, but encounter serious problems if applied to transition metals with half- and less than half-filled bands.

2. Pair interactions for transition metals

In the hybridized NFE-TB approach to interatomic forces in transition metals the total energy is given as the sum of a volume energy and a pair-interaction term [1, 2]. The volume-dependent pair potential is written in the form

$$\Phi(R) = \Phi_s(R) + \Phi_{d\text{-bond}}(R) + \Phi_{d\text{-rep}}(R). \quad (1)$$

The *s*-electron contribution is written in the standard form given by pseudopotential and linear response theories [4, 5] (assuming an empty-core form for the electron-ion pseudopotential, with core radius R_c)

$$\Phi_s(R) = \frac{2Z_s^2}{R} \left(1 + 16 \int_0^\infty \frac{\chi(q)}{\epsilon(q)} \cos^2(qR_c) \frac{\sin(qR)}{q^3} dq \right) \quad (2)$$

where $\chi(q)$ and $\epsilon(q)$ are the susceptibility and the dielectric function of the electron gas and Z_s is the number of *s* electrons per atom (we use atomic units, energies are given in Rydbergs). Exchange and correlation are included in the dielectric function by using the Ichimaru-Utsumi [6] form of the local field corrections. The bonding contribution from the *d* electrons may be written in the form

$$\Phi_{d\text{-bond}}(R) = C_{d\text{-bond}}/R^5 \quad (3)$$

The R^5 dependence arises from the distance dependence of the *d*-*d* hopping integrals, the strength of the potential is determined by the bond energy via

$$C_{d\text{-bond}} = \frac{2}{N_c} \int_{-\infty}^{E_F} (E - \epsilon_d) n_d(E) dE \quad (4)$$

where $n_d(E)$ is the density of states (DOS) of the *d* electrons, ϵ_d the *d*-electron energy in the free atom and N_c the coordination number. If we use a rectangular DOS for the *d*

Table 1. Temperature T , atomic volume Ω_a , s- and d-band occupancies Z_s , Z_d atomic d-electron energy ε_d and band width W_d for 3d and 4d transition metals.

	T (K)	Ω_a (\AA^3)	Z_s	Z_d	ε_d (Ryd)	W_d (Ryd)
Ti	1973	19.17	1.39	2.61	-0.155	0.448
V	2173	15.79	1.36	3.64	-0.194	0.499
Cr	2173	13.77	1.42	4.58	-0.231	0.483
Mn	1573	15.28	1.43	5.57		0.412
Fe	1833	13.23	1.42	6.58	-0.230	0.355
Co	1823	12.71	1.43	7.57	-0.332	0.320
Ni	1773	12.63	1.40	8.60	-0.363	0.278
Y	1773	35.75	1.31	1.69	-0.130	0.485
Zr	2173	25.55	1.30	2.70	-0.184	0.616
Nb	2773	19.71	1.29	3.71	-0.237	0.716

electrons (the Friedel model), equations (3) and (4) reduce to the form proposed by Wills and Harrison [1] and used in [2]. The disadvantage of the Friedel model is that it cannot be directly extended to binary alloys. For the binary systems we have to use a simple reference system with the proper coordination number that allows for an analytical calculation of the DOS and of the bond energy. A very convenient reference system is the Bethe lattice [7]. For a monoatomic system with only nearest-neighbour hopping integrals and large coordination numbers the Bethe lattice has a semi-elliptic DOS

$$n_d(E) = 2\sqrt{1-x}/\pi W_d \quad |x| \leq 1 \quad (5a)$$

$$x = 2(E - \varepsilon_d)/W_d \quad (5b)$$

where W_d is the width of the d band,

$$W_d = 4\sqrt{(N_c - 1)h(d)} \quad (6)$$

and $h(d)$ is the hopping integral. Using (5a) in (4) leads directly to

$$C_{d-\text{bond}} = -(2W_d/3\pi N_c)(1 - x_F)^{3/2} \quad (7a)$$

$$x_F = 2(E_F - \varepsilon_d)/W_d. \quad (7b)$$

The Fermi energy is determined by the d-band occupancy Z_d ; for the semielliptic DOS it is given by the solution of the equation

$$Z_d = \frac{1}{2} + (1/\pi) \arcsin x_F + (x_F/\pi)\sqrt{1-x_F^2}. \quad (8)$$

The repulsive energy is associated with the shift of the center of gravity of the d band. Within the same model it may be written as [1]

$$\Phi_{c-\text{rep}} = C_{d-\text{rep}}/R^8 \quad (9)$$

$$C_{d-\text{rep}} = (8/25)Z_d W_d^2 R_0^{10} \quad (10)$$

where R_0 is the atomic radius. Equation (1) gives a complete description of the effective pair interaction, depending on the numbers Z_s and Z_d of the s and d electrons, the band width W_d , the atomic electron energy ε_d , and the pseudopotential core radius R_c . The atomic d electron energies are calculated for the configuration $s^1 d^{N-1}$ (N is the group number) [8]. The d-band widths are assumed to be equal to those in the crystalline metals, our values are taken from the work of Andersen and Jepsen [9]. The s- and d-band occupancies are taken from the self-consistent calculation of Moruzzi [10]. All parameters are compiled in table 1. Note that all parameters are very close to those used

