

Recovery of an N -body potential from a universal cohesion equation

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With the use of the lattice-inversion method, we present an N -body model for interatomic potential. The model utilizes a universal cohesion equation of Rose *et al.*, with a tight-binding energy determined by the Cauchy discrepancy and the difference of the vacancy-formation energy with the sublimation energy. The lattice dynamics and the thermal expansion of the noble metals are studied based on the present model.

I. INTRODUCTION

It has been discovered by Rose, Smith, Guinea, and Ferrante (RSGF) that the total cohesive energy as a function of lattice spacing can be depicted well by a universal Rydberg function in the case of bimetallic adhesion, metallic cohesion, metallic and covalent bonds in chemisorption, and many diatomic molecules.^{1,2} The RSGF equation can be simply constructed from the equilibrium lattice constant a_e , the sublimation energy E_s , and the bulk modulus B_e . It differs from the cohesion equation of Murnaghan³ and needs no input of the pressure derivative of the bulk modulus. In the past decade, the equation was frequently applied to material simulations. For example, it was used to fit the *ab initio* cohesive energies versus lattice constants for Ni-Pt compounds,⁴ determine embedding functions for the embedded-atom method^{5,6} (EAM), and define the perturbation series in the equivalent-crystal theory.⁷

The idea of inverting the pair potential from the cohesion equation first appeared in the work of Carlsson, Gelatt, and Ehrenreich (CGE),⁸ and was immediately used to study the ideal tensile strength of copper.⁹ The CGE scheme has evident drawbacks, because it is well known that the cohesive energy cannot be merely expressed by the lattice sum of pair potentials. The pair-potential model theoretically yields two vital disagreements with experiments: the Cauchy relation and the overestimate of vacancy-formation energy.¹⁰ Instead of it, there are quite a few other methods, such as the N -body potential,¹⁰ the EAM,^{11,12} and the tight-binding model.¹³⁻¹⁵

In this work, we present an N -body potential model which is extracted from the RSGF equation by virtue of the lattice-inversion method (LIM) developed by Chen *et al.*¹⁶⁻¹⁸ The model avoids the arbitrary fitting and cutoff procedures used in many existing models by means of inverting the overlap integral and the pair potential from the respective lattice sums which can be fitted to analytical functions embodying the cohesion equation. To test the model, we study the lattice dynamics and the thermal expansion of the noble metals.

II. MODEL

The N -body method defines the cohesive energy of a d -band metal as

$$E_{\text{coh}} = \frac{1}{2} \sum_{i \neq 0} \Phi(R_i) - \sqrt{n} \quad (1)$$

with

$$n = \sum_{i \neq 0} \rho(R_i),$$

$$\rho(r) = h^2(r),$$

where $h(r)$ is the overlap integral which includes the role of s - d hybridization, $\Phi(r)$ is the pair potential, and the square-root function is to mimic the second-moment approximation of the tight-binding model.¹³

Within the framework of the N -body potential model, the elastic constants B (bulk modulus), C (tetragonal shear modulus), and C_{44} (rhombohedral shear modulus) of a cubic crystal can be formulated as

$$B = \frac{1}{18\Omega} \left[\sum_{i \neq 0} R_i^2 \left[\Phi_{\text{eff}}''(R_i) - \frac{1}{R_i} \Phi_{\text{eff}}'(R_i) \right] + \frac{1}{2\sqrt{n}^3} \left[\sum_{i \neq 0} R_i \rho'(R_i) \right]^2 \right], \quad (2)$$

$$C = \frac{1}{4\Omega} \sum_{i \neq 0} \frac{X_i^2(X_i^2 - Y_i^2)}{R_i^2} \left[\Phi_{\text{eff}}''(R_i) - \frac{1}{R_i} \Phi_{\text{eff}}'(R_i) \right], \quad (3)$$

$$C_{44} = \frac{1}{2\Omega} \sum_{i \neq 0} \frac{X_i^2 Y_i^2}{R_i^2} \left[\Phi_{\text{eff}}''(R_i) - \frac{1}{R_i} \Phi_{\text{eff}}'(R_i) \right], \quad (4)$$

