Quasiharmonic free energy and derivatives for many-body interactions: The embedded atom method

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We present a method using many-body potentials and lattice statics and quasiharmonic lattice dynamics for the calculation of the free energy of periodic crystals and its analytic derivatives with respect to *all* external and internal degrees of freedom. Derivatives are calculated by means of first-order perturbation theory and detailed expressions for the lattice sums required are presented. No approximations regarding the coupling of vibrations of different atoms are made. The approach is illustrated using the embedded atom method. As an example we calculate the temperature variation of the entropy and free energy of mixing of disordered RhPd by using configurational lattice dynamics, in which the free energies of a number of configurations is determined directly by means of fully dynamic structural minimizations. The method is particularly useful for quantities such as the vibrational contributions to the entropy of mixing.

I. INTRODUCTION

The free energy of a system is the key property from which all equilibrium thermodynamic information may be obtained. Central to this is the optimization problem of finding the equilibrium geometry of the system at a given temperature and pressure. Considerable effort has been expended to develop methods for the determination of the free energy: molecular dynamics and, to a lesser extent, Monte Carlo simulations are popular techniques. Lattice dynamics[1] has been somewhat neglected in recent years, even though it possesses a number of characteristics that make it a powerful complementary technique to molecular dynamics and Monte Carlo simulations. In particular it takes into account zero-point energy and other quantum effects and hence below the Debye temperature scores significantly over the inherently classical molecular dynamics and Monte Carlo methods. The breakdown of the quasiharmonic approximation is often indicated by the appearance of imaginary frequencies; for Rh-Pd alloys and the potential used here this happens above $T \sim 1500$ K. The investigation of normal vibrations aids interpretation and can reveal, for example, the mechanisms responsible for phase transitions and thermal expansion. Moreover, unlike molecular dynamics and Monte Carlo simulations, lattice dynamics yields absolute free energies *directly*, rather than free-energy differences, and does not rely on long runs for high precision. It is relatively inexpensive, requiring typically an order of magnitude less computation time than molecular dynamics and Monte Carlo simulations, and, moreover, avoids the critical slowing down effects and kinetic barriers suffered by those techniques.

Except at rather low temperatures, the bulk of the computational effort in lattice dynamics calculations is used in the optimization problem of determining the equilibrium geometry of the crystal. Once this is obtained, the calculation of dependent properties such as free energy, heat capacity, or thermal expansion is straightforward. Efficient optimization is only possible if derivatives of the appropriate thermodynamic potential with respect to the geometrical coordinates (or strains) are available and the generation and use of these derivatives are the main concerns of this paper. Until very recently the small number of existing generally available lattice dynamics codes[2] either neglected vibrational contributions to these derivatives or generated them *numerically*, which is prohibitively expensive for large unit cells with many internal coordinates. In Ref. 3 we developed the general theory, using lattice statics and quasiharmonic lattice dynamics, for the *analytic* calculation of the free energy and its first derivatives with respect to all parameters defining the crystal geometry, for particles interacting via long-ranged Coulomb forces[3] and short-range two-[3] and three-body[4] potentials. These expressions have formed the basis of a new code SHELL[5] developed for the efficient study of *ionic* solids and slabs[6] with many internal strains (degrees of freedom), and for the first time a full minimization of the quasiharmonic free energy for large unit cells of this type of solid is possible.

In this paper we extend this approach to many-body interactions. Many-body potentials are essential for accurate computer simulations of metals and alloys and here we present the formalism and detailed expressions required for the free energy and its derivatives in the embedded atom method.[7] In this the crystal energy is expressed as the sum of one cohesive term originating from the conduction and valence electrons and a repulsive contribution due to core-core overlap. Only a few lattice dynamics simulations using the EAM have appeared, and these have been for rather simple systems. Foiles and Adams[8] used expressions valid only for crystals with one atom per primitive unit cell, and Foiles[9] has also calculated surface and monovacancy free energies using the zero static internal stress approximation (ZSISA),[10] in which only the external strains are relaxed using fully dynamic free-energy derivatives, while all inter-

nal strains are relaxed using static energy derivatives. Najafabadi and Srolovitz[11] have applied the local harmonic model,[12] in which all terms in the dynamical matrix that couple vibrations of different atoms are neglected, to Cu (bulk, {001} surface, and vacancy formation). Barrera and de Tendler[13] have also presented a few examples, but using very small unit cells.

We do not repeat here the discussions given in Ref. 3, but in the next section summarize the essential points of quasi-harmonic free-energy minimization needed for the present work. In Sec. III the expressions required for calculating the free energy and its derivatives, assuming a EAM potential, are given. Note that no assumptions regarding the localization of the phonons are made, i.e., no elements in the dynamical matrix are neglected as in the local harmonic model. The deduction of the equations given in this paper is both time consuming and error prone. A suitable compact notation and rearrangement and identification of common terms are crucial. We present results in such a way that subsequent implementation in computer code is as efficient as possible—for example, particular attention is paid to recursion formulas which link the various derived quantities. The expressions given here for the EAM are also an essential first stage towards those in more elaborate models such as, for example, the modified embedded atom method (MEAM),[14] which is necessary for a quantitative study of hexagonal close packed structures.[15]

To illustrate the methodology, in Sec. IV we present a brief application and calculate the enthalpy, entropy, and free energy of mixing of disordered RhPd. The free energies of a number of configurations are determined directly by means of fully dynamic structural minimizations, and the thermodynamic properties of RhPd are then evaluated by suitable thermodynamic averaging. We shall see that lattice dynamics thus also provides an efficient route to the free energy of particular configurations of *disordered* solids,[16,17] and is particularly useful for assessing the importance of vibrational contributions to mixing properties.

