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Variational thermodynamic calculations for liquid transition metals

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We present calculations of the Helmholtz free energy of three series of liquid transition metals performed by using the Gibbs-Bogoliubov variational method with a hard-sphere reference system. In order to observe the role of the *s*- and *d*-like electrons, the interaction is evaluated by extending the nearly-free-electron theory of simple metals to include the effects of transition-metal *d* states. For the 3*d* series, our results for the free energy compare fairly well with those given in the literature, and the packing fraction lies in the same range as that of simple metals, for all transition metals.

I. INTRODUCTION

The thermodynamic properties of liquid metals are frequently studied by combining the Gibbs-Bogoliubov variational method and the second-order pseudopotential perturbation theory. While simple liquid metals have been fully investigated,[1-3] relatively few studies have been carried out up to now on the thermodynamics of liquid transition metals. Itami and Shimoji[4] have involved the *s*-*d* hybridization effects in the calculation of energy, by means of a term which is inversely proportional to the sixth power of the interionic distance, but they have neglected the band-structure energy. On the other hand, Aryasetiawan *et al.*[5] omitted the *s*-*d* hybridization when they combined the variational method with a semiempirical tight-binding model describing the interionic potential energy. Nevertheless, their work sheds some light on successes and shortcomings of the model and allows one to envisage further developments.

With the recent expression of the interionic pair potential for the liquid transition metals elaborated by Wills and Harrison[6] (WH) our knowledge should advance substantially, since the band-structure energy of the metal is no more than a sum of pair potentials interacting between ions, and the effect of *s*-*d* hybridization is included. The WH pair potential has been used for the determination of surface properties of noble metals[7] and for the evaluation of the structure and entropy of the 3*d* transition series, in the liquid state.[8,9]

In the present paper we use the variational method with a hard-sphere fluid as a reference system and the WH formulation of the *d*-band structure to make the calculation of the Helmholtz free energy of three series of liquid transition-metal elements. It will be seen that the theory predicts the thermodynamic properties of liquid transition metals approximately as well as the corresponding theory in the simple metals.

II. FORMALISM

The evaluation of the Helmholtz free energy F of the system of interest requires a method based on the Gibbs-Bogoliubov inequality, which states that one can reasonably approximate the free energy F by that of an appropriate reference system. In this method the free energy F of the transition metals, per ion, can be expressed in terms of the free energy of the hard-sphere (HS) reference system plus a perturbation term, and thus

$$F \le F^{\mathrm{HS}}(\eta)+E_0+\frac{N}{2V}\int d^3r\, g^{\mathrm{HS}}(r,\eta)u(r)-TS_{\mathrm{el}} . \tag{1}$$

Here $F^{\mathrm{HS}}(\eta)$ is the free energy of the HS system given by

$$F^{\mathrm{HS}}(\eta)=-k_BT\left[\ln\left[\frac{2\pi Mk_BT}{h^2}\right]^{3/2}\frac{V}{N}+1\right] +k_BT\left[\frac{(3-2\eta)}{(1-\eta)^2}-3\right] . \tag{2}$$

The first term on the right-hand side of Eq. (2) is the ideal-gas free energy, per ion, of N identical particles with mass M in the volume V, while the second term is the Carnahan-Starling[10] equation of a HS system with packing fraction as a function of diameter σ $[\eta=(\pi/6)\sigma^3N/V]$.

For simple metals, the calculations in wave-number space have proven quite successful. In contrast, for transition metals where an inverse-power form of the pair potential takes place, the calculations have to be made in real space. It is found that the HS radial distribution function, which is taken to be that given by Throop and Bearman,[11] is conveniently solvable numerically and seems to guarantee a degree of success. For the volume-dependent contribution E_0 and the effective pair potential $u(r)$, which determines the response of the metal to the arrangement of the ions at constant total volume, we used the WH expression. On the other hand, the entropy of the electron gas S_{el} cannot be neglected in the case of liquid transition metals because of the large values of the density of states for *d* bands $n_d(E_F)$, at the Fermi level. The electronic entropy may be written

$$S_{\mathrm{el}}=\frac{\pi^2}{3}k_B^2T[n_s(E_F)+n_d(E_F)] . \tag{3}$$

In order to be consistent with the WH prescription, the rectangular model, suggested by Friedel,[12] has been used to evaluate the density of d states.

