# Thermodynamics of solid and liquid embedded-atom-method metals: A variational study

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We present results of variational calculations of the Helmholtz free energy and the thermodynamic properties of a series of metallic liquids and solids (Ag, Au, Cu, Ni, Pd, Pt) described by embedded-atom-method potentials. For the solids, we use a variational procedure based on an Einstein-model reference state. The free energies of liquids are calculated with an approximate variational method proposed by Ross. At the respective melting points, the present results for the Helmholtz free energy are within about 1% of the results of accurate Monte Carlo (MC) calculations with the same interaction potentials, both for the fluid and the solid. The average error in the melting points calculated with the present procedure relative to Monte Carlo results is about 7.5%. The internal energies and entropies are compared to MC results, and show, in general, good agreement.

## I. INTRODUCTION

Many different methods have been developed to describe the thermodynamic properties of solids and liquids. For the case of perfect crystals, these include lattice dynamics in the harmonic and quasiharmonic approximations,[1] self-consistent phonon theory,[2] and classical molecular dynamics (MD) and Monte Carlo (MC) computer simulations.[3] With accurate descriptions of the interatomic interactions, these methods give calculated properties of perfect crystals in good agreement with experiment. Similarly, the thermodynamic properties of simple liquids may be determined using integral-equation methods,[4] perturbation theories,[5] and MD and MC computer simulations.[3] Apart from the simulation methods, these approaches are designed for either solids or liquids and cannot be used for both. Therefore, it is difficult to obtain consistent thermodynamics for both the solid and the liquid phases. While atomistic simulation techniques such as MD and MC may equally well be applied to solids or liquids, it is difficult and costly to use these methods to obtain the absolute free energies needed to predict phase transitions. In the present study, we report on a method to obtain the thermodynamic properties of crystalline and liquid materials, and, in particular, metals, over a wide range of temperatures and pressures.

The basis of our methods will be to calculate the Helmholtz free energy of the systems, from which all thermodynamic quantities may be derived. Free energies are not readily available from a single computer simulation; in general, a series of simulations are necessary to obtain the free energy for a given thermodynamic state. The key in all the simulation methods is to relate the free energy for the system of interest with that of a reference system for which the free energy is known. In principle, liquids are easier than solids; for a fixed temperature, one can connect to the ideal gas by integrating the pressure as a function of density, using the virial expansion at low densities and simulation data at high-

er densities.[3] A number of simulations is necessary to obtain enough data to perform an accurate integration of the pressure. The free energy of arbitrary solids can be obtained with the method of Frenkel and Ladd,[6] in which the real solid is connected to a reference system (with known free energy) by introducing a coupling parameter that can be varied to slowly turn off the true interatomic potential and turn on the reference state potential. A series of simulations is then performed as a function of that coupling parameter and the free energy determined through an integration of averages of the internal energy. Variants of the original Frenkel–Ladd method have been suggested, but are based on the same central concept.[7] All of these methods suffer from the need for large numbers of simulations. Thus, the simulation methods are quite computer intensive and not appropriate for studies of large numbers of materials.

We employ a variational procedure [which we[8] recently introduced as the variational Gaussian (VG) method] to determine the free energies of metallic solids. In the VG method, the free energy of a solid is found using an Einstein crystal as a reference state. In the Einstein model, atoms have a Gaussian probability density of being at a certain distance from their mean position. The equilibrium widths of the Gaussian distributions are obtained in the VG method by minimizing the free energy with respect to the widths of the distributions. The free energy of the solid is thus determined in terms of an Einstein model, the interaction potential between atoms, and the atomic probability densities. We have previously applied the VG method to determine the free energy of a vacancy in an fcc crystal, where atomic interactions were described in terms of a simple pair potential.[8] The first use of this method was by Monsoori and Canfield on the Lennard-Jones potential.[9] Other uses have been on perfect crystals (described either by pair potentials or as pseudopotentials),[10(a)] alloy solubility,[10(b)] and vacancies.[10(c)]

For liquids, we use a simple (and approximate) vari-

ational method introduced by Ross.[11] The simplest reference state that one could choose for a liquid would be a hard-sphere system. However, hard-sphere models are known to not give particularly good results for systems with realistic interaction potentials. Ross chose to use a $1/r^{12}$ liquid as a reference state. However, the necessary input to such a variational procedure is the radial distribution function $g_0(r)$ of the reference liquid. Until recently,[12] these were not readily available for other than hard-sphere systems. Thus, Ross approximated the $g(r)$ for a $1/r^{12}$ liquid with that of a hard-sphere system, which can be obtained analytically in the Percus–Yevick approximation. Even though it is an approximate variational theory, the Ross procedure has proven to work quite well for liquids over a wide range of densities.[11,12(b)]

Since most of the bonding in metals may be attributed to the electron gas, we abandon the pair-potential model in favor of approaches based on a description of the local electron density. In particular, we extend the VG method and the Ross procedure to cases where the atomic interactions are described by embedded-atom-method (EAM) potentials.[13] In the EAM, the total interaction energy is split into a pair term and a term that depends on the local electronic density of the system. The latter term includes many-body contributions. Both the EAM versions of the solid VG and liquid variational methods are employed to determine the free energy, entropy, and internal energy of a series of elemental transition metals (Ag, Au, Cu, Ni, Pd, and Pt) as a function of temperature. In order to test the accuracy of this approach, we compare our results with accurate Monte Carlo determinations of the free energy based on the same potentials.[14] We find that both for solids and liquids the simulation results are in excellent agreement with the Monte Carlo results. A particularly severe test of our methods is the determination of the melting points, which requires a high degree of consistency between the solid and liquid results. The melting points found using our variational approach are within about 7.5% of those determined with the MC method using the same potentials. The advantage of the variational approach is that transition temperatures, thermodynamic properties, and equations of state can be obtained orders of magnitude faster than with standard Monte Carlo or molecular dynamics methods.