II. THEORY

A. Crystal geometry

Optimization of a crystal structure involves finding the most stable state given a set of thermodynamic constraints, and hence the minimization of the appropriate thermodynamic potential. At temperature T and applied pressure P_{ext} the appropriate potential is an availability $\tilde{G}$, defined

$$\tilde{G} = A + P_{ext}V = \Phi_{stat} + A_{vib} + P_{ext}V, \qquad (1)$$

where A, the Helmholtz energy, has static and vibrational contributions, Φ_{stat} and A_{vib}. In order to proceed, A must be expressed as a function of the geometrical parameters of the structure, with respect to which A can be minimized. These coordinates may be *external*, describing macroscopic deformation of the crystal, or *internal*, describing the positions of atoms within the unit cell.

The position of the κth atom in the lth unit cell can be written[18] as

$$\mathbf{x}\begin{pmatrix} l \\ \kappa \end{pmatrix} = \mathbf{x}(l) + \mathbf{x}(\kappa) = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 + \mathbf{x}(\kappa),$$

$$\kappa = 1,2,...,N_{SL}, \qquad (2)$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the lattice vectors in a given configuration and $\mathbf{x}(\kappa)$ is the position of the κth atom in the unit cell with respect to the origin of the unit cell. There are N_{SL} sublattices or atoms in the unit cell. The three integers (l_1,l_2,l_3) define a lattice point and are collectively denoted by l. The positions of the atoms in the basis can be defined using Cartesian coordinates [as in Eq. (2)] or in relative (fractional) coordinates $\mathbf{R}$, related to $\mathbf{x}$ by

$$\mathbf{x}(\kappa) = \mathbf{R}(\kappa)\mathbf{A}, \quad \kappa = 1,2,...,N_{SL}, \qquad (3)$$

where $\mathbf{A}$ is a 3×3 matrix whose rows are the lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Since the energy depends on the relative positions of the atoms, there are only $3N_{SL} - 3$ parameters that can be used as independent variables. For this reason we take $\mathbf{R}(1)$ to be constant and define a set of $3N_{SL} + 3$ generalized coordinates $\mathcal{E}$ whose elements are $\{\mathbf{R}(\kappa), \kappa = 2,3,...,N_{SL}\}$ and six variables defining the shape and size of the unit cell. The unit cell can be specified in terms of the usual six crystallographic lattice parameters a, b, c, α, β, and γ, or equivalently, in terms of external strains $e_{\alpha\beta}$. These are defined by considering a homogeneous deformation, which deforms the lattice vectors (in a given reference configuration) such that the new lattice vectors are rows of the matrix $\mathbf{A}'$ related to $\mathbf{A}$ by

$$\mathbf{A}' = \mathbf{A}\begin{pmatrix} 1+e_{11} & e_{12} & e_{13} \\ e_{21} & 1+e_{22} & e_{23} \\ e_{31} & e_{32} & 1+e_{33} \end{pmatrix}. \qquad (4)$$

Components of the tensor $e_{\alpha\beta}$ determine both the orientation and the macroscopic state of strain of the crystal.[19] The parameters $e_{\alpha\beta}$ have been chosen because it is convenient to obtain derivatives of the free energy with respect to them and because they may be related simply to other parameters in common use such as the Voigt macroscopic infinitesimal strain coordinates. For example, the Voigt macroscopic infinitesimal strain coordinates ε_i are the components of the six-element vector:

$$\varepsilon = \begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \varepsilon_{23} \\ \varepsilon_{13} \\ \varepsilon_{12} \end{pmatrix} = \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} = \begin{pmatrix} e_{11} \\ e_{22} \\ e_{33} \\ e_{23}+e_{32} \\ e_{13}+e_{31} \\ e_{12}+e_{21} \end{pmatrix}. \qquad (5)$$

It is important to note that the last 3 elements of ε differ from those of e by a factor of 2, and that we do not define the strains ε_{32}, ε_{13}, and ε_{21}. The use of the six elements $\varepsilon_{\alpha\beta}$ defined in Eq. (5) is more convenient than the use of ε_i or $e_{\alpha\beta}$ as it leads to simpler equations.

B. Lattice dynamics

The static energy Ψ of an entire crystal is assumed to be a function of the positions $\mathbf{x}(^l_\kappa)$ of the particles comprising the crystal. The vibrational frequencies $\omega_j(\mathbf{q})$ of modes with wave vector $\mathbf{q}$ can be obtained by diagonalization of the dynamical matrix $\mathbf{D}(\mathbf{q})$ in the usual way (e.g., Ref. 1):

$$\mathbf{D}(\mathbf{q})\mathbf{e}=\omega^2(\mathbf{q})\mathbf{e}, \qquad (6)$$

where $\mathbf{D}$ is defined by

$$D^{\alpha\beta}_{\kappa_i\kappa_j}(\mathbf{q})=\frac{1}{\sqrt{m_{\kappa_i}m_{\kappa_j}}}\sum_{l_j}\Phi_{\alpha\beta}\begin{pmatrix}0 & l_i \\ \kappa_i & \kappa_j\end{pmatrix}e^{i\mathbf{q}\cdot\mathbf{r}(l_j)}. \qquad (7)$$

Throughout this paper Greek letters as subscripts α, β,... denote Cartesian coordinates x, y and z, and l_j runs over all unit cells of the crystal. The $\Phi_{\alpha\beta}(^{0\ \ l_j}_{\kappa_i\ \kappa_i})$ are second derivatives of the crystal energy with respect to atom coordinates

$$\Phi_{\alpha\beta}\begin{pmatrix}0 & l_j \\ \kappa_i & \kappa_j\end{pmatrix}=\frac{\partial^2\Psi}{\partial x_\alpha\begin{pmatrix}0 \\ \kappa_i\end{pmatrix}\partial x_\beta\begin{pmatrix}l_j \\ \kappa_j\end{pmatrix}}. \qquad (8)$$

$l_i=0$ is used to label the cell at the origin.

