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Phase transitions in a simple model ferroelectric—comparison of exact and variational treatments of a molecular-field Hamiltonian

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We pursue the qualitative features of ferroelectric phase transitions via a detailed examination of a simple model system, the Hamiltonian of which consists of a lattice of quartic anharmonic oscillators of mass M interacting via a quadratic intercell interaction term. The intercell interaction term—assumed to be long range in character—is treated in a molecular-field approximation. The eigenvalue and eigenfunction spectrum of the resulting molecular-field Hamiltonian is obtained numerically exactly. This permits us to construct the density matrix associated with the lattice of coupled oscillators, and hence calculate the related statistical properties for different values of the intercell coupling χ, the zero-point parameter $\lambda \equiv \hbar/\sqrt{M}$, and the temperature T. It is found that a second-order structural transition occurs at some finite temperature T_c if $\chi > \chi_c^{\pm}(\lambda)$, where the superscripts refer to the two cases where the local particle potential possesses a single minimum (displacive) or a double minimum (order-disorder), respectively. The functional dependence of $\chi^{+}(\lambda)$ on λ is qualitatively different from that of $\chi^{-}(\lambda)$; e.g., $\chi^{+}(0)$ is finite, whereas $\chi^{-}(0) = 0$. A variational treatment of the molecular-field Hamiltonian employing a trial density matrix of the displaced-Gaussian form yields the prediction that if a transition occurs it may be either first or second order, depending on the values of the model parameters, as compared to the exact numerical treatment, where the transition is always second order. The implications of the first-order transition are discussed, with the changeover from second- to first-order behavior being examined.

I. INTRODUCTION

With an eye towards gaining a better understanding of the qualitative features of ferroelectric phase transitions, a number of simple models have been examined in great detail recently.[1-7] Particular emphasis has been placed on determining the applicability of certain self-consistent approximation schemes when applied to a theoretical treatment of order-disorder and displacive transitions.[3-7] In two earlier works[4,6] we examined a prototype ferroelectric in which zero-point fluctuations played the role of thermal fluctuations. The primary concern there was ascertaining the range of validity of various approximation schemes when applied to a treatment of the molecular-field form of the Hamiltonian. In the present work we treat a system of coupled anharmonic oscillators at finite temperature, with the zero-point fluctuations entering as an additional parameter.[8] This is of considerable interest, since most previous works have been classical in nature and have neglected zero-point effects.[1,2,5,7] Our only approximation here will be the application of a molecular-field approximation to the intercell coupling term, which is assumed to be long range in character. One of the main thrusts of the present work will be directed toward an exact numerical evaluation of the density matrix associated with the prototype ferroelectric within the context of the molecular-field approximation, no classical assumptions being made. The results of this calculation will then provide us with a basis for discussing the range of validity of a variational treatment of the molecular-field Hamiltonian.

The model Hamiltonians which were used previously by us[4,6] as the analog of a prototype ferroelectric have the form

$$\mathcal{H}^{\pm} = \sum_{l} \left(-\tfrac{1}{2}\lambda^2 \frac{d^2}{du_l^2} \pm 4u_l^2 + 4u_l^4 \right) - \tfrac{1}{2} \sum_{ll'}{}' \chi(ll') u_l u_{l'} , \tag{1}$$

where u_l denotes the displacement of an ion in lattice cell l. The Hamiltonians (1) have been scaled such that only two parameters appear—an effective intercell coupling χ and a parameter $\lambda = \hbar/\sqrt{M}$ which is a measure of the zero-point fluctuations. Here, M is some effective (scaled) mass associated with each ion.[9] If the sign of the quadratic term in Eq. (1) is positive, each particle feels a local anharmonic potential with a single minimum, whereas if the quadratic term is negative, the local potential is double-welled in character. In the former case we refer to a "displacive" regime, whereas in the latter case we refer to an "order-disorder" regime. There is some ambiguity in this definition, of course, since if the thermal energy $K_B T$ exceeds the depth of one of the minima of the double-well potential, then the order-disorder situation goes over to a situation which is displacive in character.

In the molecular-field treatment of the crystal lattice, one approximates the density matrix ρ_c of the entire crystal by a product of single-particle density matrices localized at each lattice site; i.e.,

$$\rho_c(l_1, l_2, \ldots, l_N) \approx \prod_{m=1}^{N} \rho(l_m) . \qquad (2)$$

A minimization of the free energy of the crystal then yields an optimum form for the single-particle density matrix which is canonical in form, i.e.,

$$\rho(l) = e^{-\beta H_l^{\pm}} / \mathrm{Tr}(e^{-\beta H_l^{\pm}}), \quad \beta \equiv (K_B T)^{-1} , \qquad (3a)$$

where

$$H_l^{\pm} = -\tfrac{1}{2}\lambda^2 \frac{d^2}{du_l^2} \pm 4u_l^2 + 4u_l^4 - \chi\langle u\rangle u_l \qquad (3b)$$

and

$$\chi \equiv \sum_{l'}{}' \chi(ll') .$$

The average particle displacement $\langle u\rangle$ which appears in (3b) is evaluated using the density matrix (3a) and as such depends self-consistently on the molecular-field Hamiltonian (3b). It should be noted that when one evaluates the total energy (or free energy) per particle of the lattice one must be careful to include a term $\frac{1}{2}\chi\langle u\rangle^2$ in order to avoid overcounting the interactions.

In Sec. II we discuss the numerical evaluation of the matrix elements of the molecular-field density matrix (3a) for various values of the parameters χ and λ. Of particular note is the fact that a transition in the system of coupled oscillators from a state with $\langle u\rangle = 0$ to a state with $\langle u\rangle \neq 0$ will occur only if $\chi > \chi_c^{\pm}(\lambda)$, where the superscripts refer to the sign of the quadratic term in (3b). If this criterion is fulfilled, the transition is second order always. It should be noted that the dependence of $\chi^{+}(\lambda)$ on λ is markedly different from that of $\chi^{-}(\lambda)$ on λ. Indeed, we will find that $0 < \chi^{-}(\lambda) < \infty$ for $0 < \lambda < \infty$, whereas $\chi^{+}(\lambda)$ approaches the finite value 8 as $\lambda \to 0$.

Having determined the diagonal matrix elements of the density matrix (3a), the temperature dependence of the order parameter $\langle u\rangle$ is determined for a relatively wide range of values of the parameters χ and λ in both the order-disorder and displacive regimes. The temperature dependence of $\langle u\rangle$ obtained from the exact numerical treatment of (3b) is then compared to the behavior of $\langle u\rangle$ obtained from a variational treatment in which the density matrix (3a) is approximated by a displaced-Gaussian form. As is by now well known[3-7] this latter approximation (sometimes called the mean-field approximation or MFA) can give rise to first-order as well as second-order transitions. If the local potential in which a single particle moves has double-well character, then the MFA yields either no transition or a first-order transition. However, if the local potential possesses single-well character only, we find that if $\chi > \chi_1(\lambda)$ the transition in the MFA is always first order, whereas for $\chi_0(\lambda) < \chi < \chi_1(\lambda)$ the transition is second order, where $16 < \chi_1(\lambda) < \infty$ for $0 < \lambda < \infty$. The changeover from second- to first-order character in the MFA is discussed, together with other concluding remarks in Sec. IV.

II. NUMERICAL TREATMENT OF THE MOLECULAR-FIELD HAMILTONIAN

Assuming that it is energetically favorable for the system of coupled oscillators to undergo a transition to a statistical state in which the thermal average of u is nonzero, then within the molecular-field approximation this average displacement $\langle u\rangle$ will be determined self-consistently from the expression

$$\langle u\rangle = \mathrm{Tr}(e^{-\beta H_l^{\pm}} u) / \mathrm{Tr}(e^{-\beta H_l^{\pm}}) . \qquad (4)$$

In order to carry out the evaluation of $\langle u\rangle$ as a function of temperature for different values of the parameters λ and χ, we begin by determining the eigenfunctions and eigenvalues of the Hamiltonian

$$H_F^{\pm} \equiv -\tfrac{1}{2}\lambda^2 \frac{d^2}{du^2} \pm 4u^2 + 4u^4 - Fu \qquad (5)$$

as functions of an externally applied field F; i.e., we solve

$$H_F^{\pm}\psi_n^{\pm}(F) = E_n^{\pm}(F)\psi_n^{\pm}(F) . \qquad (6)$$

A Hamiltonian matrix is constructed by expanding $\psi_n^{\pm}(F)$ in a complete set of optimized harmonic-oscillator states[10] $\phi_m^{\pm}$; i.e.,

$$\psi_n^{\pm}(F) = \sum_m C_{nm}^{\pm}(F)\phi_m^{\pm} . \qquad (7)$$

The matrices $\| C_{nm}^{\pm}(F) \|$ were numerically diagonalized, yielding $\psi_n^{\pm}(F)$ and $E_n^{\pm}(F)$ as functions of F.

