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Structure and thermodynamics of liquid transition metals: integral-equation study of Fe, Co and Ni

N Jakse and J L Bretonnet

Laboratoire de Physique des Liquides et des Interfaces, Université de Metz, 1 bd F. Arago, 57078 Metz Cedex 3, France

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Abstract. The structure and some thermodynamic properties of iron, cobalt and nickel are investigated in the framework of integral-equation theory with the hybridized mean spherical approximation. A local form factor, which combines the empty-core model and *s*–*d* mixing through an inverse scattering approach, is used to deduce effective-pair potentials suitable for transition metals via the second-order pseudopotential perturbation method. The resulting internal energy and thermodynamic quantities, necessary to achieve thermodynamic self-consistency, contain in addition a *d*-band contribution expressed by the Friedel rectangular model for the density of *d* states. The calculated structure factors $S(q)$ of Fe, Co and Ni near the melting point are found to be in good agreement with experiment and the energies, obtained self-consistently, coincide reasonably well with other published theoretical data.

1. Introduction

The modelling of interionic interactions for transition metals is a long-standing problem, and it remains a problem of interest. Impressive progress has been made in the past ten years, and different lines of attack have appeared (see, for example, Alonso and March [1] and references therein). Effective-pair potentials, deduced from some of these models, have been a starting point for recent theoretical works on the liquid transition metals [2–6]. Most of the systematic studies have been based on the model of Wills and Harrison (WH) [7]. These authors proposed a scheme involving a separate treatment of *s* and *d* electrons and including *s*–*d* hybridization. The resulting simple expression of the internal energy has been used, in conjunction with various methods of liquid state theory, to probe thermodynamics [8, 9] as well as structure [10, 11]. Despite real success in the solid state, the latter authors reported that the WH model fails to yield reliable structure factors, $S(q)$, for the early 3*d* metals. For them, the problem lies on the position and the depth of the potential wells, which are respectively too shifted towards short distances and too deep. It is worth mentioning that the potentials developed by Moriarty [12, 13] within the model generalized pseudopotential theory (MGPT), which work fairly well for solid state properties, have similar drawbacks to the WH models. As an illustration, Moriarty [14] has obtained molten states, at normal density, only above 3528 K, in the case of molybdenum. The liquid state properties can therefore be seen to be quite severe tests for potentials, since their overall shape is needed.

Recently, Bretonnet and Silbert [15] (BS) have derived a simple electron–ion interaction model suitable for transition metals. It jointly accounts for (i) the nearly-free-electron contribution via the Ashcroft [16] empty-core model and (ii) the *s*–*d* mixing inside the core region through an inverse scattering approach. The analytical form factor can then be treated in second-order perturbation theory to get an effective-pair potential. It has been

tested on the liquid structure of the 3d series by applying the Gibbs–Bogoliubov variational scheme with a charged hard-sphere reference system [17] as well as by using the variational modified hypernetted chain (VMHNC) integral equation [18, 19]. The good agreement of the results with experiment attests that the BS potential, albeit coming from a simplified approach, possesses the right features for a liquid-state description of transition metals [17]. It is well known that interactions in systems like liquids are dominated by the short-range pair forces. Therefore, provided that the effects of the d electrons are taken into account, we believe that effective-pair potentials are sufficient to treat the structure of liquid transition metals.

In this paper, we present the results for the structure as well as the thermodynamic properties of iron, cobalt and nickel. For this purpose, we expect the internal energy (written as a volume term and a sum of effective-pair interactions), which arises from the second-order perturbation method by using the BS form factor, to be supplemented by a contribution coming from the d band. The latter is expressed by using the Friedel [20] rectangular model for the density of d states. To determine the pair-correlation function and the thermodynamic properties resulting from the above internal energy, we use integral-equation theory with the closure relation of Zerah and Hansen [21] called the hybridized mean spherical approximation (HMSA). The latter, which ensures thermodynamic self-consistency (TSC) between the virial and compressibility equations of state, allows one to treat liquid structure and thermodynamics on the same footing. It has proven to be successful for simple liquids [21, 22] and for alkali metals [23–26]. Moreover, since efficient numerical algorithms [27, 28] have been built, solving integral equations is computationally no more costly. Preliminary structure calculations with the soft-core mean spherical approximation (SMSA) and the VMHNC by Bhuiyan and co-workers [18, 19] have encouraged us to tackle thermodynamics from the HMSA as well.