From the frequencies $\omega_j(\mathbf{q})$, A_{vib} is determined from

$$A_{\text{vib}}=\sum_{\mathbf{q},j}(\{\tfrac{1}{2}\hbar\omega_j(\mathbf{q})+k_BT\ln\{1-\exp[-\hbar\omega_j(\mathbf{q})/k_BT]\}\}). \qquad (9)$$

For a macroscopic crystal the sum over $\mathbf{q}$ becomes an integral over a cell in reciprocal space, which can be evaluated by taking successively finer uniform grids until convergence is achieved.[20]

Since there is no explicit expression for A_{vib} in terms of the geometry of the lattice it is not possible to determine the strain derivatives needed for efficient minimization by direct differentiation of a lattice sum as with Φ_{stat}. Differentiating Eq. (9) with respect to an arbitrary strain $\mathcal{E}$ gives

$$\left(\frac{\partial A_{\text{vib}}}{\partial\mathcal{E}_A}\right)_{\mathfrak{R}',T}=\sum_{\mathbf{q},j}\left\{\frac{\hbar}{2\omega_j(\mathbf{q})}\left(\frac{1}{2}+\frac{1}{\exp(\hbar\omega_j(\mathbf{q})/k_BT)-1}\right)\right.$$
$$\left.\times\left(\frac{\partial\omega_j^2(\mathbf{q})}{\partial\mathcal{E}_A}\right)_{\mathcal{E}'}\right\}, \qquad (10)$$

where the subscript $\mathcal{E}'$ denotes that all the $\mathcal{E}$ are kept constant except for the differentiation variable. We thus require strain derivatives of the frequencies. The derivatives $(\partial\omega_j^2(\mathbf{q})/\partial\mathcal{E}_A)_{\mathcal{E}'}$ are obtained from the analytic expressions for the derivatives $(\partial\mathbf{D}(\mathbf{q})/\partial\mathcal{E}_A)_{\mathcal{E}'}$ by first-order perturbation theory.[1,3] A crucial point here is that for obtaining derivatives the perturbation is infinitesimal and the procedure exact. In addition, for thermodynamic properties no special consideration needs to be given to degeneracies in first-order perturbation theory, since the trace of $(\partial\mathbf{D}(\mathbf{q})/\partial\mathcal{E}_A)_{\mathcal{E}'}$ is invariant for any complete normal set of eigenvectors of $\mathbf{D}$.

To obtain the equilibrium structure a variable metric method[21] is used to minimize A with respect to the $\mathcal{E}_A$. In the

initial configuration the *static* energy Hessian, $(\partial^2\Phi_{\text{stat}}/\partial\mathcal{E}_A\partial\mathcal{E}_B)$, which is a good approximation to $(\partial^2A_{\text{stat}}/\partial\mathcal{E}_A\partial\mathcal{E}_B)$, is calculated from its analytic expression, and its inverse together with the $(\partial\Phi_{\text{stat}}/\partial\mathcal{E}_A)$ is used to obtain an improved configuration. In subsequent iterations the $(\partial\Phi_{\text{stat}}/\partial\mathcal{E}_A)$ are calculated in the new configurations and the inverse Hessian updated by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) formula.[22] An optimization therefore requires one static Hessian calculation, and a small number of dynamic gradient calculations. We have found this to be much more efficient than methods involving repeated evaluation of the Hessian or frequent line minimizations.

III. N-BODY INTERACTIONS AND THE EMBEDDED ATOM METHOD

In the EAM, the static energy per unit cell of the crystal may be written as

$$\Phi_{\text{stat}}=\sum_i F_i(\rho_i)+\frac{1}{2}\sum_i\sum_j{}'\ \phi\left(r\begin{pmatrix}l_i & l_j \\ \kappa_i & \kappa_j\end{pmatrix}\right). \qquad (11)$$

Primes on summations in this and subsequent equations indicate that terms with $r(^{l_i\ \ l_j}_{\kappa_i\ \kappa_j})=0$ are excluded. $F_i(\rho_i)$ is negative and represents the energy of "embedding" atom i in the electronic density ρ_i created by all other atoms in the crystal, and $\phi(r(^{l_i\ \ l_j}_{\kappa_i\ \kappa_j}))$ is the core-core repulsion between atoms $(^{l_i}_{\kappa_i})$ and $(^{l_j}_{\kappa_j})$, assumed to depend only on the type of the atoms and the distance between them. The electronic density ρ_i is assumed to be the sum of the electronic densities of all other atoms at the nucleus of atom i:

$$\rho_i=\sum_j{}'\ f_{\kappa_j}\left(r\begin{pmatrix}l_i & l_j \\ \kappa_i & \kappa_j\end{pmatrix}\right). \qquad (12)$$

The electron density created by atom $(^{l_j}_{\kappa_j})$ at a distance $r(^{l_i\ \ l_j}_{\kappa_i\ \kappa_j})$, $f_j(r(^{l_i\ \ l_j}_{\kappa_i\ \kappa_j}))$, is assumed to be isotropic about $(^{l_j}_{\kappa_j})$.

A. Lattice sums for short-range potentials

The two-body contribution to the energy of a unit cell can be expressed as

$$\Phi=\frac{1}{2}\sum_{\kappa_i,j}\phi\begin{pmatrix}0 \\ \kappa_i\ j\end{pmatrix}, \qquad (13)$$

where the notation

$$\phi\begin{pmatrix}0 \\ \kappa_i\ j\end{pmatrix}$$

is used to abbreviate the full expression:

$$\phi\begin{pmatrix}0 \\ \kappa_i\ j\end{pmatrix}\equiv\phi\left(r\begin{pmatrix}0 & l_j \\ \kappa_i & \kappa_j\end{pmatrix}\right) \qquad (14)$$

in which ϕ is the two-body potential, a function of the distance between atoms $(^0_{\kappa_i})$ and $j\equiv(^{l_j}_{\kappa_j})$.