## II. THEORY

The basis of our theoretical approach is the Gibbs–Bogoliubov inequality, which relates the Helmholtz free energy of a system to that of a reference state by[15]

$$A \leqslant A_0 + \langle U - U_0 \rangle_0, \qquad (1)$$

where $A$ and $U$ are the Helmholtz free energy and potential energy of the system, respectively. $A_0$ and $U_0$ are the Helmholtz free energy and potential energy of the reference system and the average is taken over the configuration of the reference system. (We use $A$ for the Helmholtz free energy to avoid confusion with the embedding energy given below.) The free energy is rigorously bounded from above by the right hand side of Eq. (1), so that if the reference system is characterized by some parameter, then the best estimate for

the free energy is found by minimizing the right-hand side of Eq. (1) with respect to that parameter. As we shall see below, there are straightforward choices for the reference system for both solid and liquid phases.

Since the present study focuses on metals, we will employ embedded-atom-method (EAM) potentials[13] to characterize atomic interactions and hence the potential energy. The potential energy of a system described by EAM potentials may be written as

$$U = \sum_{i=1}^{N} F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \phi_{ij}(r_{ij}), \qquad (2)$$

where the sum on $i$ is over all $N$ atoms in the system and the sum on $j$ is over all atoms interacting with atom $i$, $\phi_{ij}(r_{ij})$ is the pair potential contribution to the interaction between atoms $i$ and $j$ separated by distance $r_{ij}$. $F_i$ is the embedding term that approximates the energy required to embed atom $i$ in a uniform electron gas of density

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}), \qquad (3)$$

where $\rho_j(r_{ij})$ is the electron density from atom $j$ at the position of atom $i$. $F$ is a nonlinear function that is obtained, in practice, by requiring that the energy of the perfect crystal lattice matches that of the universal binding curve of Rose et al.[16]

Since $F$ is nonlinear, the evaluation of its average value is complicated by the presence of many-body terms. The average of $F$ ($\langle F \rangle$) depends on the many-body correlation functions for the system, which are not generally known, so $\langle F \rangle$ cannot be evaluated analytically. Thus, we approximate that average by first writing the electronic density as[17]

$$\bar{\rho}_i = \langle \bar{\rho}_i \rangle_0 + \sum_{j \neq i} (\rho_j(r_{ij}) - \delta), \qquad (4)$$

where $\delta$ is the mean contribution to the electron density at site $i$ from the atoms within interaction range. We then expand $F$ about $\rho_j - \delta$ and perform the configurational average. The first-order term vanishes and we are left with

$$\langle F_i(\bar{\rho}_i) \rangle_0 = F_i(\langle \bar{\rho}_i \rangle_0)$$
$$+ \frac{1}{2} \left( \frac{\partial^2 F}{\partial \bar{\rho}_i^2} \right)_{\langle \bar{\rho}_i \rangle_0} (\langle \bar{\rho}_i^2 \rangle_0 - \langle \bar{\rho}_i \rangle_0^2) + \cdots. \qquad (5)$$

The evaluation of the first term in Eq. (5) is straightforward and involves only two-body interactions, as shown below. The second-order term (involving $\langle \bar{\rho}^2 \rangle - \langle \bar{\rho} \rangle^2$) is more difficult and, as outlined in Appendix B, its evaluation requires a knowledge of three-body correlations. The rest of the terms in the series involve even higher-order correlations. As we shall see below, however, the second-order term is quite small, especially for the solid, and can be ignored with little loss in accuracy. We assume that the higher-order terms make an even smaller contribution. The results discussed herein were thus obtained including only the first term in Eq. (5). For comparison, second-order corrections were then determined. We note that since we approximate $\langle F \rangle$, we no longer have a strictly rigorous variational procedure and the final free energy need not be an absolute upper bound to the

true free energy. Nonetheless, the variational results are, indeed, greater than the true free energy (as calculated with Monte Carlo calculations) and furthermore, since the second-order terms are quite small, are a good approximation to that free energy (as shown below). A similar expansion for $\langle F \rangle$ was recently used in a study of segregation at boundaries in metallic alloys with similar conclusions as to the relative unimportance of the second-order term in Eq. (5).[18]

The success of the use of Eq. (1) as a variational procedure depends on how well the reference state approximates the properties of the system of interest. Since solids and liquids have very different physical properties, we choose different reference states for the two cases, as outlined in the next section.

We used the variational procedure to generate the best estimate of the Helmholtz free energy $A$ as a function of the volume ($V$) and temperature ($T$). The zero-pressure ($P$) properties, at each $T$, were determined by interpolating $A(V)$ and finding where $P = -(\partial A/\partial V)_T = 0$, thus giving $A(P = 0)$ and $V(P = 0)$ as a function of $T$. The entropy ($S$) and energy ($E$) were determined at each $V$ by interpolating $A$ with respect to $T$ and using the relations $S = -(\partial A/\partial T)_V$ and $E = [\partial(A/T)/\partial(1/T)]_V = A + TS$. The two expressions for $E$ were used to check the interpolation results. $E$ and $S$ were then found, for each $T$, as a function of $V$ and the $P = 0$ values determined.

