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Correlated-effective-field theory: A statistical approach for grossly anharmonic lattice vibrations

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A correlated-effective-field theory is defined for interacting oscillators each moving in a local potential well of *arbitrary* form. Correlations are introduced into an effective-field framework and determined by forcing a consistency with the fluctuation theorem. The theory is formulated for both ordered and disordered phases as a model for a structural phase transition. In the limit of a quasiharmonic local potential the linearized theory is shown to be formally equivalent to self-consistent phonon theory for classical motion. In an opposite limit of extreme anharmonicity, with a deep-double-well local potential, the method is compared to Ising theory and shown to be equivalent to the spherical approximation.

I. INTRODUCTION

As is so often the case in many-body physics, even a basic model Hamiltonian (stripped of all but its most essential features) still defies exact solution. One such example is the model Hamiltonian which embodies the essential features of a structural phase transition and is conventionally written

$$\mathcal{H}=\sum_i\left[\tfrac{1}{2}p_i^2+V(x_i)-h_ix_i\right]-\frac{1}{2}\sum_i\sum_j v_{ij}x_ix_j\,, \quad (1.1)$$

where p_i and x_i are canonically conjugate momentum and displacement operators describing the motion of ions in the ith primitive cell of a regular lattice with the symmetry of the soft mode, h_i is an applied field, $V(x_i)$ is a local-potential function of arbitrary form, and v_{ij} is an interaction potential ($v_{ii}=0$) of arbitrary range and directional dependence.

Two quite separate methods of attack have been used in the literature to probe the statistical problem defined by (1.1). One is to employ a renormalized-phonon basis with adjustable parameters which are optimized such that the low-lying excitation spectrum of this effective harmonic system approximates as closely as possible the corresponding spectrum of the actual many-body system. In this scheme, the approximated terms in (1.1) are the anharmonicities in $V(x_i)$, which are replaced by effective harmonic terms whose magnitudes depend on the thermodynamic variables. The method is now commonly termed the self-consistent-phonon approximation and has received considerable attention in recent years.[1-5]

The other approach, variously termed mean-field time-dependent Hartree or self-consistent-field methods,[6-9] concentrates upon an equilibrium picture of local ith cell motion in thermally averaged surroundings, with propagating excitations (of arbitrarily anharmonic form) defined as the response of the equilibrium distribution to a time-dependent perturbing field. This independent-cell scheme approximates the intercell interactions $v_{ij}x_ix_j$ by a mean field but allows for an exact treatment of local potential $V(x_i)$ regardless of its complexity.

Both methods can be used as zeroth-order bases for higher-order perturbational or diagrammatic representations. The primary disadvantage of the lowest-order self-consistent-phonon (SCP) approximation is its presumption of effective harmonic dynamics. Thus, although it is mathematically well defined for arbitrarily anharmonic $V(x_i)$, it is obviously a bad starting point for the description of grossly anharmonic motion such as occurs, for example, when $V(x_i)$ is of double-well form and thermal energies are of the order of the well depth (for which case the dynamic response can even be double peaked[10]). Indeed, recent classical comparison[11] of SCP and the self-consistent-field method suggests that the latter gives the lower free energy (and a better approximation to exact series expansions) at high temperatures for $V(x_i)$ of the single-well form and at both high and low temperatures for $V(x_i)$ of the deep-double-well form. There is evidence, however, that SCP is better suited for the description of low-temperature single well $V(x_i)$ (particularly, one suspects, when quantum effects are significant), and the low-temperature restriction can certaintly be removed by systematic development of SCP to higher orders.[12,13]

The weakness of the lowest-order self-consistent-field method is the fact that it is a mean-field approximation and therefore neglects, as its basic approximation, all static correlations between cells. Although some information concerning correlations is often extracted from the mean-field findings by the use of the fluctuation-response-function relation of statistical mechanics (i.e., the equality of the mean fluctuation of a coordinate to its susceptibility in response to an external field to which it is coupled), this merely implies that the method is wholly inconsistent in this respect. In other words, as has long been recognized,[14] all simple mean-field-based approximations are in violation of the fluctuation theorem.

In a recent note[15] a method has been outlined for rectifying this fundamental weakness in the self-consistent-field theory of structural phase transitions. By introducing the concept of a correlated effective field to replace the old mean field, the basic simplicity of a single-cell density matrix can be retained, while the "local-field" picture is brought into compatibility with the important exact fluctuation constraint. The strength of what we shall now call the correlated-effective-field theory (CEF) is that it retains the simplicity of an independent-cell picture and, therefore, remains tractable for arbitrarily anharmonic dynamics, while improving the local-field approach to Hamiltonian (1.1) to the point where it can compete in accuracy with SCP even in the low-temperature quasiharmonic domain where SCP is at its best.