From a knowledge of the eigenfunctions and eigenvalues of (5) as a function of field F, the average displacement as a function of field may be evaluated from

$$\langle u\rangle_F = \sum_n \langle \psi_n^{\pm}(F) | u | \psi_n^{\pm}(F)\rangle e^{-\beta E_n^{\pm}(F)} \Big/ \sum_n e^{-\beta E_n^{\pm}(F)} . \qquad (8)$$

For a given χ, λ, and T, the self-consistent $\langle u\rangle$ then results from the requirement that

$$\langle u\rangle_F = F\chi^{-1} \qquad (9)$$

for some value of F.

Obviously, the criterion that a transition occur

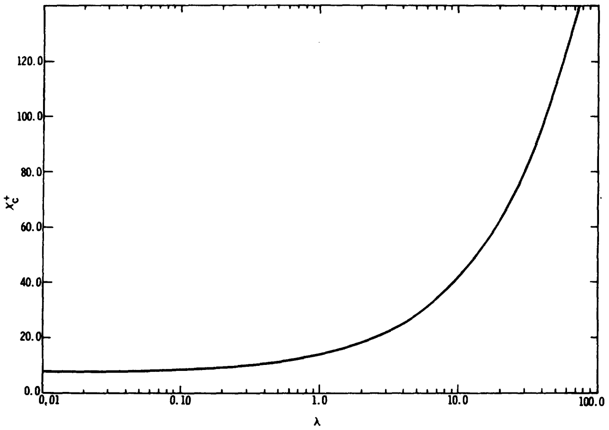

FIG. 1. λ-dependence of the critical coupling constant χ_c^+ associated with the exact treatment of H^+.

at all is simply that there must be a nonzero value of $\langle u\rangle$ at $T=0$. This translates to the requirement that for given χ and λ,

$$\lim_{F\to 0}\left(\frac{F}{\langle\psi_0^{\pm}(F)|\,u\,|\,\psi_0^{\pm}(F)\rangle}\right)\equiv\chi_c^{\pm}(\lambda)<\chi\ . \tag{10}$$

The relation (10) determines the critical values $\chi_c^{\pm}(\lambda)$ below which no transition will occur for the displacive or order-disorder case, respectively. If, however, $\chi>\chi_c^{\pm}(\lambda)$, then a classical second-order transition will occur at some finite temperature T_c, with $\langle u\rangle\propto(T_c-T)^{1/2}$ in the transition region.

In Figs. 1 and 2 we plot the behavior of $\chi_c^+(\lambda)$ and $\chi_c^-(\lambda)$ as functions of λ. It will be noticed that $\chi_c^+(\lambda)\to 8$ as $\lambda\to 0$ (classical limit), a feature which follows directly from the Hamiltonian H_l^+ if one neglects the kinetic-energy term. Furthermore, $\chi_c^+(\lambda)$ is a monotonically increasing function of λ for all λ, exhibiting positive curvature.

The behavior of $\chi_c^-(\lambda)$, illustrated in Fig. 2, is qualitatively different. From the limiting value $\chi_c^-(0)=0$, $\chi_c^-(\lambda)$ increases extremely rapidly and, in contrast to the behavior exhibited by $\chi_c^+(\lambda)$ in Fig. 1, displays negative curvature over the entire range of λ. Of course, we might expect $\chi_c^+(\lambda)$ and $\chi_c^-(\lambda)$ to asymptotically approach each other in magnitude for large λ, since it is in this large-λ regime that the order-disorder limit exhibits displacive features.

In Figs. 3(a)–3(c), 4, 7, and 8 we exhibit the temperature dependence of the order parameter $\langle u\rangle$ as obtained from the exact numerical treatment of the molecular-field Hamiltonians for various values of χ and λ. Figures 3(a)–3(c) and 4 refer to the case where the local potential has double-well character, whereas Figs. 7 and 8 are associated with the purely displacive situation, where the local potential possesses single-well character only. Also plotted in Figs. 3(a)–3(c), 4, 7, and 8 are the results of a variational treatment of the molecular-field Hamiltonians, a treatment which will be discussed in Secs. III and IV.

We have considered two values of the zero-point parameter λ: $\lambda=0.2$ and $\lambda=1.0$. For the order-disorder situation where the particle moves in a local double well the value of $\lambda=0.2$ yields a ground-state wave function which corresponds to the extreme localization of the particle at the position of one of the minima of the double-well potential.[11] When $\lambda=1.0$, the zero-point energy of the particle greatly exceeds the depth of one of the potential minima and the behavior of the system becomes displacive in character, because the particle distribution is peaked near $u=0$ rather than $u=\pm 1/\sqrt{2}$. The values of $\chi_c^-(\lambda)$ which correspond to the values $\lambda=0.2$ and $\lambda=1.0$ are 0.007 and 2.640, respectively. If $\lambda=0$ (extreme classical limit), the molecular-field approximation would predict a second-order transition for any value of χ in the double-well case (i.e., $\chi_c^-(0)=0$), with $\langle u\rangle$ approaching a saturation value of $(\chi+8)^{1/2}/4$ for $T=0$. It is clear from Figs. 3(a)–3(c) and 4 that the actual saturation value of $\langle u\rangle$ decreases from the value $(\chi+8)^{1/2}/4$ as the zero-point energy increases. This latter effect is to be expected, since the inclusion of zero-point effects tends to localize the particle distribution at a point nearer the origin. It is interesting to note that for transitions occurring in the extreme order-disorder regime, the transition is so

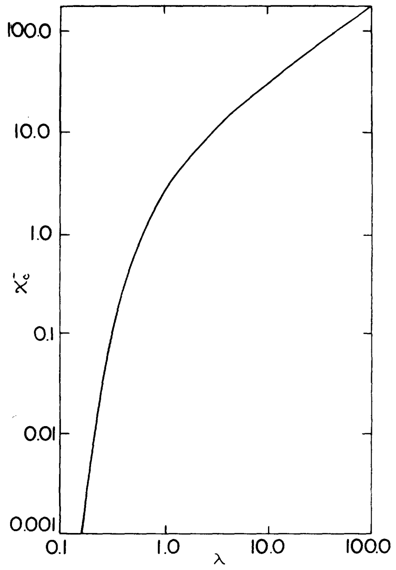

FIG. 2. λ-dependence of the critical coupling constant χ_c^- associated with the exact treatment of H^-.

abrupt that it is almost first order in character. Clearly, this latter feature has its origin in the fact that the saturation value of $\langle u\rangle$ approaches the finite value of $1/\sqrt{2}$ as $\chi\to 0$, whereas the transition temperature can be made infinitesimally small by decreasing sufficiently the value of λ.

The primary effect of increasing the magnitude of the zero-point fluctuations in the purely displacive cases (single-minimum potential) illustrated in Figs. 7 and 8 is to increase $\chi_c^+(\lambda)$ as well as to increase the second-order transition temperature T_c (for fixed χ). The critical values of $\chi_c^+(\lambda)$ corresponding to the values $\lambda = 0.2$ and $\lambda = 1.0$ are 9.509 and 13.972, respectively. In contrast to the order-disorder situation, however, the saturation value of the order parameter $\langle u\rangle$ continually approaches zero as $\chi\to 8$. For $\lambda = 0$ (classical limit) the saturation value of $\langle u\rangle$ is $(\chi-8)^{1/2}/4$, with this value being decreased with the inclusion of zero-point fluctuations. It is clear that the abrupt, almost first-order, transition which the order-disorder situation exhibits at low temperatures will not manifest itself in the purely displacive situation, since, for fixed λ, the saturation value of $\langle u\rangle$ continually approaches zero as T_c approaches zero.