## A. Variational theory for solid EAM metals

In the Einstein approximation, the vibrational density of states of a solid is approximated by a sum of delta functions centered on the local atomic vibrational frequencies. For a perfect crystal (with cubic or higher symmetry), all frequencies are equal to $\omega_0$. The time-averaged spatial distributions of atom positions in the harmonic solid consist of Gaussian functions of the form $(\alpha/\pi)^{3/2} \exp(-\alpha(\mathbf{r}_i - \mathbf{r}_i^0)^2)$ centered on the average atomic positions $\mathbf{r}_i^0$, where $\alpha = m\omega_0^2/(2k_B T)$, $m$ is the atomic mass, and $k_B T$ is the thermal energy. The classical vibrational contribution to the free energy can then be written as

$$A_v = \frac{3}{2} N k_B T \ln\left[\frac{\alpha\Lambda^2}{\pi}\right], \tag{6}$$

where $\Lambda$ is the thermal wavelength $\Lambda = h/(2\pi m k_B T)^{1/2}$. With the Einstein model as the reference system and keeping only the first term in Eq. (5), we may write the variational free energy of an EAM metal as[8]

$$\frac{A}{N} \leqslant F(\langle \bar{\rho} \rangle_0) + \frac{1}{2N} \sum_{i=1}^{N} \sum_{j \neq i}^{N} w_{ij}(r_{ij}^0)$$
$$+ \frac{3}{2} k_B T \left\{ \ln\left(\frac{\alpha\Lambda^2}{\pi}\right) - 1 \right\}. \tag{7}$$

$w_{ij}$ is an effective pair potential obtained by averaging $\phi_{ij}(r_{ij})$ over the Gaussian probability distributions of the positions of atom $i$ and $j$

$$w_{ij}(r_{ij}^0) = \left(\frac{\alpha_i}{\pi}\right)^{3/2}\left(\frac{\alpha_j}{\pi}\right)^{3/2} \int e^{-\alpha_i(\mathbf{r}_i - \mathbf{r}_i^0)^2}$$
$$\times \int e^{-\alpha_j(\mathbf{r}_j - \mathbf{r}_j^0)^2} \phi_{ij}(\mathbf{r}_{ij}) d\mathbf{r}_i \, d\mathbf{r}_j. \tag{8}$$

In applications to nonuniform solids, the vibrational frequencies will vary from atom to atom, so that the $\alpha$ parameters will also vary from site to site. The average electronic density at an atomic site is the sum of the Gaussian-averaged densities of the other atoms in the system

$$\langle \bar{\rho} \rangle_0 = \sum_{j \neq i} \psi_j(r_{ij}^0). \tag{9}$$

The $\psi_j$ are determined via Eq. (8) with $\psi_{ij}$ replacing $w_{ij}$ and $\rho_{ij}$ replacing $\phi_{ij}$. In these expressions, $r_{ij}^0$ is the distance between the average positions (i.e., the centers of the Gaussians) of atom $i$ and $j$. For convenience in evaluating the integrals in Eqs. (8) and (9), we fit $\phi$ and $\rho_j$ to a sum of Gaussian functions, as discussed in Appendix A, thus obtaining analytical expressions for $\omega_{ij}$ and $\psi_i$. Expressions for evaluating the second-order term in the average embedding energy [Eq. (5)] are given in Appendix B.

The calculation of the free energy is performed simply by summing temperature-dependent effective pair potentials and electronic densities that are only slightly more complicated than the original functions themselves. The equilibrium value of the free energy can then be determined for an atomic system at arbitrary volume and temperature by minimizing the expression on the right-hand side of Eq. (7) with respect to the mean atomic positions $\mathbf{r}_i^0$ and the local Gaussian widths $\alpha_i$.

## B. Variational theory for liquid EAM metals

For application to liquids interacting with a pair potential, $\phi_{ij}$, the Gibbs–Bogoliubov inequality takes the form[15]

$$A \leqslant A_0 + \frac{N}{2V} \int g_0(r)\{\phi(r) - \phi_0(r)\}dr, \tag{10}$$

where $V$ is the volume of the system, and $g_0$ and $\phi_0$ are the pair distribution function and potential of the reference system, respectively. To use this method, both the free energy and pair distribution function of the reference system must be known as a function of density and temperatures. We choose here to use the procedure suggested by Ross,[11] in which a reference state that approximates an atomic liquid interacting with a $1/r^{12}$ potential is used. While a recent method[12] to solve integral equations for the pair distribution functions in a $1/r^n$ fluid could obviate the approximations in the Ross method and yield a more controlled variational procedure, the Ross approach has the advantage of much greater computational simplicity. Ross[11] first approximated the free energy of a $1/r^{12}$ liquid in terms of a hard-sphere liquid by writing

$$A_{12} = A_{hs}(\eta) + \frac{N}{2V} \int g_{hs}(r,\eta)\left(\frac{1}{r}\right)^{12} dr + F_{12}(\eta), \tag{11}$$

