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Finite-Temperature Defect Properties from Free-Energy Minimization

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We present two simple, but accurate, techniques for calculating the finite-temperature atomic structure and free energy of any solid defect (point or extended). The finite-temperature equilibrium atomic structure and thermodynamic properties of defects in solids are obtained *self-consistently* by minimizing the *free energy* of the solid with respect to the coordinates of the atoms. Application of the two methods to a perfect crystal and one with a vacancy show that both methods yield excellent agreement with Monte Carlo calculations for temperatures up to at least 75% of the melting point.

Defects in solids (e.g., internal interfaces, dislocations, vacancies, etc.) are known to play crucial roles in a wide variety of material phenomena. Unfortunately, our understanding of defects in solids is far from complete. The present Letter outlines two new methods for self-consistently determining the atomic structure and thermodynamic properties of defects (point, line, plane) in solids at finite temperature. At the heart of both methods is a *local* harmonic (Einstein-like) approximation to the free energy of the solid which depends on the *local* atomic configuration. Since the free energy is determined in terms of the local atomic coordinates, a minimization of the free energy with respect to atomic coordinates yields both the equilibrium structure and free energy of the solid and the defects contained therein. These methods are compatible with a wide variety of methods for describing atomic interactions (e.g., pair, embedded atom,[1] three-body potentials) and require computational resources comparable to $T=0$ determinations of the equilibrium atomic structure.

The theoretical study of the thermodynamic properties of perfect crystals is well developed. A number of approaches have been taken, including lattice dynamics in the harmonic and quasiharmonic approximations,[2] self-consistent phonon theory,[3] and classical molecular dynamics (MD) and Monte Carlo (MC) computer simulations.[4] These methods are all, in principle, very accurate and give calculated properties of perfect crystals in good agreement with experiment. An advantage to the phonon-based methods is that the Helmholtz free energy is easily determined, while the free energy is difficult to determine using MD or MC.[5] Recently, Jacucci and co-workers[6] used quasiharmonic lattice theory to calculate the free energy of vacancies; however, the structure of the vacancy was not consistently determined. For more complicated defects, such as grain boundaries, primarily MD simulations[7] have been used at finite temperatures, though a recent application of statistical-mechanical density-functional theory has been made to dislocation structures.[8] In a spirit similar to the present work, Sutton[9] has had some success in calculating the

free energy of defects using moment expansions of the vibrational density of states. The approaches we present in this paper, which are based on a cell (local harmonic) model[10] description of the atomic vibrations, may be applied to arbitrary defects and have the advantages of both conceptual simplicity and computational efficiency.

To reasonable accuracy, the motion of an atom in a solid is harmonic. We simplify the harmonic approximation further by neglecting all terms that couple vibrations of different atoms. The Helmholtz free energy, A_0, is thus given by[11]

$$A_0 = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} u_{ij}(r_{ij}^0) + k_b T \sum_{i=1}^{N} \sum_{\beta=1}^{3} \ln\left[2\sinh\left(\frac{\hbar\omega_{\beta i}}{4\pi k_B T}\right)\right],$$

(1)

where N is the number of atoms, $k_B T$ is the thermal energy, u_{ij} is the interatomic potential, r_i^0 is the position about which particle i vibrates, $r_{ij}^0 = |r_i^0 - r_j^0|$, and $\omega_{\beta i}$ are the three vibrational frequencies of atom i. In the Einstein model all frequencies are set equal to the Einstein frequency, ω_0, which is often determined by fits to experimental data. (Note that while we assume that the atomic interactions are described by pair potentials in this Letter, the generalization to other types of potentials is straightforward.)