where R_i denotes the length of the position vector of site i , X_i and Y_i are the x and y components of the position vector \mathbf{R}_i , Ω is the atomic volume, and $\Phi_{\text{eff}}(r)$ is the effective pair potential defined by

$$\Phi_{\text{eff}}(r) = \Phi(r) - \frac{1}{\sqrt{n}} \rho(r). \quad (5)$$

The Cauchy discrepancy is then

$$C_{12} - C_{44} = \frac{1}{36\Omega} n^{-3/2} \left[\sum_{i \neq 0} R_i \rho'(R_i) \right]^2. \quad (6)$$

The vacancy-formation energy in the absence of lattice relaxation (it has been shown that the contribution of relaxation energy to the vacancy-formation energy is not more than several percent¹⁹) is

$$E_v = -\frac{1}{2} \sum_{i \neq 0} \Phi(R_i) - \sum_{i \neq 0} [\sqrt{n - \rho(R_i)} - \sqrt{n}]. \quad (7)$$

For a fcc structure whose coordination number ($=12$) is much greater than unity, Eq. (7) can be simplified to be

$$E_v = -\frac{1}{2} \sum_{i \neq 0} \left[\Phi(R_i) - \frac{1}{\sqrt{n}} \rho(R_i) \right] = -\frac{1}{2} \sum_{i \neq 0} \Phi_{\text{eff}}(R_i). \quad (8)$$

The difference of the sublimation energy and the vacancy-formation energy can be seen from Eqs. (1) and (8):

$$E_s - E_v = \frac{1}{2} \left[\sum_{i \neq 0} \rho(R_i) \right]^{1/2}. \quad (9)$$

With increasing of the lattice spacing, n , the lattice sum of $\rho(r)$, will decrease. Therefore it can reasonably be assumed to be an exponential function with respect to the nearest-neighbor distance,

$$n(R_1) = n_e \exp \left[-\alpha \left(\frac{R_1}{R_{1e}} - 1 \right) \right]. \quad (10)$$

On assuming Eq. (10) we would like to mention that Banerjee and Smith have found that the variation of the vacancy-site electron density with respect to the lattice constant exhibits a universal form of exponential function, with the scaling length taken as the Thomas-Fermi screening length.² This finding underpins our assumption very well, because the square overlap integral is also regarded to be proportional to the electron density in light of the EAM.

Another lattice sum in Eq. (6) can be found to be

$$\sum_{i \neq 0} R_i \rho'(R_i) = -n_e \left[\alpha \frac{R_1}{R_{1e}} \right] \exp \left[-\alpha \left(\frac{R_1}{R_{1e}} - 1 \right) \right]. \quad (11)$$

Noting that all the inputs are measured on the equilibrium lattice $R_1 = R_{1e}$, one can obtain the two parameters from Eqs. (6) and (9) as

$$n_e = 4(E_s^e - E_v^e)^2, \\ \alpha = \left[\frac{18\Omega_e(C_{12}^e - C_{44}^e)}{E_s^e - E_v^e} \right]^{1/2}.$$

Thus we have the analytical expressions for the lattice sums of the square overlap integral and the pair potential as

$$\sum_{i \neq 0} \rho(R_i) = 4(E_s^e - E_v^e)^2 \exp \left[-\alpha \left(\frac{R_1}{R_{1e}} - 1 \right) \right], \quad (12)$$

$$\frac{1}{2} \sum_{i \neq 0} \Phi(R_i) = -E_s^e \left[1 + \left(\frac{9B_e \Omega_e}{E_s^e} \right)^{1/2} \left(\frac{R_1}{R_{1e}} - 1 \right) \right] \\ \times \exp \left[-\left(\frac{9B_e \Omega_e}{E_s^e} \right)^{1/2} \left(\frac{R_1}{R_{1e}} - 1 \right) \right] \\ + 2(E_s^e - E_v^e) \exp \left[-\frac{1}{2} \alpha \left(\frac{R_1}{R_{1e}} - 1 \right) \right]. \quad (13)$$

In Eq. (13) the RSGF equation has been introduced.