In order to write the derivatives of the two-body potential in a compact form it is convenient to use the following notation:

$$\mathbf{x}\begin{pmatrix} l_i & l_j \\ \kappa_i & \kappa_j \end{pmatrix} = \mathbf{x}\begin{pmatrix} l_j \\ \kappa_j \end{pmatrix} - \mathbf{x}\begin{pmatrix} l_i \\ \kappa_i \end{pmatrix}, \tag{15}$$

$$r_{ij} = \left| \mathbf{x}\begin{pmatrix} l_i & l_j \\ \kappa_i & \kappa_j \end{pmatrix} \right|, \tag{16}$$

and define the functions $\phi^n(r_{ij})$ recursively as

$$\phi^0(r_{ij}) = \phi(r_{ij}), \tag{17}$$

$$\phi^n(r_{ij}) = \frac{1}{r_{ij}} \frac{\partial \phi^{n-1}(r_{ij})}{\partial r_{ij}}. \tag{18}$$

The first derivatives of the static energy with respect to external and internal coordinates are then

$$\frac{\partial \Phi}{\partial \varepsilon_{\alpha\beta}} = \frac{1}{2} \sum_{i,\kappa_j} \phi^1\begin{pmatrix} 0 \\ i \ \kappa_j \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ i \ \kappa_j \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ i \ \kappa_j \end{pmatrix}, \tag{19}$$

$$\frac{\partial \Phi}{\partial x_\alpha(\kappa_k)} = \sum_i \phi^1\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix}. \tag{20}$$

For the Hessian there are three possible different combinations:

$$\frac{\partial^2 \Phi}{\partial \varepsilon_{\gamma\delta} \partial \varepsilon_{\alpha\beta}} = \frac{1}{2} \sum_{\kappa_i, j} \left[\phi^2\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right.$$
$$\left. \times x_\delta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} + \frac{1}{2} \phi^1\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \frac{\partial^2 r^2\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix}}{\partial \varepsilon_{\gamma\delta} \partial \varepsilon_{\alpha\beta}} \right], \tag{21}$$

$$\frac{\partial^2 \Phi}{\partial x_\beta(\kappa_l) \partial x_\alpha(\kappa_k)} = \sum_i \left\{ \left[\phi^2\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} \right. \right.$$
$$\left. \left. + \delta_{\alpha\beta} \phi^1\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} \right] (\delta_{\kappa_k \kappa_l} - \delta_{\kappa_i \kappa_l}) \right\}, \tag{22}$$

$$\frac{\partial^2 \Phi}{\partial x_\gamma(\kappa_k) \partial \varepsilon_{\alpha\beta}} = \sum_i \left\{ \phi^2\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} \right.$$
$$\left. + \phi^1\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} \left[\delta_{\alpha\gamma} x_\beta\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} + \delta_{\beta\gamma} x_\alpha\begin{pmatrix} 0 \\ i \ \kappa_k \end{pmatrix} \right] \right\}. \tag{23}$$

On the derivation of Eqs. (18), (20), and (21), it is useful to remember that derivatives correspond to changes in (static) energy when *all* atoms of the crystal in a given sublattice are moved by an infinitesimal amount. Equations (17), (19), and (21) are expressions for derivatives with respect to ε_i, i.e., the change in energy when the unit cell is deformed by an infinitesimal amount.

The derivatives needed to evaluate the dynamical matrix involve changes in the crystal energy when only atoms $\begin{pmatrix} 0 \\ \kappa_i \end{pmatrix}$ and $\begin{pmatrix} l_j \\ \kappa_j \end{pmatrix}$ are moved:

$$\Phi_{\alpha\beta}\begin{pmatrix} 0 & l_j \\ \kappa_i & \kappa_j \end{pmatrix} = -\phi^2\begin{pmatrix} 0 \\ j \ \kappa_i \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ j \ \kappa_i \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ j \ \kappa_i \end{pmatrix}$$
$$- \delta_{\alpha\beta} \phi^1\begin{pmatrix} 0 \\ j \ \kappa_i \end{pmatrix}. \tag{24}$$

Equation (24) is valid only for $\begin{pmatrix} 0 \\ \kappa_i \end{pmatrix} \neq \begin{pmatrix} l_j \\ \kappa_j \end{pmatrix}$. Terms with $\begin{pmatrix} 0 \\ \kappa_i \end{pmatrix} = \begin{pmatrix} l_j \\ \kappa_j \end{pmatrix}$ are calculated from the condition of translational invariance:[23]

$$\sum_{\kappa_j} \Phi_{\alpha\beta}\begin{pmatrix} 0 & l_j \\ \kappa_i & \kappa_j \end{pmatrix} = 0 \tag{25}$$

The two dynamical matrix derivatives necessary involve changes in the dynamical matrix when all atoms in the crystal in a given sublattice are moved or when the unit cell is deformed, both by infinitesimal amounts:

$$\frac{\partial^3 \Phi}{\partial \varepsilon_{\gamma\delta} \partial x_\alpha\begin{pmatrix} 0 \\ \kappa_i \end{pmatrix} \partial x_\beta\begin{pmatrix} l_j \\ \kappa_j \end{pmatrix}}$$
$$= -\phi^3\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\delta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\delta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix}$$
$$- \phi^2\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \left[\delta_{\alpha\beta} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\delta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right.$$
$$+ \delta_{\alpha\gamma} x_\beta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} + \delta_{\alpha\delta} x_\beta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix}$$
$$\left. + \delta_{\beta\gamma} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\delta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} + \delta_{\beta\delta} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right]$$
$$- \phi^1\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}), \tag{26}$$

$$\frac{\partial^3 \Phi}{\partial x_\gamma(\kappa_k) \partial x_\beta\begin{pmatrix} l_j \\ \kappa_j \end{pmatrix} \partial x_\alpha\begin{pmatrix} 0 \\ \kappa_i \end{pmatrix}}$$
$$= (\delta_{\kappa_i \kappa_k} - \delta_{\kappa_j \kappa_k}) \left\{ \phi^3\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\beta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right.$$
$$+ \phi^2\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \left[\delta_{\alpha\gamma} x_\beta\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} + \delta_{\beta\gamma} x_\alpha\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right.$$
$$\left. \left. + \delta_{\alpha\beta} x_\gamma\begin{pmatrix} 0 \\ \kappa_i \ j \end{pmatrix} \right] \right\}. \tag{27}$$