We have taken a different approach, which we call the local harmonic (LH) model. For a given perfect crystal structure at a volume V and temperature T, one can determine $\omega_{\beta i}$ by diagonalizing the local dynamical matrix for each independent atom in the unit cell. These local frequencies, inserted into Eq. (1), yield the Helmholtz free energy, from which all other thermodynamic quantities are determined. In the classical limit, Eq. (1) can be simplified to

$$A_0 = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} u_{ij}(r_{ij}^0) + 3k_B T \sum_{i=1}^{N} \ln\left[\frac{D_i^{1/6}}{k_B T}\right],$$

(2)

where $D_i = [\omega_{1i}\omega_{2i}\omega_{3i}]^2$ is the determinant of the local dynamical matrix of particle i. As demonstrated below, this very simple model yields accurate free energies and

equations of state. Application to imperfect systems, such as solids with vacancies or grain boundaries, is straightforward, since all of the variables in Eq. (2) are completely specified by the interatomic potential and the *local* atomic configurations. We note that by neglecting the coupling of vibrations of different atoms, the free energy of a configuration of N atoms is simplified to the calculation of the determinants of N (3×3) matrices. The equilibrium atomic structure and corresponding thermodynamic properties are determined by minimizing the *free energy* at *any temperature* with respect to the atomic coordinates.

If we restrict the frequencies in Eq. (1) to a local Einstein model, with only one frequency per independent atom, the potential energy can be written classically (assuming pairwise interactions) as

$$U_0(\mathbf{r}^N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq 1} u_{ij}(r_{ij}^0) + \frac{1}{2} \sum_{i=1}^{N} k_i (\mathbf{r}_i - \mathbf{r}_i^0)^2 , \quad (3)$$

where k_i ($= \omega_i^2 m$, where m is the atomic mass) is the

harmonic force constant associated with atom i. An atom vibrating in such a harmonic potential has a spherically symmetric Gaussian atomic density profile. Our second approximate technique, the variational Gaussian (VG) method, is a variational theory that takes advantage of these Gaussian distributions. From the Gibbs-Bogoliubov inequality,[11] the free energy of a system is constrained such that $A \leq A_0 + \langle U - U_0 \rangle_0$, where $\langle \rangle_0$ indicates that the average is performed over the harmonic reference system [Eq. (3)] and U is the total potential energy of the system of interest. Thus $A_0 + \langle U - U_0 \rangle_0$ is a rigorous upper bound to the true free energy of the system. A takes on the simple form

$$A \leq \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq 1} w_{ij}(r_{ij}^0) + \frac{3}{2} k_B T \sum_{i=1}^{N} \left[\ln \left(\frac{\alpha_i \Lambda^2}{\pi} \right) - 1 \right] , \quad (4)$$

where $\alpha_i = k_i / 2 k_B T$, Λ is the thermal DeBroglie wavelength, and w_{ij} is the interaction between atoms at sites i and j whose distributions have been broadened into Gaussians by their vibrational motion,

$$w_{ij}(r_{ij}^0) = \left[\frac{\alpha_i}{\pi} \right]^{3/2} \left[\frac{\alpha_j}{\pi} \right]^{3/2} \int e^{-\alpha_i(\mathbf{r}_i - \mathbf{r}_i^0)^2} \int e^{-\alpha_j(\mathbf{r}_j - \mathbf{r}_j^0)^2} u_{ij}(r_{ij}) d\mathbf{r}_i d\mathbf{r}_j . \quad (5)$$

The variational Gaussian potential, w_{ij}, is determined one time for each *form* of pair potential, u_{ij}, by evaluating the integrals over the highly peaked Gaussian distributions. For an exponential potential $\exp(-\gamma r_{ij})$, w_{ij} takes on the simple form

$$w_{ij} = (1 - \gamma \theta / r_{ij}^0) \exp(-\gamma r_{ij}^0 + \gamma^2 \theta / 2) ,$$

where $\theta = (1/\alpha_i + 1/\alpha_j)/2$, with additional correction terms that are negligible for the narrow Gaussian distributions found in solids.

In the VG method calculation of the free energy is then just a sum of *temperature-dependent effective pair potentials* which are only slightly more complicated than the original pair potentials 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. (4) with respect to the mean atomic positions $\mathbf{r}_i^0$ and the local Gaussian widths α_i.