where $\eta = \pi N d^3/6V$, $d$ is the diameter of the reference hard spheres, the free energy of the hard-sphere liquid is $\beta A_{hs}[ = \eta(4 - 3\eta)/(1 - \eta)^2]$, and $F_{12}$ is a function of $\eta$ that ensures that the expression agrees with the known free energy of the $1/r^{12}$ liquid $[F_{12} = -(\eta^4/2 + \eta^2 + \eta/2)]$. The optimal value for $A_{12}$ is found by minimizing the right-hand side with respect to $\eta$. Ross then approximates the pair

distribution function for the $1/r^{12}$ liquid with that for a hard-sphere fluid $g_{hs}(r,\eta)$, which, for EAM potentials, yields

$$A \leqslant A_{hs}(\eta) + F_{12}(\eta) + \frac{N}{2V}\int g_{hs}(r,\eta)\phi(r)dr$$

$$+ F(\langle\bar{\rho}\rangle_0) + k_B T\left[\ln\left(\frac{N\Lambda^3}{V}\right) - 1\right], \qquad (12)$$

where $\eta$ is the variational parameter and $V$ is the volume. The last term is that for an ideal gas. In Eq. (12), the average embedding energy is approximated with the first term in Eq. (5) and the average electron density is given by

$$\langle\bar{\rho}\rangle_0 = \frac{N}{V}\int g_{hs}(r,\eta)\rho(r)dr. \qquad (13)$$

Note that since an approximate value for the reference $g(r)$ is used, the Ross procedure is not a strict variational theory. However, it has been shown to work well for a number of potentials. We evaluated the integrals in Eqs. (12) and (13) with a Gauss–Legendre quadrature, using the Percus–Yevick solution for $g_{hs}(r)$.[19] Expressions for the second-order term in the average embedding energy [Eq. (5)] are given in Appendix B in terms of the three-body correlation functions.

## III. APPLICATION TO EAM METALS

Since we are concerned here with the quality of the variational procedures, we need to compare our results to accurate free energies based on the same interaction potentials as used in our study. Such a comparison is more appropriate than with experimental data, since the potentials represent an uncertain description of the real system. We thus applied the present variational methods to a series of transition metals (Ag, Au, Cu, Ni, Pd, and Pt) described by the EAM potentials of Foiles, Daw, and Baskes[13] for which the free energies of the solid and liquid are available from the extensive Monte Carlo (MC) simulations by Foiles and Adams.[14] In their paper,[14] (hereafter referred to as FA) Foiles and Adams demonstrate that the EAM potentials yield thermodynamics of solid and liquid metals that are in reasonably good agreement with existing experimental data. A particularly sensitive test of the potentials, however, is the prediction of melting points, since small errors in the free energy can lead to large errors in transition temperatures. In Table I, we show the melting points for these six materials, as determined experimentally[20] and from the MC-EAM calculations. We see that the MC results are in only fair agreement with experiment, with average errors of 13% and a maximum error more than twice as large. As pointed out by Foiles and Adams, however, an error of only 0.01 eV in the free energy (about 0.2%) can lead to an error of order 100 °K in the melting point. Fortuitous cancellation of errors between the fluid and solid can, of course, enable more accurate determinations.

In Fig. 1, we show the results of our variational calculations for the zero-pressure free energy of the solid phases of Ag, Au, Cu, Ni, Pd, and Pt, all of which have a face-centered-cubic crystal structure. Two curves are shown for each material; one for the variational results (solid curve) and the other for the Monte Carlo simulation results (dashed curve) of Foiles and Adams. Not surprisingly, the results agree well

TABLE I. Comparison of calculated and experimental melting points (°K).

| Element | $T_m$ (expt) | $T_m$ (MC) | $T_m$ (Variational) |
|---------|-------------|------------|---------------------|
| Ag | 1234 | 1150 | 1100 |
| Au | 1338 | 1090 | 1150 |
| Cu | 1358 | 1340 | 1290 |
| Ni | 1726 | 1740 | 1665 |
| Pd | 1825 | 1390 | 1505 |
| Pt | 2045 | 1480 | 1740 |

at low temperatures (they must agree exactly at 0 °K), with the error increasing as the temperature is increased. At the appropriate melting points found in the MC study (Table I), the errors in the present results are: Ag–0.04 eV/atom (1.22%), Au–0.03 eV/atom (0.61%), Cu–0.05 eV/atom (1.11%), Ni–0.06 eV/atom (1.17%), Pd–0.05 eV/atom (1.0%), Pt–0.05 eV/atom (0.64%). As discussed in Appendix B, the second-order terms for the average embedding energy in the solid can be evaluated exactly, though they involve sums over three-body interactions and require considerably more computer time than the rest of the calculations. These terms are small and positive and range from a low of 0.001 eV/atom in Cu to a high of 0.048 eV/atom in Pt at their respective melting points. Since these terms are positive, their inclusion slightly increases the error relative to the MC results. At the melting points of the materials, the average errors in the free energy are 0.97% with the first-order term and 1.22% with the second-order correction. We have not evaluated the contribution of the higher-order terms, though we expect these will be smaller than the second-order
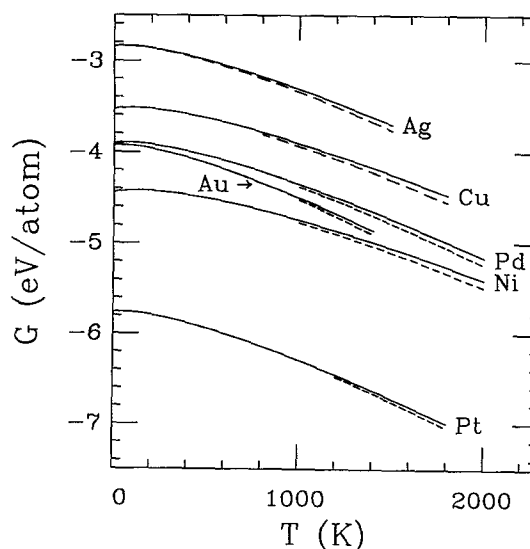