In section 2, we outline the theoretical basis of our work, which is twofold. On one hand, we give the effective-pair potential for transition metals; on the other hand, we briefly present the HMSA and the thermodynamic quantities playing an important role in the achievement of the TSC. In section 2, we compare the results of the structure factors and pair-correlation functions with molecular dynamics (MD) results and discuss the behaviour of some thermodynamic quantities for iron, cobalt and nickel. In section 4 we present our conclusions.

2. Theory

2.1. The BS pseudopotential and effective-pair potential

In transition metals, the tightly bound d electrons hybridize with the nearly-free electrons and form a partially filled d band, crossing the Fermi energy. This situation has been a serious impediment to the use of the pseudopotential perturbation method because of d resonance. The latter, completely defined by the δ_2 scattering phase shift as a function of energy E , behaves as

$$\tan \delta_2 = \frac{\Gamma}{2(\varepsilon_d - E)} \quad (1)$$

where ε_d is the resonance energy corresponding to the d-band centre and Γ is related to the d-band width. Bretonnet and Silbert [15] treat the sp states by the Ashcroft [16] empty-core model of core radius R_c as WH, although they take account of the s–d mixing by an

approximate potential, $u_c(r)$, inside the core. The term $u_c(r)$ is represented by the first two terms of (1) expanded as a Dirichlet series of short-range exponential functions. The superposition of these two potentials results in the following expression:

$$w(r) = \begin{cases} \sum_{n=1}^2 B_n \exp(-r/na) & r < R_c \\ -Z_s/r & r > R_c. \end{cases} \quad (2)$$

All quantities are expressed in Hartree atomic units ($m = \hbar = e = 1$); Z_s represents the effective number of conducting electrons per ion. For transition metals, it takes non-integer values [12] to account for hybridization. If we denote by $Z(= Z_s + Z_d)$ the number of s and d electrons of the free atom, Z_d will be the number of remaining d electrons per ion in the metal, which do not participate in conduction. Continuity of $w(r)$ and its first derivative at $r = R_c$ is required, thus defining B_1 and B_2 :

$$B_1 = \frac{Z_s}{R_c} \left(1 - \frac{2a}{R_c}\right) \exp\left(\frac{R_c}{a}\right) \quad (3)$$

and

$$B_2 = \frac{2Z_s}{R_c} \left(\frac{a}{R_c} - 1\right) \exp\left(\frac{R_c}{2a}\right). \quad (4)$$

The weakness of $w(r)$ allows a second-order perturbation treatment. Consequently, the local form factor

$$w(q) = 4\pi a^3 \frac{N}{V} \left(\frac{B_1 J_1}{(1 + a^2 q^2)^2} + \frac{8B_2 J_2}{(1 + 4a^2 q^2)^2} \right) - \frac{4\pi Z_s N}{q^2 V} \cos(q R_c) \quad (5)$$

obtained by Fourier transformation of (2), where

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

gives rise to an effective-pair potential taking the standard form:

$$u(r) = \frac{1}{8\pi^3} \int d^3q \frac{4\pi Z_s^2}{q^2} \left(1 - F_N(q)\right) e^{iq \cdot r}. \quad (7)$$

In equation (7) $F_N(q)$ is the normalized energy-wavenumber characteristic, written as

$$F_N(q) = \left(\frac{q^2}{4\pi Z_s}\right)^2 \left(1 - \frac{1}{\epsilon(q)}\right) \left(\frac{1}{1 - G(q)}\right) w^2(q) \quad (8)$$

which includes screening via the dielectric function $\epsilon(q)$ and its related local field correction, $G(q)$, given by Ichimaru and Utsumi [29]. The potential $u(r)$ contains three parameters: the core radius R_c , the softness parameter a and the number of conducting electrons Z_s . In the next section we discuss in detail their numerical values for each system.