In this paper we extend the work of Ref. 15 to define CEF for all temperatures, including ordered and disordered phases. For the quasiharmonic limit of $V(x_i)$ at low temperatures we also define a linearized (effective-harmonic) approximation to the general CEF scheme, since in this linear form the CEF theory is directly comparable to SCP. We emphasize very strongly, however, that this linearization is performed *solely* to enable a direct comparison with SCP in the harmonic limit. It is not required for solution to the CEF equations nor is it an approximation which one would otherwise make. Thus, for example, in the long-range or mean-field limit $v_{ij} = \text{const}$ for all $j-i$, CEF theory is exact whereas linearized CEF (like SCP) leads to spurious (first-order transition) discontinuities near the critical point.

After defining both CEF and SCP we demonstrate the formal equivalence of linearized CEF and SCP (with quasiharmonic potential) for describing linear response for *classical* motion. In quantum theory the two methods are in accord at high temperatures but deviate at low temperatures. In the opposite extreme of an Ising limit (deep double well) $V(x_i)$, we establish the formal equivalence of general CEF and the spherical approximation.

Throughout this paper CEF theory is discussed only in its lowest order, for which the field dependence of correlations is neglected. Work in the next higher order (including the linear dependence of correlations on field) is now in progress. This is particularly important since both the spherical and SCP theories exhibit questionable properties close to a phase transition.[14,16] In view of the close relationship demonstrated in this paper between lowest-order CEF and these more conventional schemes, we hope later to achieve some deeper understanding of these difficulties by studying higher-order CEF.

II. CORRELATED-EFFECTIVE-FIELD THEORY

In CEF theory we concentrate on describing the motion of the *i*th "particle" in the many-body system as moving in the correlated effective field of its neighbors. From (1.1) the effective field at site i is $\sum_j v_{ij} x_j$ and, without restricting the range or structure of the interaction potential v_{ij}, we approximate this statistically in the equation of motion for the *i*th particle by replacing the operator x_j of an arbitrary (interacting) neighbor by its ensemble average $\langle x_j \rangle$ together with a correlated contribution $A_{ij}(x_i - \langle x_i \rangle)$, as yet of unspecified amplitude A_{ij}, proportional to the instantaneous deviation of the *i*th particle from its averaged position $\langle x_i \rangle$. The resulting equation of motion is

$$\dot{p}_i = h_i - \frac{dV(x_i)}{dx_i} + \sum_j v_{ij}[\langle x_j \rangle + A_{ij}(x_i - \langle x_i \rangle)] \tag{2.1}$$

and is valid both classically and quantum mechanically [at least to the extent that $V(x_i)$ is expandable as a Maclauren series about the origin of x_i].

We now note that this same equation of motion can be obtained quite formally from an effective "*i*th particle" Hamiltonian,

$$\mathcal{H}_i = \tfrac{1}{2} p_i^2 + V(x_i) - h_i x_i - \sum_j v_{ij} x_i \times [\langle x_j \rangle + \tfrac{1}{2} \alpha x_i - \alpha \langle x_i \rangle], \tag{2.2}$$

where $\alpha = \sum_j v_{ij} A_{ij} / \sum_j v_{ij}$. Writing $\langle x_i \rangle = \langle x \rangle_0 + m_i$ to define the zero-field static order parameter $\langle x \rangle_0$, it follows from (2.2) and the use of formal statistical mechanics that

$$\langle x_i \rangle z = \mathrm{Tr}\left\{ x_i \exp\left[\frac{-1}{kT} \left(\frac{1}{2} p_i^2 + V(x_i) - \tfrac{1}{2} \alpha v(0) x_i^2 - x_i \langle x \rangle_0 (1-\alpha) v(0) - h_i x_i - \sum_j v_{ij} x_i (m_j - \alpha m_i) \right) \right] \right\}, \tag{2.3}$$

where z is the partition function, given by the trace of unit times the exponential function of (2.3) and where $v(0)$ is the zero-wave-vector limit of the Fourier transform

$$v(\vec{q}) = \sum_{j-i} v_{ij} e^{i\vec{q}\cdot(\vec{i}-\vec{j})}, \tag{2.4}$$

with respect to the lattice, of the interaction potential v_{ij}. Writing

$$\mathcal{H}_i = V_i' - x_i \Gamma_i, \tag{2.5}$$

defining

$$V_i' = \tfrac{1}{2} p_i^2 + V(x_i) - \tfrac{1}{2} \alpha v(0) x_i^2 - x_i \langle x \rangle_0 (1-\alpha) v(0), \tag{2.6a}$$

$$\Gamma_i = h_i + \sum_j v_{ij}(m_j - \alpha m_i), \qquad (2.6\text{b})$$

and verifying, by formal differentiation (noting the noncommutation of V_i' and x_i in quantum theory), the equation

$$\frac{\partial}{\partial \beta} e^{\beta V_i'} e^{-\beta \mathcal{H}_i} = e^{\beta V_i'} x_i \Gamma_i e^{-\beta \mathcal{H}_i}, \qquad (2.7)$$

we establish the relationship

$$e^{-\beta \mathcal{H}_i} = e^{-\beta V_i'}\left(1 + \int_0^\beta e^{\lambda V_i'} x_i \Gamma_i e^{-\lambda V_i'}\, d\lambda\right), \qquad (2.8)$$

correct to first order of smallness in field h_i and response m_i.

