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Phase Transitions in the Self-Consistent Phonon Approximation and a Mean-Field Approximation

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An analysis is made of the possible structural transformations in the self-consistent phonon approximation, in a mean-field approximation, and in an exactly solvable model. The character of the transition is found to depend both on the theoretical treatment and on the parameters used in the model Hamiltonians.

Several recent studies[1-4] of displacive transitions have used closely related model Hamiltonians which can be represented schematically by

$$H = K + V_2 + V_4. \tag{1}$$

Here V_4 represents a positive, quartic, short-range interaction, while the harmonic V_2 term includes both a short-range interaction and a long-range dipolar interaction. Since the lattice is stabilized by the quartic term, the force constant matrix in V_2 need not be positive definite.

In Refs. 1 and 2, a mean-field approximation (MFA) was used, and a second-order displacive transition was found; in Ref. 4, the self-consistent phonon approximation (SPA) was used and a first-order transition was found. It has recently been suggested[5] that long-range fluctuations are responsible for the first-order character of the transition in SPA, whereas the MFA yields a second-order transition because these fluctuations are effectively cut off. Unfortunately, Ref. 5 is completely qualitative and does not indicate whether the transitions are found in the same temperature regime in which long-range fluctuations are important.

Reference 5 used a variational treatment of a Hamiltonian of the form (1) containing a single collective degree of freedom of optic phonon character. As in Ref. 4, a displaced oscillator form was used for the trial density matrix. Minimization of the free energy yielded

$$\omega_q^2 = \Omega_0^2 - v(q) + 3\gamma\Delta + 3\gamma Q_0^2 \tag{2}$$

for the optic-mode frequency and

$$Q_0[\Omega_0^2 - v(0) + 3\gamma\Delta + \gamma Q_0^2] = 0 \tag{3}$$

for Q_0, the order-parameter conjugate to the $q = 0$ optic mode. The bare frequency Ω_0 and the quartic constant γ are associated with the intracell short-range interaction, and $v(q)$ is the Fourier transform of the harmonic intercell interaction $v_{ll'}$. The correlation function $\Delta = \langle (Q_l - Q_0)(Q_l - Q_0)\rangle$ depends implicitly on the mode frequency ω_q via the relation

$$\Delta = \frac{1}{2N}\sum_q \frac{1}{\omega_q}\coth\frac{\beta\omega_q}{2} \sim \frac{k_B T}{M}\sum_q \frac{1}{\omega_q^2}. \tag{4}$$

The difference between the MFA and the SPA is the way in which Δ is evaluated. The MFA uses what we will call the flat-spectrum approximation and replaces ω_q in (4) with a constant frequency $\Omega = [\omega_0^2 + v(0)]^{1/2}$ so that

$$\Delta_{MFA} = k_B T/[\omega_0^2 + v(0)]. \tag{5}$$

The SPA, on the other hand, evaluates the sum in (4) exactly. The MFA is equivalent to SPA with the approximation $v_{ll'} = v(0)/N$ so that $v(q) = \delta(q) \times v(0)$ and $\omega_q^2 = \omega_0^2 + v(0)$, $q \neq 0$. The flat-spectrum approximation has another implication: One can write $\sum_{ll'} v_{ll'} Q_l Q_{l'} \simeq v(0) \sum_l Q_l \sum_{l'} (Q_{l'}/N) = \sum_l v(0) \times \langle Q_{l'} \rangle Q_l$, which introduces a symmetry-breaking field in the Hamiltonian.

