

Correlated Einstein model for the equilibrium properties of solids

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(Received 8 August 1983; revised manuscript received 20 October 1983)

The correlated Einstein model (CEM) is a new approach to the problem of determining the equilibrium properties of anharmonic solids. It is based on the use of the zeroth-order term in an expansion for the average of a product of one- and two-particle functions, where the average is a classical canonical average for a system of independent Einstein oscillators. The parameters that characterize the oscillators are chosen so that the first- and second-order terms in the expansion vanish. A diagrammatic representation of the expansion is given. Explicit formulas for determining the Helmholtz free energy of a monatomic cubic crystal are given and are evaluated both for a Lennard-Jones and a $1/r^{12}$ potential. The results obtained are compared with available Monte Carlo values. The CEM is found to be at least as accurate as the uncorrelated-pairs approximation, the cell-cluster method, the simple cell model, and improved self-consistent phonon theory.

I. INTRODUCTION

This paper introduces a new method for calculating the equilibrium properties of anharmonic solids. The method is based on the exact result

$$\left\langle \prod_j f_j(\vec{x}_j) \prod_{\substack{k,l \\ k < l}} f_{kl}(\vec{x}_k, \vec{x}_l) \right\rangle_0 = e^{\lambda[R(\vec{\nabla})+A(\vec{\nabla})]} \times \prod_j \langle f_j(\vec{x}_j) \rangle_0 \prod_{\substack{k,l \\ k < l}} \langle f_{kl}(\vec{x}_k, \vec{x}_l) \rangle_0 \Big|_{\lambda=1}, \quad (1.1)$$

where the angular brackets indicate a classical equilibrium average for a system of N independent Einstein oscillators. \vec{x}_i is the displacement of particle i from lattice site i ($i = 1, \dots, N$), and the $f_j(\vec{x}_j)$ and $f_{kl}(\vec{x}_k, \vec{x}_l)$ are arbitrary one- and two-particle functions. The derivation of Eq. (1.1), which makes critical use of Fourier transforms and the special properties of harmonic averages, is given in Sec. II. Also given are the definitions of the differential operators $A(\vec{\nabla})$ and $R(\vec{\nabla})$, which operate on the particle variables \vec{x}_i before the averages are performed. $A(\vec{\nabla})$ is a sum of elementary operators each of which acts on a pair of two-particle functions. The interrelations or connections between pairs of functions made by these elementary operators correct for the correlations between different two-particle functions that are neglected in the product of averages on the right-hand side of Eq. (1.1). Similarly, the elementary operators that make up $R(\vec{\nabla})$ correct for the neglected correlations between one-particle functions and two-particle functions.

The above new and somewhat abstract result can be applied to the task of determining the equilibrium properties of a system whose true potential energy Φ is not of the Einstein type by using the relationship

$$F = F_0 - \beta^{-1} \ln \langle e^{-\beta(\Phi - \Phi_0)} \rangle_0. \quad (1.2)$$

Φ_0 is an approximate potential-energy function. F and F_0

are the true and approximate Helmholtz free energies, which are given by

$$F = F_{\text{ideal gas}} - \beta^{-1} \ln \left[V^{-N} \int d^3N x e^{-\beta\Phi} \right] \quad (1.3)$$

and

$$F_0 = F_{\text{ideal gas}} - \beta^{-1} \ln \left[V^{-N} \int d^3N x e^{-\beta\Phi_0} \right]. \quad (1.4)$$

V is volume, T is temperature, k_B is Boltzmann's constant, and $\beta = 1/k_B T$. When both Φ_0 and Φ are sums of two-particle functions, so that

$$\Phi_0 = \sum_{\substack{k,l \\ k < l}} \phi_{kl}^0(\vec{x}_k, \vec{x}_l) \quad (1.5)$$

and similarly for Φ , it follows that

$$F = F_0 - \beta^{-1} \ln \left\langle \prod_{\substack{k,l \\ k < l}} \exp[-\beta(\phi_{kl} - \phi_{kl}^0)] \right\rangle_0. \quad (1.6)$$

An Einstein model connects each particle to a lattice site by a spring, and the associated potential energy is most naturally written as a sum of one-particle functions. However, a sum of one-particle functions can always be rewritten as a sum of two-particle functions, so that the potential energy of a collection of Einstein oscillators can always be assumed to have the form given by Eq. (1.5). By letting

$$f_{kl}(\vec{x}_k, \vec{x}_l) = \exp[-\beta(\phi_{kl} - \phi_{kl}^0)], \quad (1.7)$$

the average in Eq. (1.6) becomes the same as the average on the left-hand side of Eq. (1.1). These comments suggest that the one-particle functions in Eq. (1.1) could be ignored, or equivalently that one could set all $f_j(\vec{x}_j) = 1$. It is found, however, that it is not always desirable to do so.