In the WH formulation of the transition-metal potential the nearly-free-electron theory of the simple metals is extended to include the effects of the transition-metal d band, so that the pair potential can be written (in atomic units)

$$u(r)=u_{\mathrm{SM}}(r)-\frac{28.1}{\pi}\left[\frac{12}{n}\right]^{1/2} Z_d\left[1-\frac{Z_d}{10}\right]\frac{r_d^3}{r^5}+\frac{225}{\pi^2}Z_d\frac{r_d^6}{r^8}\ . \tag{4}$$

The first term $u_{\mathrm{SM}}(r)$, which corresponds to the effective pair potential in the simple metals, is given by

$$u_{\mathrm{SM}}(r)=\frac{Z_s^2}{r}\left[1-\frac{2}{\pi}\int F_N(q)\frac{\sin(qr)}{q}dq\right] \tag{5}$$

and must be numerically calculated with the classical expression of the normalized wave-number–energy characteristic,

$$F_N(q)=\left[\frac{q^2}{4\pi e^2 Z_s}\frac{V}{N}\right]^2 w_0^2(q)\left[1-\frac{1}{\epsilon(q)}\right]\left[\frac{1}{1-G(q)}\right], \tag{6}$$

where $w_0(q)$ is the form factor and $\epsilon(q)$ is the dielectric function. To perform our calculations we used the Ashcroft[13] empty-core model potential and the two functions of Vashishta and Singwi[14] (VS) and of Ishimaru and Utsumi[15] (IU) as the local-field exchange-correlation function $G(q)$. The second term in Eq. (4) results from a treatment of the overlap between d states on different ions combined with Friedel's rectangular model of the density of d states. The third term, varying as r^{-8}, is a correction to the previous term and can be seen as a shift of the d-band center due to nonorthogonality of d-like states. The last two terms involve the coordination number n, the d-state radius r_d, and the number of valence electrons Z_s on each ion site.

Except for a slight modification of the s-like electrons term, the volume-dependent contribution E_0 is given, according to the WH description, by

$$E_0=E_{\mathrm{EG}}-\frac{1}{2V}\sum_q{}'\frac{4\pi Z_s^2 e^2}{q^2}F_N(q)-\lim_{q\to 0}\left[2\pi Z_s^2 e^2\frac{N}{V}\left[\frac{\pi\hbar^2}{4me^2k_F}-\frac{G(q)}{q^2}\right]\right]\ . \tag{7}$$

In this equation E_{EG} is the sum of the kinetic energy and the exchange-correlation energy of the uniform electron gas. Its explicit expression is (in atomic units)

$$E_{\mathrm{EG}}=\frac{Z_s}{2}\left[\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+0.031\ln r_s-0.115\right], \tag{8}$$

where r_s, such as $r_s^3=(3/4\pi)V/NZ_s$, is the radius of the sphere that contains one electron, on average. The second term in Eq. (7) represents the self-energy between an ion and its surrounding cloud of charge, whereas the last term corresponds to the rearrangement of various energetic contributions that come from the standard derivation performed by Hasegawa and Watabe.[16] We have to note that in their formulation the parameter R_c of the empty-core model potential, usually contained in the Hartree energy, is missing. On the other hand, the long-wavelength limit of the local-field exchange-correlation function appears in Eq. (7) through the parameter γ, since

$$G(q)\cong\gamma\frac{q^2}{k_F^2}+O(q^4)\ . \tag{9}$$

III. APPLICATION TO THE LIQUID TRANSITION METALS

From the form of the expressions of $u(r)$ and E_0, we can see that only a small number of parameters are necessary to predict the transition-metal energy. We believe that certain parameters can be kept for the liquid state,

TABLE I. Transition-metal parameters of the $3d$ series. Z_d is the number of d electrons, d is the nearest-neighbor distance, r_d is the d-state radius, P_d and P_{HS} are the contributions to pressure from the d electrons and the hard-sphere model, respectively (in 10^{-3} energy a.u. per volume a.u.), r_s is the electron-density parameter, and R_c is the empty-core radius.

	Z_d	d (a.u.)	r_d (a.u.)	P_d	P_{HS}	r_s (a.u.)	R_c (a.u.)
Sc	1.5	6.253	2.344	−0.727	0.374	2.841	1.461
Ti	2.5	5.578	2.042	−1.716	0.446	2.748	1.731
V	3.5	4.957	1.853	−2.760	0.630	2.537	1.656
Cr	4.5	4.722	1.701	−3.346	0.685	2.450	1.625
Mn	5.5	4.234	1.626	−2.694	0.442	2.532	1.674
Fe	6.5	4.692	1.512	−2.184	0.603	2.421	1.372
Co	7.5	4.739	1.437	−1.429	0.614	2.388	1.170
Ni	8.5	4.711	1.342	−0.596	0.608	2.378	0.965
Cu	9.5	4.832	1.267	+0.164	0.449	2.427	0.807

TABLE II. Transition-metal parameters of the 4d series. Symbols are as in Table I.