The individual functions of the overlap integral and pair potential are uniquely governed by the above two equations. The potentials defined as such can in principle include as many neighbors as possible. They can be obtained by using the LIM of Chen *et al.*¹⁸ The basic equation of the LIM can be expressed by

$$F(\gamma x) = \sum_{n=1}^{\infty} w(n) f(\sqrt{n} x) \iff f(x) \\ = \sum_{n=\beta}^{\infty} \mu(n) F(\gamma \sqrt{n} x / \beta), \quad (14)$$

where γx is the lattice constant, $\sqrt{n} x$ is the radius of the n th shell centered at a given lattice site, $w(n)$ is the corresponding number of atoms on the n th shell [$w(n)$ vanishes if n cannot be decomposed into a sum of three square non-negative integers], and $\mu(n)$ is the modified Möbius function, which can be decided from a recursion formula

$$\sum_{n/\beta k} w(n) \mu(\beta k / n) = \delta_{\beta k}, \quad (15)$$

where $\beta=1$, $\gamma=1$ for sc structures, and $\beta=2$, $\gamma=2$ for fcc and $L1_2$ structures.

The experimental data for the lattice constants a_e , the sublimation energies E_s , the vacancy-formation energies E_v , the bulk moduli B_e , and the Cauchy discrepancies $C_{12} - C_{44}$ for Cu, Ag, and Au as the inputs are taken from Ref. 6 and listed in Table I (for convenience we have

TABLE I. The model inputs a_e , E_s , B_e , E_v , and $\Delta C = C_{12} - C_{44}$ and the predicted elastic constants C_{11} , C_{12} , and C_{44} (the first row) by comparison with the experimental values (the second row). The elastic constants are in 10^{11} erg/cm³, E_s and E_v in eV, and a_e in Å. All the experimental values are taken from Ref. 6.

Atom	a_e	E_s	B_e	E_v	ΔC	C_{11}	C_{12}	C_{44}
Cu	3.61	3.54	1.38	1.3	0.467	1.75	1.18	0.71
						1.70	1.225	0.758
Ag	4.09	2.85	1.04	1.1	0.473	1.19	0.95	0.48
						1.24	0.934	0.461
Au	4.08	3.93	1.67	0.9	1.150	1.82	1.59	0.44
						1.86	1.57	0.42