We have been studying[6] a model system of interacting anharmonic oscillators described by the Hamiltonians[7]

$$H_+ = -\tfrac{1}{2}\lambda^2 d^2/dx^2 + 4x^2 + 4x^4 - \alpha\langle x\rangle x, \quad (6a)$$

$$H_- = -\tfrac{1}{2}\lambda^2 d^2/dx^2 - 4x^2 + 4x^4 - \alpha\langle x\rangle x, \quad (6b)$$

where the term $-\alpha\langle x\rangle x$ is the result of treating a bilinear interaction term in a molecular-field approximation. The relationship to (1) is through the symmetry-breaking term introduced by the flat-spectrum approximation and the term $\alpha\langle x\rangle x$. Both α and $v(0)$ are assumed to be positive. The particles have unit mass and $\hbar$ is replaced by the variable λ. Thus a possible displacive transition will be driven by λ and zero-point energy will take the place of thermal energy.

The Hamiltonian (6) contains the essential physics of (1), but is exactly solvable by numerical methods. Thus we believe that the exact solutions of (6) are a reliable guide to the results of an exact solution of (1) if such were possible. Also, one can treat (6) approximately by using a trial ground-state wave function of the displaced-oscillator form $\Psi_\pm = \exp[-\tfrac{1}{2}g(x \pm x_0)^2]$ with g and x_0 chosen to minimize the ground-state energy. This is analogous to the displaced-oscillator density matrix used in Ref. 4. We will call the two treatments of (6) the exact and variational treatments.

These treatments, together with further investigations of the SPA and the MFA, have provided us with a much clearer picture of the relationship among the character of the displacive transition, the theoretical method, and the parameters in the model Hamiltonians. A summary of these results is given in Table I. The contents of this table, as well as other of our most important new conclusions, will be discussed in the points (a)–(f) below.

(a) Since the Hamiltonian (1) is symmetric, the state of lowest free energy must also be symmetric. Thus, any displacive transition which is found is due either to an approximation or to the implicit introduction of a symmetry-breaking term. The flat-spectrum approximation does the latter. As an example of the former, the exact solution of (6b) yields no transition for $\alpha = 0$, whereas the variational calculation yields a first-order transition for $\alpha \geq 0$. As will be seen in (c), the transition for $\alpha = 0$ is due to the restricted form of the variational wave function as it is readily shown that the properly symmetrized function $\Psi_S = \Psi_+ + \Psi_-$ gives a lower energy when $\alpha = 0$.

(b) The Hamiltonians (1) and (6) can each describe physical systems which are qualitatively different. When the quadratic term is negative, a physical picture is presented in which each atom in the most symmetric structure is at a classically unstable region of negative curvature —a hump. Hence, the system has built-in instability, and whenever the zero-point or thermal energy can be made small enough to permit localization of the particles in one of the wells of the double minimum potential, a displacement is likely to occur. When $\alpha = 0$, symmetry prevents the distortion, but for any finite, arbitrarily small α a transition ultimately occurs. Therefore, in a real physical system, something should break the symmetry and a distortion should occur. This is the physical picture of what we will call an instability-driven transition. In addition, if the symmetry-breaking term is short range

TABLE I. The values of the parameters in the model Hamiltonians (1) and (6) for which transitions of a particular character are found in the SPA and MFA treatments of (1) and the exact and variational treatments of (6).

Character of transition	SPA	MFA	Exact	Variational
No transition	$\Omega_0^2 \geq v(0)$	$\Omega_0^2 \geq v(0)$	$\alpha = 0$ (6b) $0 < \alpha \leq 8$ (6a)	$0 < \alpha \leq 8$ (6a)
First-order	$\Omega_0^2 < v(0)$	$v(0) > 2\Omega_0^2$		$\alpha \geq 0$ (6b)
Second-order		$\Omega_0^2 < v(0) \leq 2\Omega_0^2$	$\alpha > 0$ (6b) $\alpha > 8$ (6a)	$\alpha > 8$ (6a)

and random, the possibility of an order-disorder transition is introduced.

When the quadratic term is positive, the situation is quite different. The system is inherently stable and a strong enough field to overcome the natural stability must be imposed. We will call this a field-driven transition.