	Z_d	d (a.u.)	r_d (a.u.)	P_d	P_{HS}	r_s (a.u.)	R_c (a.u.)
Y	1.5	6.718	2.987	−0.549	0.221	3.369	1.987
Zr	2.5	6.010	2.665	−1.345	0.358	3.039	2.034
Nb	3.5	5.403	2.420	−2.301	0.603	2.785	1.934
Mo	4.5	5.151	2.268	−2.672	0.727	2.660	1.805
Tc	5.5	5.110	2.098	−2.334	0.702	2.579	1.598
Ru	6.5	5.009	1.985	−1.478	0.717	2.554	1.329
Rn	7.5	5.085	1.872	−0.612	0.616	2.580	1.100
Pd	8.5	5.200	1.777	+0.134	0.478	2.626	0.850
Ag	9.5	5.461	1.682	+0.542	0.283	2.744	0.694

while others have to be changed. Thus, as has been advocated by WH, the number of electrons per ion in free-electron-like states (Z_s) is taken to be 1.5 for all transition metals, with the exception of gold, for which $Z_s=2$. The number of d electrons (Z_d) can then be easily obtained since the total number (Z) of s and d electrons is known ($Z_d=Z-Z_s$). On the other hand, though $u(r)$ is not strictly structure independent, because of the presence of $n^{-1/2}$, we have maintained n constant to 12 for all transition metals in the liquid state. In fact, we have numerically checked that the results are not too sensitive to the choice of the value of n lying between 8 and 12.

It emerges from the WH work that the model is specified by two other parameters obtainable from the free-atom characteristics. One parameter is the radius R_c of the empty-core model potential and the other is the d-state radius r_d, which can be directly calculated in terms of atomic wave functions. However, for the latter, it is preferable to use adjusted values in fitting the d bandwidth.[17] To treat all the transition metals on an equal footing, we have adopted the values of r_d quoted by WH and we have fitted the core radius R_c, in requiring the cohesive energy to be the minimum at the observed volume of each liquid metal. This procedure of fitting is based on the condition

$$p=-\frac{\partial}{\partial V}(E_f+E_b+E_c+F^{\mathrm{HS}})=0\ , \tag{10}$$

where E_f consists of the electron-gas energy E_{EG} and of the contributions of the simple metals, namely, the Madelung energy and the Hartree energy

$$E_f=\frac{Z_s}{2}\left[\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+0.031\ln r_s-0.115-\frac{1.8Z_s^{2/3}}{r_s}+\frac{3R_c^2}{r_s^3}\right]\ . \tag{11}$$

The two following terms in Eq. (10) account for the effects of transition-metal d bands and are connected to the last two terms of Eq. (4). They are written as follows:

$$E_b=-15.45n^{1/2}Z_d\left[1-\frac{Z_d}{10}\right]\frac{r_d^3}{d^5}\ , \tag{12}$$

$$E_c=11.4nZ_d\frac{r_d^6}{d^8}\ , \tag{13}$$

where d is the nearest-neighbor distance. The last term in Eq. (10) is the free energy of the HS fluid, already given by Eq. (2). Resolving Eq. (10), we find the core radius R_c for the liquid state, such as

$$R_c^2=\tfrac{1}{9}[-4.42r_s+(0.916+1.8Z_s^{2/3})r_s^2+0.031r_s^3]-\frac{8\pi r_s^6}{9}(p_d+p_{\mathrm{HS}})\ , \tag{14}$$

where

$$p_d=-\frac{\partial}{\partial V}(E_b+E_c),\quad p_{\mathrm{HS}}=-\frac{\partial F^{\mathrm{HS}}}{\partial V}\ . \tag{15}$$

In estimating the HS contribution to the pressure we have adopted the value of $\eta=0.45$ for all transition met-

TABLE III. Transition-metal parameters of the 5d series. Symbols are as in Table I.

