

Calculating Accurate Free Energies of Solids Directly from Simulations

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We have developed and tested a new, accurate technique for determining free energies of solid phases using simulations. Our method uses correlation functions available in the simulations, and yields an upper bound on the entropy. We use our approach to calculate the free energy of a simple model of structural phase transitions, and compare with exact calculations of the free energy for the same model.

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Much current theoretical work in condensed matter physics and computational materials science requires the determination of a model material's structure and other properties at a given pressure and temperature. An accurate and general method of determining the free energy of a material would greatly aid work in solid-solid transformations, alloy design, surface reconstructions, and many other areas. Any calculation of a phase diagram (away from $T = 0$) requires knowledge of the relevant free energies.

The difficulty is that, typically, there are many possible structures for a given material or defect; the observed structure will depend upon its energy and, for $T > 0$, its entropy. The energy can often be determined, either by first-principles calculations or by more empirical models. The entropy cannot be calculated directly, however, as it cannot be written in terms of an ensemble average. Therefore, either some indirect approach must be used or a physical approximation must be made.

One approach is to use a series of simulations to calculate a *difference* in free energies. If we have a model potential V_0 for which we know the free energy F_0 at some temperature, and wish to know the free energy F of a different potential V at the same potential, then we may, in principle, calculate the free energy using the relation

$$F - F_0 = \int_0^1 d\lambda \langle V - V_0 \rangle_\lambda. \quad (1)$$

This approach is straightforward, assuming that there are no irreversible processes (such as phase transitions) occurring as the system is perturbed in the path from $\lambda = 0$ to $\lambda = 1$. The difficulty in this approach is that multiple simulations with different values of λ are required in order to evaluate the integral in Eq. (1). For solids, the free energy is usually found by perturbing from an Einstein solid or some other harmonic solid [1–6]. Once $F(T)$ is known for one temperature, it may be determined at other temperatures using a relation similar to Eq. (1).

In this Letter, we (1) present an approach which allows us to calculate an approximate free energy from a *single* simulation; (2) prove that this provides an upper bound to the entropy; and (3) demonstrate the power of this technique by comparing it with an exactly solvable

model of structural phase transitions. Anharmonic terms are included in the quantities calculated during the simulation, affecting both the energy and the entropy. These properties make our approach quite useful.

We begin by considering a system with a single degree of freedom x . We assume that the particle is in some external potential $V(x)$ that has a local minimum which confines the particle to some region of phase space. Classically, the partition function is

$$Z = \frac{1}{\lambda} \int dx \exp[-\beta V(x)] = \exp[-\beta F]. \quad (2)$$

Here, the thermal de Broglie wavelength is $\lambda = h/(2\pi mT)^{1/2}$ and $\beta = 1/T$. (Note that we have used $k_B = 1$ for convenience.)

To calculate an approximate free energy, we use the Gibbs-Bogoliubov inequality [7] that is used in many approaches, including self-consistent phonon theory (SCPT) [8]. This variational principle is normally written as

$$F \leq F_0 + \langle V - V_0 \rangle_0, \quad (3)$$

where the average is with respect to a *trial* potential $V_0(x)$ with a known free energy F_0 . We will reverse the roles of the trial and actual potentials, to write this principle as

$$F_0 \leq F + \langle V_0 - V \rangle. \quad (4)$$

All expectation values are calculated using the *actual* potential $V(x)$. We may write this equation as

$$S \leq S_0, \quad (5)$$

where $S \equiv -\beta[F - \langle V(x) \rangle - \langle E_K \rangle]$ is the real entropy of the system, and $S_0 \equiv -\beta[F_0 - \langle V_0(x) \rangle - \langle E_K \rangle]$ is a *trial* entropy of the system. Here, the average kinetic energy will classically have the value $\langle E_K \rangle = T/2$.

We now consider the specific case of a harmonic trial potential $V_0(x) = \frac{1}{2}m\omega^2 x^2$. (For convenience, we choose the origin of x such that $\langle x \rangle = 0$.) For this case, the trial entropy is

$$S_0 = \frac{1}{2} + \frac{1}{2} \ln\left(\frac{2\pi T}{m\omega^2 \lambda^2}\right) + \frac{m\omega^2 \langle x^2 \rangle}{2T}. \quad (6)$$

Minimizing S_0 with respect to ω , we obtain

$$\omega^2 = \frac{T}{m\langle x^2 \rangle}, \quad (7)$$

which is exactly what we would expect for a harmonic system. Equation (7) then simply states that for a classical harmonic oscillator, $\langle x^2 \rangle$ grows linearly with temperature.

