Exactly Solvable Heterophase Fluctuations at a Vibrational-Entropy-Driven First-Order Phase Transition

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We propose a new Hamiltonian (intended to mimic solid-to-solid diffusionless martensitic transitions) that displays a vibrational-entropy-driven, first-order phase transition. This model employs anharmonic intersite couplings that alter the stiffness of the vibrations in the product phase relative to the (high-temperature) parent phase. Our studies (of a one-dimensional, pseudotransition) clearly show (i) that the heterophase fluctuations connecting the parent and product phases are an equilibrium property, and (ii) the associated central peak in $S(q,\omega)$ has a very unusual temperature dependence.

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The theory of the dynamics of first-order phase transitions relies on many standard models that dominate statistical mechanics.[1] However, for studies concerning the modeling of diffusionless structural phase transitions, so-called martensitic transformations,[2] none of the existing models are adequate. To see this, consider a sequence of transitions undergone by the simple metals. Upon solidification, Li, Na, as well as many other metals, assume the bcc form. With further cooling these materials change to their (presumed) $T=0$ form, viz., one of the close-packed layered structures, e.g., the $9R$ lattice.[3] The equilibrium aspects of these transitions are well described by conventional theories, and rely on the low vibrational energies of the bcc phase; i.e., these structures are stabilized by the large entropy of the relatively soft bcc lattice.[4] To be specific, there is a low-lying phonon branch, corresponding to the Zener elastic mode,[5] present in the bcc but not the low-temperature phases. Thus, one should envision such solid-to-solid transformations as occurring from a change of the phonon-dispersion curves. In order to model such transitions in a simple way one must begin with a model that possesses the ability to show a change in the vibrational entropy. Such a simple model Hamiltonian was recently proposed by one of us,[6] and here we display the interesting dynamics obtained in a study of this model.

Consider the following (temperature-independent) Hamiltonian[6] for an arbitrary lattice with sites labeled by index i:

$$H=\sum_i\left[\frac{p_i^2}{2m}+V_{\mathrm{os}}(u_i)\right]+\sum_{\langle ij\rangle}V(u_i,u_j)\,,$$

where

$$V_{\mathrm{os}}(u_i)=\tfrac{1}{2}Au_i^2-\tfrac{1}{4}Bu_i^4+\tfrac{1}{6}Cu_i^6$$

and

$$V(u_i,u_j)=\tfrac{1}{2}k(u_i-u_j)^2+\tfrac{1}{4}\alpha(u_i^2+u_j^2)(u_i-u_j)^2\,;\qquad(1)$$

the symbol $\langle i,j\rangle$ denotes near-neighbor pairs. The constant u_i can be viewed as the displacement of an ion from its lattice position. The on-site potential $V_{\mathrm{os}}(u)$ with A, B, and C all positive is chosen to have a metastable minimum at $u=0$, and doubly degenerate stable minima at $u=\pm u_0$. Further, these three parameters may be selected to specify a length scale, an energy scale, and the ratio of the barrier-height to the well-depth energies. We have assigned the length scale such that $u_0=1$. Setting the barrier height to 300 (in temperature units) determines the energy scale. We are interested in the case where the intersite coupling strength is much stronger than the on-site potential's localization energy. This is known as the displacive limit,[7] and in this limit we expect only weakly anharmonic vibrations.

Note that under $u_i\to -u_i$ for all i, H is invariant, and thus $\langle u_i\rangle=0$ for all temperatures; consequently, any low-temperature transition to the stable wells of V_{os} must be a true symmetry-breaking phase transition. To be specific, V_{os} is the simplest potential with this character relevant to a first-order phase transition. However, it is the intersite couplings which furnish us with the interesting behavior.

In order to understand the new intersite coupling term, first consider the case $\alpha=0$. The coupling above and below the transition is purely harmonic, with strength k. The effect of α is to produce an effective intersite coupling that is different above and below the transition. Above the transition, $\langle u^2\rangle\ll 1$, so the coupling strength is $\sim k$. However, below the transition, $\langle u^2\rangle\sim 1$, and thus $\langle u_i^2+u_j^2\rangle\sim 2$; therefore, the coupling is essentially $k+\alpha$. This increased coupling strength produces stiffer phonons, and thereby lowers the vibrational entropy.

This entropy difference plays an important role in "driving" the transition. In the absence of the new term ($\alpha=0$), there is a change of the system's behavior as the temperature is varied when the temperature is of the same order as the energy difference between the stable and metastable wells. The temperature regime over which the change occurs is broad. By adding the new term ($\alpha \neq 0$), the vibrational entropy of the low-temperature phase is lowered, and thus this enhanced difference in free energies as a function of temperature sharpens the transition. Our exact calculation demonstrates that this new term provides a modification to the harmonically coupled Hamiltonian that displays these effects.