In Eqs. (20) we need the derivatives:

$$\frac{\partial^2 r^2}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\delta}} = \frac{1}{2} x_\alpha x_\gamma \delta_{\beta\delta} + \frac{1}{2} x_\alpha x_\delta \delta_{\beta\gamma} + \frac{1}{2} x_\beta x_\gamma \delta_{\alpha\delta}$$

$$+ \frac{1}{2} x_\beta x_\delta \delta_{\alpha\gamma}. \tag{28}$$

If required, derivatives with respect to the $R(\kappa)$ rather than the $x(\kappa)$ may be obtained from the latter and the chain rule. For example,

$$\frac{\partial^2 \Phi}{\partial R_\beta(\kappa_i) \partial R_\alpha(\kappa_j)} = \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \frac{\partial^2 \Phi}{\partial x_\delta(\kappa_j) \partial x_\gamma(\kappa_i)} A_{\alpha\gamma} A_{\beta\delta}. \tag{29}$$

Similarly, derivatives with respect to the lattice parameters can be obtained from the derivatives with respect to the $\varepsilon_{\alpha\beta}$ and the chain rule using Eq. (4).

B. Lattice sums for embedding interactions

We start by rewriting the embedding contribution to Φ_{stat}, i.e., the first term on the right-hand side of Eq. (11), as

$$E = \sum_{\kappa_i} \left\{ F_{\kappa_i}\left(\rho\left(\begin{array}{c} 0 \\ \kappa_i \end{array} \right) \right) \right\}. \tag{30}$$

For convenience we define, analogously to the $\phi^n(r_{ij})$ in the previous section, a set of quantities $f_{\kappa_i}^n(ij)$, such that

$$f_{\kappa_i}^0(ij) = f_{\kappa_i}(ij) = f_{\kappa_i}\left(r\left(\begin{array}{cc} l_i & l_j \\ \kappa_i & \kappa_j \end{array} \right) \right), \tag{31}$$

$$f_{\kappa_i}^n(ij) = \frac{1}{r_{ij}} \frac{\partial f_{\kappa_i}^{n-1}(ij)}{\partial r_{ij}}. \tag{32}$$

The contributions of the many-body forces to the static energy, the dynamical matrix, and the strain derivatives of both are much more expensive to evaluate than the two-body contributions [Eq. (13)] because now each term in the sum given by Eq. (30) requires the calculation of another sum over *all* atoms of the crystal. To allow the evaluation of these sums in an efficient way so as to be able to simulate cells with a large number of atoms, it is convenient to define the following sums:

$$S^0(\kappa_i, \kappa_j) = \sum_{l_j} f_{\kappa_j}(ij), \tag{33}$$

$$S^1(\kappa_i, \kappa_j) = \sum_{l_j} f_{\kappa_j}^1(ij), \tag{34}$$

$$S_\alpha^1(\kappa_i, \kappa_j) = \sum_{l_j} f_{\kappa_j}^1(ij) x_\alpha(ij), \tag{35}$$

$$S_{\alpha\beta}^1(\kappa_i, \kappa_j) = \sum_{l_j} f_{\kappa_j}^1(ij) x_\alpha(ij) x_\beta(ij), \tag{36}$$

$$S_{\alpha\beta\gamma}^1(\kappa_i, \kappa_j) = \sum_{l_j} f_{\kappa_j}^1(ij) x_\alpha(ij) x_\beta(ij) x_\gamma(ij), \tag{37}$$

and

$$S^0(\kappa_i) = \sum_{\kappa_j} S^0(\kappa_i, \kappa_j), \tag{38}$$

$$S^1(\kappa_i) = \sum_{\kappa_j} S^1(\kappa_i, \kappa_j), \tag{39}$$

$$S_\alpha^1(\kappa_i) = \sum_{\kappa_j} S_\alpha^1(\kappa_i, \kappa_j), \tag{40}$$

$$S_{\alpha\beta}^1(\kappa_i) = \sum_{\kappa_j} S_{\alpha\beta}^1(\kappa_i, \kappa_j), \tag{41}$$

and similarly for other terms not explicitly given. It is important to note that the sums in Eqs. (33)–(41) do not depend on the index l_i and l_j.

In turn, derivatives of the static energy with respect to both internal and external strains requires the calculation of derivatives of the electronic density with respect to the set of $\mathbf{x}(\kappa_i)$ and $\varepsilon_{\alpha\beta}$. In terms of the S's given above they can be evaluated as

$$\rho(i) = S^0(\kappa_i), \tag{42}$$

$$\frac{\partial \rho(i)}{\partial \varepsilon_{\alpha\beta}} = S_{\alpha\beta}^1(\kappa_i), \tag{43}$$

$$\frac{\partial \rho(i)}{\partial x_\alpha(\kappa_k)} = S_\alpha^1(\kappa_i, \kappa_k) - \delta_{\kappa_i, \kappa_k} S_\alpha^1(\kappa_i), \tag{44}$$

$$\frac{\partial^2 \rho(i)}{\partial \varepsilon_{\alpha\beta} \partial \varepsilon_{\gamma\delta}} = S_{\alpha\beta\gamma\delta}^2(\kappa_i) + \frac{1}{4} (\delta_{\beta\delta} S_{\alpha\gamma}^1(\kappa_i) + \delta_{\beta\gamma} S_{\alpha\delta}^1(\kappa_i)$$
$$+ \delta_{\beta\gamma} S_{\alpha\delta}^1(\kappa_i) + \delta_{\alpha\gamma} S_{\beta\delta}^1(\kappa_i)), \tag{45}$$