The *correlated Einstein model* (CEM) is obtained by expanding Eq. (1.1) in a Taylor series of powers of the artificially introduced parameter λ and keeping only the zeroth-order term. The parameters in the Einstein

potential-energy function Φ_0 are then chosen so that all first- and second-order terms in the resulting series vanish. This choice sets the average and mean-square displacements of the i th Einstein oscillator (i.e., $\langle \bar{x}_i \rangle_0$ and $\langle \bar{x}_i \bar{x}_i \rangle_0$) equal to averages that are modulated by the Boltzmann factors $\exp[-\beta(\phi_{ij} - \phi_{ij}^0)]$. When the zeroth-order term in the expansion is substituted into Eq. (1.6), one obtains

$$F = F_0 - \beta^{-1} \sum_{\substack{k,l \\ k < l}} \ln \langle \exp[-\beta(\phi_{kl} - \phi_{kl}^0)] \rangle_0. \quad (1.8)$$

This is the CEM approximation for the free energy. It is accurate through second order. Effectively, it replaces the average of a product of two-particle functions by a product of their averages. Correlations are accounted for by the choice of Φ_0 and by the averages of $\exp[-\beta(\phi_{kl} - \phi_{kl}^0)]$.

We call the series obtained by expanding in powers of λ the *correlated-particles expansion* (CPE). The parameter λ orders the terms in the expansion according to the number of elementary connections between pairs of functions that are in the term. A useful property of the expansion is that the maximum dimensionality of the integrals that require numerical integration is 3, independent of the order of the term considered. To help understand the expansion we introduce a set of diagrams in Sec. II that can be put in one-to-one correspondence with the terms in the expansion.

The CPE is similar to the first type of correlated-pairs expansion described in an earlier paper.¹ The main difference is that the earlier expansion required that the approximate potential-energy function be harmonic, not that it be of the Einstein type. Since an Einstein model is a special case of a harmonic model, the CPE is in a sense less general than the earlier expansion. The advantage of the CPE is that it is simpler and therefore easier to apply.

The parameters in Φ_0 must be chosen self-consistently. This is described in Sec. III, and the formulas needed to calculate the equilibrium properties of a monatomic crystal with cubic symmetry are given. In Sec. IV the predictions of the CEM are compared with Monte Carlo (MC) results. Both a Lennard-Jones and a simple $1/r^{12}$ potential are considered. For the latter potential we find that nontrivial one-particle functions [i.e., $f_j(\bar{x}_j) \neq 1$] must be included in Eq. (1.1) in order to obtain self-consistency. The predictions of the CEM are found to be quite accurate. For the Lennard-Jones solid a comparison is made with the predictions of the uncorrelated-pairs approximation (UPA) (Ref. 2), the cell-cluster method (CCM) (Ref. 3), the simple cell model (CM) (Ref. 3), and improved self-consistent phonon theory (ISC) (Ref. 4). The advantages and disadvantages of the different approximations are discussed in Sec. V.

II. CPE

A. Exact result

We begin the proof of the exact result given by Eq. (1.1) with some comments on notation. For convenience we let A_{Π} designate the average of the product on the left-hand

side of Eq. (1.1) and omit the subscripts on $f_j(\bar{x}_j)$ and $f_{kl}(\bar{x}_k, \bar{x}_l)$:

$$A_{\Pi} = \left\langle \prod_j f(\bar{x}_j) \prod_{\substack{k,l \\ k < l}} f(\bar{x}_k, \bar{x}_l) \right\rangle_0. \quad (2.1)$$

It is left implicit that the functions $f(\bar{x}_k, \bar{x}_l)$ for different variables \bar{x}_k and \bar{x}_l are in general different, and similarly for the $f(\bar{x}_j)$. For $k > l$, we define

$$f(\bar{x}_k, \bar{x}_l) = f(\bar{x}_l, \bar{x}_k). \quad (2.2)$$

Since only functions $f(\bar{x}_k, \bar{x}_l)$ with $k < l$ occur in Eq. (2.1), this involves no loss of generality.

Angular brackets with subscript zero indicate harmonic averages of functions of the particle variables of the form

$$\langle F(\bar{x}_1, \dots, \bar{x}_N) \rangle_0 = \frac{\int d^{3N}x [e^{-\beta\Phi_0} F(\bar{x}_1, \dots, \bar{x}_N)]}{\int d^{3N}x e^{-\beta\Phi_0}}, \quad (2.3)$$

where

$$\Phi_0 = \sum_i \left(\frac{1}{2} \bar{x}_i \cdot \vec{K}_i \cdot \bar{x}_i - \vec{\Gamma}_i \cdot \bar{x}_i \right). \quad (2.4)$$

These averages are unaffected by the addition of an arbitrary constant to Φ_0 . The force constant tensor \vec{K}_i is a symmetric matrix with positive eigenvalues. The vector $\vec{\Gamma}_i$ represents a constant force that determines the mean value of the variable \bar{x}_i . In particular, it follows from Eqs. (2.3) and (2.4) that

$$\langle \bar{x}_i \rangle_0 = \vec{K}_i^{-1} \cdot \vec{\Gamma}_i \quad (2.5)$$

and

$$\langle (x_i^\alpha - \langle x_i^\alpha \rangle_0)(x_j^\gamma - \langle x_j^\gamma \rangle_0) \rangle_0 = (\vec{K}_i^{-1})^{\alpha\gamma} k_B T \delta_{ij}, \quad (2.6)$$

where α and γ label different spatial components ($\alpha, \gamma = 1, 2, 3$) and δ_{ij} is a Kronecker δ function.