In order to establish a relevant value for α, we note that above the transition the anharmonic coupling produces a temperature-dependent dispersion relation (within self-consistent phonon theory; see below). For $\alpha \sim k$, the zone-boundary phonons change relative to the zone-center phonons by $\sim 50\%$ for a temperature change of ~ 1000 (in our temperature units). This corresponds to changing the effective coupling by $\sim 25\%$ over this temperature interval. Thus, choosing $\alpha = k$ allows for a reasonable relative temperature variation of the quasiharmonic restoring force.

In one dimension the partition function may be solved exactly using the transfer-integral (TI) technique.[8] Although there is no true transition in one dimension, due to the domain-wall entropy, the exact calculation demonstrates the effect of the new term on the thermodynamic quantities. The partition function may be written as $Z = Z_p Z_u$, where Z_p is the one-dimensional free-particle partition function

$$Z_p = \left[\int e^{-p^2/2mk_BT} dp \right]^N = (2\pi m k_B T)^{-N/2}. \tag{2}$$

This gives the usual contribution to the specific heat of $\frac{1}{2} k_B$; there is no interesting behavior from this term, and it will henceforth be ignored. However, the configurational partition function

$$Z_u = \int \prod_{i=1}^{N} \exp\{-\beta[V_{\rm os}(u_i) + V(u_i, u_{i+1})]\} du_i \tag{3}$$

leads to nontrival behavior. Following the prescription for a TI calculation of Z_u, we choose functions $\phi_n(u)$ to satisfy the eigenvalue equation

$$\int \exp\{-\beta[V_{\rm os}(u_i)/2 + V_{\rm os}(u_j)/2 + V(u_i, u_j)]\} \phi_n(u_i) du_i = \lambda_n \phi_n(u_j), \tag{4}$$

and relabel the ϕ_n such that

$$\lambda_0 > |\lambda_1| > \cdots .$$

In the thermodynamic limit, the configurational partition function is then

$$\lim_{N \to \infty} Z_u = \lambda_0^N. \tag{5}$$

The eigenfunctions and corresponding eigenvalues may be found numerically, and thus all equilibrium thermodynamic properties may be found exactly.[8]

In Fig. 1 the heat capacity for the system is shown as a function of temperature, for the cases $\alpha = 0$ and k. For $\alpha = 0$, there is a broad peak in the heat capacity. This is related to the Schottky anomaly.[9] The case of nonzero α shows a very narrow peak, with a very large maximum at $T = T_1 \approx 138.7$. For a real first-order transition, this peak would be a delta function, with integrated area equal to the latent heat. We have calculated the mean-square displacement and find that this peak corresponds

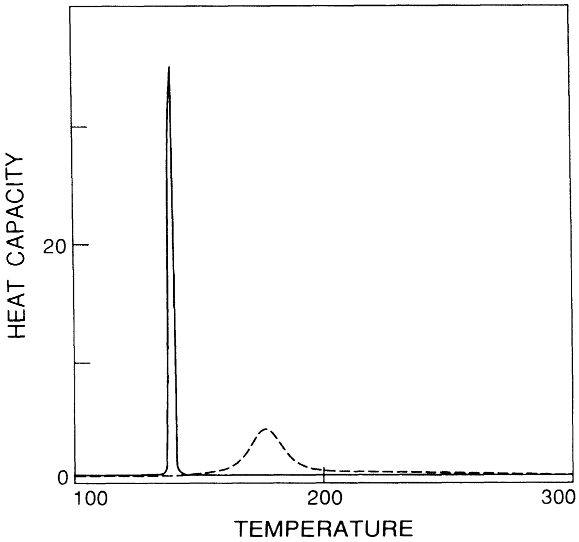

FIG. 1. The specific heat vs temperature of the $\alpha = 0$ (dashed curve) and $\alpha = k$ (solid curve) systems. The parameters appearing in the on-site potential in Eq. (1) have been taken to have the values $B/A = 4.209$ and $C/A = B/A - 1$ (ensuring the minima appear at $u = \pm 1$), and A is chosen to lead to a barrier height of 300, and a well depth of 75. Also, $k/A = 0.921$, corresponding to the displacive limit.