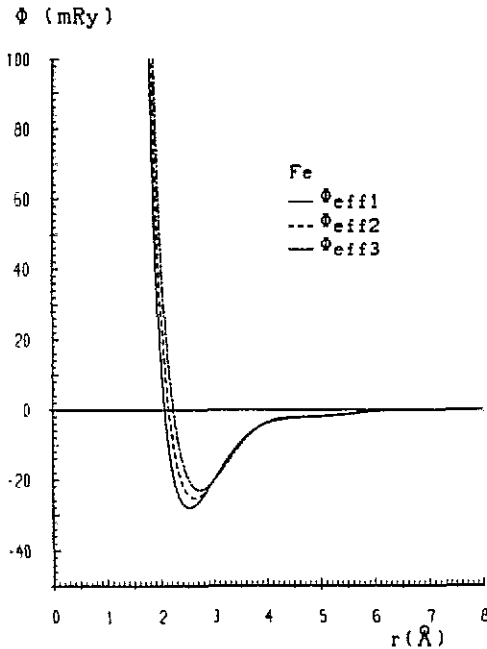


Figure 1. Effective interatomic pair potential for liquid Fe at $T = 1833$ K, calculated with different s-electron pseudopotential radii R_c : — $R_c = R_c(p = 0) = 0.77$ Å, - - - $R_c = 0.80$ Å, - · - $R_c = 0.85$ Å.

in [2]. The largest difference is in the s-band occupancy. The self-consistent calculations yield values of Z_s which are consistently lower than the constant value of $Z_s = 1.5$ proposed by Wills and Harrison and used in [2]. The only parameter that cannot be fixed *a priori* is the pseudopotential core radius. We previously [2] proposed to determine R_c from a first-order approximation to the zero-pressure condition. Combined with the soft-sphere variational method the resulting interatomic potentials give a quite realistic description of the liquid structure. However, if we use the same potential in molecular dynamics simulations we find that the attractive forces neglected in the variational approach lead to a large negative pressure and a clustering of the atoms. No homogeneous solution is possible, the reason being that the interatomic potentials bind the atoms too strongly and at distances which are too short. This may be corrected by choosing a larger core radius. A larger R_c shifts the position of the first minimum of $\Phi(R)$ to greater distances and makes the potential less attractive. This is illustrated in figure 1 for the example of Fe, figure 2 shows the decomposition of the effective potential into s- and d-electron contributions. It is clear that the precise form of the total potential depends in a rather delicate way on the interplay of the repulsive s- and attractive d-electron forces around the nearest-neighbour distance. With an appropriate choice of R_c , reasonably accurate liquid structures are found for all 3d and 4d elements. The values adopted in this work are compiled in table 2. Note that Wills and Harrison [1] and Regnaut [3] had pointed out that the simple one-parameter form of the pair interaction does not allow a simultaneous fit of the pressure and the bulk modulus. We find that the values resulting from the molecular dynamics fit fall between these two values (table 2), hence they represent a reasonable compromise for the thermodynamic properties.

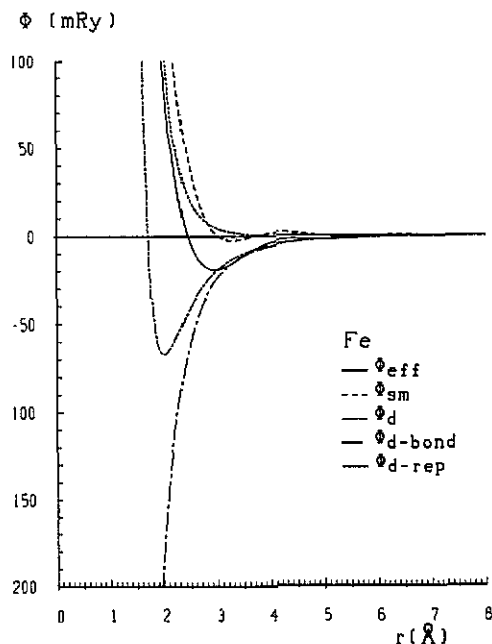


Figure 2. Individual contributions to the effective pair interaction in liquid Fe. Symbols as indicated.

Table 2. Core radii R_c for the s -electron pseudopotential in transition metals: $R_c(\rho)$, $R_c(B)$ calculated by fitting the first-order approximation to the pressure (ρ) and bulk modulus (B). R_c determined by the optimal MD fit to the liquid structure (see text).