The potential in Eq. (3) also serves as the reference system in the method suggested by Frenkel and Ladd[5] for calculating free energies of solids with computer simulations. In principle, the free energies determined with their method are exact, subject only to numerical uncertainties, but it necessitates a fairly large number of simulations (of order 10) for each V, T state point.

We tested the LH and VG methods on a simple model for Cu, using a pairwise Morse potential truncated between the second and third nearest neighbors,

$$u_{ij} = D_0 \{ \exp[-2\beta(r - r_0)] - 2\exp[-\beta(r - r_0)] \} ,$$

with $D_0 = 0.3429$ eV, $\beta = 1.3588$ Å^{-1}, and $r_0 = 2.866$ Å.

We note that since this is a very approximate description of the interactions in Cu, we do not compare with experiment but rather to accurate MC calculations with the same potential. The results for the free energy of the perfect solid at pressures of -3.2, 0, and 80 GPa are shown in Fig. 1 as a function of temperature. The agree-
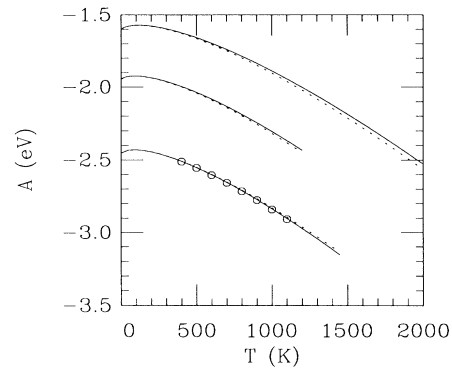

FIG. 1. Calculated free energy vs temperature for a perfect Cu crystal using a truncated Morse potential. The upper curve is for a pressure of 80 GPa, the middle curve for -3.2 GPa, and the lower curve for zero pressure. The values for the -3.2-GPa results have been shifted by $+0.5$ eV to separate them from the zero-pressure results. The solid curves are from the local harmonic model, the dashed curves from the variational Gaussian method, and the circles from the Frenkel-Ladd Monte Carlo procedure. We note that the MC results require ten full length simulations per point. The estimated errors in the MC calculations are smaller than the symbol size.
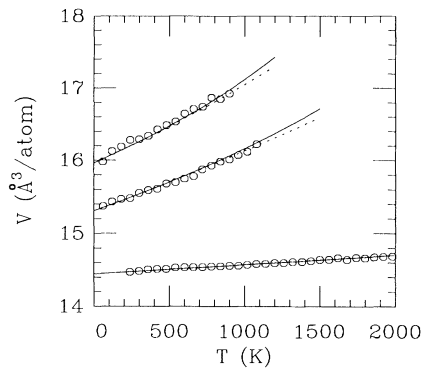
FIG. 2. Calculated volume per atom for a perfect Cu crystal using a Morse potential truncated at the second-nearest neighbors. The upper curve is for a pressure of −3.2 GPa, the middle curve at zero pressure, and the lower curve at 80 GPa. The values for the 80-GPa results have been shifted up by 4 Å³/atom to compress the scale. The line and symbol types are the same as for Fig. 1.

FIG. 3. Vacancy formation free energy for one atom removed from a 108-particle system (periodic boundary conditions), $\Delta A_v = (107/108)A_p - A_v$, where A_p is the free energy of a perfect 108-particle system and A_v is the free energy of the 107-particle system with a vacancy at the same volume. The solid curves are from the local harmonic model, the dashed curves from the variational Gaussian method, and the circles from the Frenkel-Ladd Monte Carlo procedure. The estimated errors in the MC results are smaller than the symbol size.

ment between both the LH and VG methods and our nominally exact Frenkel-Ladd MC results are excellent, with the VG method giving a slightly larger error at $P = 0$ and better results at both higher and lower pressures. The thermal expansion of this model of Cu is shown in Fig. 2, where we plot the volume versus temperature at the same three pressures. Once again, the agreement between all three methods is excellent, especially at high pressures, where the results are nearly indistinguishable. The frequencies calculated from the α_i parameter in the variational Gaussian method are within a few percent of those calculated with the local harmonic model over the range of temperatures and pressures studied. At zero pressure, for instance, the VG frequencies are larger by about 1.5% at 250 K and 6% at 1000 K.