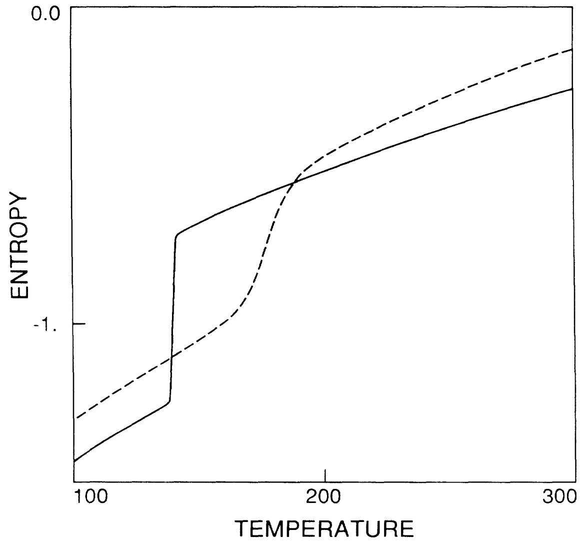

FIG. 2. The entropy vs temperature for $\alpha = 0$ (dashed curve) and $\alpha = k$ (solid curve) for the same values as used in Fig. 1. The broad "transition" found for $\alpha = 0$ is sharpened to a near step for $\alpha = k$.

to a sudden increase in $\langle u^2\rangle$. Figure 2 shows the entropy for these two situations. The nonzero-α case appears discontinuous; for dimensions greater than one, we expect a true discontinuity corresponding to a real transition. More importantly, we see that the new term has indeed increased the change in entropy, relative to the $\alpha=0$ case, and that the increased entropy difference has stabilized the high-temperature phase. The sharpness of the transition due to the enhanced entropy change is manifest.

The above equilibrium properties show that we are studying a vibrational-entropy-driven first-order phase transition. We may also use the TI technique to show the existence of heterophase fluctuations for temperatures near T_1. The probability density $P(u)$ of finding a particle in the range from u to $u+du$ is given by[8]

$$P(u)\propto|\phi_0(u)|^2, \tag{6}$$

where ϕ_0 is the eigenfunction with the dominant eigenvalue. Figure 3 shows this distribution for $T=138.5$ and 138.9. These temperatures are just above and just below T_1, where the peak in the specific heat occurs. The figure shows just above the transition the system is almost completely localized in the center well, with small dynamical fluctuations into the side wells. *These are long-lived, heterophase fluctuations.* For slightly higher temperatures, these fluctuations decrease dramatically until the probability density in the side wells is essentially zero. Just below the transition, analogous but opposite behavior is found, with the system mainly in the side wells, but with small fluctuations into the metastable minimum. For $\alpha=0$ the distribution broadens severely as the temperature is decreased, slowly spreading out into the side wells. The change in behavior is very gradual, and in essence $P(u)$ is simply $\exp\{-\beta V_{\rm os}(u)\}$: Minimal vibrational-entropy effects are present.

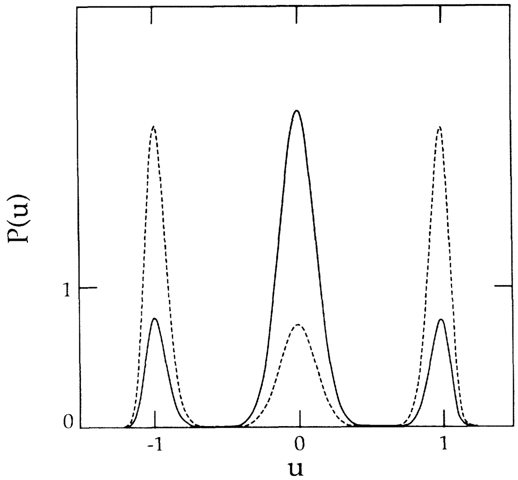

FIG. 3. The probability distribution function $P(u)$ for $\alpha=k$ at $T=138.5$ (dashed curve) and $T=138.9$ (solid curve). The specific heat peak in Fig. 1 occurs at $T=T_1\equiv138.7$. The heterophase fluctuations, both above and below the transition, corresponding to parent-to-produce phase motion, are evident.

The above results show that away from the immediate region of T_1, the system is highly localized in one of the wells. This suggests that the system is *harmonic* away from T_1. Thus, we have performed self-consistent phonon calculations,[10] i.e., a harmonic theory that includes the lowest-order renormalization of the Hamiltonian by thermal effects. We use the trial Hamiltonian

$$H_t=\sum_i[\tfrac{1}{2}p_i^2+\tfrac{1}{2}\Omega^2(u_i-\bar{u})^2+\tfrac{1}{2}\phi(u_i-u_{i+1})^2]\,. \tag{7}$$

Here, $\bar{u}$ is the average displacement. The true free energy F satisfies the variational equation

$$F\leq -k_BT\ln Z_t+\langle H-H_t\rangle_t\equiv F_t\,, \tag{8}$$

where Z_t is the partition function for the trial Hamiltonian, and the average is with respect to the phonon basis. By varying the trial free energy F_t with respect to the parameters $\bar{u}$, ϕ, and Ω^2, we derive self-consistent equations for these parameters. The high-temperature phase is characterized by $\bar{u}=0$. In the low-temperature phase, we have allowed $\bar{u}$ to vary as a function of temperature. This allows for the fact that the side wells are not symmetric about their minima, $u=\pm1$.