	$R_c(\rho)^a$ (Å)	$R_c(B)^b$ (Å)	R_c (Å)
Ti	0.97 (0.90)	(1.09)	1.06
V	1.01 (0.90)	(1.10)	1.08
Cr	0.92 (0.85)	(1.04)	0.94
Mn	0.86 (0.80)	(0.88)	0.87
Fe	0.77 (0.72)	(0.94)	0.80
Co	0.64 (0.63)	(0.82)	0.69
Ni	0.52 (0.53)	(0.70)	0.58
Y	1.23		1.30
Zr	1.18 (1.12)		1.30
Nb	1.15		1.26

^a after [2]

^b after [3]

Values in brackets calculated assuming a constant number of s electrons of $Z_s = 1.5$ as in [1–3].

3. Molecular dynamics simulations

We have performed microcanonical molecular dynamics simulations (MD) of liquid 3d and 4d transition metals. Our molecular dynamics routines are based on a fourth-order

predictor–corrector algorithm for the integration of the equation of motion, and on an efficient network-cube algorithm for determining the neighbours within the interaction sphere and for storing the nearest-neighbour information [11]. All simulations were performed for $N = 1372$ particles in a periodically repeated cubic cell, with a time increment of $\delta t = 10^{-15}$ s. The interatomic potential was set to zero for distances larger than about 25% of the diameter of the MD cell. Typical runs took 3–4000 steps for melting and equilibration and about as many for production. Pair correlation functions are based on averages over about 40 independent configurations taken at intervals of 100 time steps. The pair correlation function $g(R)$ and the static structure factor $S(q)$ calculated for all 3d and some 4d transition metals are given in figures 3 to 5. Except for the lightest 3d metals Ti and V, the MD simulations achieve a good fit to the diffraction data. Note that the results are quite sensitive to the precise form of the pair potentials, see section 2. The rather poor agreement between the simulation results and experiment for Ti and V remains puzzling, especially as we find a very good agreement for the homologous elements Zr and Nb. Note that the structure factor of liquid Ti reported in the literature [12] is definitely anomalous: the ratio of the position of the first two peaks is $q_2/q_1 \approx 1.76$ against a value of $q_2/q_1 \approx 1.83$ – 1.86 for all other transition metals. Except for these two problematic cases we now have a set of interatomic interactions that can serve as a basis for reliable simulations of the liquid transition metals.

4. Thermodynamic perturbation theory and integral equations

4.1. Variational calculations

With the revised potentials, the variational approach yields rather poor results both in the hard- and in the soft-sphere form (figure 6). The hard-sphere reference system is clearly inappropriate for these rather soft interactions, the soft-sphere (HSY) reference system fits the first peak in $g(R)$ much better, but still overestimates the long-range oscillations. Clearly this is related to the neglect of the attractive forces: $\Phi(R)$ is still quite strongly attractive between 3 and 4 Å (see figures 1 and 2) and this tends to increase $g(R)$ in the region of the first minimum and to flatten the second peak.

4.2. ORPA

In the WCA–ORPA perturbation theory [5, 13, 14] the total pair interaction $\Phi(R)$ is decomposed into a purely repulsive short-range potential $\Phi_0(R)$ and a predominantly attractive long-range part $\Phi_1(R)$. $\Phi_0(R)$ corresponds to a soft-core fluid which is treated as a perturbation to the HS fluid in the WCA [13] method. The ORPA is defined by the closure relations

$$c_1(R) = -\beta\Phi_1(R) \quad R > \sigma \quad (11a)$$

$$g_1(R) = 0 \quad R < \sigma \quad (11b)$$

to the residual Ornstein–Zernike equation for the Φ_1 interaction. $c(R)$ and $g(R)$ are the direct correlation function and pair correlation function, σ is the hard-core diameter of the reference system. In the original version of the WCA theory the corrections are added in the pair correlation function. In the Jacobs–Andersen (JA) variant [15] (corresponding to a partial resummation of higher order terms) the corrections are added in the direct correlation function (for details see e.g. [5, 14, 15]). Figure 7 shows the different levels