Putting $\beta = 1/kT$ and neglecting any possible field dependence of α, this result can be substituted into Eq. (2.3) when we obtain

$$\langle x_i\rangle = \langle x\rangle_0 + \frac{1}{kT}\left(\langle x:x\rangle_0 - \langle x\rangle_0^2\right)\left(h_i + \sum_j v_{ij}(m_j - \alpha m_i)\right), \qquad (2.9\text{a})$$

where

$$\langle x\rangle_0 = \mathrm{Tr}(x_i\, e^{-V_i'/kT})/\mathrm{Tr}(e^{-V_i'/kT}) \qquad (2.9\text{b})$$

and

$$\beta\langle x:x\rangle_0 = \mathrm{Tr}\left(e^{-\beta V_i'} \int_0^\beta e^{\lambda V_i'} x_i e^{-\lambda V_i'} x_i\, d\lambda\right)/\mathrm{Tr}(e^{-\beta V_i'}), \qquad (2.9\text{c})$$

$\langle \cdots\rangle_0$ referring to an ensemble average in the absence of applied field. Recognizing that such averages are independent of site i and recalling the definition of m_i as $\langle x_i\rangle - \langle x\rangle_0$, Eq. (2.9a) can be Fourier transformed to give

$$\langle m(\vec q)\rangle = (1/kT)\left(\langle x:x\rangle_0 - \langle x\rangle_0^2\right) \times\left[h(\vec q) + v(\vec q)m(\vec q) - \alpha v(0) m(\vec q)\right], \qquad (2.10)$$

where

$$m(\vec q) = \left(\frac{1}{N}\right)^{1/2} \sum_i m_i e^{i\vec q\cdot\vec r} \qquad (2.11)$$

and N is the number of "particles" in the macroscopic lattice.

Writing a wave-vector-dependent susceptibility $\chi(\vec q) = m(\vec q)/h(\vec q)$ we calculate from (2.10) the form

$$[\chi(\vec q)]^{-1} = \tau + \alpha v(0) - v(\vec q), \qquad (2.12)$$

in which

$$\tau = kT/\left(\langle x:x\rangle_0 - \langle x\rangle_0^2\right). \qquad (2.13)$$

To this point the parameter α remains a free variable in the theory. It is now determined, and the theory thereby closed, by requiring the susceptibility $\chi(\vec q)$ of (2.12) to obey an exact fluctuation-dissipation relationship derivable as follows.

From Hamiltonian (1.1) we can calculate $\chi(\vec q)$ directly as

$$\chi(\vec q) = \frac{\partial}{\partial h(\vec q)} \frac{\mathrm{Tr}[x(\vec q)\rho]}{\mathrm{Tr}\rho}, \qquad (2.14)$$

where $x(\vec q)$ is the Fourier transform of displacement x_i with respect to the lattice, and $\rho/\mathrm{Tr}(\rho)$ is the normalized density matrix, where

$$\rho = \exp\left[\frac{-1}{kT}\left(\sum_i[\tfrac{1}{2}p_i^2 + V(x_i)] - \frac{1}{2}\sum_i\sum_j v_{ij}x_i x_j - \sum_{\vec q} h(\vec q)x(-\vec q)\right)\right]. \qquad (2.15)$$

Differentiating directly we obtain, to lowest order

$$kT\chi(\vec q) = \langle x(-\vec q) : x(\vec q)\rangle_0 - \langle x(-\vec q)\rangle_0 \langle x(\vec q)\rangle_0, \qquad (2.16\text{a})$$

in which

$$\beta x(-\vec q) : x(\vec q) = \int_0^\beta e^{\lambda \mathcal{H}_0} x(-\vec q) e^{-\lambda \mathcal{H}_0} x(\vec q)\, d\lambda, \qquad (2.16\text{b})$$

where $\mathcal{H}_0$ is the exact Hamiltonian for zero field and where $\langle \cdots\rangle_0$ indicates ensemble averages in the absence of field. Noting that

$$\sum_{\vec q}\left(\langle x(-\vec q) : x(\vec q)\rangle_0 - \langle x(-\vec q)\rangle_0\langle x(\vec q)\rangle_0\right) = N\left(\langle x_i : x_i\rangle_0 - \langle x_i\rangle_0^2\right), \qquad (2.17\text{a})$$

we find the exact result

$$\sum_{\vec q} kT\chi(\vec q) = N\left(\langle x_i : x_i\rangle_0 - \langle x_i\rangle_0^2\right). \qquad (2.17\text{b})$$

Approximating this exact result by its CEF form (i.e., replacing $\mathcal{H}_0$ by V_i' in $\langle x_i : x_i\rangle_0$ and $\langle x_i\rangle_0$), Eqs. (2.12), (2.13), and (2.17b) can now be combined to give

$$\frac{N}{\tau} = \sum_{\vec q}[\tau + \alpha v(0) - v(\vec q)]^{-1}. \qquad (2.18)$$

Equations (2.6a), (2.9b), (2.9c), (2.13), and (2.18) are now closed and define the correlated effective-field approximation in lowest order.