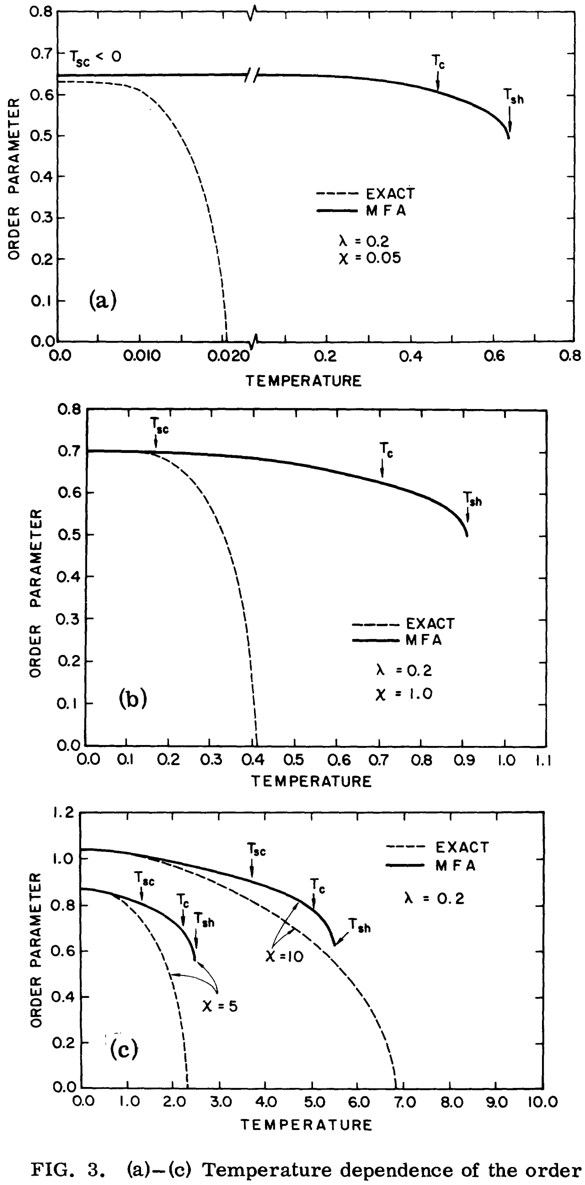

FIG. 3. (a)–(c) Temperature dependence of the order parameter as predicted by the exact and MFA treatments of the molecular-field Hamiltonian H^*. The parameter λ is fixed at the value 0.2 while the intercell coupling χ assumes the values 0.05, 1.0, 5.0, and 10.0, respectively. Both the order parameter and the temperature are expressed in the reduced units discussed in the text.

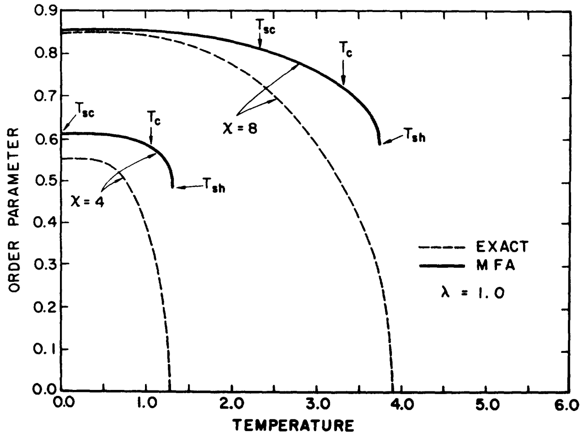

FIG. 4. Same as Fig. 3, but with λ fixed at the value 1.0 while χ assumes the values 4.0 and 8.0.

For the numerical calculations reported in this section a 200×200 matrix was diagonalized to obtain the first 50 eigenvalues and eigenfunctions of the Hamiltonians (5). These lowest 50 eigenfunctions and eigenvalues were then used in the construction of $\langle u\rangle_F$ using Eq. (8).

III. VARIATIONAL TREATMENT OF THE MOLECULAR-FIELD HAMILTONIANS

A natural approach to the treatment of the Hamiltonians (1) within the context of the molecular-field approximation is to introduce a *trial* form for the single-particle density matrix 3(a) and then determine the optimum density matrix of this form through the application of a variational principle. Recently, the terminology *mean-field approximation* (MFA) has appeared in the literature,[3] referring to a variational treatment of the molecular-field approximation in which one assumes a displaced-Gaussian form for the trial single-particle density matrix. In this section we wish to examine the content of this approximation in some detail and, in particular, compare our results with the results of the exact numerical treatment of the molecular-field Hamiltonians discussed in Sec. IV.

We begin by assuming that the trial single-particle density matrix is to be constructed from a trial Hamiltonian harmonic in form: i.e.,

$$\rho(l) \approx e^{-\beta h_l}/\mathrm{Tr}(e^{-\beta h_l}) , \tag{11}$$

where

$$h_l = -\tfrac{1}{2}\lambda^2 \frac{d^2}{du_l^2} + \frac{1}{2\lambda^2}\,\Omega^2(u_l - \langle u\rangle)^2 \tag{12}$$

and the frequency Ω and the relative displacement $\langle u\rangle$ are to be treated as variational parameters. The free energy per particle may be constructed as

$$f^{\pm} = \frac{1}{N}\,\mathrm{Tr}\left\{\prod_l \rho(l)\left[\mathcal{H}^{\pm} + \beta^{-1}\ln \prod_l \rho(l)\right]\right\} \quad , \tag{13}$$

where the form of $\rho(l)$ is taken from (11). This expression can be immediately rewritten as

$$\begin{aligned} f^{\pm} = {}& -\beta^{-1}\ln \mathrm{Tr}(e^{-\beta h_l}) + \mathrm{Tr}\left\{\rho(l)\left[\pm 4u_l^2 + 4u_l^4 - \frac{1}{2\lambda^2}\,\Omega^2 u_l^2\right]\right\} \\ & - \frac{1}{2N}\,\mathrm{Tr}\left\{\prod_l \rho(l) \sum_{n\neq n'} \chi(n,n')u_n u_{n'}\right\} \\ = {}& f_0 \pm 4\langle(u+\langle u\rangle)^2\rangle_0 + 4\langle(u+\langle u\rangle)^4\rangle_0 \\ & - \frac{1}{2\lambda^2}\,\Omega^2\langle(u+\langle u\rangle)^2\rangle_0 - \tfrac{1}{2}\langle u\rangle^2\left(\sum_n{}' \chi(n,n')\right), \end{aligned} \tag{14}$$

where the subscript zero refers to a statistical average using the density matrix $\rho(l)$ with $\langle u\rangle = 0$. Also,

$$f_0 \equiv -\beta^{-1}\ln \mathrm{Tr}(e^{-\beta h_l}) .$$

If we define $\Delta \equiv \langle u^2\rangle_0$ and note that for harmonic averages $\langle u^4\rangle_0 = 3\langle u^2\rangle_0^2$, then (14) takes the form

$$\begin{aligned} f^{\pm} = {}& f_0 \pm 4\Delta \pm 4\langle u\rangle^2 + 12\Delta^2 + 24\Delta\langle u\rangle^2 \\ & + 4\langle u\rangle^4 - (1/2\lambda^2)\Delta\Omega^2 - \tfrac{1}{2}\langle u\rangle^2\chi . \end{aligned} \tag{15}$$

Using the evaluations

$$f_0 = \beta^{-1}\ln(2\sinh\tfrac{1}{2}\beta\Omega) \tag{15a}$$

and

$$\Delta = (\lambda^2/2\Omega)\coth\tfrac{1}{2}\beta\Omega , \tag{15b}$$

we may minimize $f^{\pm}$ with respect to $\langle u\rangle$ and Ω. The result is

$$\frac{\delta f^{\pm}}{\delta\langle u\rangle} = 0 = \langle u\rangle\,[\pm 8 + 48\Delta + 16\langle u\rangle^2 - \chi] , \tag{16a}$$

$$\frac{\delta f^{\pm}}{\delta\Omega} = 0 = \left[\pm 4 + 24\Delta + 24\langle u\rangle^2 - \frac{1}{2\lambda^2}\,\Omega^2\right]\frac{\delta\Delta}{\delta\Omega} \quad . \tag{16b}$$

Equations (16a) and (16b) yield two solutions: an undisplaced solution with

$$\begin{aligned} &\langle u\rangle = 0 , \\ &\Omega^2 = \lambda^2[\pm 8 + 48\Delta] , \end{aligned} \tag{17a}$$

and a displaced solution with

$$\begin{aligned} &\langle u\rangle^2 = -\tfrac{1}{16}[\pm 8 + 48\Delta - \chi] , \\ &\Omega^2 = \lambda^2[\pm 8 + 48\Delta + 48\langle u\rangle^2] . \end{aligned} \tag{17b}$$

The frequency Ω which appears in Eqs. (17a) and (17b) is *not* the usual "soft-mode" frequency; i.e., Ω does not vanish at the transition temperature if the transition is second order, nor does it vanish at the supercooling point if the transition is first order. In order to properly identify the long-wavelength "soft" collective mode associated with the system of interacting oscillators, we calculate the static susceptibility of the system. If we apply an external field F_0 to our system of oscillators, this has the effect of adding a term $-F_0\langle u\rangle$ to (15). Thus, the minimization of (16a) yields the equation

$$F_0 = \langle u\rangle[\pm 8 + 48\Delta + 16\langle u\rangle^2 - \chi] . \tag{18}$$

Differentiating both sides of (18) with respect to F_0 and setting $\langle u\rangle = 0$, we obtain

$$\left(\frac{\delta\langle u\rangle}{\delta F_0}\right)_{\langle u\rangle=0} = [\pm 8 + 48\Delta - \chi]^{-1} = \frac{\lambda^2}{\Omega^2 - \lambda^2\chi} \quad . \tag{19}$$

Thus, if the divergence of the static susceptibility is to be associated with a long-wavelength phonon becoming soft, then the quantity $\Omega^2 - \lambda^2\chi \equiv \omega_0^2$ should be identified with the soft mode. That this is indeed the case is derived independently in Appendix A via a dynamic-linear-response analysis.