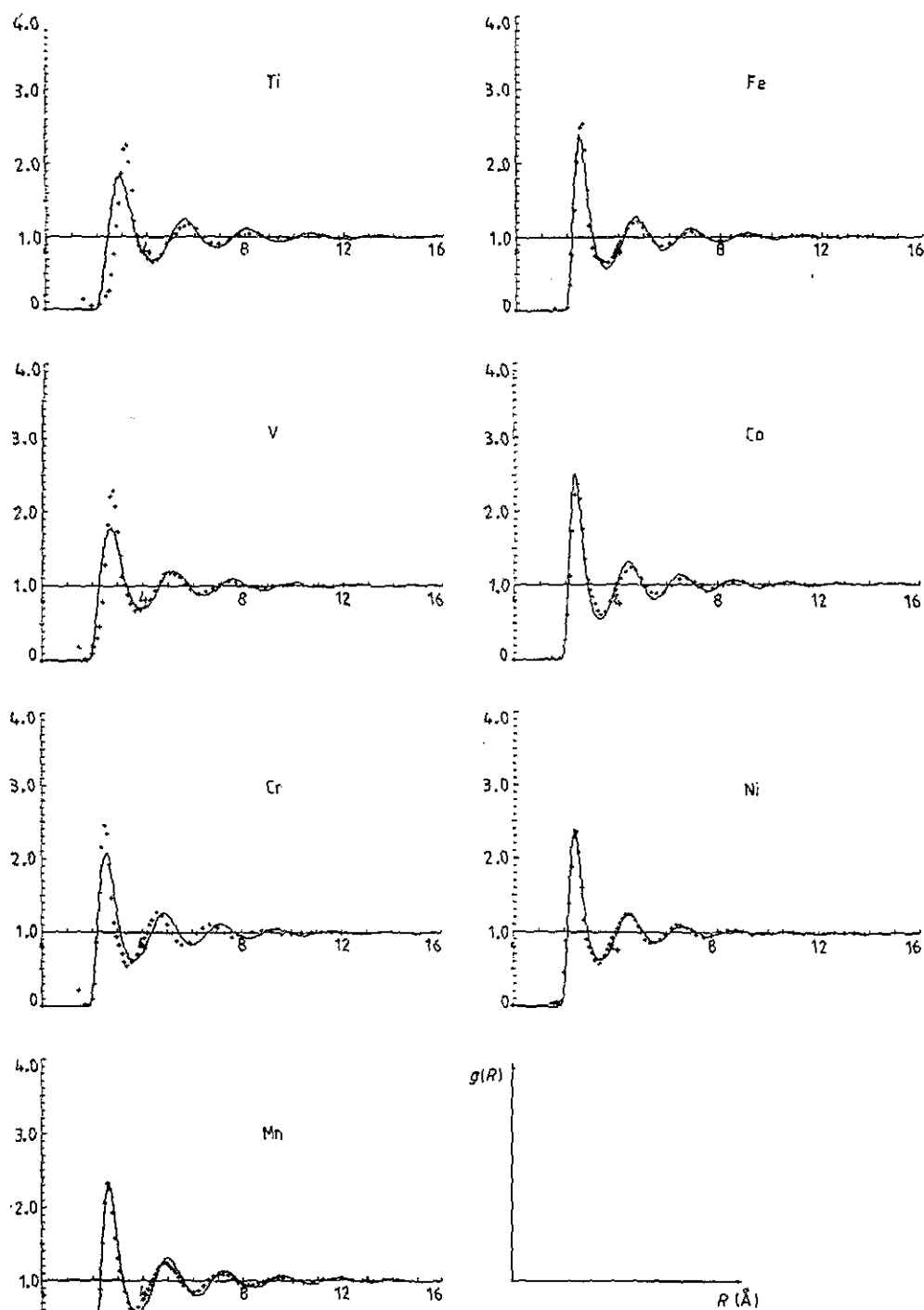


Figure 3. Pair correlation function $g(R)$ for the liquid 3d transition metals from Ti to Ni. Full curves: MD simulation, crosses: experiment [12].