2.2. Liquid state theory

2.2.1. *Integral equations.* Central to the theory of simple liquids is the pair-correlation function, $g(r)$, which can be related to the direct correlation function, $c(r)$, through the Ornstein-Zernike [30] (OZ) equation:

$$g(r) - 1 - c(r) = \rho \int d^3r' (g(r') - 1) c(|r - r'|) \equiv \gamma(r) \quad (9)$$

which is taken as a definition. The number density, ρ , is related to the electronic density n by $n = \rho Z_s$. The integral-equation method consists in solving the OZ equation in conjunction with an approximate closure relation [31]. In this work, we choose the hybridized mean spherical approximation (HMSA) of Zerah and Hansen [21]:

$$g^{\text{HMSA}}(r) = \exp(-\beta u_1(r)) \left(1 + \frac{\exp[f_0(\gamma(r) - \beta u_2(r))] - 1}{f_0} \right) \quad (10)$$

where $\beta = 1/k_B T$, with T and k_B being respectively the temperature and the Boltzmann constant. According to Weeks and co-workers [32], the effective-pair potential may be written as $u(r) = u_1(r) + u_2(r)$, where

$$u_1(r) = \begin{cases} u(r) - u(r_0) & r < r_0 \\ 0 & r > r_0 \end{cases} \quad (11)$$

represents its repulsive short-range part, and

$$u_2(r) = \begin{cases} u(r_0) & r < r_0 \\ u(r) & r > r_0 \end{cases} \quad (12)$$

is its weak long-range attractive part, r_0 being the position of the principal minimum of $u(r)$. The HMSA, given by (10), interpolates between two standard closure relations by means of the variation of f_0 , the mixing parameter. When f_0 tends to zero, the HMSA reduces to the SMSA [33], and when $f_0 = 1$ it becomes the hypernetted chain (HNC). The interpolation is carried out to achieve thermodynamic self-consistency (TSC), which consists in finding the equality between the isothermal compressibilities coming from two independent methods (see Egelstaff [34]). On the one hand we take the well known compressibility route:

$$\rho k_B T \chi_T = S(0) \quad (13)$$

where $S(0)$ is the long-wavelength limit of the structure factor. On the other hand we use the derivative with respect to density of the virial pressure P expressed in the grand-canonical ensemble of partition functions Ξ by

$$P = \rho k_B T - \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \exp(-\beta U_N(\mathbf{r}^N)) \frac{dU_N}{dV} d\mathbf{r}^N \quad (14)$$

where U_N is the N -particle potential energy for a system of volume V . A detailed description of the above two thermodynamic relations, for the case of transition metals, is given in the next subsection.

For a given f_0 , the system formed by (9) and (10) is solved numerically by employing a fast algorithm due to Labik and co-workers [28], which takes advantage of the combination, primarily proposed by Gillan [27], of the Newton-Raphson and successive substitution methods.

2.2.2. *Thermodynamic properties.* The second-order pseudopotential perturbation method gives a contribution to the total potential energy, U_N , that depends only upon the volume of the metal plus a sum of effective-pair potentials (see, for example, Ashcroft and Stroud [35] and Finnis [36]). It results in a term

$$U_0(\rho) = E_{eg} - \rho^{-1} B_{eg} + \phi(r=0) \quad (15)$$

where E_{eg} and B_{eg} are respectively the energy and the bulk modulus of the homogeneous electron gas. The last term is one half the electrostatic energy between the ion and its surrounding cloud; it is

$$\phi(r=0) = -\frac{Z^2}{\pi} \int_0^\infty F_N(q) dq \quad (16)$$

where $U_0(\rho)$ represents the energy arising from the Z_s conducting electrons per ion. To complete the potential energy of a transition metal, we have to include the effects of the remaining Z_d electrons. Following WH, it can be approximately accounted for by a contribution

$$E_d = -53.59Z_d \left(1 - \frac{Z_d}{10}\right) \frac{r_d^3}{D^5} + 136.8Z_d \frac{r_d^6}{D^8} \equiv E_b + E_c \quad (17)$$

where r_d is the so-called d-state radius and D is the nearest-neighbour separation (the coordination number is taken to be 12). Equation (17) is derived by combining the treatment of the overlap between d states on different ion sites with the Friedel [20] rectangular model for the density of d states, $n_d(E)$, ($= 10/W_d$ if $\varepsilon_d - W_d/2 < E < \varepsilon_d + W_d/2$, and 0 otherwise, where W_d is the d-band width). The first term, E_b , is a bonding energy proportional to the filling of the d band across the transition series and the second, E_c , is a correction due to the shift of the d-band centre of gravity. Finally, the internal energy per ion is

$$\frac{E}{\langle N \rangle} = \frac{3}{2} k_B T + U_0(n) + E_d + 2\pi\rho \int u(r; n) g(r; \rho) r^2 dr. \quad (18)$$

The first term of the right-hand side of (18) is the kinetic energy and the last term is the structure-dependent energy corresponding to the sum of pair interactions.