Since the theory is defined for all temperatures and for arbitrary local potential $V(x_i)$ it is of great interest to relate it, where possible, to existing statistical approximations derived under more restrictive circumstances. Two points of contact are immediately evident. For a quasiharmonic $V(x_i)$, Hamiltonian (1.1) is of a form suitable for approximation by self-consistent linearization of the normal mode equations of motion. This is the SCP approximation originally introduced by Boccara and Sarma[1] and since studied in detail by several authors.[2-5] In an opposite limit of extreme anharmonicity we can take $V(x_i)$ in the form of a deep and narrow double well, when the ensemble average $\langle x:x\rangle_0$ becomes independent of temperature and we regenerate an Ising problem, the literature of which spans almost a half-century. Let us first direct our attention to the quasiharmonic situation and solve (1.1) in SCP approximation.

III. SELF-CONSISTENT-PHONON THEORY

Consider a local potential function of the form

$$V(x_i) = a_1 x_i^2 + a_2 x_i^4, \qquad (3.1)$$

with a_1 positive. The equation of motion for (1.1) with local potential (3.1) results from

$$\dot{x}_i = \frac{\partial \mathcal{H}}{\partial p_i}\,,\quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial x_i}\quad \text{(classical)}, \tag{3.2}$$

or

$$\dot{x}_i = (i/\hbar)[\mathcal{H},\, x_i]_-\,,\quad \dot{p}_i = (i/\hbar)[\mathcal{H},\, p_i]_-\quad \text{(quantum)}, \tag{3.3}$$

where $[\;,\;]_-$ denotes a commutator and is

$$\ddot{x}_i = h_i - 2a_1 x_i - 4a_2 x_i^3 + \sum_j v_{ij} x_j \tag{3.4}$$

for both schemes. Writing

$$x_i = \langle x\rangle_h + u_i\,, \tag{3.5}$$

where $\langle x\rangle_h = \langle x_i\rangle$ and is assumed independent of i (i.e., letting $h_i = h$ be a uniform field or zero) we find

$$\ddot{u}_i = h - 2a_1(\langle x\rangle_h + u_i) - 4a_2(\langle x\rangle_h^3 + 3\langle x\rangle_h^2 u_i + 3\langle x\rangle_h u_i^2 + u_i^3) + \sum_j v_{ij}(\langle x\rangle_h + u_j)\,. \tag{3.6}$$

Taking ensemble averages on both sides and assuming quasiharmonic motion such that $\langle \ddot{u}_i\rangle = \langle u_i\rangle = 0$ gives

$$h = [2a_1 - v(0) + 12a_2\langle u_i^2\rangle]\langle x\rangle_h + 4a_2\langle x\rangle_h^3\,, \tag{3.7}$$

and subtracting (3.7) from (3.6) leaves a motion

$$\ddot{u}_i = \sum_j v_{ij}u_j - 2a_1 u_i - 12a_2\langle x\rangle_h^2 u_i - 4a_2 u_i^3 - 12a_2\langle x\rangle_h(u_i^2 - \langle u_i^2\rangle)\,. \tag{3.8}$$

Introducing running waves

$$u_i = \left(\frac{1}{N}\right)^{1/2} \sum_{\vec{q}} u(\vec{q})e^{-i\vec{q}\cdot\vec{i}} \tag{3.9}$$

and linearizing the resulting equation of motion by replacing $u(\vec{q}\,')u(\vec{q}\,'')$ by its ensemble average for all $\vec{q}\,'$ and $\vec{q}\,''$, we find

$$\ddot{u}(\vec{q}) = v(\vec{q})u(\vec{q}) - 2a_1 u(\vec{q}) - 12a_2\left(\langle x\rangle_h^2 + \frac{1}{N}\sum_{\vec{q}\,'}\langle u(\vec{q}\,')u(-\vec{q}\,')\rangle\right)u(\vec{q})\,, \tag{3.10}$$

where $v(\vec{q})$ is defined in (2.4). Using the fact that

$$\sum_{\vec{q}}\langle u(\vec{q})u(-\vec{q})\rangle = N\langle u_i^2\rangle\,, \tag{3.11}$$

we rewrite (3.10) in simple oscillator form

$$\ddot{u}(\vec{q}) = -\Omega^2(\vec{q})u(\vec{q})\,, \tag{3.12}$$

with

$$\Omega^2(\vec{q}) = 2a_1 + 12a_2\langle x\rangle_h^2 + 12a_2\langle u_i^2\rangle - v(\vec{q})\,. \tag{3.13}$$

Using the text-book statistical result for quantum harmonic oscillators

$$\langle u(\vec{q})u(-\vec{q})\rangle = [\hbar/2\Omega(\vec{q})]\coth[\hbar\Omega(\vec{q})/2kT]\,, \tag{3.14}$$

the SCP picture is completed by the equation

$$N\langle u_i^2\rangle = \sum_{\vec{q}}\langle u(\vec{q})u(-\vec{q})\rangle = \sum_{\vec{q}} \frac{\hbar}{2\Omega(\vec{q})}\coth\frac{\hbar\Omega(\vec{q})}{2kT}\,, \tag{3.15}$$

which closes the set of Eqs. (3.7), (3.13), and (3.15) for the temperature dependence of $\langle x\rangle_h$, $\langle u_i^2\rangle$, etc.