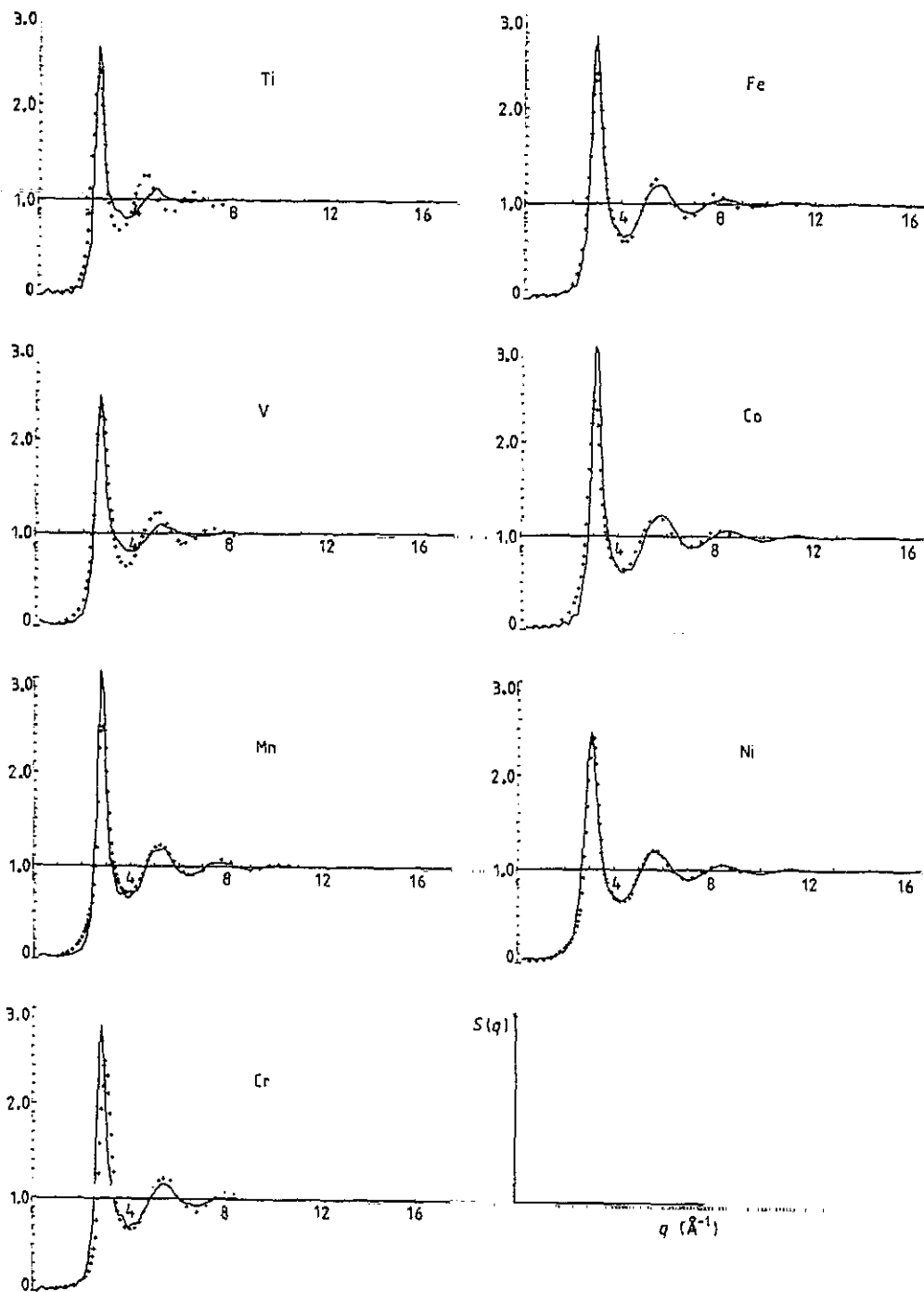


Figure 4. Static structure factor $S(q)$ for the liquid 3d transition metals from Ti to Ni. Full curves: MD simulation, crosses: experiment [12].

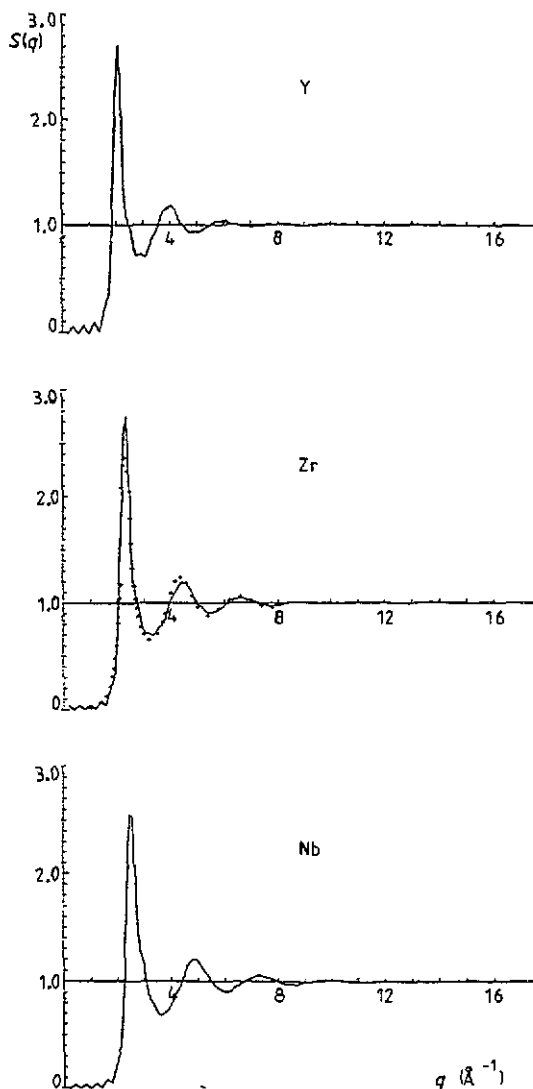


Figure 5. Static structure factor $S(q)$ for the liquid 4d transition metals Y, Zr and Nb. Symbols are as in figure 4.

of approximation to the ORPA for Fe, Co and Ni. The HS and WCA approximations are very similar to the hard- and soft-sphere variational calculations. It is essential to use the JA variant of the theory to eliminate the broad unphysical hump in $S(q)$ near $q \sim 1 \text{ \AA}^{-1}$. The comparison of the WCA and JA variants of the ORPA gives a rather nice illustration of the interplay of soft repulsive and attractive forces. Including the attractive forces in the ORPA leads to a strong increase of the first peak in $S(q)$ if the correction $B_0(R)$ for the softness of the repulsive forces is included only the linear approximation of WCA [13]. In the JA approach a partial summation of terms up to infinite order in $B_0(R)$ leads to a substantial damping of the first and second peaks in $S(q)$, demonstrating that the effect of strong covalent attraction is partially compensated by the exceptional softness of the potential. The full solution of the JA-ORPA represents a good approxi-