By means of (18), the virial pressure is derived from (14) to get

$$P = \rho\beta^{-1} + P_0 + P_d + P_{i-i}. \quad (19)$$

The different volume terms are as follows:

$$P_0 = \rho^2 \frac{\partial U_0(\rho)}{\partial \rho} \quad (20)$$

$$P_d = \frac{1}{3} \rho r \left. \frac{\partial E_d}{\partial r} \right|_{r=D} = \frac{1}{3} \rho 3(5E_b + 8E_c) \quad (21)$$

and the structure-dependent term P_{i-i} , is divided into two parts:

$$P'_{i-i} = -\frac{2\pi\rho^2}{3} \int \frac{\partial u(r; \rho)}{\partial r} g(r; \rho) r^3 dr \quad (22)$$

$$P''_{i-i} = 2\pi\rho^2 \int \frac{n \partial u(r; n)}{\partial n} g(r; \rho) r^2 dr. \quad (23)$$

This formulation is due to Hasegawa and Watabe [37] for the case of simple metals, and we have extended it to transition metals by adding P_d , the d-band contribution to the pressure.

We now turn to the bulk modulus. As pointed out in the previous subsection, it can be obtained by the compressibility route:

$$\beta \left. \frac{\partial P}{\partial \rho} \right|_T = 1 - 4\pi\rho \int c(r)r^2 dr = \frac{1}{S(0)} \quad (24)$$

as well as by the virial equation of state, which is at present given by (19):

$$\beta \left. \frac{\partial P}{\partial \rho} \right|_T = 1 + B_0 + B_d + B_{i-i} \quad (25)$$

where

$$B_0 = 2\frac{\beta}{\rho} P_0 + \beta\rho^2 \frac{\partial^2 U_0(\rho)}{\partial \rho^2} \quad (26)$$

$$B_d = \frac{8\beta}{3\rho} P_d + \frac{8\beta}{3} E_c. \quad (27)$$

The term B_{i-i} contains all the terms arising from the derivation with respect to the density of P'_{i-i} and P''_{i-i} :

$$B_{i-i} = 2\frac{\beta P'_{i-i}}{\rho} + 3\frac{\beta P''_{i-i}}{\rho} + \sum_{p=1}^4 B_p \quad (28)$$

where

$$B_1 = -2\pi\beta\rho \int r^2 g(r; \rho) \frac{r\rho}{3} \frac{\partial^2 u(r; \rho)}{\partial \rho \partial r} dr \quad (29)$$

$$B_2 = 2\pi\beta\rho \int r^2 g(r; \rho) \rho^2 \frac{\partial^2 u(r; \rho)}{\partial \rho^2} dr \quad (30)$$

$$B_3 = -2\pi\beta\rho^2 \int r^2 \frac{\partial g(r; \rho)}{\partial \rho} \frac{r}{3} \frac{\partial u(r; \rho)}{\partial r} dr \quad (31)$$

$$B_4 = 2\pi\beta\rho^2 \int r^2 \frac{\partial g(r; \rho)}{\partial \rho} \rho \frac{\partial u(r; \rho)}{\partial \rho} dr. \quad (32)$$

Note that, if the density dependence of the pair potential, the volume terms and the effect of the d band are dropped, expression (25) reduces to that of simple liquids [34].

3. Results and discussion

3.1. Fitting of the parameters

The input data for iron, cobalt and nickel are listed in table 1. The first two columns report the thermodynamic states, given by $V/(N)$ and T , under which the systems are investigated. These correspond to states just above the melting point.

Table 1. Input data of the calculations: atomic volume $V/(N)$, temperature T , effective valence Z_s , pseudopotential parameters a and R_c , TSC parameter f_0 , number of d electrons Z_d , interatomic distance D and d-state radius r_d .

	$V/(N)$ (au ³)	T (K)	Z_s	a (au)	R_c (au)	f_0	Z_d	D (au)	r_d (au)
Fe	89.356 98	1833	1.4	0.363	1.540	0.272	6.6	4.692	1.512
Co	85.837 20	1823	1.4	0.393	1.641	0.490	7.6	4.739	1.437
Ni	85.295 30	1773	1.4	0.207	1.030	-0.076	8.6	4.711	1.342

We have constructed the pair potentials by specifying the three parameters Z_s , a and R_c . To choose the effective valence, Z_s , we follow the prescriptions of Moriarty [12, 13]. His self-consistent calculations of Z_s , Z_d and E_F (the Fermi energy) have given Z_s values situated in a narrow range $1.1 < Z_s < 1.7$ for the 3d and 4d transition metals. Therefore, we take in all cases a typical value of 1.4, thus fixing the number of d electrons, Z_d , since $Z = Z_s + Z_d$ is a constant.