	Z_d	d (a.u.)	r_d (a.u.)	P_d	P_{HS}	r_s (a.u.)	R_c (a.u.)
La	1.5	7.057	2.987	−0.675	0.136	3.466	2.328
Hf	2.5	5.911	2.722	−1.427	0.446	2.983	1.948
Ta	3.5	5.406	2.533	−2.372	0.689	2.818	1.985
W	4.5	5.181	2.401	−2.460	0.868	2.717	1.791
Re	5.5	5.181	2.268	−1.676	0.919	2.610	1.388
Os	6.5	5.057	2.136	−0.907	0.924	2.566	1.086
Ir	7.5	4.110	2.042	+0.134	0.750	2.579	0.697
Pt	8.5	5.246	1.966	+0.954	0.525	2.641	0.781
Au	9	5.452	1.909	+1.249	0.312	2.479	0.633

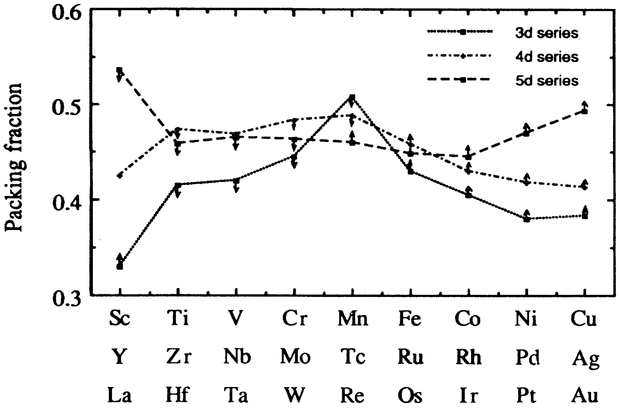

FIG. 1. Packing fraction obtained from the variational method with the Ichimaru-Utsumi local-field exchange and correlation function, for the three series of liquid transition metals. The arrows indicate the tendency observed when the exchange-correlation effect is absent.

als. Besides this, since the d bands are likely to be little modified from the solid state to the disordered state, we have taken the values of p_d from WH. All the relevant parameters used for the calculations are displayed in Tables I–III.

IV. RESULTS AND DISCUSSION

The free energy has been calculated variationally, as described in Sec. II, with the Hartree dielectric function as well as both the VS and IU local-field exchange-correlation functions, in order to investigate the effect of the interacting electron gas. In Fig. 1, we have represented the variation of the packing fraction calculated with the IU local-field function, across the three transition-metal series. The first point revealed in Fig. 1 is that η passes through a maximum in the middle of the 3d and 4d series, while the tendency is inverted for the 5d series. The second point concerns the local-field function. With the exception of Sc and Y, it is found that the exchange-correlation effect gives the greatest value of η when the d band is half empty, and the smallest one when the d band is filled to a large extent. While the difference between the two local-field functions is very small, we notice that the values $\eta_{\rm VS}$ obtained with the VS function lie between $\eta_{\rm IU}$ and η_H.

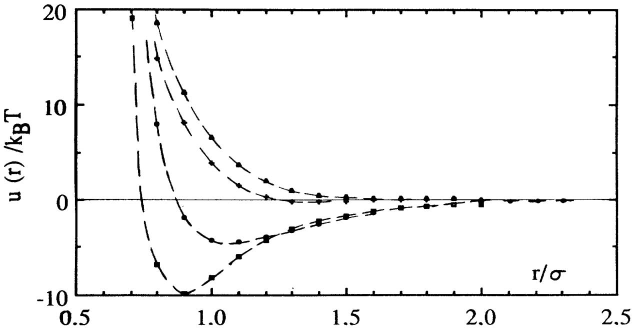

FIG. 2. Pair potential of Sc. The closed circles correspond to the total potential, the triangles to the s-like contribution without exchange-correlation effect, the crosses to the s-like contribution with IU dielectric function, and the squares to the d-band contribution.

We have displayed in Tables IV–VI the values of the packing fraction and the free energy calculated with Eq. (1). The values of $\eta^{\rm HS}$, obtained by fitting to the first peak of the liquid structure factor,[18] have also been reported for the 3d transition series. Although slightly smaller, the calculated packing fractions are reasonably close to that of $\eta^{\rm HS}$, except for Sc, Mn, and Ni. Hence, we expect that the results for entropy are in as good agreement with experiments as those of Meyer *et al.*[18] Incidentally, note the very good agreement for Pt with a value of $\eta^{\rm HS}=0.468$ quoted by the authors.

The electronic contribution to the entropy, which remains a small correction to that of the HS reference fluid ($\sim 10\%$), has been calculated using the rectangular model for the density of d-like states $[n_d(E_F)=10/W_d]$ with the bandwidth W_d taken from Harrison.[19] It is worth noting that the d-band contribution to the entropy is about five times that for the electron gas.