Applying this to an anharmonic system, however, results in an effective frequency that is temperature dependent. In the general case, $\langle x^2 \rangle$ is not proportional to the temperature. Defining the frequency by Eq. (7) provides for the best possible harmonic approximation of the system. This is analogous to the approach of SCPT, in which temperature-dependent phonons are calculated using Eq. (3). SCPT produces an upper bound to the free energy. Our approach produces a lower bound, making the techniques complementary.

Inserting Eq. (7) into Eq. (6) to eliminate the frequencies, we obtain the following upper bound to the entropy:

$$S \leq S_0, \quad S_0 \equiv \frac{1}{2} \ln \left(\frac{2\pi\langle x^2 \rangle}{\lambda^2} \right) + 1. \quad (8)$$

This equation is straightforward to evaluate from a simulation, which would give a time-averaged value for the potential energy, for the temperature, and for $\langle x^2 \rangle$.

We now generalize to a system with N degrees of freedom $x_j, j = 1, \dots, N$. We define the correlation matrix

$$C_{ij} = \langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle. \quad (9)$$

As C_{ij} is symmetric and real, we are free to change our coordinate system to a set of variables y_j which diagonalizes the correlation matrix. This corresponds to choosing a set of modes for the system that are approximately decoupled. Further, we may choose the coordinates such that $\langle y_j \rangle = 0$.

We may then choose a trial potential that is harmonic in this basis. Repeating the analysis as before, we find a set of frequencies specified by

$$\omega_j^2 = \frac{T}{m\langle y_j^2 \rangle}, \quad (10)$$

where $\langle y_j^2 \rangle$ are simply the eigenvalues of the correlation matrix. From Eq. (9) it is apparent that all eigenvalues will be positive. The product of the eigenvalues is simply the determinant of the correlation matrix, so the generalization of Eq. (8) is

$$S \leq S_0, \quad S_0 \equiv \frac{N}{2} \ln \left(\frac{2\pi}{\lambda^2} \right) + \frac{1}{2} \ln(\det C) + N. \quad (11)$$

The corresponding free energy bound may then be expressed quite simply as

$$F \geq \langle V \rangle - \frac{NT}{2} - \frac{T}{2} \ln \left[\left(\frac{2\pi}{\lambda^2} \right)^N \det C \right]. \quad (12)$$

This is a powerful approach: While based on the harmonic approximation, it directly incorporates finite tem-

perature effects, allowing for temperature-dependent frequencies. At any given temperature, the instantaneous correlation matrix may be determined from a simulation. The entropy of the system is then estimated from a harmonic system which, at that temperature, exactly reproduces the correlation matrix. Anharmonic terms will be accounted for by affecting the correlations, which will then affect the entropy calculation. Thus, this is very comparable to SCPT, yet the method of calculation allows for significantly broader applications.

The similarity of this approach to SCPT and quasiharmonic theory has been used previously by Sutton [9,10]. The work of Sutton used quasiharmonic theory to derive a free energy which, in the classical limit, gives the entropy in the form shown in Eq. (11). His motivation was to use this as an analytic approach to calculating temperature-dependent relaxations near defects. Our derivation demonstrates that this bounds the entropy and indicates how it may be used in combination with simulations.

We note that, in practice, this bound may not be a good approximation for the true free energy. If the system is not approximately harmonic, then the results will be poor. In particular, diffusion will cause this approach to produce entropies much higher than the real entropy of the system. Further, the bound is based upon accurate values of the equilibrium correlation function. If the system is not in equilibrium, then the calculated entropy may be lower than the actual value. This may occur when simulating metastable phases.

To demonstrate how our approach may be applied, and to test the accuracy of the approximation, we have used a simple model of first-order structural transitions [11–14] which may be solved *exactly* in 1D using transfer matrix methods [12,13]. By comparing our approach with exact calculations that are not based upon simulations, we may demonstrate the accuracy and usefulness of the approach.