The parameter a has an influence on the softness of the potential $u(r)$. A larger value of a gives rise to a softer $u(r)$ without changing the position of its first node. As a consequence, the oscillations of the pair-correlation function, $g(r)$, shift towards smaller r and damp more rapidly. However a is restricted to the domain $4 < R_c/a < 5$, preventing an unrealistic pair potential. Regarding this restriction, we choose a values that best reproduce the oscillations of $g(r)$ for each system. Bretonnet and co-workers [17], in the framework of the GB scheme, have employed a similar adjustment since they choose the values of a in order to fit the low- q region of $S(q)$.

The core radius, R_c , is fitted to reproduce numerically the observed isothermal compressibility. At the same time, the mixing parameter of the HMSA, f_0 , is fixed to achieve the TSC. This procedure, in which the TSC is obtained at the experimental χ_T , has been previously employed by Bretonnet and Jakse [26] for the alkali metals. In this scheme, the pressure calculated by using (19) does not vanish, being in contradiction with the experimental conditions. This is a consequence of the pseudopotential theory leading to an electronic inconsistency (EI) (see Browman and Kagan [38]) and preventing the two equations of state given by (24) and (25) to be fully consistent. Therefore, to reduce the effects of the EI as well as of shortcomings of the model and numerical inaccuracies, the zero-pressure condition is applied to (25), which is, finally, rewritten as

$$\beta \frac{\partial P}{\partial \rho} \Big|_T = \frac{8}{3} \beta \frac{P}{\rho} + \beta \rho^2 \frac{\partial^2 U_0(\rho)}{\partial \rho^2} + \frac{8}{3} \beta E_c + \frac{1}{3} B_p + \sum_{k=1}^4 B_k \quad (33)$$

where

$$B_p = -2 \frac{\beta P_0}{\rho} - 2 \frac{\beta P'_{i-i}}{\rho} + \frac{\beta P''_{i-i}}{\rho} - 5. \quad (34)$$

Finally, the two last columns report the values taken by the parameters of the d-band energy, namely the nearest-neighbour separation D and the d-state radius r_d . For the latter, we take those used by WH, which have been fitted to the known d-band width in the solid state [39]. We believe that the r_d values can be kept in the liquid state.

3.2. Structure factors

In figures 1(a), 2(a) and 3(a) we present a comparison of our calculated $S(q)$ HMSA results, for Fe, Co and Ni, and the experimental data of Waseda [40], which are, to our present knowledge, the only ones that are available in the literature.

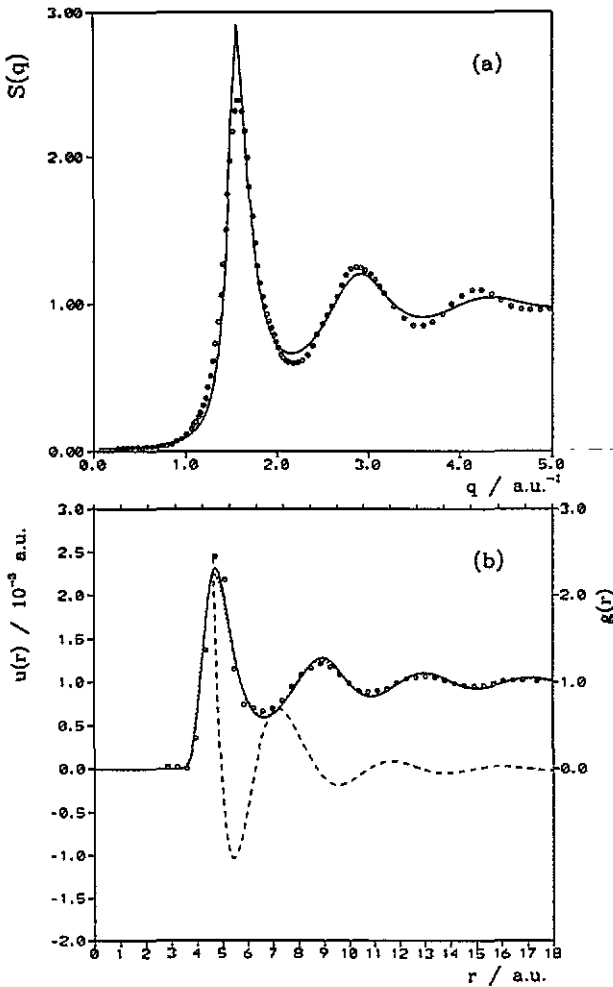


Figure 1. (a) Structure factor of liquid Fe (HMSA: full curve). (b) Effective-pair potential $u(r)$ (broken curve) and pair distribution function $g(r)$ (full curve: HMSA; dotted curve: MD simulation) of liquid Fe. The open dots correspond to the experimental data of Waseda [40].