TABLE IV. Packing fractions and free energies (in a.u.) calculated with the variational method, for 3d transition series (H, Hartree; VS, Vashishta and Singwi; IU, Ichimaru and Utsumi; $\eta_{\rm HS}$, packing fraction fitted to the experimental structure factor).

	η_H	F_H	$\eta_{\rm VS}$	$F_{\rm VS}$	$\eta_{\rm IU}$	$F_{\rm IU}$	$\eta_{\rm HS}$
Sc	0.3525	−0.7347	0.3300	−0.7546	0.3250	−0.7558	0.43
Ti	0.4150	−0.7042	0.4150	−0.7304	0.4175	−0.7344	0.437
V	0.4175	−0.7652	0.4200	−0.7983	0.4250	−0.8029	0.436
Cr	0.4425	−0.7573	0.4450	−0.7939	0.4450	−0.7988	0.445
Mn	0.5000	−0.6864	0.5075	−0.7205	0.5150	−0.7258	0.449
Fe	0.4350	−0.7430	0.4300	−0.7762	0.4300	−0.7781	0.438
Co	0.4200	−0.7519	0.4050	−0.7845	0.4000	−0.7852	0.444
Ni	0.4050	−0.7564	0.3800	−0.7901	0.3725	−0.7913	0.442
Cu	0.4175	−0.7456	0.3825	−0.7797	0.3700	−0.7827	

TABLE V. Packing fractions and free energies (in a.u.) calculated with the variational method, for 4*d* transition series (symbols are as in Table IV).

	η_H	F_H	η_{VS}	F_{VS}	η_{IU}	F_{IU}
Y	0.4250	−0.6369	0.4250	−0.6508	0.4250	−0.6538
Zr	0.4645	−0.7112	0.4725	−0.7344	0.4775	−0.7404
Nb	0.4645	−0.8000	0.4675	−0.8291	0.4725	−0.8357
Mo	0.4745	−0.8435	0.4825	−0.8748	0.4875	−0.8807
Tc	0.4850	−0.8437	0.4875	−0.8515	0.4900	−0.8555
Ru	0.4600	−0.8502	0.4575	−0.8770	0.4575	−0.8781
Rh	0.4400	−0.8122	0.4300	−0.8372	0.4275	−0.8379
Pd	0.4400	−0.7896	0.4175	−0.8165	0.4100	−0.8196
Ag	0.4500	−0.7501	0.4125	−0.7784	0.4000	−0.7843

The treatment of the exchange-correlation effects contributes to the lowering of the free energy on the order of 5%. Our results of the free energy for the 3*d* series compare fairly well with those of Hausleitner and Hafner.[8] According to the calculations, the IU local-field function leads to a lower variational upper bound to the free energy than the VS function, for all transition and noble metals. However, in contradistinction to what happens in the simple metals, the VS function yields the lowest minimum variational for the volume-independent contribution of the free energy. This point reveals the primordial role of the volume-dependent contribution [Eq. (7)] to the energy.

Considering that the free energy does not change very much when we take into account the exchange-correlation effects, it seems most useful to inspect the pair potential that would be more sensitive to them, although it is not clear to what extent the pair-potential concept is justified, due to the strong mixture of fairly-localized-*d* and nearly-free electrons in the transition metals. Some authors proposed new promising techniques for calculating some properties, such as the structure of defects in crystalline solids,[20,21] which avoid the ambiguities of the pair potential. Nevertheless, one usually expects transition-metal potentials to be much shorter ranged than for simple metals. In Figs. 2–4, we compare the contribution of the *d* band, $u_d(r)$, to the total pair potential $u(r)$ for three representative 3*d* transition metals. It is found that the *d* band has a similar effect to that of the exchange-correlation, though amplified when the *d* band is half filled, in the sense that the repulsive part of $u(r)$ is drawn into lower *r* and that its attractive part is deeper. Thus both the *d*-band and exchange-correlation effects tend to reduce noticeably the range of the strong screened Coulomb repulsion between ions. In the case of the *d* band we can provide a general argument about the magnitude of its effect on $u(r)$ by calculating the position r_m and the depth $u_d(r_m)$ of the attractive well associated with the *d* band,

$$r_m = 1.598 \frac{r_d}{\left[1-\dfrac{Z_d}{10}\right]^{1/3}} , \tag{16}$$

$$u_d(r_m) = -0.322 Z_d \left[1-\frac{Z_d}{10}\right]^{8/3} \frac{1}{r_d^2} . \tag{17}$$