In our model, the state of each particle is characterized by a scalar displacement u . We have chosen a Hamiltonian that is invariant under $u \rightarrow -u$, with two absolute minima at $u = \pm u_0$, but also has a metastable minima at $u = 0$. The model is based upon a phenomenological expansion of the energy at $T = 0$ (with all parameters independent of T). In 1D, the energy may be written as

$$U = \sum_i V_{os}(u_i) + \frac{k}{2} (u_i - u_{i+1})^2 + \frac{\alpha}{4} (u_i^2 + u_{i+1}^2)(u_i - u_{i+1})^2, \quad (13)$$

where the on-site energy, shown in Fig. 1, is given by

$$V_{os}(u) = (V_0 u^2 + E_{well}/u_0^4)(u^2 - u_0^2)^2 - E_{well}. \quad (14)$$

This potential can be characterized by setting the depth of the minima E_{well} , the value of u_0 , and the barrier height to well depth ratio $E_{barrier}/E_{well}$. For the purposes of this paper, we will set $u_0 = 1$, $E_{well} = 75$, and $E_{barrier}/E_{well} = 4$, following Ref. [12].

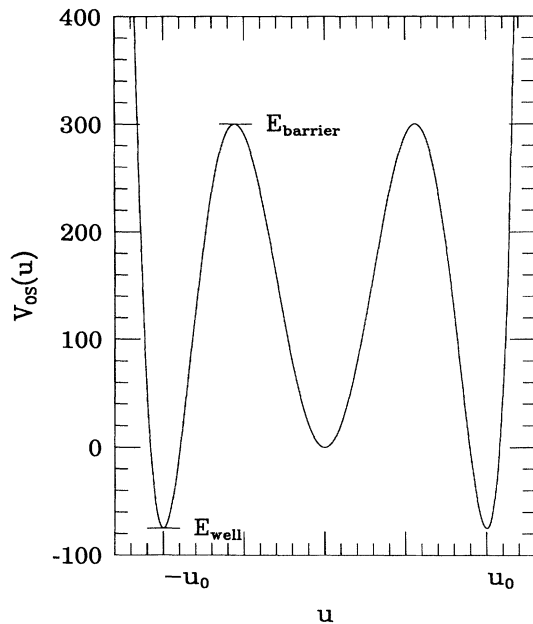


FIG. 1. On-site energy $V_{os}(u)$ of the model Hamiltonian as a function of the scalar displacement u . Note that at low temperatures, the system will break the $u \rightarrow -u$ symmetry by choosing one of the degenerate absolute minima.

There are two parameters controlling the intersite couplings. The first of these, k , is the strength of the usual harmonic coupling between sites. The second, α , models the change in phonons that typically occurs at a first-order structural transition. At low temperatures, when $\langle u^2 \rangle \approx 1$ for all i , the intersite terms are nearly harmonic with strength $k + \alpha$. At high temperatures, when $\langle u^2 \rangle \approx 0$, the second term is negligible. Thus, the high-temperature phase has softer phonons than the low-temperature phase. The resulting large vibrational entropy difference between the two phases helps stabilize the high-temperature phase, as in many real systems [11–16]. We will use $k = \alpha = 4000$ in this work.

With this choice of parameters [12], the exact $d = 1$ results show that there is a dramatic change in the behavior of the system in the vicinity of the $d = 2$ transition temperature [13,14]. (For $d = 1$, systems with short-range interactions cannot have phase transitions due to the entropy of domain wall formation [17].) This is demonstrated in Fig. 2, which shows the mean squared displacement $\langle u^2 \rangle$ versus temperature. At $T \approx 140$, the equilibrium system changes from $\langle u^2 \rangle \approx 0.95$ at low temperatures (corresponding to $u \approx \pm 1$) to $\langle u^2 \rangle \approx 0$ at higher temperatures. The exact results demonstrate that while $\langle u^2 \rangle$ is continuous, the change in behavior occurs over a very narrow range of temperature.