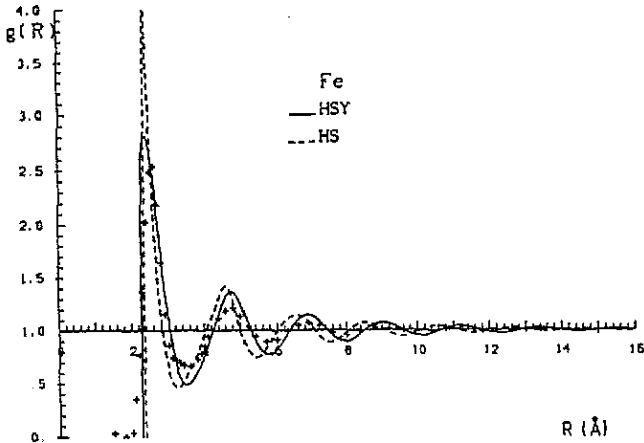


Figure 6. Pair correlation function $g(R)$ for liquid Fe determined by a thermodynamic variational calculation using the hard-sphere (HS) and a soft-sphere (HSY) reference system ($\eta_{HS} = 0.512$, $\eta_{HSY} = 0.465$, $\epsilon = 200$ mRyd, $\kappa = 1.51 \text{ \AA}^{-1}$).

mation to the simulation data for liquid Ni, but some distinct differences exist in Co and Fe. For the transition metals from the middle of the series we could not find a stable solution of the ORPA.

4.3. Integral equations

Recently several attempts [16–18] have been made to construct improved integral equations for liquids, based on the fact that an Ornstein–Zernike equation together with the hypernetted chain (HNC) closure ($h(R) = g(R) - 1$)

$$g(R) = \exp[-\beta\Phi(R)] \exp[h(R) - c(R)] \quad (12)$$

works well for systems with soft repulsive interactions, whereas systems with attractive interactions are better described by the soft mean spherical approximation (SMSA) defined by

$$g(R) = \exp[-\beta\Phi_0(R)][1 + h(R) - c(R) - \beta\Phi_1(R)]. \quad (13)$$

Zerah and Hansen [17] proposed to interpolate smoothly between (12) at long and (13) at short distances

$$g_{ZH}(R) = \exp[-\beta\Phi_0(R)][1 + \{\exp[(h(R) - c(R) - \beta\Phi_1(R))f(R)] - 1\}/f(R)] \quad (14)$$

with $f(R) = \tanh(\alpha R)$ [19]. The parameter α of the interpolation function is determined by imposing thermodynamic self-consistency. For liquid Ni the SMSA works reasonably well, but the HNC result leads to only moderate agreement with experiment (figure 8). It is characteristic that the HNC equation underestimates the amplitude of the first peak and predicts long-wavelength density fluctuations which do not appear in the MD simulations, nor in the SMSA solution. The difficulties with the HNC solution arise from the fact that the softness of the potential is overestimated by the HNC closure. With the Zerah–Hansen closure the best fit to the MD results is obtained with $\alpha \approx 0.135$ which also leads to a thermodynamically self-consistent result (figure 8). With this value of α , $f(R) > 0.5$ for distances $R > 11.1$, so that the HNC behaviour is dominant for these