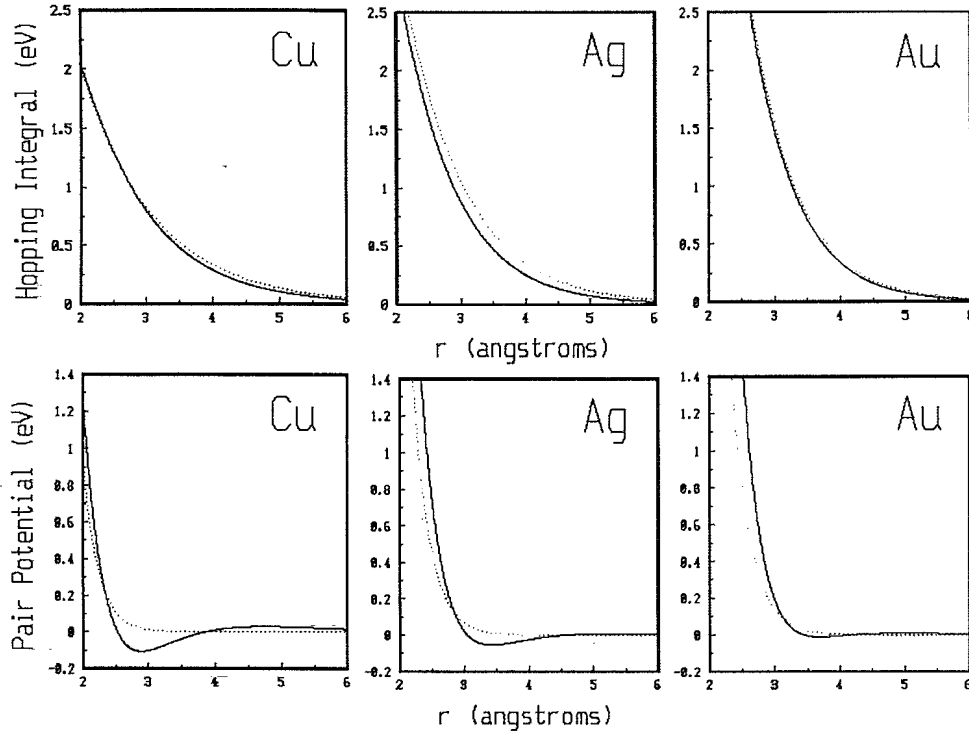


FIG. 1. The solid lines are the inverted overlap integrals and pair potentials for Cu, Ag, and Au. The dotted lines are the corresponding potential plots according to Cleri and Rosato (Ref. 15).

dropped out the superscript e). The elastic constants C_{11} , C_{12} , and C_{44} calculated by the present model are also tabulated in Table I, in comparison to the experimental values.

The inverted overlap integrals and pair potentials for Cu, Ag, and Au are plotted in Fig. 1, for comparison with the plots of potentials according to Cleri and Rosato.¹⁵ In Fig. 1 it is shown that the shapes of the two overlap integrals are generally similar to each other. Unlike the pure repulsive characteristic of the pair potentials in Ref. 15, the present pair potentials exhibit attractive regions. They have a minimum and a maximum, and feature a slightly oscillatory behavior. The oscillatory behaviors of Cu and Ag are evident, whereas that of Au is not quite evident. The pair potential of this form may be understandable, because it has been established that a pair potential of oscillatory form is due to the s -electron contribution, which generates a pair potential with a substantial attractive well and an oscillatory tail, according to the second-order perturbation approximation of pseudopotential theory.²⁰

III. APPLICATIONS

A. Phonon dispersion

Similar to the derivation of the EAM,²¹ the N -body dynamical matrix for a cubic metal can be obtained from Eq. (1) as

$$D(\mathbf{K}) = 2 \sum_{i \neq 0} A_i \sin^2 \left[\frac{\mathbf{K} \cdot \mathbf{R}_i}{2} \right] + \frac{1}{4\sqrt{n^3}} \mathbf{X}(\mathbf{K}) \mathbf{X}(\mathbf{K}), \quad (16)$$

where

$$A_i = \Phi''_{\text{eff}}(R_i) \frac{\mathbf{R}_i \mathbf{R}_i}{R_i^2} + \frac{\Phi'_{\text{eff}}(R_i)}{R_i} \left[\hat{\mathbf{I}} - \frac{\mathbf{R}_i \mathbf{R}_i}{R_i^2} \right]$$

and

$$\mathbf{X}(\mathbf{K}) = \sum_{i \neq 0} \rho'(R_i) \sin(\mathbf{K} \cdot \mathbf{R}_i) \frac{\mathbf{R}_i}{R_i}.$$

The phonon dispersion relations in the equilibrium lattice for the noble metals are plotted in Fig. 2. The results are in perfect agreement with the experimental values of Nilsson and Rolandson for Cu,²² and of Kamitakahara and Brockhouse for Ag.²³ The predicted results of Au are not good compared with the experimental results of Lynn, Smith, and Nicklow.²⁴

B. Phonon density of states

We know that the alteration of the lattice constant will result in a change of the phonon spectrum. The relation is generally described by the simplified Grüneisen approximation, which assumes the negative of the first derivative of the logarithm of the eigenfrequencies with respect to the logarithm of the unit-cell volume to be a constant, the Grüneisen constant. The Grüneisen constant is positive, implying that the phonon frequencies will decrease when the lattice expands. Alternatively, this effect can be elucidated by introducing a density of states (DOS) considered as a function of both vibrational frequency and lattice constant, $g(\omega, a)$. Starting from the dynamical matrix, the DOS as a function of the lattice constant can be calculated. Figure 3 shows these relations for the noble metals.