As we examine the figures, it appears that the low- q region is well reproduced in all cases, being a consequence of the fitting to the observed $S(0)$. The oscillations are also in good agreement with experiment. For Fe and Co, the position of the main peak is at the right place, but for Ni a slight shift towards small q is visible with respect to the experimental value. Bhuiyan and co-workers [19] have also observed this shift with the VMHNC integral equation, even by using a different parametrization of the pair potentials. Incidentally, we used the local-field correction of Vashishta and Singwi [41] for the screening. The curves are indistinguishable on the scale of the plots, particularly in the low- q region as a consequence of the TSC procedure. For this reason, these are not shown in the figures.

However, as a general feature, the height of the principal peak of $S(q)$ is overestimated. This could arise from either the error involved in the measurements, carried out in the early 1970s, or as a shortcoming of the BS model. We keep in mind the discussion by Singh and Holz [42], who have pointed that the height of the first peak of $S(q)$, for alkali metals, varies by about 40% in some cases, due to the different resolutions of the detection systems. On the other hand, since the shape of the first peak of $S(q)$ results from the interplay between the repulsive part, $u_1(r)$, and the attractive part, $u_2(r)$, of the effective-pair potential, it is difficult to attribute the discrepancy to the short-range or to the long-range oscillatory part

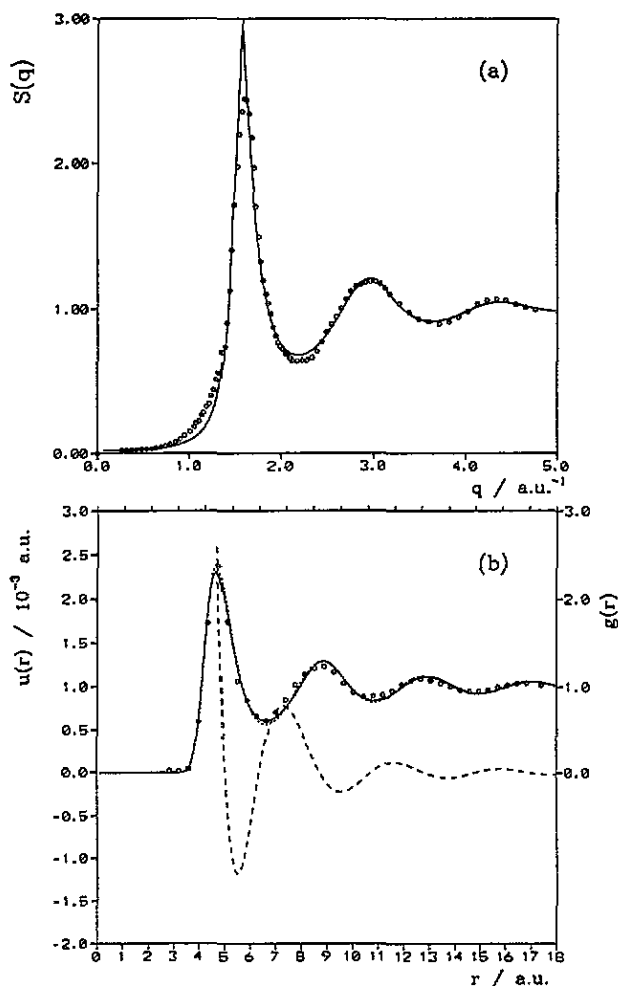


Figure 2. Same as in figure 1 for Co.

of $u(r)$.

Our effective-pair potentials $u(r)$ possess the so-called Friedel oscillations beyond the potential well, which are inherent in metallic systems. It is worth noting that other models, describing correctly the structure of liquid transition metals [2,5], do not exhibit these oscillations. It would therefore be interesting to compare the two classes of potentials on various physical properties.