FIG. 1. Comparison of the zero-pressure Gibbs free energy $G$ in eV/atom as a function of temperature for a series of solid metals described by EAM potentials. The solid curves were calculated with the variational method and the dashed curves are from accurate Monte Carlo calculations (Ref. 14).

terms. Thus, we presume the results with the second-order corrections to be upper bounds to the true free energy.

The results for the liquid EAM metals are shown in Fig. 2, where once again the solid curves are the variational results and the dashed curves are the MC results by FA. Overall, the agreement between the variational results and the MC data is quite good. However, the disagreement between MC and variational results for the liquid is somewhat larger than for the solid (Fig. 1). At the MC melting points, the average error was 0.97% with the first-order term in $\langle F \rangle$ and 1.52% when the second-order correction to $\langle F \rangle$ is included. The contributions from the second-order term for $\langle F \rangle$ is somewhat larger in the liquid than in the solid, ranging between 0.01 eV/atom in Ag and Ni to 0.06 eV/atom in Pt at their respective melting points. We used, however, a rather severe approximation for the three-body correlation functions needed in the evaluation of the second-order term for the liquid, as discussed in Appendix B, and thus the calculated values for this term are suspect. Though the Ross procedure is not a true variational method, the present results do lie above the MC results.

A sensitive test of any free energy method is its usefulness in determining phase transitions. In Table I, we compare the estimated melting points for the six EAM metals with both MC results and experiment. Comparison of the variational results with the MC melting points indicates that the variational method does reasonably well for all metals but Pt, where the results are a factor of two worse. The average error for all six materials was about 100 K or 7.5%. Excluding the Pt results, we find that the variational and MC results agree to within approximately 75 K or about 6%. Why the results for Pt should have a larger error remains unclear. On average, the variational results underestimate the MC determined melting points. Inclusion of the
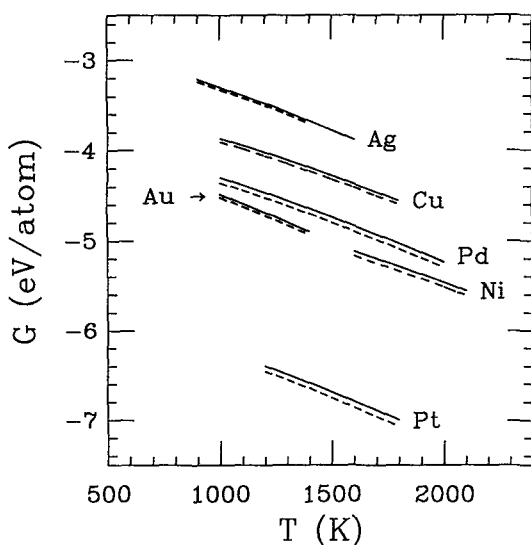
second-order terms slightly increases the overall error in the melting points (compared with the MC results), to about 10%. However, as noted previously, the values for the second-order term for the liquid are of uncertain quality and so calculations based on them are somewhat suspect.

The internal energies $E$ were determined from the variational free energies as described in Sec. II and are plotted in Fig. 3 for both the solid and liquid states (solid curves). Also plotted on that figure are the results from the MC calculations (FA). We see that the agreement between the variational results and the MC studies is excellent for the solid materials. They do, however, consistently, underestimate the MC internal energies with an average deviation of only about 0.03 eV/atom, or about 0.84%, at the MC melting points. The variational results for the internal energy of the liquids are in less good agreement. They are always overestimated, with an average error at the MC melting points of about 0.045 eV/atom, or about 1.28%.

The calculated entropies $S$, which were determined from the variational free energies as outlined above, are shown in Fig. 4. In this case, the agreement between the variational results for the liquids and that from the MC calculations is remarkably good, with an average error of only $3.3 \times 10^{-6}$ eV/(°K atom), or 0.47%, at the MC melting points. The variational solid entropies are consistently too low and the errors are roughly an order of magnitude worse than for the liquids, with an average error at the MC melting points of $5.3 \times 10^{-5}$ eV/( K atom), or 6.3%.

## IV. DISCUSSION

Overall, the agreement between the free energies predicted by the variational method and the Monte Carlo simu-



FIG. 2. Comparison of the zero-pressure Gibbs free energy $G$ in eV as a function of temperature for a series of liquid metals described by EAM potentials. The solid curves were calculated with the variational method and the dashed curves are from accurate Monte Carlo calculations (Ref. 14).
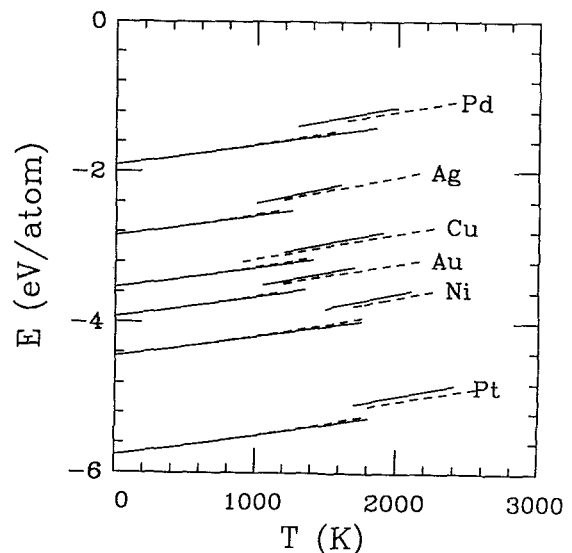