The molecular dynamic simulations demonstrate the difficulty in determining the transition temperature. Two sets of simulations were performed: One set of data

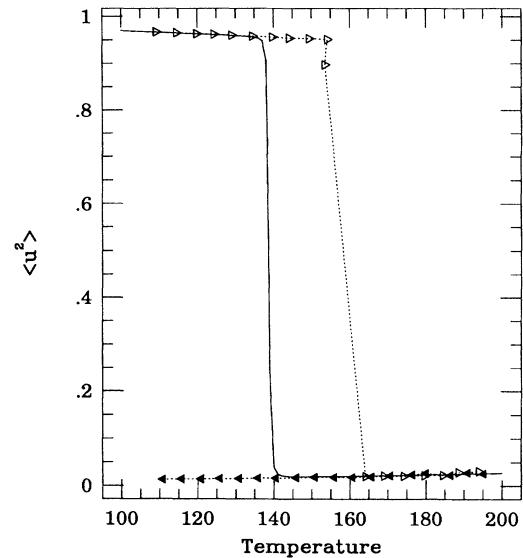


FIG. 2. Mean squared displacement $\langle u^2 \rangle$ as a function of temperature. The solid line indicates exact results, obtained from transfer-integral calculations. The open symbols are results from simulations of heating the low-temperature phase; the closed symbols are results from simulations of cooling the high-temperature phase.

shows the results obtained by heating the system from the low-temperature phase, the other by cooling the high-temperature phase. We simulated 512 atoms, and allowed the system to equilibrate for 50 000 time steps at each temperature, then calculated averages over the next 64 000 time steps. From these simulation data, shown in Fig. 2, we cannot determine the transition temperature, despite the long equilibration time.

The hysteresis demonstrated here will occur in most simulations of systems undergoing first-order phase transitions, and is due to the fact that the equilibration times near the transition temperature are much longer than practical simulation times. For our model, the high-temperature phase is metastable at all temperatures, and no transition to the low-temperature phase is observed. The low-temperature phase remains stable to some temperature above the transition temperature, and then transforms.

In Fig. 3 we show the exact results for the free energy, along with the approximate free energies calculated from the techniques presented in this paper. The exact results show a rounded cusp near $T \approx 140$, corresponding to the change in behavior. From the simulations, we obtained two free energy curves, one corresponding to the low-temperature phase and one to the high-temperature phase. These curves cross at $T \approx 145$, near the cusp in the exact results. Taking the lower of the free energy curves on each side of the crossing produces a good approximation to the exact results.

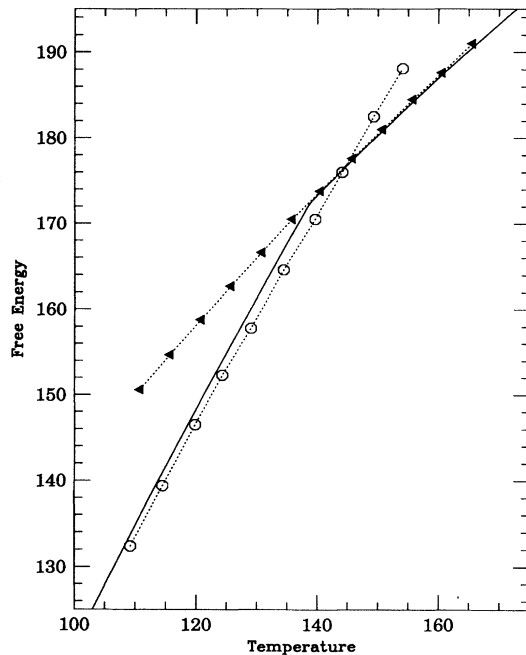


FIG. 3. Free energy as a function of temperature. The solid line indicates exact results, obtained from transfer-integral calculations. The open symbols are results from simulations of heating the low-temperature phase; the closed symbols are results from simulations of cooling the high-temperature phase.

The high-temperature simulation results are in particularly good agreement with the exact results for $T \geq 140$, while the low-temperature results are not as good. The errors are on the same order of magnitude as errors from SCPT [12,14]. The larger error for the low-temperature phase is due to the fact that the expansion of the potential about $u = u_0$ has odd-power terms, which are not fully taken into account in first-order perturbation schemes such as our technique. A fuller account of how this occurs in SCPT, and how higher order terms may be incorporated, is given in Ref. [14]. Similar difficulties have been noticed in defect free energy calculations [6].

In conclusion, our paper has demonstrated that the use of Eq. (11) is a good approximation for the exact results, for solids which may be approximated by an effectively harmonic Hamiltonian. This approach is more convenient than SCPT and does not require a series of simulations. Further, it provides for temperature-dependent phonon frequencies, which makes it more adaptable than other approximate harmonic techniques [18]. We have also successfully applied this approach to embedded atom

method models of Al [5] and Cu [6]; this will be described in a forthcoming paper.

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