Consistency of the SCP scheme with the fluctuation theorem can be tested for as follows. Using the relationship

$$\langle x(-\vec{q}) : x(\vec{q})\rangle - \langle x(-\vec{q})\rangle\langle x(\vec{q})\rangle = \langle u(-\vec{q}) : u(\vec{q})\rangle\,, \tag{3.16}$$

the fluctuation result (2.16a) for SCP becomes

$$\chi(\vec{q})\,\mathrm{Tr}\,e^{-\beta\mathcal{H}_0} = \mathrm{Tr}\int_0^\beta e^{\lambda\mathcal{H}_0}u(-\vec{q})e^{-\lambda\mathcal{H}_0}u(\vec{q})e^{-\beta\mathcal{H}_0}\,d\lambda\,. \tag{3.17}$$

For harmonic $\mathcal{H}_0$, the trace in (3.17) is easily evaluated in the coordinate basis for which the energy is diagonal to give

$$\chi(\vec{q}) = 1/\Omega^2(\vec{q})\,, \tag{3.18}$$

from which, in particular, the uniform static susceptibility $\chi(0)$ follows [using (3.13)] as

$$[\chi(0)]^{-1} = 2a_1 - v(0) + 12a_2\langle u_i^2\rangle + 12a_2\langle x\rangle_h^2\,. \tag{3.19}$$

This same equation can also be obtained directly from (3.7) by differentiation with respect to h if $d\langle u_i^2\rangle/dh = 0$ when $h = 0$. This is so only if $\langle x\rangle_0 = 0$ and it follows that the basic SCP equations conform to the fluctuation theorem only in the disordered phase.

IV. COMPARISON OF CEF AND SCP THEORIES

It is evident that no matter how small the anharmonic coefficient a_2 in (3.1) the basic anharmonic character must eventually destroy the validity of any linearized approximation (such as SCP) at sufficiently high temperatures. Since the CEF approximation makes no essential use of linearization it is not restricted in this way. Nevertheless, in this and the following section, it will prove convenient to define a "linearized CEF," since in this form the theory is most easily compared with the SCP scheme, and we shall use the abbreviation LCEF to denote this restricted scheme in Secs. IV and V.

A. LCEF theory, $T \geqslant T_c$, $\langle x\rangle_0 = 0$, $h = 0$

With local potential (3.1) the equation of motion for a particle at site i in the CEF approximation is

$$\ddot{x}_i = -2x_i[a_1 - \tfrac{1}{2}\alpha v(0)] - 4a_2 x_i^3\,. \tag{4.1}$$

Linearizing the equation gives simple harmonic motion with frequency Ω, where

$$\Omega^2 = 2a_1 - \alpha v(0) + 12a_2\langle x^2\rangle_0\,, \tag{4.2}$$

and where $\langle x^2\rangle_0$ in this harmonic approximation, becomes

$$\langle x^2\rangle_0 = (\hbar/2\Omega)\coth(\hbar\Omega/2kT)\,. \tag{4.3}$$

In the high-temperature limit, as mentioned, this quasiharmonic scheme must break down and the essentially anharmonic nature of (3.1) take over. Such a situation is readily handled in CEF theory but, since our present concern is a direct comparison with SCP, we shall use (4.2) and (4.3) to arbitrarily high temperatures to define a linearized CEF approximation.

From (2.12) in the $q = 0$ limit, Eq. (2.18) can be written

$$\frac{N}{\tau} = \sum_{\vec{q}} \{[\chi(0)]^{-1} + v(0) - v(\vec{q})\}^{-1}, \tag{4.4}$$

where, in the disordered phase,

$$\tau = kT/\langle x : x\rangle_0 , \tag{4.5}$$

and (4.2) becomes

$$\Omega^2 = 2a_1 + \tau - v(0) + 12a_2\langle x^2\rangle_0 - [\chi(0)]^{-1}, \tag{4.6}$$

thereby eliminating α. Now, as in (3.17), direct evaluation of $\langle x : x\rangle_0$ for the quasiharmonic motion and substitution in (4.5) gives

$$\tau = \Omega^2\,. \tag{4.7}$$

As a result, Eq. (4.6) reduces to

$$[\chi(0)]^{-1} = 2a_1 + 12a_2\langle x^2\rangle_0 - v(0)\,, \tag{4.8}$$

and from (4.4) we have

$$\frac{N}{\Omega^2} = \sum_{\vec{q}} \{[\chi(0)]^{-1} + v(0) - v(\vec{q})\}^{-1}. \tag{4.9}$$

Equations (4.3), (4.8), and (4.9) now determine the linearized CEF theory for the disordered phase.