FIG. 3. Internal energy $E$ in eV/atom for solid and liquid metals described by EAM potentials. The solid curves were derived (as described in the text) from the variational free energies. The dashed curves are the results from MC simulations (Ref. 14). There are two sets of curves associated with each material. The curves to low temperatures are for the solids and the curves extending to higher temperatures are for the liquids. The results for Pd have been shifted up by 2 eV/atom to separate them from the results for Au.
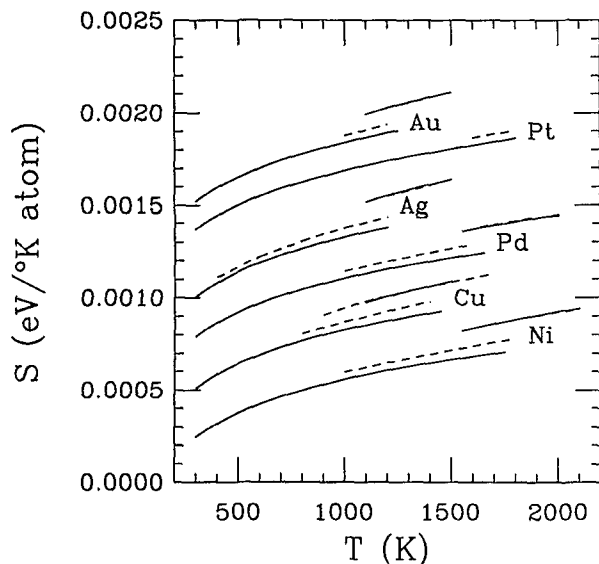
FIG. 4. Entropy $S$ in eV/( K atom) for solid and liquid metals described by EAM potentials. The solid curves were derived (as described in the text) from the variational free energies. The dashed curves are found from the results of MC simulations (Ref. 14), using $S = (E - A)/T$. There are two sets of curves for each material, except for Pt, where only the results for the solid are shown. The curves to low temperatures are for the solids and the curves extending to higher temperatures are for the liquids. The results have been shifted to separate the curves. The shifts are Ag, 0.0006; Au, 0.0010; Cu, 0.0002; Ni, 0.0; Pd, 0.0004; Pt, 0.0009, with all units in eV/( K atom).

lation results are excellent, with errors typically of only 1% at the melting points. The errors in the solid and liquid variational free energies arise from different causes, which can be understood in part by comparing the internal energy and entropy in Figs. 3 and 4 with our approximation for A. First, we see in Fig. 3 that the internal energies of the solids agree very well with MC results, with a somewhat greater error for the liquids, while the entropies are almost exact for the liquids and in error for the solids. Another way of writing the Gibbs–Bogoliubov inequality is $A \leqslant \langle U \rangle_0 - TS_0$. Given that the temperature dependence of the variational parameters ($\alpha$ for the solid and $\eta$ for the liquid) and hence $\langle U \rangle_0$ is small, then the entropy is dominated by $S_0$. Using Eq. (7) for the free energy of the solid and Eq. (12) for the liquid (with the right-hand sides at their minimum), we can analytically differentiate $A$ with respect to $T$ to evaluate the contributions of the various terms to the entropy. For example, for Ag at its melting point, the contributions to the entropy from the reference states are about 85% of the total entropy for both the solid and the liquid. It is clear then, that the $1/r^{12}$ fluid (as approximated in the Ross procedure) represents the entropy of the liquid very well, while the assumption of independent, harmonically vibrating atoms leads to errors in the solid state entropy. In our approximation, $A = E - TS = \langle U \rangle_0 - TS_0$, so that if $S \approx S_0$, then $E \approx \langle U \rangle_0$. Since our results for the solid are in good agreement with the MC values, it thus appears that a Gaussian description of the atomic distribution functions is accurate for a solid, even at the melting point. Similar conclusions have been drawn by those using a Gaussian description of the distributions in statistical–mechanical density–func-

tional theories of melting.[21] That the results for the internal energy of the liquids are somewhat less accurate than the solid may be due largely to the approximations inherent in the Ross procedure, where the real $g(r)$ is replaced by that of a hard-sphere liquid. Indeed, errors may well have been introduced even if we had used a real $1/r^{12}$ potential, since the EAM potentials are less steep than $1/r^{12}$.

In this paper, we have only examined the variational prediction by comparison with zero-pressure results. We expect that at high pressures, where the atomic motions are more constrained and harmonic, the variational procedure will improve. For the same reasons, we expect that the variational approach will work less well for systems that are not as close packed, and therefore not as harmonic, as the fcc structures studied here.

The agreement between the melting points calculated here and those from the MC calculations is very good, especially considering the simplicity of the present approach and the sensitivity of melting points to very small errors. However, since our errors in the free energy at the melting points are about 0.04 eV/atom which, according to Foiles and Adams,[14] should lead to an error of about 400 K in the melting point, considerable cancellation of errors is present, since the variational and MC melting points typically differ by only 75 °K. This cancellation is obvious from Figs. 1 and 2, where both the liquid and solid variational results lie above the MC values. Thus, the free energies in both cases are too high.