Equations (15b), (17a), and (17b) must be solved self-consistently for the quantities Δ, Ω, and $\langle u\rangle$. For convenience, we rewrite the equations in terms of $\overline{\omega}^2 = \omega_0^2/\lambda^2$, so that for the disordered state ($\langle u\rangle = 0$) we have

$$\Delta = \tfrac{1}{48}[\overline{\omega}^2 + \chi \mp 8] , \tag{20a}$$

$$\Delta = \frac{\lambda}{2[\overline{\omega}^2 + \chi]^{1/2}}\coth[\tfrac{1}{2}\lambda\beta(\overline{\omega}^2 + \chi)^{1/2}] \tag{20b}$$

and for the ordered state ($\langle u\rangle \neq 0$)

$$\Delta = \tfrac{1}{48}[-\tfrac{1}{2}\overline{\omega}^2 + \chi \mp 8] , \tag{21a}$$

$$\Delta = \frac{\lambda}{2[\overline{\omega}^2 + \chi]^{1/2}}\coth[\tfrac{1}{2}\lambda\beta(\overline{\omega}^2 + \chi)^{1/2}] . \tag{21b}$$

In Fig. 5 we illustrate the graphical solution of these two sets of equations. Subsections III A and III B will be devoted to a discussion of the order-disorder and displacive situations, respectively. Particular emphasis will be placed on three points: (i) the criterion for a transition to occur at all, (ii) the order of the transition if it

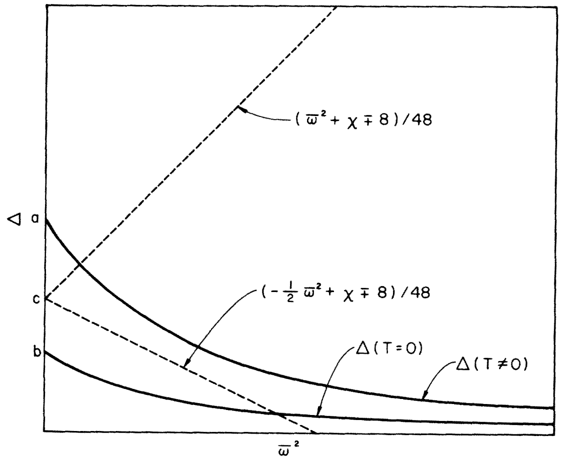

FIG. 5. Graphical solution of the MFA equations (10a)–(21b). The points a and b are the limiting values of $\Delta(T\neq 0)$ and $\Delta(T=0)$ as $\overline{\omega}^2\rightarrow 0$, respectively. At point a $\Delta(T)$ assumes the value $[\lambda\coth(\lambda\chi^{1/2}/2T)]/(2\chi^{1/2})$, while at the point b $\Delta(0)$ has the value $\lambda/(2\chi^{1/2})$. A solution with a vanishing mode frequency $\overline{\omega}$ can occur only at the point c, where $\Delta(T)$ assumes the value $(\chi\mp 8)/48$ for the order-disorder and displacive situations, respectively. If the transition is first order, the temperature at which the point c is reached is the supercooling temperature, whereas if the transition is second order this temperature is the transition temperature.

occurs, and (iii) the criterion for the supercooling temperature to be positive in the case where the transition is first order.

A. Order-disorder case: local double-minimum potential

In Sec. I we found that for the system of coupled oscillators moving in local double-minimum potentials, a classical second-order transition occurs if $\chi>\chi_c^-(\lambda)$. We wish now to establish the analogous criterion for the variational approximation. From Eqs. (21a) and (21b) and Fig. 5 we may establish a necessary criterion for an ordered solution to exist at $T=0$. We require that $\Delta(T=0)\equiv\lambda/[2(\overline{\omega}^2+\chi)^{1/2}]$ be tangent to the straight line $\Delta=(-\overline{\omega}^2/2+\chi+8)/48$. Thus, we obtain the two equations

$$\frac{\lambda}{2(\overline{\omega}^2+\chi)^{1/2}}=\frac{(-\overline{\omega}^2/2+\chi+8)}{48} \tag{22a}$$

and

$$\frac{\lambda}{4(\overline{\omega}^2+\chi)^{3/2}}=\frac{1}{96}\ . \tag{22b}$$

Eliminating $\overline{\omega}^2$ from (22a) and (22b) yields a critical value $\tilde{\chi}_c^-(\lambda)$ defined as

$$\tilde{\chi}_c^-(\lambda)=(24\lambda)^{2/3}-\tfrac{16}{3}\ . \tag{23}$$

If for a given value of λ, $\chi<\tilde{\chi}_c^-(\lambda)$, then no ordered solution is possible at $T=0$ within the context of the variational treatment. For $\lambda=1$, $\tilde{\chi}_c^-(\lambda)=2.987$, which compares with the value 2.640 obtained from the exact numerical treatment of the molecular-field Hamiltonian H^-. We might also note that for $\lambda\leqslant 24(\frac{16}{3})^{3/2}\approx 0.5132$, an ordered solution is always possible at $T=0$.

We now demonstrate that for the order-disorder situation the MFA yields only first-order transitions. From Fig. 5 we see that a necessary criterion for the transition to be *second order* is that the curve of Δ vs $\overline{\omega}^2$ must at some temperature intersect the ordinate at the point c. Furthermore, the slope $d\Delta/d(\overline{\omega}^2)$ must exceed the slope of the lower dashed straight line at this point. These two requirements lead to the two conditions

$$\frac{\lambda}{2\chi^{1/2}}\coth\left(\frac{\lambda\chi^{1/2}}{2T}\right)=\tfrac{1}{48}(\chi+8) \tag{24a}$$

and

$$\left\{\frac{d}{d(\overline{\omega}^2)}\left[\frac{\lambda}{2[\overline{\omega}^2+\chi]^{1/2}}\coth\left(\frac{\lambda}{2T}[\overline{\omega}^2+\chi]^{1/2}\right)\right]\right\}_{\overline{\omega}^2=0}>-\frac{1}{96}. \tag{24b}$$

If the transition were second order, the temperature determined from (24a) would be the second-order transition temperature, whereas for first-order transitions the temperature so determined is the supercooling temperature. We now wish to demonstrate that (24a) and (24b) cannot be simultaneously satisfied and hence the predicted transition, if it occurs at all, is first order. Evaluating the derivative in (24b) yields the inequality

$$\left\{\frac{\lambda}{4\chi^{3/2}}\coth\left(\frac{\lambda\chi^{1/2}}{2T}\right)+\frac{\lambda^2}{8\chi T}\left[\coth^2\left(\frac{\lambda\chi^{1/2}}{2T}\right)-1\right]\right\}<\frac{1}{96}. \tag{25}$$

The second term in the parentheses of Eq. (25) is always greater than zero. The first term may be rewritten, using Eq. (24a), as

$$\frac{\lambda}{4\chi^{3/2}}\,\frac{\chi^{1/2}}{24\lambda}(\chi+8)=\frac{1}{96\chi}(\chi+8)>\frac{1}{96}\ .$$

Hence, the inequality (25) is always violated and the transition is necessarily first order. Having established this fact concerning the character of the transition, it is now of interest to inquire into what conditions must be met in order that the supercooling temperature associated with the first-order transition be positive. By the supercooling temperature T_{sc} we of course mean the temperature at which the disordered solution becomes unstable—this is represented by the point c in Fig. 5. We had mentioned previously that if the transition is first order, then T_{sc} is deter-

TABLE I. Values of T_{sc}, T_c, and T_{sh} for various values of λ and χ within the context of the MFA treatment of the Hamiltonian $\mathcal{H}^-$.