Application of traditional lattice dynamics methods to systems with defects are difficult due to the low symmetry of the system and the large $(3N \times 3N)$ matrices that must be diagonalized. Because our methods depend only on a local description of the atomic vibrations, calculations of defects structures and thermodynamics are not much more challenging than for the perfect system. In order to test the LH and VG methods on a defect (where anharmonic effects are more important), we studied a vacancy in Cu, using the same pair potential as for the perfect system. We created the vacancy by removing one of the particles from the 108-particle system used in the MC calculations for the perfect crystal. In Fig. 3 we compare the vacancy formation *free* energy, ΔA_v $= (107/108)A_p - A_v$ calculated with the LH, VG, and Frenkel-Ladd MC methods. A_p is the free energy of the perfect 108-particle system and A_v is the free energy of a 107-particle system at the same total volume. The agreement between the approximate methods and the more accurate MC results is not as good for this system
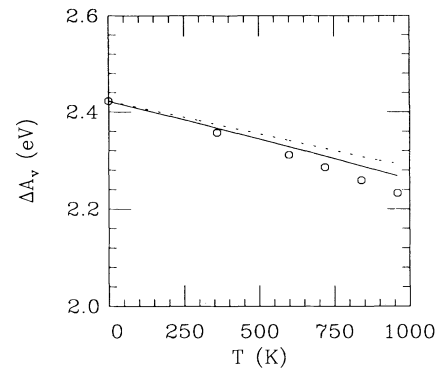
as for the perfect system. The errors range from 0 to 2.5% and 0 to 1.2% for the variational Gaussian model and the local harmonic model, respectively, as the temperature is increased from 0 to 960 K, which is approximately 75% of the melting point of this model for Cu. This increased error may be due in part to the increased anharmonicity of the lattice around the vacancy. However, the disagreement is somewhat misleading in that ΔA_v is defined as the difference between two relatively large numbers, and so any errors are greatly magnified. Indeed, the calculated free energies for the full 107-particle system are within about 0.15% with the LH model and about twice that with the VG model of the accurate MC determinations at $P = 0$.

For the atoms nearest to the vacancy, the LH model yields three vibrational frequencies, with a spread of about ± 10% relative to their geometric mean. This mean is about 0.5% less than the perfect-crystal value. The frequency derived from the α parameter in the VG method is reduced by about 4% relative to the perfect crystal. We note, however, that fixing the Gaussian widths of every atom in the VG model to their perfect-crystal value increases the vacancy free energy by only 0.01 eV. Comparison of atomic structure of the atoms around the defect shows excellent agreement between our two methods. For instance at 960 K, the distance between the center of the vacancy and its nearest-neighbor shell of atoms decreases by about 0.019 and 0.021 Å in the LH and VG calculations, respectively, relative to the perfect crystal. We note that the MC vacancy simulation results required approximately a factor of 200 more computer time to obtain than did either the VG or LH model computations. This large computational advantage enjoyed by the LH and VG methods in-

creases dramatically with increasing complexity of the defect studied (e.g., tens of thousands of atoms are required to study a low-angle grain boundary).

In summary, we have developed two approaches for self-consistently calculating the atomic structure and free energy of defects in solids at finite temperature. Both of these techniques are based upon minimizing the *free energy* with respect to atomic positions. Since the resultant simulations are simply minimizations, atomic structures and all thermodynamic properties are as simple and as fast to calculate at arbitrary temperature as $T = 0$ defect relaxations. While the LH and VG methods have been applied to the relatively simple cases of perfect crystals and vacancies, these methods are equally applicable to more complicated defects. Current work is focusing on the application of the LH and VG methods to grain boundaries with nonpair potentials (e.g., the embedded atom method[1]). At this time, we do not know whether one method or the other will be more useful. However, either approach is very much more efficient than any competing method for calculating free energies of solids, including the recent statistical-mechanical density-functional methods.[8,12]

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