B. SCP theory, $T \geqslant T_c$, $\langle x\rangle_0 = 0$, $h = 0$

From (3.13) and (3.18) we can write

$$[\chi(0)]^{-1} = 2a_1 - v(0) + 12a_2\langle x^2\rangle_0 , \tag{4.10}$$

and

$$\Omega^2(\vec{q}) = 2a_1 + 12a_2\langle x^2\rangle_0 - v(\vec{q})\,. \tag{4.11}$$

where we have noted that $\langle u_i^2\rangle = \langle x^2\rangle_0$ when $T > T_c$ and $h = 0$. Also, from (3.15),

$$N\langle x^2\rangle_0 = \sum_{\vec{q}} \frac{\hbar}{2\Omega(\vec{q})}\coth\frac{\hbar\Omega(\vec{q})}{2kT}\,. \tag{4.12}$$

Equations (4.10)–(4.12) now determine the temperature dependence of $\langle x^2\rangle_0$ and the uniform static susceptibility above T_c in the SCP approximation.

Now, comparing Eqs. (4.3), (4.8), and (4.9), with Eqs. (4.10)–(4.12), we see that for general v_{ij} they are identical in, but only in, the limits $\hbar \to 0$ (classical theory) *or* $T \to \infty$. The coincident classical equations are

$$[\chi(0)]^{-1} = 2a_1 + 12a_2\langle x^2\rangle_0 - v(0) \tag{4.13}$$

and

$$N\langle x^2\rangle_0 = \sum_{\vec{q}} \frac{kT}{\chi(0)^{-1} + v(0) - v(\vec{q})}\,. \tag{4.14}$$

C. LCEF theory, ordered phase, $\langle x\rangle_0 \neq 0$, $h = 0$

In the ordered phase the equation of motion for the ith particle in CEF approximation is

$$\ddot{x}_i = -2a_1x_i + \alpha v(0)x_i + (1-\alpha)v(0)\langle x\rangle_0 - 4a_2x_i^3\,. \tag{4.15}$$

Putting $x_i = \langle x\rangle_0 + u_i$ we find

$$\begin{aligned}\ddot{u}_i = \langle x\rangle_0[v(0) - 2a_1] - 2a_1u_i + \alpha v(0)u_i \\ - 4a_2(\langle x\rangle_0 + u_i)^3\,.\end{aligned} \tag{4.16}$$

Assuming quasiharmonic motion we take $\langle\ddot{u}_i\rangle = \langle u_i\rangle = 0$ and deduce

$$v(0) = 2a_1 + 4a_2\langle x\rangle_0^2 + 12a_2\langle u_i^2\rangle \tag{4.17}$$

and

$$\ddot{u}_i = -[2a_1 - \alpha v(0) + 12a_2\langle x\rangle_0^2]\,u_i - 4a_2u_i^3\,. \tag{4.18}$$

Linearizing (4.18) allows for simple harmonic motion with frequency Ω', where

$$\Omega'^2 = 2a_1 - \alpha v(0) + 12a_2\langle x\rangle_0^2 + 12a_2\langle u_i^2\rangle\,, \tag{4.19}$$

from which it follows that

$$\langle u_i^2\rangle = (\hbar/2\Omega')\coth(\hbar\Omega'/2kT)\,. \tag{4.20}$$

Using (2.12) and (2.18) we can again eliminate correlation α to obtain

$$\frac{N}{\tau} = \sum_{\vec{q}} \{[\chi(0)]^{-1} + v(0) - v(\vec{q})\}^{-1} \tag{4.21}$$

and

$$\begin{aligned}\Omega'^2 = 2a_1 + \tau - v(0) + 12a_2\langle x\rangle_0^2 \\ + 12a_2\langle u_i^2\rangle - [\chi(0)]^{-1}\,,\end{aligned} \tag{4.22}$$

where

$$\tau = kT/(\langle x : x\rangle_0 - \langle x\rangle_0^2) = kT/\langle u_i : u_i\rangle. \tag{4.23}$$

By direct evaluation in the basis for which the oscillator energy is diagonal we find

$$\langle u_i : u_i\rangle/kT = \left\langle \int_0^\beta e^{\lambda\mathcal{H}_0}u_ie^{-\lambda\mathcal{H}_0}u_i\,d\lambda\right\rangle = 1/\Omega'^2\,, \tag{4.24}$$

and hence

$$\tau = \Omega'^2\,. \tag{4.25}$$

Equation (4.22) now simplifies by use of (4.17) and (4.25) to

$$[\chi(0)]^{-1} = 8a_2\langle x\rangle_0^2 \tag{4.26}$$

and relates reciprocal susceptibility directly with the square of the order parameter. Finally (4.21) can be rewritten

$$\frac{N}{\Omega'^2} = \sum_{\vec{q}} [8a_2\langle x\rangle_0^2 + v(0) - v(q)]^{-1}, \qquad (4.27)$$

when (4.17), (4.20), and (4.27) are now a closed set of equations in Ω', $\langle x\rangle_0$, and $\langle u_i^2\rangle$ and define the linear CEF theory for the ordered phase.