According to Eqs. (16) and (17) we observe that the more pronounced is the $u_d(r_m)$ the more the position r_m moves toward low *r*. In addition, for the three transition-metal series, the attractive well is smaller at the end than at the beginning of the row, but it is for the elements of the middle of each row that the minimum is deeper [i.e., $u_d(r_m) = 0.057$ a.u. for Sc, 0.102 a.u. for Cr and 0.010

TABLE VI. Packing fractions and free energies (in a.u.) calculated with the variational method, for 5*d* transition series (symbols are as in Table IV).

	η_H	F_H	η_{VS}	F_{VS}	η_{IU}	F_{IU}
La	0.5300	−0.5573	0.5375	−0.5768	0.5525	−0.5841
Hf	0.4525	−0.7720	0.4575	−0.7950	0.4650	−0.8002
Ta	0.4600	−0.8306	0.4650	−0.8595	0.4675	−0.8665
W	0.4575	−0.9016	0.4625	−0.9303	0.4650	−0.9355
Re	0.4625	−0.9631	0.4600	−0.9883	0.4600	−0.9896
Os	0.4550	−0.9602	0.4475	−0.9854	0.4450	−0.9861
Ir	0.4600	−0.9371	0.4450	−0.9681	0.4400	−0.9728
Pt	0.4850	−0.8078	0.4700	−0.8348	0.4650	−0.8384
Au	0.5150	−1.3295	0.4925	−1.4038	0.4975	−1.4185

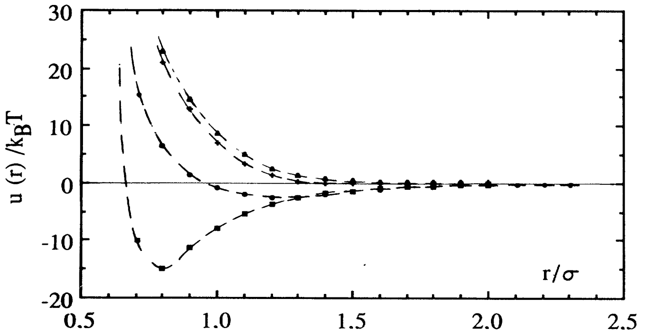

FIG. 3. Pair potential of Cr (symbols are as in Fig. 2).

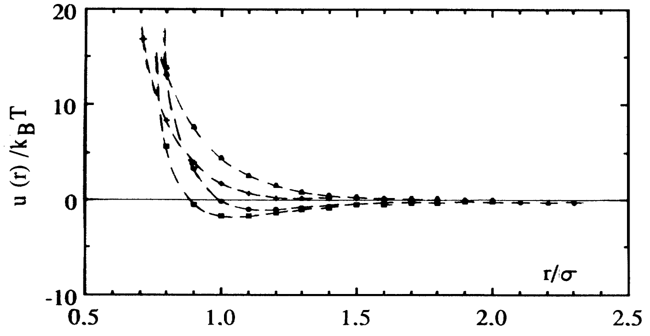

FIG. 4. Pair potential of Ni (symbols are as in Fig. 2).

a.u. for Ni].

Another feature that is apparent in Figs. 2–4 is the displacement of the pair potential curve $u(r)$ underneath the abscissa axis, in the range of r between the first- and the second-nearest neighbors. This behavior, induced by the d-band contribution, might have an influence on the calculation of certain selected physical properties. The WH potential has already been tested with respect to the structure of liquid $3d$ transition metals by means of perturbation theory[9] and it has been pointed out that if the WH potential is good enough for the repulsive-core approximation, no decisive improvement is obtained when the attractive tail is considered. Nevertheless, the new thermodynamically self-consistent integral equation[22,23] for the determination of the structural properties of liquids appears to be a more promising procedure. This scheme, which combines the hypernetted-chain and the Percus-Yevick equations, leads to a significant improvement compared to conventional approximations. Calculations using this integral equation with the WH pair potential are in progress and are planned to be published shortly.

In summary, the WH pair potential has been used to perform the calculations of the thermodynamic properties of liquid transition metals and the results point to a qualitative agreement in the packing fraction for the three series. On the other hand, the role of the exchange-correlation contribution has also been clearly shown, although the most important effect is that of the d band, which is particularly sensitive in the middle of each row.

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