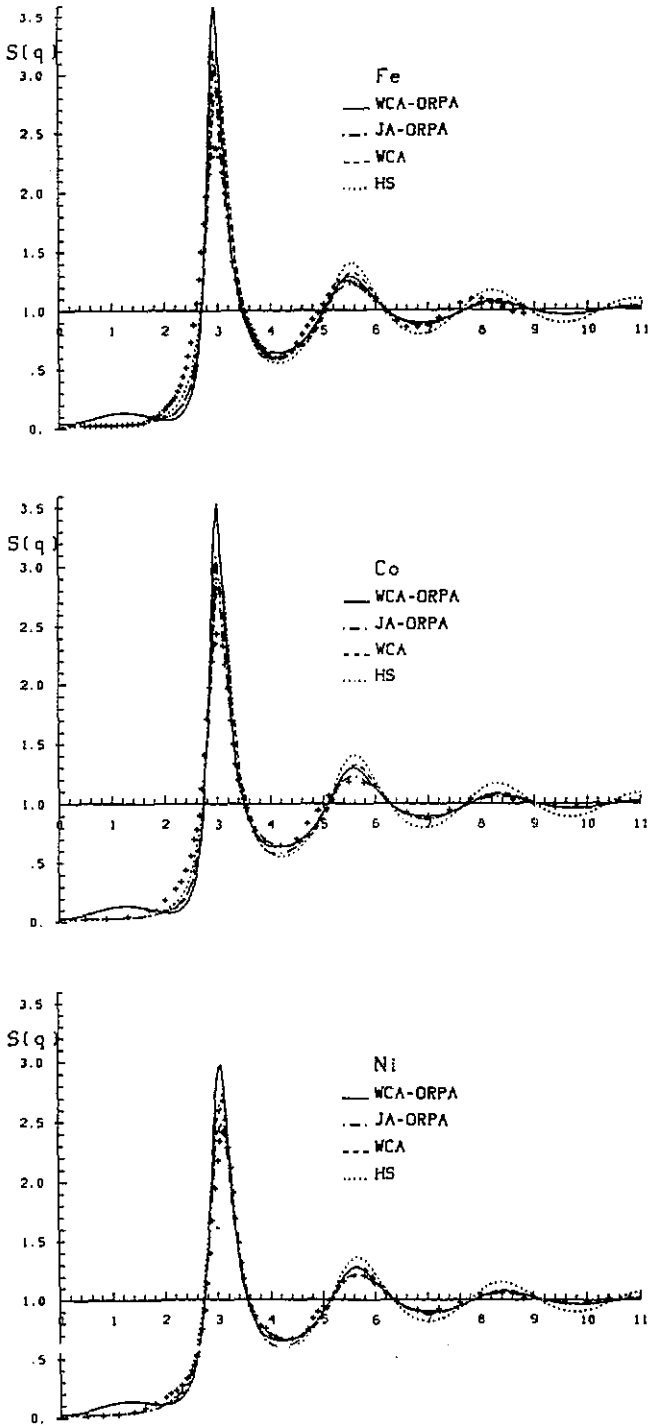


Figure 7. Static structure factor $S(q)$ for liquid Fe (a), Co (b) and Ni (c) calculated in the HS, the WCA, the ORPA-WCA and the ORPA-JA approximations.

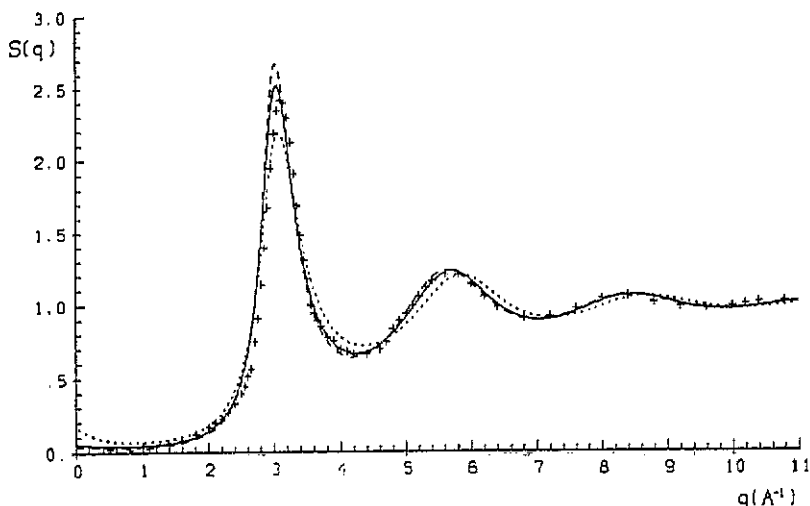


Figure 8. Static structure factor $S(q)$ for liquid Ni, calculated using the SMSA (broken curve), HNC (dotted curve) and the Zerah-Hansen closure (equation (16)) (full curve with $\alpha = 0.135$).

distances. Ni with a nearly full d band and relatively weak covalent interactions is a bit of a special case. Transition metals with an only half-filled band are much more difficult to handle. In nearly all cases the HNC approach fails, and the SMSA grossly overestimates the amplitudes of peaks in $S(q)$ demonstrating the overestimate of the attractive forces. The mixed closure (14) leads to a rather good fit at large q , but the form of the $S(q)$ in the region of main peak remains unsatisfactory (figure 9). This reflects only in part a failure of the integral equations. The sharp spike appearing at the first peak, exactly at $q = 2k_F$ is an unphysical consequence of the long-range Friedel oscillations which in reality are screened out by the d electrons. In the MD-simulations this effect was included by introducing a cut-off in the pair potential. If the Friedel oscillations are damped out exponentially, we eliminate the sharp spike in $S(q)$, without improving the general results (figure 9(b)). We have also made some calculations using the modified HNC of Rosenfeld and Ashcroft [18]. We found results very similar to the HNC. This shows that the hard-core bridge functions used in the MHNC are inappropriate for systems with interactions that are as soft as those of the transition metals. Our findings relate to recent results of Levesque *et al* [20] who found in a study on Morse systems—which have an even softer core than transition metals—that HS bridge functions cannot be used to satisfy the thermodynamic self-consistency requirement of soft potentials. Altogether we find that the characteristic features of the interionic interactions in transition metals—extreme softness of the repulsive part, very strong attractive forces—make the application of integral-equation techniques very difficult. Except for systems with a nearly full d band and hence relatively weak covalent interactions all existing integral equations fail to describe the structure of the liquid transition metals.