Our results show that in all cases the second order term in $\langle F \rangle$ [Eq. (5)] is small and positive, and thus inclusion of this term results in slightly worse agreement between the thermodynamic functions determined with the variational and MC results. For the solid, these increased errors are small. They are larger for the liquid, but as discussed in Appendix B, our evaluation of the second order term in $\langle F \rangle$ for the liquid required the introduction of a new approximation, i.e., replacing the three-body correlation functions with the product of three two-body correlation functions. Such an approximation is unnecessary for the solid and the free energies including that term are in better agreement with the MC data than those for the liquid.

Besides the surprisingly high degree of accuracy provided by the variational method, its real advantage over competing methods is its simplicity and computational efficiency. The Monte Carlo results with which we compare our variational method were obtained by performing a large number of time-consuming simulations representing hours of supercomputer time. On the other hand, the variational results require just minutes of computer time on inexpensive computer work stations. Therefore, the variational method is the method of choice for problems in which a significant quantity of thermodynamic data is required and accuracy of order 1% is adequate.

While the variational method works quite well for the perfect crystal, there are other, equally easy, methods that work about as well. Recently we presented results for the free energy of gold using a local-Einstein model with the same potential as used here.[22] In that method, the Einstein expression for the free energy is used with the vibrational frequency determined at each volume by ignoring all terms in the dy-

namical matrix coupling the vibrations of different atoms and diagonalizing the remaining $3 \times 3$ matrix to find the frequency. That approach gave results essentially identical with the variational method (without the second-order term). All other quantities determined with that method also agree well with those from the variational procedure, including lattice expansion. This agreement indicates that the lattice is very harmonic, which indeed may explain the overall high quality results obtained with the variational method as well, since it is based on a harmonic reference system.

## V. SUMMARY AND CONCLUSIONS

We have presented a new variational method for calculating the free energies of a series of solid and liquid metals (Ag, Au, Cu, Ni, Pd, Pt) described by embedded-atom-method (EAM) potentials, which incorporate a more realistic description of atomic bonding in metals than do pair potentials. Both the EAM versions of the solid VG and liquid variational methods were employed to determine the free energy, entropy, and enthalpy of a series of elemental metals as a function of temperature. In order to test the accuracy of this approach, we compare our results with accurate Monte Carlo determinations and find that the present results are in good agreement with the Monte Carlo results, with an error in free energies at the melting points of about 1% for both solids and liquids.

A particularly severe test of our methods is the determination of the melting points of these metals. Accurate melting point determinations require a high degree of consistency between the solid and liquid results. The melting points found using our variational approach are within about 7.5% of those determined with the MC method using the same potential. Why the Pt results are somewhat less accurate is not clear.

One of the main advantages our variational methods enjoy over other methods, such as Monte Carlo or molecular dynamics, is the efficiency with which transition temperatures, thermodynamic properties, and equations of state can be determined. The calculations required to obtain the results in this paper for all six systems (at any pressure) take far less time than a simulation at any one state point for these materials.

## APPENDIX A

To facilitate evaluation of the integrals in Eqs. (8) and (9), we fit the EAM pair potentials and electronic densities with sums of Gaussian functions of the interatomic distance of the form

$$\phi(r) = \sum_{i=1}^{6} c_i e^{-\gamma_i r^2}; \quad \rho(r) = \sum_{i=1}^{5} d_i e^{-\delta_i r^2}. \quad (A1)$$

The number of functions for $\phi$ and $\rho$ were chosen to give reasonable fits and a combination of a nonlinear least-squares fit for the exponents ($\gamma$ and $\delta$) and a linear least-squares fit for the coefficients ($c$ and $d$) was used. The relative standard deviations of the fits were less than 0.001 in all cases. The potential and density averaged over the Gaussians [Eqs. (8) and (9)] then take on the simple forms (for isotropic vibrations)

$$w(r) = \sum_{i=1}^{6} \frac{c_i}{\sqrt{(1 + 2\gamma_i/\alpha)^3}} e^{-\gamma_i r^2/(1 + 2\gamma_i/\alpha)} \quad (A2)$$

and

$$\psi(r) = \sum_{i=1}^{5} \frac{d_i}{\sqrt{(1 + 2\delta_i/\alpha)^3}} e^{-\delta_i r^2/(1 + 2\delta_i/\alpha)}, \quad (A3)$$

where $\alpha$ is related to the width of the atomic distributions as discussed in Sec. II A above.

The embedding function in the EAM potential, $F(\bar{\rho})$, is determined from results on the perfect crystal for a series of volumes by subtracting the pair energy from the total energy of the universal binding curve of Rose et al.[16] Since we introduce small errors in both the pair and the density terms because of the fitting procedure, we redetermined $F$ with these representations. The changes in $F$ from those used by Foiles et al.[13] were quite small.

## APPENDIX B

To evaluate the second-order term in Eq. (5) for the average embedding energy, the fluctuation in the density, i.e. $\langle\bar{\rho}^2\rangle - \langle\bar{\rho}\rangle^2$, is needed. Using Eq. (3) for the density, we find

$$\langle\bar{\rho}_i^2\rangle_0 = \sum_{j\neq i=1}^{N} \langle\rho_j^2(r_{ij})\rangle_0$$
$$+ \sum_{j\neq i=1}^{N} \sum_{k\neq j\neq i=1}^{N} \langle\rho_j(r_{ij})\rho_k(r_{ik})\rangle_0. \quad (B1)$$

The first term is a sum of two-body terms, while the second term involves three-body interactions.