$$\frac{\partial^2 \rho(i)}{\partial x_\alpha(\kappa_k) \partial \varepsilon_{\beta\gamma}} = S_{\alpha\beta\gamma}^2(\kappa_i, \kappa_k) + \delta_{\alpha\beta} S_\gamma^1(\kappa_i, \kappa_k)$$
$$+ \delta_{\alpha\gamma} S_\beta^1(\kappa_i, \kappa_k) - \delta_{\kappa_i \kappa_k}(S_{\alpha\beta\gamma}^2(\kappa_i)$$
$$+ \delta_{\alpha\gamma} S_\beta^1(\kappa_i) + \delta_{\alpha\beta} S_\gamma^1(\kappa_i)), \tag{46}$$

$$\frac{\partial^2 \rho(i)}{\partial x_\beta(\kappa_l) \partial x_\alpha(\kappa_k)} = \delta_{\kappa_k \kappa_l}(S_{\alpha\beta}^2(\kappa_i, \kappa_k) + \delta_{\alpha\beta} S^1(\kappa_i, \kappa_k))$$
$$- \delta_{\kappa_i \kappa_l}(S_{\alpha\beta}^2(\kappa_i, \kappa_k) + \delta_{\alpha\beta} S^1(\kappa_i, \kappa_k))$$
$$- \delta_{\kappa_i \kappa_k}(S_{\alpha\beta}^2(\kappa_i, \kappa_l) + \delta_{\alpha\beta} S^1(\kappa_i, \kappa_l))$$
$$+ \delta_{\kappa_i \kappa_k} \delta_{\kappa_i \kappa_l}(S_{\alpha\beta}^2(\kappa_i) + \delta_{\alpha\beta} S^1(\kappa_i)). \tag{47}$$

For the evaluation of the dynamical matrix and its derivatives, the following derivatives of the electronic density with respect to the coordinates of a particular atom are required:

$$\frac{\partial \rho(i)}{\partial x_\alpha(k)} = f^1_{\kappa_k}(ik) x_\alpha(ik) - \delta_{l_i,l_k} \delta_{\kappa_i,\kappa_k} S^1_\alpha(\kappa_i), \quad (48)$$

$$\frac{\partial^2 \rho(i)}{\partial x_\beta(l) \partial x_\alpha(k)} = -\delta_{il}(f^2_{\kappa_k}(ik) x_\alpha(ik) x_\beta(ik) + f^1_{\kappa_k}(ik) \delta_{\alpha\beta})$$
$$- \delta_{ik}(f^2_{\kappa_l}(il) x_\alpha(il) x_\beta(il) + f^1_{\kappa_l}(il) \delta_{\alpha\beta}), \quad (49)$$

$$\frac{\partial^2 \rho(i)}{\partial \varepsilon_{\alpha\beta} \partial x_\gamma(k)} = f^2_{\kappa_k}(ik) x_\alpha(ik) x_\beta(ik) x_\gamma(ik)$$
$$+ f^1_{\kappa_k}(ik)(\delta_{\alpha\gamma} x_\beta(ik) + \delta_{\beta\gamma} x_\alpha(ik))$$
$$- \delta_{ik}[S^2_{\alpha\beta\gamma}(\kappa_i) + (\delta_{\alpha\gamma} S^1_\beta(\kappa_i) + \delta_{\beta\gamma} S^1_\alpha(\kappa_i))], \quad (50)$$

$$\frac{\partial^2 \rho(i)}{\partial x_\beta(\kappa_l) \partial x_\alpha(k)} = (\delta_{\kappa_k \kappa_l} - \delta_{\kappa_i \kappa_l})(f^2_{\kappa_k}(ik) x_\alpha(ik) x_\beta(ik)$$
$$+ f^1_{\kappa_k}(ik) \delta_{\alpha\beta}) - \delta_{ik}[S^2_{\alpha\beta}(\kappa_i,\kappa_l)$$
$$+ \delta_{\alpha\beta} S^1(\kappa_i,\kappa_l)] + \delta_{ik}\delta_{\kappa_i\kappa_l}[S^2_{\alpha\beta}(\kappa_i)$$
$$+ \delta_{\alpha\beta} S^1(\kappa_i)], \quad (51)$$

$$\frac{\partial^3 \rho(i)}{\partial x_\delta(l) \partial x_\gamma(k) \partial \varepsilon_{\alpha\beta}} = -\delta_{il} f^3_{\kappa_k}(ik) x_\alpha(ik) x_\beta(ik) x_\gamma(ik) x_\delta(ik) - \delta_{il} f^2_{\kappa_k}(ik)(\delta_{\alpha\delta} x_\beta(ik) x_\gamma(ik) + \delta_{\beta\delta} x_\alpha(ik) x_\gamma(ik)$$
$$+ \delta_{\gamma\delta} x_\alpha(ik) x_\beta(ik) + \delta_{\alpha\gamma} x_\beta(ik) x_\delta(ik) + \delta_{\beta\gamma} x_\alpha(ik) x_\delta(ik)) - \delta_{il} f^1_{\kappa_k}(ik)(\delta_{\alpha\gamma} \delta_{\beta\delta}$$
$$+ \delta_{\beta\gamma} \delta_{\alpha\delta}) - \delta_{ik} f^3_{\kappa_l}(il) x_\alpha(il) x_\beta(il) x_\gamma(il) x_\delta(il) - \delta_{ik} f^2_{\kappa_l}(il)(\delta_{\alpha\delta} x_\beta(il) x_\gamma(il) + \delta_{\beta\delta} x_\alpha(il) x_\gamma(il)$$
$$+ \delta_{\gamma\delta} x_\alpha(il) x_\beta(il) + \delta_{\alpha\gamma} x_\beta(il) x_\delta(il) + \delta_{\beta\gamma} x_\alpha(il) x_\delta(il)) - \delta_{ik} f^1_{\kappa_l}(il)(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\beta\gamma} \delta_{\alpha\delta}), \quad (52)$$

$$\frac{\partial^3 \rho(i)}{\partial x_\gamma(\kappa_m) \partial x_\beta(l) \partial x_\alpha(k)} = -\delta_{il}(\delta_{\kappa_k \kappa_m} - \delta_{\kappa_i \kappa_m})(f^3_{\kappa_k}(ik) x_\alpha(ik) x_\beta(ik) x_\gamma(ik) + f^2_{\kappa_k}(ik)(\delta_{\alpha\gamma} x_\beta(ik) + \delta_{\beta\gamma} x_\alpha(ik) + \delta_{\alpha\beta} x_\gamma(ik)))$$
$$- \delta_{ik}(\delta_{\kappa_l \kappa_m} - \delta_{\kappa_i \kappa_m})(f^3_{\kappa_k}(il) x_\alpha(il) x_\beta(il) x_\gamma(il) + f^2_{\kappa_k}(il)(\delta_{\alpha\gamma} x_\beta(il) + \delta_{\beta\gamma} x_\alpha(il) + \delta_{\alpha\beta} x_\gamma(il))). \quad (53)$$