5. Conclusion

We have presented a comprehensive investigation of the structure of the liquid transition metals, using a variety of theoretical tools. A simple hybridized nearly-free-electron

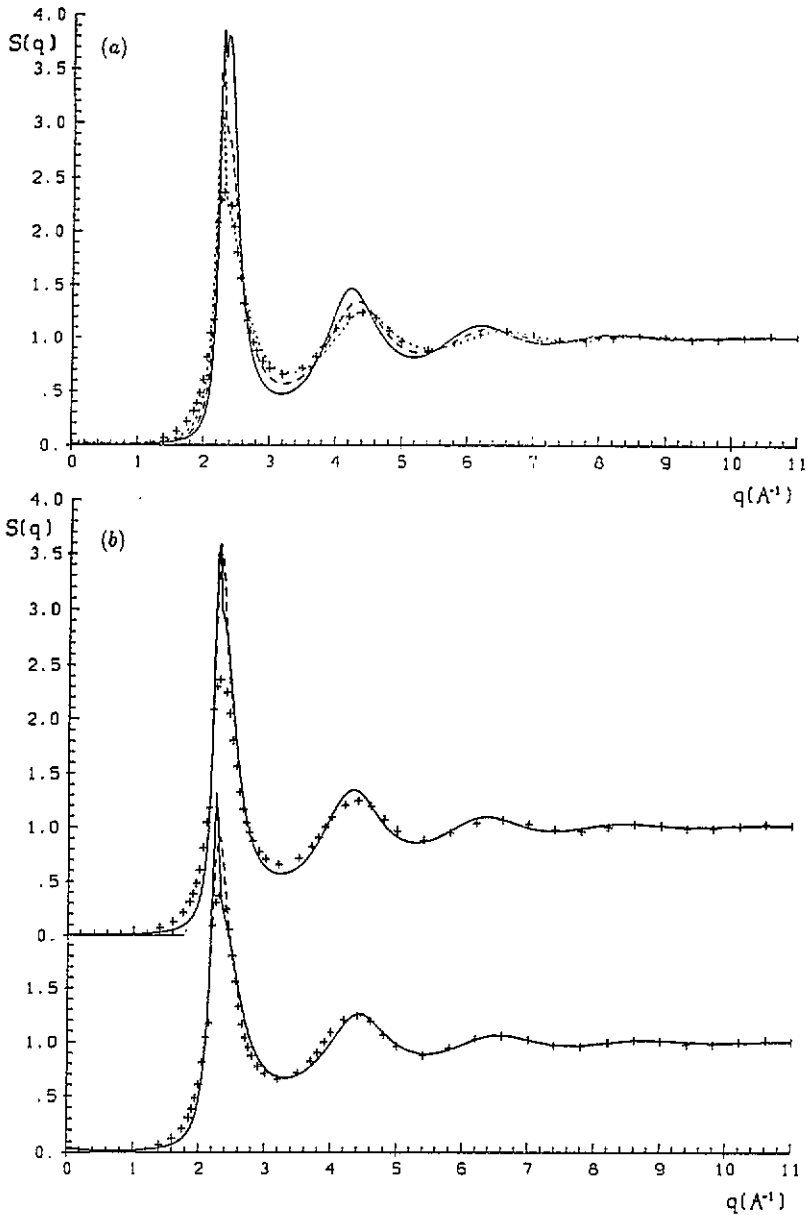


Figure 9. Static structure factor $S(q)$ for liquid Zr, calculated assuming the Zerah-Hansen closure relation (equation (14)): (a) with $\alpha = 0$ (SMSA—full curve), $\alpha = 0.1$ (broken curve) and $\alpha = 0.3$ (dotted curve); (b) with exponential dampening of the Friedel oscillations (for $R > R_{\text{cut}}$): full potential ($R_{\text{cut}} \approx 150$ a.u.): full curve, truncated potential ($R_{\text{cut}} = 10$ a.u. ($\alpha = 0.1$) and $R_{\text{cut}} = 6$ a.u. ($\alpha = 0.3$)): broken curve, for two different mixing parameters ($\alpha = 0.1$: top and $\alpha = 0.3$: bottom).

tight-binding theory has been used to determine the effective interatomic interactions. The parameters determining the d electron contributions are derived from the electronic structure, the pseudopotential core radius entering the s-electron contribution is obtained via a molecular dynamics fit to the liquid structure. It turns out that for all 3d

and 4d metals (except for Ti and V) we can find a potential that describes the liquid structure with good accuracy. The application of competitive techniques such as the embedded atom approximation [21, 22] has been limited up until now to the liquid elements of the Ni group. The resulting potentials have been used to test the applicability of existing liquid-state theories (Gibbs–Bogoljubov variational approach, WCA–ORPA-type perturbation theory, integral equations) to liquid transition metals. It turns out that among all ‘simple’ monatomic liquids, transition metal melts are the most difficult case. The actual liquid structure is influenced to a large degree by the extreme softness of the repulsive interactions and the strong covalent interactions. However, these effects compensate each other to a large degree. This is best seen in those cases where the ORPA works best: including the attractive forces and only first-order corrections for the softness of the potential (WCA–ORPA) leads to large amplitudes of the structure factor; if the corrections for the softness are included to all orders (JA–ORPA) the heights of the first and the second peaks are reduced close to the observed amplitudes. For these metals from the end of the transition metal series the mixed-closure integral equation of Zerah and Hansen works quite well, but for really strong attractive interactions the integral equation fails in the same way as the perturbation theories.

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