For the solid, the two-body terms can be evaluated with expressions similar to those in Eq. (A3), i.e.,

$$\langle\rho_j^2(r)\rangle_0 = \sum_{a=1}^{5} \sum_{b=1}^{5} \frac{d_a d_b}{\sqrt{(1 + 2(\delta_a + \delta_b)/\alpha)^3}}$$
$$\times e^{-(\delta_a + \delta_b)r^2/(1 + 2(\delta_a + \delta_b)/\alpha)}. \quad (B2)$$

The three-body terms can be determined analytically and take the form

$$\langle \rho_j(r_{ij})\rho_k(r_{ik})\rangle_0$$

$$= \sum_{a=1}^{5} \sum_{b=1}^{5} \frac{d_a d_b}{\sqrt{g^3}} \exp\left[ -\left( \delta_a r_{ij}^{02} + \delta_b r_{ik}^{02} \right.\right.$$

$$\left.\left. + \frac{2\delta_a \delta_b}{\alpha} \{ r_{ij}^{02} + r_{ik}^{02} - \mathbf{r}_{ij}^0 \cdot \mathbf{r}_{ik}^0 \} \right) g \right], \quad (B3)$$

where

$$g = 1 + \frac{2\delta_a}{\alpha} + \frac{2\delta_b}{\alpha} + \frac{3\delta_a \delta_b}{\alpha^2}$$

and $\mathbf{r}_{ij}^0$ is the vector connecting the centers of the distributions of atom $i$ and $j$.

For the liquid, the first term in Eq. (B1) takes the same form as in Eq. (13), with $\rho$ replaced by $\rho^2$. The second term becomes

$$\frac{N^2}{V^2} \int d\mathbf{r}_j \int d\mathbf{r}_k \, \rho(\mathbf{r}_j)\rho(\mathbf{r}_k) g_0^{(3)}(\mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_j - \mathbf{r}_k) \quad (B4)$$

In general, three-body correlation functions are not readily available. Here, we use the superposition approximation[19] and take $g^{(3)} = g(r_{12})g(r_{13})g(r_{23})$, using the Percus–Yevick solution for the hard-sphere $g(r)$.[19] This approximation is of uncertain quality.

[1] T. H. K. Barron and M. L. Klein, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North Holland, Amsterdam, 1974), Vol. 1, pp. 391–450.

[2] T. R. Koehler, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North Holland, Amsterdam, 1975), Vol. 2, pp. 1–104.

[3] *Simulation of Liquids and Solids*, edited by G. Ciccotti, D. Frenkel, and I. R. McDonald (North Holland, Amsterdam, 1987).

[4] J. Talbot, J. L. Lebowitz, E. M. Waisman, D. Levesque, and J.-J. Weis, J. Chem. Phys. **85**, 2187 (1986).

[5] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971); J. A. Barker and D. Henderson, Annu. Rev. Phys. Chem. **23**, 439 (1972).

[6] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984).

[7] E. J. Meijer, D. Frenkel, R. LeSar, and A. J. C. Ladd, J. Chem. Phys. **92**, 7570 (1990).

[8] R. LeSar, R. Najafabadi, and D. J. Srolovitz, Phys. Rev. Lett. **63**, 624 (1989).

[9] G. A. Monsoori and F. B. Canfield, J. Chem. Phys. **51**, 4967 (1969).

[10] (a) H. D. Jones, Phys. Rev. A **8**, 3215 (1973); M. Hasegawa, M. J. Stott, and W. H. Young, J. Phys. F **9**, 1 (1979); W. Y. Shih, W-H. Shih, and I. A. Aksay, J. Chem. Phys. **90**, 4506 (1989); (b) W. Y. Shih and D. Stroud, Phys. Rev. B **32**, 7779 and 7785 (1985); (c) J. F. Dobson and N. W. Ashcroft, Phys. Rev. B **16**, 5326 (1977).

[11] M. Ross, J. Chem. Phys. **71**, 1567 (1979).

[12] (a) F. J. Rogers and D. A. Young, Phys. Rev. A **30**, 999(1984); (b) G. Zerah and J.-P. Hansen, J. Chem. Phys. **84**, 2336(1986); (c) D. B. Boercker and D. A. Young, Phys. Rev. A **40**, 6379 (1989).

[13] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[14] S. M. Foiles and G. B. Adams, Phys. Rev. B **40**, 5909 (1989).

[15] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[16] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).

[17] S. M. Foiles, Phys. Rev. B **32**, 3409 (1985).

[18] H. Y. Wang, R. Najafabadi, D. Srolovitz, and R. LeSar, J. Mater. Res. (submitted).

[19] D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976). The program used to calculate the Perkus–Yevick solution for the hard-sphere radial distribution function was taken from this book.

[20] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly, and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973).

[21] See, for example, W. A. Curtin, Phys. Rev. B **39**, 6775 (1989).

[22] R. Najafabadi, D. Srolovitz, and R. LeSar, J. Mater. Res. **5**, 2663 (1990); R. Najafabadi, D. Srolovitz, and R. LeSar, J. Mater. Res. (submitted).