Equations (51)–(53) are valid only for $k \neq l$. Terms with $k = l$ are obtained from the condition of translational invariance as given in Eq. (25).

In the two last sets of equations it is important to note once more the difference between derivatives with respect to the position of all atoms in a given sublattice, $\mathbf{x}(\kappa_i)$, and with respect to a particular atom of the crystal, $\mathbf{x}\binom{l_i}{\kappa_i}$.

In terms of derivatives of the electronic densities given in Eqs. (48)–(53), it is now straightforward to calculate the static energy, the dynamical matrix, and their derivatives. The first derivatives of the static energy are, for instance,

$$\frac{\partial E}{\partial x_\alpha(\kappa_k)} = \sum_{\kappa_i} F'_{\kappa_i}\left(\rho\binom{0}{\kappa_i}\right) \frac{\partial \rho\binom{0}{\kappa_i}}{\partial x_\alpha(\kappa_k)}, \quad (54)$$

$$\frac{\partial E}{\partial \varepsilon_{\alpha\beta}} = \sum_{\kappa_i} F'_{\kappa_i}\left(\rho\binom{0}{\kappa_i}\right) \frac{\partial \rho\binom{0}{\kappa_i}}{\partial \varepsilon_{\alpha\beta}}, \quad (55)$$

while the second-order derivatives necessary to calculate the dynamical matrix are

$$\frac{\partial^2 E}{\partial x_\beta(\kappa_l) \partial x_\alpha(\kappa_k)} = \sum_{\kappa_i} F''_{\kappa_i}\left(\rho\binom{0}{\kappa_i}\right) \frac{\partial \rho\binom{0}{\kappa_i}}{\partial x_\beta(\kappa_l)} \frac{\partial \rho\binom{0}{\kappa_i}}{\partial x_\alpha(\kappa_k)}$$
$$+ F'_{\kappa_i}\left(\rho\binom{0}{\kappa_i}\right) \frac{\partial^2 \rho\binom{0}{\kappa_l}}{\partial x_\beta(\kappa_l) \partial x_\alpha(\kappa_k)}. \quad (56)$$

By carrying out the evaluation of the static energy, the dynamical matrix and their derivatives as indicated above it is possible to implement a fairly efficient algorithm in which sums over, in principle, all cells of the crystal are carried out only once and for all derivatives, for a given configuration. The final sums as those required in Eqs. (54) and (55), for instance, are only over all atoms in one unit cell.

IV. FREE ENERGY OF MIXING OF RhPd

We end with a brief example, our treatment here being illustrative rather than comprehensive. Though the use of

lattice dynamics techniques has largely been restricted to the perfect crystals, we have shown previously[17] that it can be used also for solid solutions. In Ref. 17 we considered a very different type of system (MgO-MnO) in which the atoms interacted via only pairwise interactions. Here we concentrate on Rh-Pd, a system that phase separates at low temperatures and which forms a solid solution at temperatures above ~1200 K (for example, Refs. 24, 25, 26). Results for the 50-50 mixture are given here.

We represent the electronic densities as simple exponentials:

$$f_j(r) = D_j \exp(-r_{ij}/\zeta_j) \qquad (57)$$

with different parameters D_j and ζ_j for each metal (j = Pd,Rh). The embedding energy [Eq. (11)] is given by

$$F_j(\rho_j) = -C_j\sqrt{\rho_j} \qquad (58)$$

with different parameters C_j again for Pd and Rh. The repulsive potential in Eq. (11) is also given a simple form,

$$\phi_{ij}(r) = A_{ij}\exp(-r_{ij}/\sigma_{ij}), \qquad (59)$$

where A_{ij} and σ_{ij} are different for each type of interaction (Pd-Pd, Rh-Rh, Pd-Rh). A cutoff of 6 Å was used for both electronic densities and repulsive potentials. The values of the model parameters were fitted to reproduce the results of *ab initio* calculations and are reported in Ref. 27.

In order to simulate disordered RhPd we used cubic unit cells containing 32 atoms, with atom positions as in a face-centered cubic lattice. We generated a set of configurations k, in each of which the location of the sixteen Rh (or Pd) atoms within the unit cell was chosen at random. At each temperature a full dynamic optimization of the structure of each configuration was carried out, calculating at the same time several thermodynamic properties such as the Gibbs energy, G_k, the enthalpy, H_k and the entropy, S_k. The ensemble average of an observable, the enthalpy, for instance, is calculated from

$$H = \frac{\Sigma_k^K H_k \exp(-\beta G_k)}{\Sigma_k^K \exp(-\beta G_k)}, \qquad (60)$$

while the ensemble average of the Gibbs energy is given by

$$G = -k_B T \ln K - k_B T \ln\left(\sum_k^K \exp(-\beta G_k)/K\right) \qquad (61)$$

where K is the total number of possible configurations for the supercell considered. Because it is in general not possible to carry out the summation in Eqs. (44) and (45) over all configurations, they are carried out over a subset K'. Consistently, K, the denominator of Eq. (45), is replaced by K'. The first term of Eq. (45) represents the ideal contribution while the second term is the deviation from ideality.