C. Thermal expansion

It has been concluded by Marchese, Jacucci, and Flynn²⁵ and Sutton²⁶ that the original N -body potential of Finnis and Sinclair¹⁰ causes incorrect predictions when applied to the calculation of linear thermal expansion. In their calculation for the same item,^{27,28} Foiles and co-workers pointed out that the errors might originate from the fact that the potentials of the Finnis-Sinclair N -body method are only fitted to elastic constants so that they fail in depicting anharmonicity effects. To reflect the anharmonicity, they used the RSGF function to adjust their EAM and gained excellent agreement with experimental values for thermal expansion.

We will use the present model to study the temperature behavior of linear thermal expansion of the noble metals. With the above-defined DOS function, one can write the

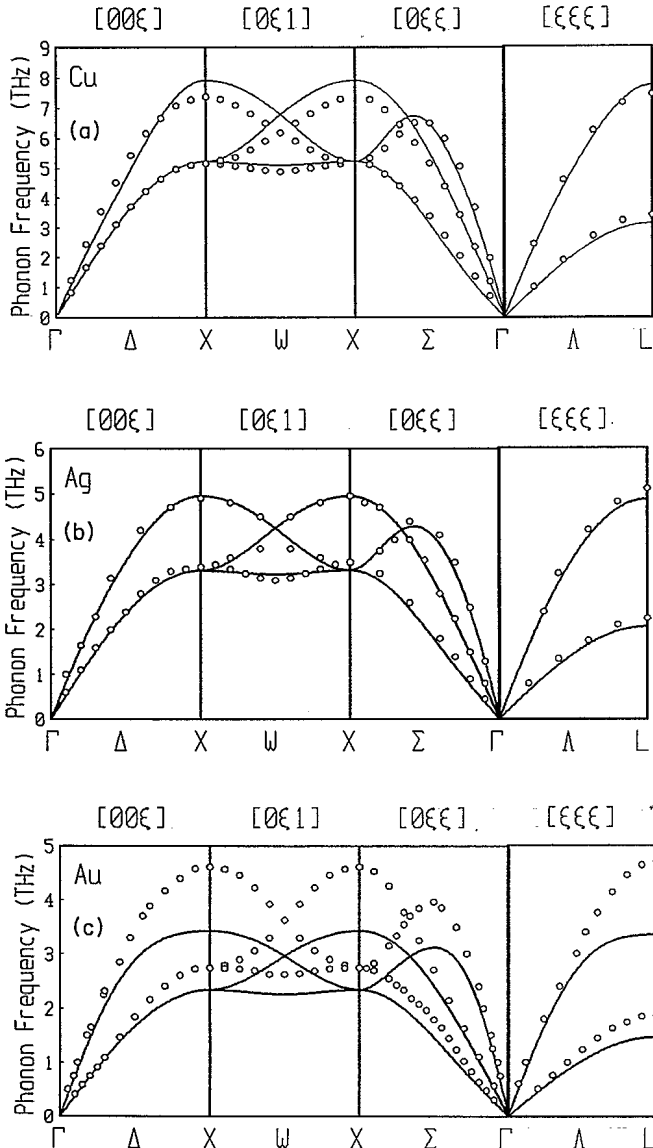


FIG. 2. Phonon dispersions for Cu, Ag, and Au. The open circles are the experimental values. (a) Cu; (b) Ag; (c) Au.