(c) A first-order transition is found in the variational calculation of Ref. 4 because the trial density matrix corresponding to the displaced system is a better variational form than is the symmetric one. We draw this conclusion because we find that, when the variational treatment of (6) predicts a transition, the exact ground-state wave function is quite similar to Ψ_S in the vicinity of the potential minimum and that the energy derived from the displaced solution differs from the true energy (or from the energy obtained using Ψ_S) by terms proportional to the overlap $\langle\Psi_+|\Psi_-\rangle \sim \exp(-gx_0^2)$, which is numerically quite small, whereas the undisplaced energy and the true energy differ by terms proportional to x_0^2. Thus Ψ_+, Ψ_-, and Ψ_S are almost equally good variational wave functions and all are superior to the undisplaced wave function.

(d) Contrary to the conclusion of Ref. 5, the transition found in Ref. 4 takes place at a temperature which is sufficiently high that the effects of long-range fluctuations can be completely ignored. Reference 5 employed a Debye approximation to evaluate Δ_{SPA} as

$$\Delta_{SPA} \sim \frac{3k_BT}{\omega_D^2}\left[1+\frac{\omega_0}{\omega_D}\tan^{-1}\left(\frac{\omega_D}{\omega_0}\right)\right], \qquad (7)$$

where ω_D is some effective Debye frequency. This shows the influence of the fluctuations associated with the soft mode on the behavior of the intercell correlation function in the region where $\hbar\omega_0 \ll k_BT$, a behavior which can be noted in the graphs of the correlation function in Ref. 3. However, the transition found in Ref. 4 took place in the vicinity of $\hbar\omega_0 \sim k_BT$,[8] where the behavior of Δ_{MFA} and Δ_{SPA} are similar. This is illustrated in Fig. 1 where the behavior of these quantities as functions of ω_0^2 is depicted. The plots show that both are monotonically decreasing, convex upward functions of ω_0^2 with the same large ω_0^2 behavior. Deviations between the behavior of the two occur only for $\hbar\omega_0 \ll k_BT$.

(e) Depending on the magnitudes of certain quantities in (1), the MFA may give rise to a first- or second-order transition or to no transition at all and the SPA may lead to a first-order transition or to no transition. This can be seen

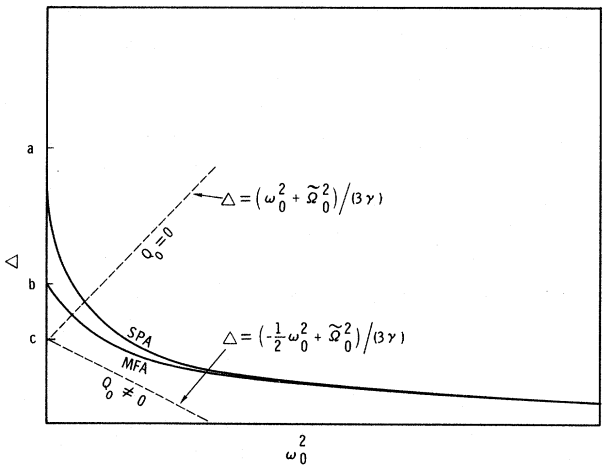

FIG. 1. Graphical solution of Eqs. (2)–(4) in both the SPA and the MFA. The solid curves represent plots of Δ_{MFA} and Δ_{SPA} versus ω_0^2 at a single temperature. The points a and b are the limiting values of Δ_{SPA} and Δ_{MFA}, respectively, as $\omega_0 \to 0$. A solution with a vanishing order parameter Q_0 can occur only at the point c, where $\Delta = \tilde{\Omega}_0^2/(3\gamma)$, with $\tilde{\Omega}_0^2 \equiv v(0) - \Omega_0^2$.

from the low-temperature behavior of the correlation functions as shown in Fig. 1. Here, Δ_{SPA} intersects the ordinate at $3k_BT/\omega_0^2$ with a slope of $-\infty$, whereas Δ_{MFA} intersects the ordinate at $k_BT/v(0)$ with a finite negative slope equal to $-k_BT/v(0)^2$. The dashed linear plots arise from the coupled solutions of (2) and (3) for the two cases $Q_0=0$ and $Q_0\neq 0$. The allowable self-consistent solutions for Δ and ω_0^2 are given by the intersection of the dashed lines with the appropriate temperature parametrized curve of Δ versus ω_0^2. Since $d\Delta_{SPA}/d(\omega_0^2) \to -\infty$ as $\omega_0^2 \to 0$, the SPA yields first-order transitions only.