D. SCP theory, ordered phase, $\langle x\rangle_0 \neq 0, h=0$

For SCP theory in the ordered phase the relevant equations can be taken directly from Sec. III. Rewriting (3.7) for $\langle x\rangle_0 \neq 0$, $h=0$, as

$$v(0) = 2a_1 + 4a_2\langle x\rangle_0^2 + 12a_2\langle u_i^2\rangle, \qquad (4.28)$$

[which is exactly (4.17) of LCEF theory], we see that this equation, together with (3.13) and (3.15) determines the susceptibility and order parameter for the ordered phase in the SCP approximation.

Comparing (4.17), (4.20), and (4.27), of LCEF theory with (4.28), (3.13), and (3.15) of SCP, we see again that for general v_{ij} they are identical in, but only in, the classical or high-temperature limits. In this limit the coincident classical equations are (4.17) and

$$N\langle u_i^2\rangle = \sum_{\vec{q}} \frac{kT}{8a_2\langle x\rangle_0^2 + v(0) - v(\vec{q})}, \qquad (4.29)$$

and together determine $\langle u_i^2\rangle$ and $\langle x\rangle_0$ self-consistently.

As an extreme example of the differences between quantum LCEF and quantum SCP which develop at lower temperatures we consider the zero-point motion. In SCP, from (3.13), (3.15), and (4.28) for $T=0$ we find

$$\langle u_i^2\rangle = \tfrac{1}{2}\hbar \frac{1}{N}\sum_{\vec{q}} [8a_2\langle x\rangle_0^2 + v(0) - v(\vec{q})]^{-1/2}, \quad T=0 \qquad (4.30)$$

while the equivalent LCEF finding, from (4.20) and (4.27) is

$$\langle u_i^2\rangle = \tfrac{1}{2}\hbar\left(\frac{1}{N}\sum_{\vec{q}} [8a_2\langle x\rangle_0^2 + v(0) - v(\vec{q})]^{-1}\right)^{1/2}, \quad T=0. \qquad (4.31)$$

V. DYNAMICS

Whereas the dynamical situation for SCP is immediately apparent, with $\Omega(\vec{q})$ describing the frequency of normal modes of the wave vector $\vec{q}$ and with $\Omega(0)$, in particular, being the "soft-mode" frequency which goes to zero as $[\chi(0)]^{-1/2}$ [see Eqs. (4.10) and (4.11)] on approach to the transition temperature, an analysis of the dynamical situation for CEF approximation requires a little thought. It is, for example, immediately evident that Ω of (4.6) is not the soft-mode frequency nor, in fact, the frequency of any wave-vector lattice mode. The latter, however, are readily described within CEF theory by use of linear response theory. In addition, as with the static properties, the method is not restricted to the quasiharmonic limit, but may be formally set out for local potential $V(x_i)$ of any form.

Consider the effective Hamiltonian (2.2) for particle i. It is conveniently thought of as describing an isolated particle moving in a local potential $V(x_i) - \frac{1}{2}\alpha v(0)x_i^2$ and perturbed by an effective field

$$h_{\text{loc}} = h_i e^{-i\omega t} + \sum_j v_{ij}(\langle x_j\rangle - \alpha\langle x_i\rangle), \qquad (5.1)$$

where we have now allowed for a time-dependent applied field.

We now define a linear response $\langle x_i\rangle$ in the form

$$\langle x_i\rangle = \phi(\omega)\left(h_i e^{-i\omega t} + \sum_j v_{ij}(\langle x_j\rangle - \alpha\langle x_i\rangle)\right), \qquad (5.2)$$

where $\phi(\omega)$ is the dynamic polarizability of an ensemble of *noninteracting* oscillators each subject to a local potential $V(x) - \frac{1}{2}\alpha v(0)x^2$. Fourier transforming (5.2) with respect to the lattice we get

$$\langle x(\vec{q})\rangle = \phi(\omega)\{h(\vec{q})\, e^{-i\omega t} + [v(\vec{q}) - \alpha v(0)]\langle x(\vec{q})\rangle\} \qquad (5.3)$$

and can define a dynamic polarizability $\chi(\vec{q}, \omega)$ as

$$\chi(\vec{q}, \omega) = \frac{\langle \chi(\vec{q})\rangle}{h(\vec{q})e^{-i\omega t}} = \frac{\phi(\omega)}{1 - \phi(\omega)[v(\vec{q}) - \alpha v(0)]}. \qquad (5.4)$$

Since $\phi(\omega)$ can be calculated directly by standard textbook procedures for the noninteracting ensemble, Eq. (5.4) defines the many-body dynamic solution within the CEF approximation. For a potential $V(x)$ of general form it is necessary to solve for the "isolated" local motion $x(t)$, in terms of which the noninteracting polarizability $\phi(\omega)$ can be formally cast as[17]

$$\phi_R(\omega) = (1/\pi)\mathcal{P}\int_{-\infty}^{\infty} \phi_I(E)\,dE/(E-\omega), \qquad (5.5)$$

$$\phi_I(\omega) = \tfrac{1}{2}\tanh(\hbar\omega/2kT)\int_{-\infty}^{\infty}\langle x(0)x(t) + x(t)x(0)\rangle\, e^{i\omega t}\,dt, \qquad (5.6)$$

where subscripts I and R refer to the imaginary and real parts of the susceptibility $\phi(\omega)$, respectively, and $\mathcal{P}$ signifies the principal value of the integral.