The HMSA procedure employed here could also be questioned. Therefore, we performed the calculation of the structure by MD simulations, with the same pair potential, in order to test the approximation. To this end, we use a cubic cell containing 666 particles, subject to periodic boundary conditions. The volume of the box is chosen to reproduce the desired liquid density for each system. The initial positions are set randomly and the initial velocities are those of a Maxwellian distribution. A phase-space trajectory is then produced in the microcanonical NVE ensemble by the standard Verlet algorithm in velocity form [44]. The typical duration of a run is about 5×10^4 steps of 10^{-15} s. After an equilibration time at the right temperature, 300 independent configurations are retained to calculate the average $g(r)$.

In figures 1(b), 2(b) and 3(b), the pair correlation functions, $g(r)$, as well as the

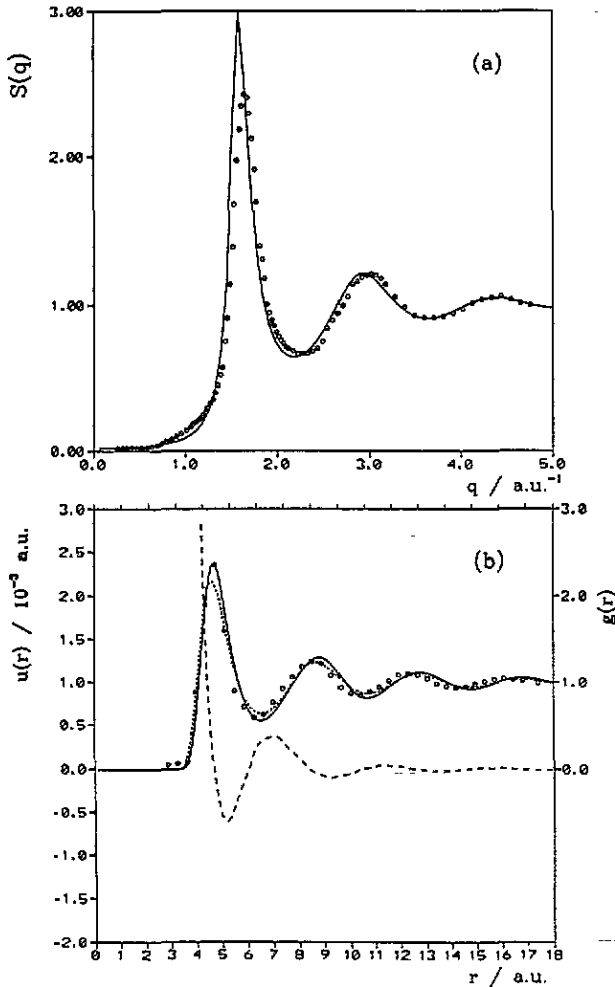


Figure 3. Same as in figure 1 for Ni.

associated effective-pair potentials, $u(r)$, are presented. The first peak of $g(r)$ obtained with HMSA coincides fairly well with experiment for Fe, Co and Ni. Its position is always at a shorter distance than the position of the corresponding potential well and the mean position of the nearest neighbours is situated within the repulsive part of $u(r)$. This fact gives rise to an important positive contribution to the structure-dependent pressure and partly accounts for the large values of the bulk modulus of transition metals. For Fe and Co, the curves of $g(r)$ of HMSA compare favourably with those of molecular dynamics while, for Ni, there is an appreciable difference that could reveal a weakness of HMSA in this case.

The HMSA involves two standard integral equations: the SMSA and the HNC. The mixing parameter f_0 measures the degree of contribution of those closure relations. The values listed in table 1 are below 0.5, indicating that the SMSA is better able to describe liquid transition metals than the BS model. Nevertheless, the very small negative value for Ni ($f_0 = -0.076$), which is an extrapolated value, could also reveal a weakness of the BS model for Ni. Hausleitner and co-workers [11] have used the HMSA with a modified WH model, and report that their results show an HNC-like behaviour, forcing us to remark that the kind of integral equations to use depends on the model potential. Consequently, once more one can see that the WH and BS effective-pair potentials are different in nature.

Table 2. Contributions to the internal energy per ion given in 10^{-3} au, according to (18). E_{BD} stand for the values obtained by Bretonnet and Derouiche [9].