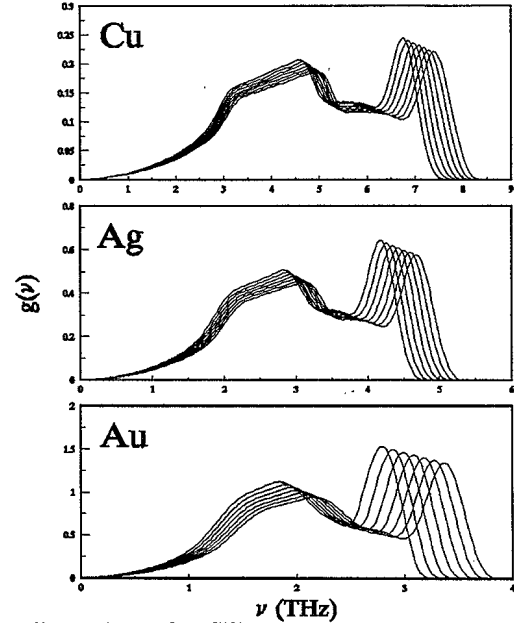


FIG. 3. Illustration of the changes of the phonon DOS of the noble metals with respect to lattice constants.

free energy as a function of lattice constant and temperature,

$$F(a, T) = E_{\text{coh}}(a) + F_T(a, T), \quad (17)$$

with

$$F_T(a, T) = k_B T \int_0^{\infty} \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] g(\omega, a) d\omega.$$

To get the thermal expansion, we have to minimize the free energy so as to find the equilibrium lattice constant under a given temperature. For performing the numerical differentiation of the free energy with respect to the lattice constant, we first select n lattice constants near equilibrium as the samples and calculate the DOS's for the selected samples. For arbitrary lattice constant inside the interval of sampling length, we suppose that the corresponding DOS can be given by using the Lagrange interpolation

$$g(\omega, a) = \sum_{i=1}^n \left[\prod_{j \neq i} \frac{a - a_j}{a_i - a_j} \right] g(\omega, a_i). \quad (18)$$

Figure 4 shows the calculated relations of linear thermal expansion with temperature for the noble metals. The predicted results are all greater than experimental data.²⁹ The errors may be due to the fact that the inputs for the model are all measured under finite temperature and therefore must be different from the actual ones under zero temperature.

IV. DISCUSSION

It should be pointed out that, despite the purely empirical treatment in the above sections, the present method may represent a possible connection between total-energy

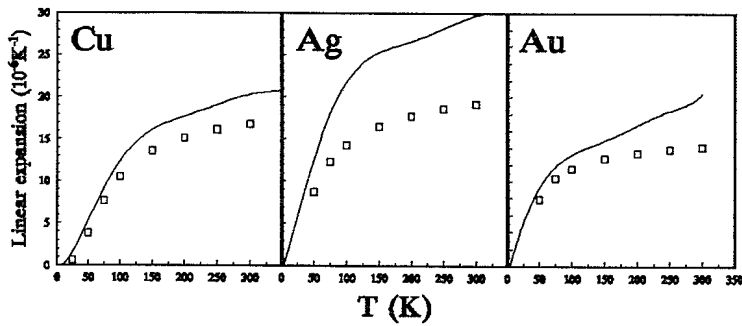


FIG. 4. The linear thermal expansions as a function of temperature for the noble metals. The open squares are the experimental data (Ref. 29) and the full lines denote the calculated results.

computation from first-principles and the interatomic force method. As we know, although the developing band theory has enabled us to study materials from the viewpoint of electronic structure, it is not always applicable, especially when the system in consideration becomes complicated. As a result, the phenomenological concept of the interatomic potential still remains as a practical groundwork for simulating material properties such as elastic constants, phonon spectra, thermodynamics, and even the energetics of surfaces, interfaces, fractures, and grain boundaries. The present method may be a useful step to facilitate simulations for complex systems at finite temperature on the basis of less time-consuming first-principles calculations for selected simple systems as references. If *ab initio* results for a_e , E_s , B_e , C_{12} , C_{44} ,

and E_b are available, we can construct an *ab initio* N -body potential, and since the *ab initio* N -body potential takes the many-body interaction into account, it will be more applicable than the previous *ab initio* two-body potential used by CGE. Finally, it should be added that the present method has been extended to the study of alloy systems.³⁰

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