An excellent exact classical treatment for the highly anisotropic noninteracting ensemble has been given by Onodera.[10] For the quasiharmonic limit the theory is simple in the extreme. If $\phi(\omega)$ is the dynamic susceptibility for an ensemble of undamped independent harmonic oscillators of frequency Ω, then it is real and takes the form

$$\phi(\omega) = \phi(0)\Omega^2/(\Omega^2 - \omega^2), \qquad (5.7)$$

where

$$\phi(0) = \langle x : x\rangle_0/kT \qquad (5.8)$$

is the static susceptibility.

From (5.4) the dynamic susceptibility for the interacting oscillators in LCEF approximation now follows immediately. In particular, the $\vec{q}=0$ susceptibility diverges at a frequency Ω_s (defining the soft mode) given by

$$\Omega^2 - \Omega_s^2 = \langle x : x\rangle_0 \Omega^2 (1-\alpha) v(0)/kT, \tag{5.9}$$

which, using (4.5), (4.7), and (2.12) for the $\vec{q}=0$ limit, reduces to

$$\Omega_s^2 = \Omega^2 [\chi(0)]^{-1}/\tau = [\chi(0)]^{-1}, \tag{5.10}$$

in the disordered phase. It follows that within LCEF (as with SCP) the soft-mode frequency tends to zero as the square root of the reciprocal susceptibility as the transition is approached.

VI. ISING LIMIT

The Ising model results within the present framework when we consider the local potential $V(x)$ to have the form of a double δ function, i.e., $V(x) = -\delta(x_i^2 - x_c^2)$, where x_c is a constant. In this limit the dynamics and quantum aspects play no part in the discussion and it follows immediately that (2.9c) can be replaced by

$$\langle x : x\rangle_0 = x_c^2 . \tag{6.1}$$

As a result the series of coupled equations which define the CEF approximation for general local potential $V(x)$ simplify markedly in the Ising model.

A. Disordered phase

In the disordered phase, where order parameter $\langle x\rangle_0$ is zero in the absence of field, Eq. (2.13) reduces to

$$\tau = kT/x_c^2, \tag{6.2}$$

and is independent of correlation α. Now, combining (2.12) for $\vec{q}=0$ with (2.18) and (6.2) allows us to write an equation,

$$\frac{Nx_c^2}{kT} = \sum_{\vec{q}} \{[\chi(0)]^{-1} + v(0) - v(\vec{q})\}^{-1}, \tag{6.3}$$

which directly relates static uniform susceptibility to temperature. In addition, since

$$\langle x_i x_{i+R}\rangle = N^{-1} \sum_{\vec{q}} \langle x(\vec{q}) x(-\vec{q})\rangle e^{i\vec{q}\cdot\vec{R}}$$

$$= \frac{kT}{N} \sum_{\vec{q}} \chi(\mathrm{q}) e^{i\vec{q}\cdot\vec{R}}, \tag{6.4}$$

using the fluctuation result for the disordered phase, an expression can also be written for the static correlation between the motion at sites with the relative position vector $\vec{R}$, in the form

$$\langle x_i x_{i+R}\rangle = \frac{kT}{N} \sum_{\vec{q}} \frac{e^{i\vec{q}\cdot\vec{R}}}{\chi(0)^{-1} + v(0) - v(\vec{q})} . \tag{6.5}$$

Equations (6.3) and (6.5) together define these correlations directly as a function of temperature.

Finally, using (6.3) in the limit of diverging $\chi(0)$, we locate the Curie temperature T_C in the form

$$\frac{Nx_c^2}{kT_C} = \sum_{\vec{q}} [v(0) - v(\vec{q})]^{-1} . \tag{6.6}$$

B. Ordered phase, $\langle x\rangle_0 \neq 0, h=0$

From (2.9b) we obtain

$$\langle x\rangle_0 = x_c \tanh[v(0) x_c \langle x\rangle_0 (1-\alpha)/kT], \tag{6.7}$$

as the equation for order parameter $\langle x\rangle_0$. In order to eliminate α we make use of (2.18) which, for the Ising case, can be rewritten

$$N = \sum_{\vec{q}} \frac{kT}{kT + (x_c^2 - \langle x\rangle_0^2)[\alpha v(0) - v(\vec{q})]} . \tag{6.8}$$

Equations (6.7) and (6.8) now together determine $\langle x\rangle_0$ directly as a function of temperature.

Students of the Ising problem will immediately recognize these equations as those resulting from the generalized spherical model.[14,18] In the latter, the Ising restriction $x_i^2 = x_c^2$ for all i is replaced by the weaker constraint $\sum_i x_i^2 = Nx_c^2$ thereby allowing x_i to become a continuous variable. The spherical model is exactly soluble and of some considerable importance in the theory of critical phenomena.[19] Finally we note the formal equivalence of the CEF theory in the Ising limit to the Onsager reaction-field approach. The derivation of the spherical equations from the use of the reaction-field concept for the Ising many-dipole problem was demonstrated by Brout and Thomas.[20]

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