λ	χ	T_{sc}	T_c	T_{sh}
0.2	0.05	<0	0.46	0.64
	1.00	0.168	0.71	0.91
	5.00	1.34	2.20	2.49
	10.00	3.74	5.04	5.50
1.00	4.00	0	1.07	1.32
	8.00	2.39	3.35	3.75

mined from the relation (24a). It follows immediately, then, that a necessary condition for T_{sc} to be positive is

$$\lambda < \tfrac{1}{24}\chi^{1/2}(\chi + 8) . \tag{26}$$

For $\lambda = 1$, we must have $\chi > 4$ and for $\lambda = 0.2$ we require $\chi > 0.332$ in order that $T_{sc} > 0$.

For a given value of the coupling χ, we may distinguish two critical values of the zero-point parameter. First, from Eq. (26) we define

$$\lambda_1 = \tfrac{1}{24}\chi^{1/2}(\chi + 8) \tag{27}$$

above which the supercooling temperature is negative. Second, we define from Eq. (23) the value

$$\lambda_2 = \tfrac{1}{24}(\chi + \tfrac{16}{3})^{3/2} \tag{28}$$

above which no ordered solution is possible. Noting that $\lambda_1 < \lambda_2$, we have three possible cases: (i) $\lambda < \lambda_1 < \lambda_2$, for which an ordered solution is possible with $T_{sc} > 0$; (ii) $\lambda_1 < \lambda < \lambda_2$, for which an ordered solution is possible, but $T_{sc} < 0$; (iii) $\lambda_1 < \lambda_2 < \lambda$, for which no ordered solution at all is possible.

Finally, we consider the definition of the superheating temperature T_{sh}, i.e., the temperature at which the ordered solution (if it exists) becomes unstable. The superheating temperature is the temperature at which one of the temperature-parametrized curves of Fig. 5 becomes tangent to the lower dashed line. This requires the simultaneous satisfaction of

$$\frac{\lambda}{2[\overline{\omega}^2 + \chi]^{1/2}} \coth\left(\frac{\lambda}{2T}[\overline{\omega}^2 + \chi]^{1/2}\right) = \tfrac{1}{48}[-\tfrac{1}{2}\overline{\omega}^2 + \chi + 8] \tag{29a}$$

and

$$\left\{\frac{d}{d(\overline{\omega}^2)} \frac{\lambda}{2[\overline{\omega}^2 + \chi]^{1/2}} \coth\left(\frac{\lambda}{2T}[\overline{\omega}^2 + \chi]^{1/2}\right)\right\} = -\frac{1}{96} . \tag{29b}$$

The simultaneous solution of (29a) and (29b) for T_{sh} can be carried out numerically. In Table I we summarize the results of the calculation of T_{sc}, T_c, and T_{sh} for the MFA treatments illustrated in Figs. 3(a)–3(c) and 4.

B. Displacive case: local single-minimum potential

It might be anticipated that the MFA treatment of the Hamiltonian $\mathcal{H}^+$ would yield quantitatively better results than the same treatment of $\mathcal{H}^-$, the reason being that an optimized-Gaussian density matrix provides a better representation of the true single-particle density matrix if the local potential is an anharmonic single-well potential rather than a potential which is double well in character. This is indeed the case as we shall see.

The exact numerical treatment of the Hamiltonian H^+ predicted a second-order transition if $\chi > \chi^+(\lambda)$ and no transition otherwise. In order to determine whether the MFA treatment of $\mathcal{H}^+$ yields a second-order transition or not we proceed as we did in the Sec. III A. From the discussion preceding Eqs. (24a) and (24b), together with Fig. 7, we see that the necessary criterion for the transition to be second order is that the following two relations be satisfied:

$$\frac{\lambda}{2\chi^{1/2}} \coth\left(\frac{\lambda\chi^{1/2}}{2T}\right) = \tfrac{1}{48}(\chi - 8) \tag{30a}$$

and

$$\left\{\frac{d}{d(\overline{\omega}^2)}\left[\frac{\lambda}{2(\overline{\omega}^2 + \chi)^{1/2}} \coth\left(\frac{\lambda}{2T}(\overline{\omega}^2 + \chi)^{1/2}\right)\right]\right\}_{\overline{\omega}^2=0} > -\frac{1}{96} . \tag{30b}$$

Equations (24b) and (30b) are the same, whereas (30a) is obtained from (24a) by replacing the right-hand side of (24a) by $(\chi - 8)/48$. The inequality (25) must again be satisfied. However, whereas the first term in the parentheses of Eq. (25) was greater than $\frac{1}{96}$ for the order-disorder case we now have that

$$\frac{\lambda}{4\chi^{3/2}} \coth\left(\frac{\lambda\chi^{1/2}}{2T}\right) = \frac{1}{96\chi}(\chi - 8) ,$$

and this last quantity may be either greater than or less than $\frac{1}{96}$. Thus, we have the possibility of *either* a first- or second-order transition occurring. In order to determine whether a transition occurs at all, we require that the temperature (T_c or T_{sc}) determined from (30a) be positive. Thus, since $\coth x > 1$ for $x > 0$, we must have

$$\lambda < \tfrac{1}{24}\chi^{1/2}(\chi - 8) . \tag{31}$$

For fixed λ, Eq. (31) determines a limiting value $\chi_0(\lambda)$ of the coupling strength such that if $\chi < \chi_0(\lambda)$ no transition will occur. The dashed plot in Fig. 6 displays the λ dependence of $\chi_0(\lambda)$—the values of $\chi_0(\lambda)$ corresponding to $\lambda = 0.2$ and $\lambda = 1.0$ are

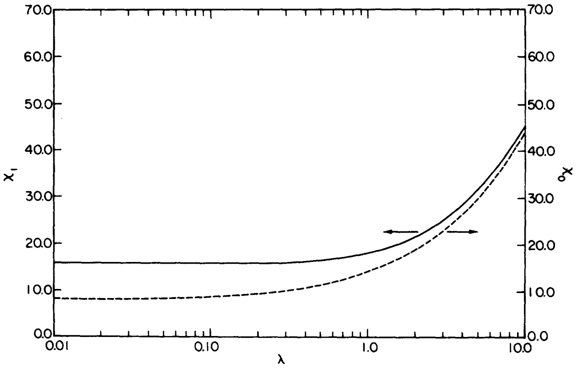

FIG. 6. λ-dependence of the critical coupling constants χ_0 and χ_1 associated with the MFA treatment of H^+. If $\chi_0(\lambda)<\chi<\chi_1(\lambda)$, the transition predicted by the MFA is second order.

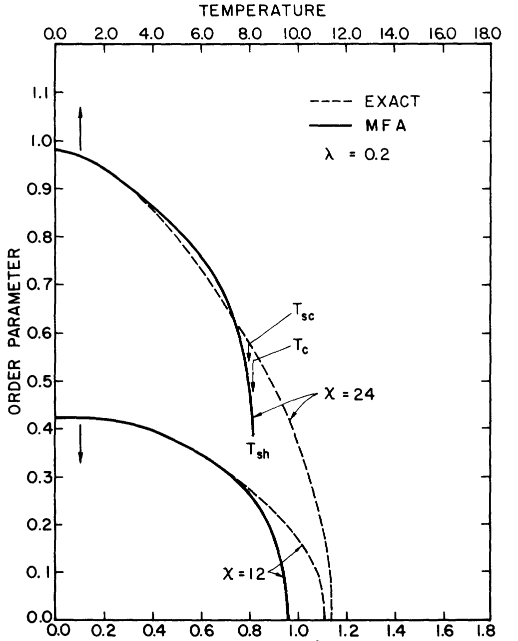

FIG. 7. Temperature dependence of the order parameter as predicted by the MFA treatment of H^+. The parameter λ is fixed at the value 0.2 while χ assumes two values 12.0 and 24.0 such that $\chi_0(0.2)<12.0<\chi_1(0.2)<24.0$. These plots illustrate how the transition predicted by the MFA changes from second- to first-order character as the coupling strength is increased beyond the critical value $\chi_1(0.2)$. Also plotted is the temperature dependence of the order parameter obtained from the exact numerical treatment of H^+. The reduced units discussed in the text are used.