	E_{id}	E_{cg}	$-\rho^{-1}B_{cg}$	$\phi(r=0; \rho)$	E_d	E_{str}	$E/\langle N \rangle$	$E^{BD}/\langle N \rangle$
Fe	8.71	-67.73	-77.41	-465.89	-138.03	11.99	-728.36	-708.84
Co	8.66	-64.68	-80.42	-461.06	-85.37	17.89	-664.98	-713.38
Ni	8.42	-64.18	-80.91	-626.75	-38.86	5.17	-797.12	-725.66

3.3. Thermodynamic properties

We come now to our results for the thermodynamic properties. In table 2 we present the different contributions to the internal energy, $E/\langle N \rangle$, (expressed in 10^{-3} au) according to (18). The values of $E/\langle N \rangle$ for Fe, Co and Ni are compared to those obtained by Bretonnet and Derouiche [9], $E^{BD}/\langle N \rangle$. These authors have used a modified WH model in the Gibbs–Bogoliubov variational scheme with a hard-sphere reference system. The two sets of results coincide within a range of 10%. The ideal part, E_{id} , and the structure-dependent part, $E_{str} = 2\pi\rho \int r^2 u(r)g(r)dr$, contribute moderately to the internal energy (only a few per cent); $\phi(r=0, \rho)$ and E_d , which contain the s–d mixing and the d-band energy respectively, are the most important contributions to $E/\langle N \rangle$. As expected, going from Fe to Ni, the d-band fills up and E_d increases. For Ni, it provides the smallest term of the negative contributions, while $\phi(r=0, \rho)$ becomes the essential term.

Table 3. Contributions to the pressure corresponding to (19).

	$\beta P_{id}/\rho$	$\beta P_0/\rho$	$\beta P_d/\rho$	$\beta P'_{i-i}/\rho$	$\beta P''_{i-i}/\rho$	$\beta P/\rho$
Fe	1	-21.20	-31.38	11.96	0.21	-39.41
Co	1	-21.93	-18.41	15.75	0.75	-22.84
Ni	1	-47.57	-6.50	8.40	-0.12	-44.79

In table 3 we present the virial pressure, $\beta P/\rho$, and its different contributions expressed by (20)–(23). Contrary to the case of internal energy, the volume-dependent and structure-dependent parts of the pressure are comparable and of opposite signs for Fe and Co. As a result, the large negative values come from the d-band pressure. For Ni, because the d band has little influence, $\beta P_d/\rho$ takes a moderate value and $\beta P_0/\rho$ is the most important term. Note that, as for simple metals, $\beta P'_{i-i}/\rho$ arising from the derivative of $u(r)$ with respect to density is always negligible.

Finally, in table 4 we list the terms of the bulk modulus written in (33). We recall that the self-consistent values of $\beta(\partial P/\partial\rho)_T$ coincide with the experimental ones [43] since these correspond to the fitting of R_c ; $\beta\partial P/\partial\rho|_T$ is composed of two dominant terms: B_3 , which was the sole important term in the case of alkali metals [26] by using the same procedure, and the d-band contribution $8\beta E_c/3$.

Table 4. Contributions to the bulk modulus $\beta\partial P/\partial\rho|_T$ defined in (33), that have been fitted to experimental values [43].

	$B_p/3$	B_1	B_2	B_3	B_4	$\beta\rho^2\partial^2 U_0(\rho)/\partial\rho^2$	$8\beta E_c/3$	$\beta\partial P/\partial\rho _T = 1/S_{exp}(0)$
Fe	4.56	-4.80	10.15	18.31	-0.83	1.52	21.09	50.00
Co	2.70	-4.75	15.07	20.90	0.38	1.72	16.61	52.63
Ni	24.49	-5.23	6.72	15.10	-2.02	0.13	13.44	52.63

4. Conclusion

In this paper, the structure as well as some thermodynamic properties for iron, cobalt and nickel have been studied with the HMSA integral equation. The good agreement of our calculated $S(q)$ attests to the fact that this closure relation, which has previously proven to be successful for simple liquids and alkali metals, is also valid for transition metals. It should therefore be widely applied to various kinds of potentials. Our procedure has also provided, in a thermodynamically self-consistent manner, reliable results for thermodynamic quantities. These are deduced from the internal energy including, albeit in a simplified way, three important features for transition metals: hybridization, s-d mixing and a d-band contribution.

We are exploring two possible extensions of the HMSA procedure. First, we are introducing an inversion technique in order to get direct information on the shape of the potentials of the transition metals, which can be compared to different types of models. Second, we are trying to generalize the HMSA to the case of liquid binary mixtures and alloys.

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