With as few as 200 configurations used in the ensemble average, the value of G at 1000 K is converged to better than 0.01 kJ/mol. Similar convergence is observed at other tem-
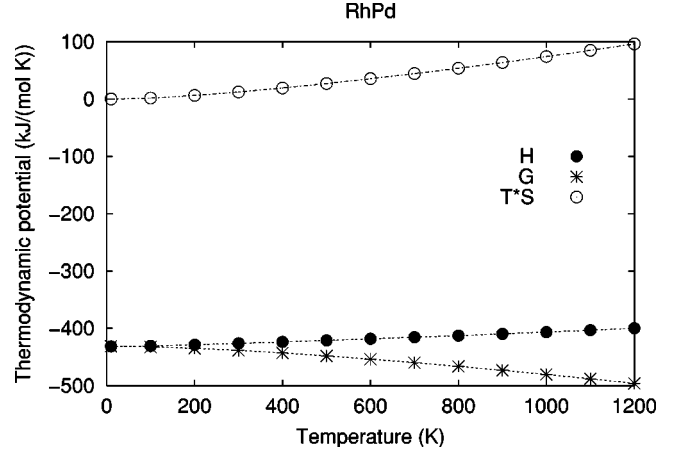

FIG. 1. Enthalpy, entropy (*TS*), and the Gibbs energy of disordered RhPd as a function of temperature.

peratures. All subsequent averages presented here were done using 1000 configurations, which ensures very well converged values.

From the results of optimizations over a wide range of temperatures, we show in Fig. 1 the temperature dependence of the enthalpy, the entropy (as the product *TS*) and the free energy of disordered RhPd. Again using a simulation cells with 32 atoms, it is straightforward also to calculate *G, H*, and *S* for the pure metals over the same temperature range and so determine the corresponding values of ΔG_{mix}, ΔH_{mix}, and ΔS_{mix}, which are plotted in Fig. 2. Note the absolute values of the quantities in Fig. 1 are of the order of several hundred kJ mol^{-1}, while the thermodynamic potentials of mixing in Fig. 2 are smaller by two orders of magnitude. ΔH_{mix} increases slightly with temperature.

The value of ΔG_{mix} becomes negative at $\approx$1100 K, which is of course a necessary but not sufficient condition for the formation of a solid solution. Analogous free-energy minimizations over a range of composition would allow calculation of the phase diagram. At lower temperatures, ΔS_{mix} is less than the ideal value while at 1200 K it is larger than the ideal value by more than 1 J K^{-1} mol^{-1} ($\approx$17%). It is important to

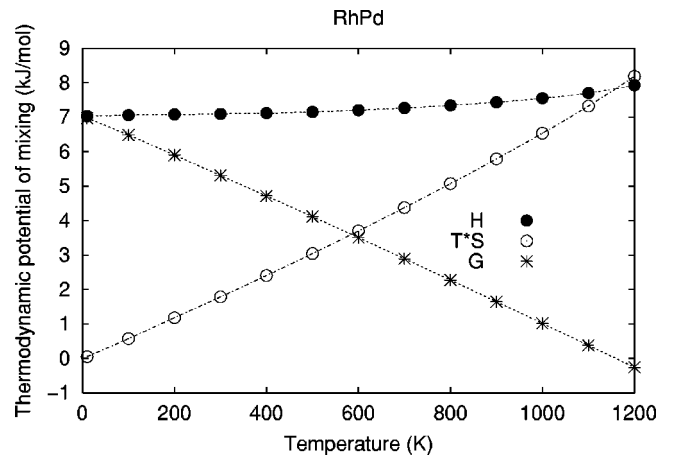FIG. 2. Enthalpy, entropy (*TS*), and Gibbs energy of mixing of disordered RhPd as a function of temperature.

note also that the calculated ΔS_{mix} includes *both* configurational *and* vibrational terms. The latter are often neglected. Vibrational contributions to the thermodynamic properties of mixing can be estimated quantitatively by comparing results obtained from fully dynamic optimizations with those obtained using static-limit optimizations of each configuration in the static limit and replacing G_k in Eqs. (60) and (61) by the static enthalpy $H_{k(static)}$. This procedure leads to values of ΔS_{mix} of 5.3 $\mathrm{J\,K^{-1}\,mol^{-1}}$, which is $\approx$77% of the total value at this temperature. Vibrational contributions to the enthalpy of mixing are smaller.

V. CONCLUSIONS

We have discussed a method for the calculation of the free energy of solids and its analytic derivatives with respect to arbitrary strain using a many-body potential model together with lattice statics and quasiharmonic lattice dynamics. No approximations are made regarding coupling of vibrations of atoms on different sites. Detailed expressions have been given for the embedded atom method and a computer program has been written for this purpose.[28]

By way of example, we have examined the thermodynamics of disordered RhPd. The free energy is determined directly from fully dynamic structural minimizations of a number of randomly chosen configurations, followed by thermodynamic averaging. This approach is particularly useful for quantities such as the vibrational contributions to the entropy of mixing. The values of ΔG_{mix} for RhPd agree well with those obtained from semigrand ensemble canonical Monte Carlo calculations,[27] obtained with the same set of potentials as used here. The availability of the Monte Carlo data was a major reason for our choice of example. It remains to examine carefully the convergence of different thermodynamic properties with cell size and with number of configurations, both of which may well vary with composition.

The direct minimization of the free energy via this method is quick and precise. Key to this has been the rearrangement of the complex expressions for the derivatives in such a way that common terms have been identified and recursion relationships obtained. In total, all the calculations reported in Sec. IV took only a few hours on a typical modern PC. Increasing the number of configurations sampled by an order of magnitude would be straightforward, and these new methods can readily applied to much more complex examples than that reported in this study. The expressions presented here are also an essential first step towards the implementation of more elaborate models such as the modified embedded atom method for the study of hexagonal systems.

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[28] The code is intended to be available for use by other groups: academic groups interested in obtaining a copy should contact G.D. Barrera. Further information may also be found at http://quimica.unp.edu.ar/eamld.