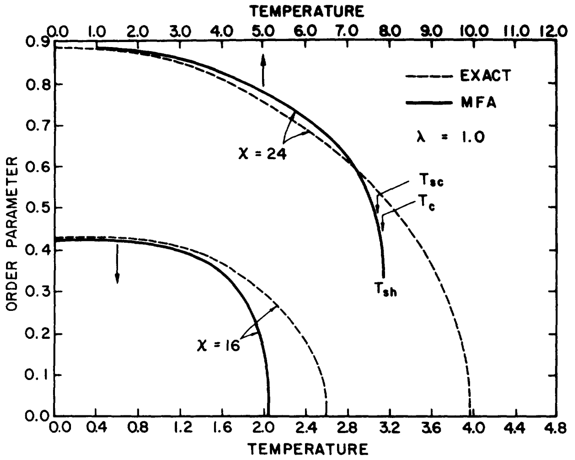

FIG. 8. Same as Fig. 7, but with λ fixed at the value 1.0 and χ assuming the values 16.0 and 24.0 such that $\chi_0(1.0)<16.0<\chi_1(1.0)<24.0$.

9.553 and 14.338, respectively. In the classical limit, $\lambda\rightarrow 0$ and $\chi_0(\lambda)\rightarrow 8$. Assuming now that $\chi>\chi_0(\lambda)$ so T_c or T_{sc} is positive, we may eliminate the temperature from (30a) and (30b). This yields the inequality

$$\frac{3\lambda}{\chi^{1/2}}\left\{\coth^{-1}\left(\frac{\chi^{1/2}}{24\lambda}(\chi-8)\right)\right\}\left(\frac{\chi}{(24\lambda)^2}(\chi-8)^2-1\right)<1\,, \tag{32}$$

which must be satisfied if the transition is to be second order.

Equation (32) may be solved numerically, yielding an upper critical value $\chi_1(\lambda)$ above which the transition is first order. Thus, we conclude that for $\chi<\chi_0(\lambda)$ no transition is possible, whereas for $\chi_0(\lambda)<\chi<\chi_1(\lambda)$ the transition is second order. If χ exceeds the critical value $\chi_1(\lambda)$ the transition is always first order. A plot of $\chi_1(\lambda)$ vs λ is given by the solid plot in Fig. 6. It is to be noted that in the classical limit $(\lambda\rightarrow 0)$, $\chi_1(\lambda)\rightarrow 16$. The corresponding values of $\chi_1(\lambda)$ for $\lambda=0.2$ and $\lambda=1.0$ are 16.2 and 18.21, respectively. In Figs. 7 and 8 we illustrate the changeover from second- to first-order character for two values of the zero point parameter λ. Table II summarizes the values of T_{sc}, T_c, and T_{sh} associated with the MFA cases treated in Figs. 7 and 8.

IV. DISCUSSION

In the previous sections we have treated the two molecular-field Hamiltonians $H^{\pm}$ of our model ferroelectric numerically exactly and also variationally. An important difference between this treatment and previous treatments is that we do not neglect zero-point fluctuations at finite temperature; i.e., no classical approximation is made. A classical molecular-field treatment of the order-disorder Hamiltonian $\mathcal{H}^-$ predicts that a second-order transition occurs at some temperature T_c for any value of the coupling strength

TABLE II. Character of the transition predicted by the MFA treatment of $\mathcal{H}^+$ for various values of λ and χ.

λ	χ	Character of transition	T_{sc}	T_c	T_{sh}
0.2	12.0	second		0.960	8.2
	24.0	first	8.0	8.1	8.2
1.0	16.0	second		2.056	
	24.0	first	7.74	7.84	7.88

$\chi > 0$. The inclusion of zero-point fluctuations, however, prevents the particle from becoming localized if the coupling strength is too small. Thus, we found that for λ finite, no transition occurred if $\chi < \chi_c^-(\lambda)$ and a second-order transition occurred otherwise. The behavior of $\chi_c^-(\lambda)$ as a function of λ is summarized in Fig. 2. The striking feature of this plot is the extremely rapid increase of $\chi_c^-(\lambda)$ for λ small—thus, in the extreme order-disorder limit the zero-point fluctuations play an important role. For $\lambda \gtrsim 1.0$, the particles no longer "feel" the hump in the double-well potential and we have effectively entered the displacive regime. In this regime the effect of zero-point fluctuations on $\chi_c^-(\lambda)$ is less marked.

An analog of the displacive ferroelectric is provided by the model Hamiltonian H^+. The exact numerical treatment of this molecular-field Hamiltonian indicated that a second-order transition would occur if the coupling strength χ exceeded some critical value $\chi_c^+(\lambda)$ which depended on the magnitude of the zero-point fluctuations. In the classical, $\lambda \to 0$, limit χ_c^+ approaches the value 8. The behavior of χ_c^+ as a function of λ is summarized in Fig. 1. The effect of zero-point fluctuations on the magnitude of χ_c^+ is not as marked as was the effect on χ_c^-. This is to be expected, since the particles are already localized in local single-minimum potentials centered at $u=0$. Indeed, from Fig. 1 we see that the increase of χ_c^+ with λ is quite slow until $\lambda \gtrsim 10.0$.

The temperature dependence of the order parameter $\langle u\rangle$ predicted by the molecular-field treatment of the model Hamiltonians $\mathcal{H}^\pm$ in the region near the second-order-transition point is

$$\langle u\rangle = a^\pm(\lambda)(T_c - T)^{1/2} , \tag{33}$$

where $a^\pm(\lambda)$ is some function of λ. In order to demonstrate that Eq. (33) holds, we refer to Eq. (8) in the form

$$\langle u\rangle_F = \Phi^\pm(F, \lambda, T) , \tag{34}$$

where $\Phi^\pm(F, \lambda, T)$ is an analytic function of F and T. Expand (34) about $F=0$,

$$\langle u\rangle = \left[\frac{d\Phi^\pm(F, \lambda, T)}{dF}\right]_0 F + B(\lambda, T)F^3 + \cdots . \tag{35}$$

Only odd powers of F occur because $\Phi^\pm(F, \lambda, T)$ and all even derivatives thereof vanish at $F=0$. The transition temperature T_c is determined from the relation

$$\chi^{-1} = \left[\frac{d\Phi^\pm(F, \lambda, T_c)}{dF}\right]_{F=0} . \tag{36}$$

Thus, we expand the first term in (35) in powers of $(T - T_c)$, obtaining

$$\langle u\rangle = [\chi^{-1} + (T - T_c)B(\lambda, T_c) + \cdots]F + A(\lambda, T_c)F^3 ,$$

and we have evaluated $A(\lambda, T)$ at $T = T_c$. Inserting now the self-consistent value (9) for F we have that

$$\chi^{-1}\langle u\rangle = [\chi^{-1} + (T - T_c)B(\lambda, T_c)]\langle u\rangle + A(\lambda, T_c)\chi^2\langle u\rangle^3 . \tag{37}$$

Equation (37) yields two solutions:

$$\langle u\rangle = 0 \tag{38a}$$

and

$$\langle u\rangle^2 = \chi^{-2}\,\frac{B(\lambda, T_c)}{A(\lambda, T_c)}\,(T_c - T) . \tag{38b}$$

Equation (33) follows immediately from (38b).

In Ref. 6 we evaluated the true ground-state wave function associated with the molecular-field Hamiltonian H^- in the extreme order-disorder limit. We examined how this ground-state wave function evolved for various values of λ in the presence of a linear symmetry-breaking term. The important point to note is that in the order-disorder limit the particle distribution defined by the molecular-field wave function is two peaked in character, the two peaks being approximately centered at the minima of the double-well potential. Because of the presence of the linear symmetry-breaking field the two peaks will have different amplitudes, of course. When the molecular-field wave function was compared with an optimized variational function of Gaussian structure it was found that the variational function, which was single peaked in character, overestimated the particle localization for $u \neq 0$ and severely underestimated the overlap near $u=0$. The same qualitative conclusions hold at finite temperatures; i.e., the density matrix (11) yields a particle distribution which exhibits only a single peak near one of the minima of the local double well. In contrast to this, the molecular-field density matrix (3a) has a two peaked structure. Hence, the variational density matrix underestimates the overlap of the particle distribution at $u=0$. This has important consequences which we now discuss.

Referring to Figs. 3(a)–3(c) and 4, and Table I, we see that for λ small the MFA treatment of H^- is an extremely poor approximation in the transition region. Indeed, the MFA yields first-order transitions only, whereas the exact molecular-field treatment yields no transition or a classical second-order transition if $\chi \lessgtr \chi_c^-(\lambda)$, respectively. An extreme effect of the overlocalization of the variational density matrix for $u \neq 0$ can be seen from Fig. 3(a). While the molecular-field treatment predicts a transition at $T \approx 0.02$, the first-order transition of the variational treatment does not occur unitl $T \approx 0.40$. Because the variational density matrix is so localized for $\lambda = 0.2$, there is virtually no temperature dependence to the order parameter at all up to the first-order transition point—$\langle u \rangle$ essentially remains at its saturation value at $T = 0$ until it becomes energetically favorable to make a first-order transition to a disordered state. Again, because the variational density matrix is more localized than the molecular-field distribution, the saturation value of $\langle u \rangle$ at $T = 0$ predicted by the variational treatment is larger than the molecular-field value.