This approximate treatment agrees *quantitatively* with the exact calculation, except for temperatures very close to T_1. Above T_1 the predicted free energy is within 0.05% of the exact value. Slightly below T_1, where the method is least accurate, this gives the correct free energy within ~2%. The predictions for the average energy per particle, the entropy, and the heat capacity are also very close to the exact values. Below T_1, this calculation does not allow for the domain-wall entropy. This causes a small discrepancy between the approximate treatment and the exact calculation. Also, the theory is not as accurate for the asymmetric minima. The exceptional agreement between the two calculations shows that away from T_1 the system is effectively harmonic.

Although the static equilibrium properties may be calculated using the TI technique, this method does not provide for an examination of the dynamics near the transition. Clearly, we would like to understand the character of the heterophase fluctuations near the transition. To study these dynamical properties we have performed molecular-dynamics (MD) simulations for our 1D system. As a check of the accuracy of these simulations, we have found that they exactly reproduced the TI results for the internal energy and heat capacity. We have also reproduced the susceptibility and the probability density for $T>T_1$.

Our principle interest in performing the MD simulations is to calculate the dynamical structure factor:

$$S(q,\omega)=\frac{1}{N}\sum_j\int\langle u_j(t)u_0(0)\rangle e^{i(qj-\omega t)}dt\,. \tag{9}$$

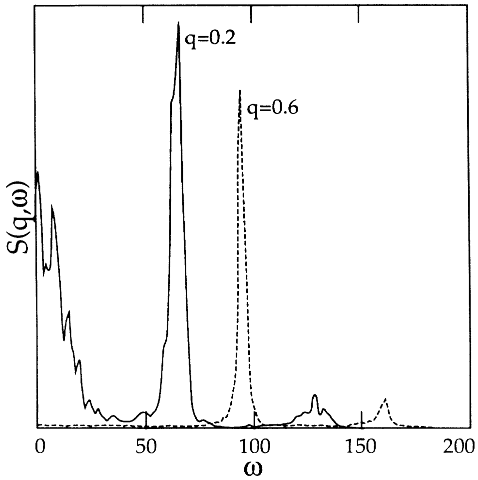

FIG. 4. The dynamical structure factor $S(q,\omega)$ at one degree above T_1 at $q=0.2$ (solid curve) and $q=0.6$ (dashed curve), where $q=1$ corresponds to the zone boundary. The central peak is present in the $q=0.2$ spectra, and product-phase phonons are in evidence at high frequencies.

In practice, we have calculated $S(q,\omega)$ for each of a set of different time periods to produce an averaged spectrum. In addition, we convolute the data with a smoothing function to eliminate noise from the data.

For $T > T_1$, $S(q,\omega)$ shows sharp peaks corresponding to long-lived phonons. The phonon frequencies correspond very closely to those predicted by self-consistent phonon theory [see Eq. (7)]. The lifetimes of the phonons increase as the system is cooled from high temperatures, viz., as the system becomes more localized within the central well. In addition to the phonon peaks, $S(q,\omega)$ has structure near $\omega=0$ for small q that is associated with the heterophase fluctuations. One such spectrum is shown in Fig. 4, which corresponds to *one* degree above the transition temperature. We have been able to fit the central peak by a diffusive mode's dynamical structure factor[11] where the linewidth varies as $\Gamma \sim D_0 + D_1 q^2 + D_2 q^4$; this width is effectively independent of temperature. However, the intensity of the peak is strongly temperature dependent, and the central peak is only observed over a small temperature range above T_1. In fact, below T_1 the central peak disappears, and one only obtains the product-phase phonon peaks.

One of the most informative aspects of Fig. 4 is the explicit proof these data provide of the long-lived nature of the heterophase fluctuations. To be specific, the two high-frequency peaks correspond to the product-phase phonons, and thus the system is diffusing from the parent (central) well into the product (side) well (recall that this is the stiffer phase and thus the corresponding phonon frequencies are higher), and then staying there long enough to fluctuate as if it were product phase. The lifetimes of these fluctuations are long enough for the product-phase phonon peaks to be well formed.

In conclusion, we have introduced a new Hamiltonian that produces a vibrational-entropy-driven first-order phase transition with long-lived heterophase fluctuations of a diffusive character in only a very small region around the transition.

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