The MFA, however, admits the possibility of a second-order transition because $d\Delta_{MFA}/d(\omega_0^2)$ is negative *finite* at $\omega_0=0$. The various possibilities in the MFA are summarized in Table I. One should particularly note that if $\Omega_0^2<0$ (which is the case treated in Ref. 4) the transition in MFA is always first order, just as in the SPA, and that if $v(0) \leq \Omega_0^2$, no transition occurs in either the SPA or the MFA. Thus the MFA as employed in Refs. 1, 2, and 5 does not unambiguously yield a second-order transition since these calculations do not start from a well-defined model of the interatomic forces.

(f) The exact treatment of Eqs. (6) yields a second-order transition or no transition. The variational treatment yields a first- or second-order transition or no transition. Our exact numerical

analysis of (6b) shows that for $\alpha \neq 0$, a continuous displacive transition will occur at some $\lambda_c(\alpha)$ with $\lambda_c(\alpha)$ an increasing function of α. An interesting feature of this instability-driven transition is that the transition becomes increasingly sharp as $\alpha \to 0$. Thus, if this were used to model a real physical system, a case could occur in which it would be impossible experimentally to determine that the transition was not first order. The results for (6b) are as shown in Table I.

In conclusion, a clearer picture of the transition found in Ref. 4 is now available. In the absence of a symmetry-breaking term there should be no transition. In the presence of one (which could be implicitly introduced through the MFA), there should be a second-order transition. These results are for an idealized model. In a real, physical system, there should be at least a weak symmetry-breaking term. Then, since the transition is of the instability-driven type (with the instability of the Coulomb lattice providing an effective "hump" for the TO mode) there would be a sharp second-order transition with almost a first-order character. If this were accompanied by, for example, a lattice distortion, the transition could be a real, first-order transition. Thus, the first-order character of either the MFA or SPA treatment of the instability-driven transition should not be considered spurious, but rather a strong indication of the inherent instability of the system.

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[8]This is also the region where $k_B T$ is of the order of the depth of one of the minima of the effective double-well potential associated with the long-wavelength optic mode.

Half-Life of ^{10}Be

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The half-life of ^{10}Be has been measured to be $(1.5 \pm 0.3) \times 10^6$ yr, a value in significant disagreement with the previously accepted value of $(2.7 \pm 0.4) \times 10^6$ yr. We discuss several implications of the revised half-life.

Cosmogenic radionuclides having very long half-lives can be useful dating tools in a number of astrophysical, geophysical, and cosmochemical problems. One of the most prominent of such species is the nuclide ^{10}Be, which has significant applications in studying the history of cosmic rays,[1] meteorites,[2] lunar samples,[3] marine sediments,[4] and polar deposits.[5]

The generally accepted[6] half-life of ^{10}Be is $(2.7 \pm 0.4) \times 10^6$ yr, a value based on two separate experiments carried out more than 20 years ago.[7,8] We have become interested in the question of the accuracy of this number because of its importance in trying to "date" cosmic-ray ages.[1] Although we had no reason to suspect a large error in the accepted value, we felt its widespread use warranted an attempt to reduce the error limits. While we have not yet succeeded in that goal, we have found a value which is in strong disagreement with the older number, and which should have important implications in a number of fields of study.

The two essential quantities in the determination of any half-life which is too long to be followed directly are the decay rate and the number of atoms of the decaying species. Usually the former can be measured directly, while the latter is obtained by a mass-spectrometric comparison of the radioactive nuclide and a stable isotope. The main problem with the second step is the