As we pointed out in the discussion following Eq. (23), for λ values $\lesssim 0.5$, a first-order transition always occurs in the variational treatment—even for $\chi = 0$. This is in direct contrast to the molecular-field treatment, where χ must exceed $\chi_c^-(\lambda)$ in order for a transition to occur. However, it is to be noted that for small enough λ, the molecular-field transition is almost first order in character as can be seen from Figs. 3(a) and 3(b) for $\chi = 0.05$ and $\chi = 1.0$. This is because the saturation value of $\langle u \rangle$ approaches a constant value as $\chi \rightarrow \chi_c^-(\lambda)$, whereas T_c can be made to approach zero as $\chi \rightarrow \chi_c^-(\lambda)$. In any case there seems to be little connection between the molecular field T_c and T_c(MFA), at least for small λ and χ. We note that for $\chi = 0.05$, $\lambda = 0.2$ the two predicted transition temperatures differ by over an order of magnitude.

The supercooling temperature of the MFA may be negative, zero, or positive depending on the values of the model parameters. Figure 3(a), which illustrates the extreme order-disorder limit, presents a case where the effective supercooling temperature is negative. In Fig. 3(b) we have increased the magnitude of the coupling χ by a factor of 20 and the supercooling temperature becomes positive in accordance with Eq. (26). In Fig. 4 we have increased the zero-point parameter λ to the value 1.0 and have illustrated two cases where T_{sc} is zero or positive for values of $\chi = 4$ and 8, respectively.

It is clear that for small values of χ and λ, the extreme order-disorder case, the first-order transition point of the MFA gives no hint as to what the true transition temperature might be—the two transition temperatures do not agree at all. However, for larger χ values such as we have in Figs. 3(c) and 4 the first-order transition temperature agrees reasonably well with the transition temperature associated with the molecular-field second-order transition.

In retrospect, the fact that the MFA provides a poor description of the order-disorder regime was to be expected. Indeed, as we have seen, the variational density matrix exhibits the incorrect symmetry in the ordered state. The true particle distribution immediately below the second-order transition point is a nearly symmetric two-peaked structure with non-negligible overlap at $u = 0$. In contrast to this, the variational density matrix is a single peaked-Gaussian structure for all values of the displacement. It is thus to be expected that the variational treatment will not describe the transition region adequately. As the temperature is lowered, the true distribution becomes more like a displaced-Gaussian structure. Thus, near $T = 0$ and far from the transition the variational treatment is expected to work best. This expectation is borne out in Figs. 3(a)–3(c) and 4, where we see that the temperature dependence of the order parameter as predicted by the MFA is a reasonable facsimile of the molecular-field temperature dependence far from the transition.

Before proceeding to discuss the extreme displacive limit, it is of interest to examine the temperature dependence of the correlation function Δ. Remembering that Δ has an implicit as well as explicit temperature dependence we evaluate the temperature derivative using Eq. (15b). Thus,

$$\frac{d\Delta}{dT} = \frac{\partial}{\partial \Omega^2}\left(\frac{\lambda^2}{2\Omega} \coth \frac{\Omega}{2T}\right)\frac{d\Omega^2}{dT} + \frac{\lambda^2}{4T^2} \operatorname{csch}^2 \frac{\Omega}{2T} \quad . \tag{39}$$

Using Eq. (17b), we may express $d\Omega^2/dT$ in terms of $d\Delta/dT$ as

$$\frac{d\Omega^2}{dT} = -96\lambda^2 \frac{d\Delta}{dT} \quad . \tag{40}$$

Inserting (40) in (39) we obtain

$$\frac{d\Delta}{dT} = \frac{\lambda^2}{4T^2} \operatorname{csch}^2 \frac{\Omega}{2T}\left(1 + 96\lambda^2 \frac{\partial}{\partial \Omega^2} \Delta\right)^{-1} \quad . \tag{41}$$

There are two points to note: (i) As $T \rightarrow 0$, Ω remains finite and $\operatorname{csch}^2(\Omega/2T) \rightarrow 0$. Thus, $(d\Delta/dT) \rightarrow 0$ as $T \rightarrow 0$. (ii) From Fig. 5, as $T \rightarrow T_{sh}$, $\partial\Delta/\partial(\Omega^2) \rightarrow -1/(96\lambda^2)$. Thus, $(d\Delta/dT) \rightarrow \infty$ as $T \rightarrow T_{sh}$. From Eq. (17b) we see that the temperature derivative of the squared order parameter is directly proportional to $(d\Delta/dT)$; i.e.,

$$\frac{d\langle u \rangle^2}{dT} = -3 \frac{d\Delta}{dT} \quad . \tag{42}$$

Thus, we see that

$$\frac{d\langle u\rangle^2}{dT} \to \begin{cases} 0, & T \to 0 \\ \infty, & T \to T_{\rm sh} \end{cases} \tag{43}$$

a feature which is obvious in Figs. 3(a)–3(c) and 4.

Referring now to Figs. 6–8 and Table II we find that with certain exceptions the MFA applied to the purely displacive situation yields results which agree reasonably well with the predictions of the exact treatment of the molecular-field Hamiltonian H^+. This is to be expected, simply on the basis that the variational density matrix mirrors the exact distribution obtained from H^+ more closely than that obtained from H^-. Thus, the temperature dependence of $\langle u\rangle$, obtained within the framework of the MFA, should be at least quantitatively similar to the temperature dependence predicted by the exact molecular-field treatment. For the most part this is true—however, exceptions occur for large values of the coupling strength χ. We saw in the discussion following Eq. (30b) that if, for fixed λ, the coupling exceeded $\chi_1(\lambda)$ then the transition was first order, in contrast to the classical second-order transition predicted by the molecular-field treatment. Furthermore, for $\chi < \chi_0(\lambda)$ no transition at all occurred. Thus, the MFA in this situation yields a second-order transition only if χ is restricted to the interval $\chi_0(\lambda) < \chi < \chi_1(\lambda)$. In this region the MFA yields qualitatively correct results for the temperature dependence of u, although the predicted transition temperature is always too low. If the MFA transition is second order, then the transition temperature T_c is determined by Eq. (30a). On the other hand, if the MFA transition is first order, then Eq. (30a) determines the supercooling temperature T_{sc}.

One can easily produce an argument as to why the T_c (or T_{sc}) derived from the MFA is less then the T_c predicted by the exact molecular-field treatment. In Ref. 6 we demonstrated that the "two-level" approximation was a very satisfactory approximation in the molecular-field transition region. The finite temperature extension of the two-level approximation yields the formula[12]

$$(\epsilon_1^- - \epsilon_0^-)^{-1} \tanh \frac{(\epsilon_1^- - \epsilon_0^-)}{2T_c} = [2\chi |\langle \phi_0^- | u | \phi_1^-\rangle|^2]^{-1} \tag{44}$$

for the molecular-field transition temperature. In Eq. (44) ϵ_0, ϵ_1 and ϕ_0, ϕ_1 are the ground- and first-excited-state energies and eigenfunctions, respectively, of the Hamiltonian H^- [see Eq. (3b)] with $\langle u\rangle = 0$. In the MFA the excitation energy $(\epsilon_1^- - \epsilon_0^-)$ is approximated by a variationally determined excitation energy. In general, this variational energy will exceed $(\epsilon_1^- - \epsilon_0^-)$ and hence, from Eq. (44), the MFA T_c must be lower. Here, we have assumed that $\langle \phi_0 | u | \phi_1\rangle$ is unaffected when we replace the true wave functions by their variational counterparts. However, as was argued in Ref. 6 (pp. 4994 and 4995) this is an excellent approximation.

From Fig. 6 we see that the range of χ values for which the MFA yields a second-order transition becomes increasingly smaller as λ becomes large. In Figs. 7 and 8 we explicitly show the changeover from second- to first-order character for two values of the zero-point parameter λ. For $\lambda = 0.2$ a second-order transition requires that $9.55 < \chi < 16.12$, whereas for $\lambda = 1.0$ we must satisfy the inequality $14.34 < \chi < 18.21$ in order that the transition be second order. For λ values greater than 1.0 the allowed χ interval becomes rapidly smaller.

In a recent work[7] Eisenriegler has shown (in the classical limit) that the molecular-field approach provides a good description of the order-disorder regime. If it is true that the molecular-field solution mirrors the exact solution well in this regime, then we have shown here that the MFA yields a relatively poor description of order-disorder transitions, although it provides a qualitatively reasonable description of displacive transitions if the zero-point fluctuations are not too large. Furthermore we have demonstrated what effect these zero-point fluctuations have on the characteristics of the transition in both displacive and order-disorder regime and have found that the effect of zero-point fluctuations can be extremely important in this latter regime.

APPENDIX

We wish to calculate the response of the average particle displacement to some externally applied time-dependent perturbation $-\sum_l \delta F_l(t) u_l$. The response function so calculated, when Fourier transformed in time and space, will exhibit resonances—one of which can be identified as the "soft" collective mode of the system of coupled oscillators. Introducing the time-dependent field $-\sum_l \delta F_l(t) u_l$ into the Hamiltonian (3b), the linear response of the statistically averaged particle displacement is given by

$$\delta\langle u_l\rangle(t) = -i \int_{-\infty}^{t} dt' \langle [u_l(t), \delta H(t')]\rangle \ , \tag{A1}$$

where the ensemble average is taken using the molecular-fluid density matrix (2), and δH has the form

$$\delta H(t) = -\sum_{ll'} \chi(ll') u_l \delta\langle u_l\rangle(t) - \sum_l F_l(t) u_l \ . \tag{A2}$$

We express the single-particle density matrix (3a) in the diagonal form

$$\rho = \sum_{\alpha} |\phi_\alpha^\pm\rangle f_\alpha^\pm \langle\phi_\alpha^\pm| \;,$$

where

$$f_\alpha^\pm = e^{-\beta\epsilon_\alpha^\pm} \Big/ \sum_{\alpha} e^{-\beta\epsilon_\alpha^\pm} \;,$$

and $\epsilon_\alpha^\pm$ and $\phi_\alpha^\pm$ are the energies and eigenfunctions associated with (3b). Introducing a set of intermediate states $\phi_\alpha^\pm$ into the commutator in (A1) and subsequently Fourier transforming all lattice and time-dependent quantities, we obtain the following expression for the frequency- and wave-vector-dependent response function:

$$\frac{\delta\langle u_q\rangle(\omega)}{\delta F_q(\omega)} = \sum_{\alpha\alpha'} \frac{(f_\alpha^\pm - f_{\alpha'}^\pm)|\langle\phi_\alpha^\pm|u|\phi_{\alpha'}^\pm\rangle|^2}{\omega - \epsilon_\alpha^\pm + \epsilon_{\alpha'}^\pm} \times\left[1 - \chi(q)\sum_{\alpha\alpha'} \frac{(f_\alpha^\pm - f_{\alpha'}^\pm)|\langle\phi_\alpha^\pm|u|\phi_{\alpha'}^\pm\rangle|^2}{\omega - \epsilon_\alpha^\pm + \epsilon_{\alpha'}^\pm}\right]^{-1} . \tag{A3}$$

The energies associated with the collective modes of the system are defined by the position of the poles in the frequency space of the response function (A3). These poles are determined by the solutions to the equation

$$\sum_{\alpha\alpha'} \frac{(f_\alpha^\pm - f_{\alpha'}^\pm)|\langle\phi_\alpha^\pm|u|\phi_{\alpha'}^\pm\rangle|^2}{\omega - \epsilon_\alpha^\pm + \epsilon_\alpha^\pm} = \chi^{-1}(q) \;. \tag{A4}$$

The solutions to (A4) can be represented graphically in a manner similar to that discussed in Ref. 6. However, here we are primarily interested in evaluating the long-wavelength collective mode of the system within the context of the MFA. Setting $q=0$ in Eq. (A4) determines the long-wavelength modes associated with the exact numerical treatment of the molecular-field Hamiltonians (3b). In order to revert to the MFA, we interpret the spectrum of energies $\epsilon_\alpha^\pm$ and wave functions $\phi_\alpha^\pm$ as arising from the Hamiltonian (12). For simplicity we consider the disordered phase ($\langle u\rangle = 0$) only. Thus,

$$\left(-\tfrac{1}{2}\lambda^2 \frac{d^2}{du^2} + \frac{1}{2\lambda^2}\,\Omega^2 u^2\right)\phi_\alpha = \epsilon_\alpha\phi_\alpha \tag{A5a}$$

determines a set of oscillator states ϕ_α with energies

$$\epsilon_\alpha = (\alpha + \tfrac{1}{2})\Omega, \quad \alpha = 0,\ 1,\ 2,\ \ldots \;. \tag{A5b}$$

The only nonzero matrix elements are

$$\langle\phi_\alpha|u|\phi_{\alpha+1}\rangle = \lambda[(\alpha+1)/2\Omega]^{1/2} \;. \tag{A6}$$

Thus,

$$\sum_{\alpha\alpha'} \frac{(f_\alpha - f_{\alpha'})|\langle\phi_\alpha|u|\phi_{\alpha'}\rangle|^2}{\omega - \epsilon_\alpha + \epsilon_{\alpha'}} = \sum_{\alpha=0}^{\infty} (f_\alpha - f_{\alpha+1})|\langle\phi_\alpha|u|\phi_{\alpha+1}\rangle|^2 \frac{2(\epsilon_\alpha - \epsilon_{\alpha+1})}{\omega^2 - (\epsilon_\alpha - \epsilon_{\alpha-1})^2} = \frac{2\Omega}{\omega^2 - \Omega^2} \sum_{\alpha=0}^{\infty} (f_{\alpha+1} - f_\alpha)|\langle\phi_\alpha|u|\phi_{\alpha+1}\rangle|^2 \;.$$

Introducing the expression (A6) for the matrix elements, we obtain

$$\sum_{\alpha=0}^{\infty} (f_{\alpha+1} - f_\alpha)|\langle\phi_\alpha|u|\phi_{\alpha+1}\rangle|^2 = \frac{\lambda^2}{2\Omega}\sum_{\alpha=0}^{\infty}(e^{-\beta\epsilon_{\alpha+1}} - e^{-\beta\epsilon_\alpha})(\alpha+1)\Big/\sum_{\alpha=0}^{\infty} e^{-\beta\epsilon_\alpha} = \frac{\lambda^2}{2\Omega}(e^{-\beta\Omega} - 1)\sum_{\alpha=0}^{\infty}(\alpha+1)e^{-\alpha\beta\Omega}\Big/\sum_{\alpha=0}^{\infty} e^{-\alpha\beta\Omega} = \frac{\lambda^2}{2\Omega} \;.$$

Thus,

$$\sum_{\alpha\alpha'} \frac{(f_\alpha - f_{\alpha'})|\langle\phi_\alpha|u|\phi_{\alpha'}\rangle|^2}{\omega - \epsilon_\alpha + \epsilon_{\alpha'}} = -\frac{\lambda^2}{\omega^2 - \Omega^2}$$

and

$$\frac{\delta\langle u_q\rangle(\omega)}{\delta F_q(\omega)} = \frac{-\lambda^2}{\omega^2 - \Omega^2 + \lambda^2\chi(q)} \;. \tag{A7}$$

This MFA response function exhibits resonances at the frequencies ± Ω_q, where

$$\Omega_q^2 = \Omega^2 - \lambda^2\chi(q) \;. \tag{A8}$$

In the long-wavelength limit, the squared frequency defined by (A8) is proportional to the inverse of the static susceptibility defined in Eq. (19), which is what we set out to prove.

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[9] Starting with the Hamiltonian $\mathcal{H}^{\pm}=\sum_l(-\frac{1}{2}\lambda^2 d^2/du_l{}^2+\frac{1}{2}au_l^2+4\phi u_l^4)-\frac{1}{2}\sum_{ll'}\chi(ll')u_l u_{l'}$ we introduce the scale changes $u\rightarrow[|a|/(8\phi)]^{1/2}u$, $\lambda\rightarrow\phi^{-1}(|a|/8)^{3/2}\lambda$, $\chi\rightarrow(|a|/8)\chi$, and $\mathcal{H}^{\pm}\rightarrow[a^2/(64\phi)]\mathcal{H}^{\pm}$. The reduced temperature to be used in our later discussion is obtained by expressing K_BT in the energy units $[|a|^2/(64\phi)]$.

[10] See Ref. 6, p. 7, for a discussion of how these oscillator states are constructed.

[11] See Fig. 1, Ref. 6.

[12] Equation (44) is arrived at as follows. We first diagonalize H_F^- of Eq. (5) in the 2×2 subspace defined by the ground and first excited states of $H_F^-(F=0)$. The new ground and first excited states and energies are then used to construct the density matrix (8). Reasons for why this gives a good estimate of T_c are detailed in Ref. 6.