Fourier transforms will be designated by tildes, so that the inverse transformations are given by

$$f(\bar{x}_j) = (2\pi)^{-3/2} \int d^3s_{jj} e^{i\vec{s}_{jj} \cdot \bar{x}_j} \tilde{f}(\vec{s}_{jj}) \quad (2.7)$$

and

$$f(\bar{x}_k, \bar{x}_l) = (2\pi)^{-3} \int d^3s_{kl} \int d^3s_{lk} e^{i(\vec{s}_{kl} \cdot \bar{x}_k + \vec{s}_{lk} \cdot \bar{x}_l)} \times \tilde{f}(\vec{s}_{kl}, \vec{s}_{lk}). \quad (2.8)$$

The first subscript on the transform variables \vec{s}_{kl} indicates the particle variable \bar{x}_k that has been replaced, while the second subscript indicates the function $f(\bar{x}_k, \bar{x}_l)$ that has been transformed. The repeated subscripts on \vec{s}_{jj} indicate that a one-particle function has been transformed.

The first step in the proof is to introduce the inverse transformations into the average A_{Π} . After combining the product of the exponentials $\exp(i\vec{s}_{jk} \cdot \bar{x}_j)$ into a single exponential, one obtains

$$A_{\Pi} = \left\langle (2\pi)^{-M/2} \int d^M s \exp \left[i \sum_{j,k} \vec{s}_{jk} \cdot \vec{x}_j \right] \right. \\ \left. \times \prod_j \tilde{f}(\vec{s}_{jj}) \prod_{\substack{k,l \\ k < l}} \tilde{f}(\vec{s}_{kl}, \vec{s}_{lk}) \right\rangle_0, \quad (2.9)$$

where $M = 3N^2$. Note that there are N^2 independent transform or integration variables \vec{s}_{jk} , while there are only N independent particle variables \vec{x}_i . The transformation of the N one-particle functions $f(\vec{x}_j)$ gives $3N$ of the integration variables, while the transformation of the $N(N-1)/2$ two-particle functions $f(\vec{x}_k, \vec{x}_l)$ gives the remaining $3N(N-1)$ integration variables.

We now use the exponential averaging theorem for harmonic averages, which is crucial to the theory of the Debye-Waller factor. It states that

$$\left\langle \exp \left[i \sum_{j,k} \vec{s}_{jk} \cdot \vec{x}_j \right] \right\rangle_0 = \exp \left[-\frac{1}{2} k_B T \sum_{j,k,l} \vec{s}_{jk} \cdot \vec{K}_j^{-1} \cdot \vec{s}_{jl} + i \sum_{j,k} \vec{s}_{jk} \cdot \langle \vec{x}_j \rangle_0 \right], \quad (2.11)$$

where the single, double, and triple sums are unrestricted and where Eq. (2.6) has been used. By rearranging the triple sum in Eq. (2.11) and again using the exponential averaging theorem (in reverse) it follows that

$$\left\langle \exp \left[i \sum_{j,k} \vec{s}_{jk} \cdot \vec{x}_j \right] \right\rangle_0 = e^{-[R(\vec{s}) + A(\vec{s})]} \prod_j \langle e^{i \vec{s}_{jj} \cdot \vec{x}_j} \rangle_0 \prod_{\substack{k,l \\ k < l}} \langle e^{i(\vec{s}_{kl} \cdot \vec{x}_k + \vec{s}_{lk} \cdot \vec{x}_l)} \rangle_0, \quad (2.12)$$

where the symbols $R(\vec{s})$ and $A(\vec{s})$ have the following meaning:

$$R(\vec{s}) = k_B T \sum'_{j,k} \vec{s}_{jj} \cdot \vec{K}_j^{-1} \cdot \vec{s}_{jk}, \quad (2.13)$$

$$A(\vec{s}) = k_B T \sum_j \sum_{\substack{k,l \\ k < l}}^{(j)} \vec{s}_{jk} \cdot \vec{K}_j^{-1} \cdot \vec{s}_{jl}. \quad (2.14)$$

The primed double sum over j and k in Eq. (2.13) excludes terms with $j = k$, and the superscripted double sum over k and l in Eq. (2.14) excludes terms with either $k = j$ or $l = j$. Using the above results in Eq. (2.9) gives

$$A_{\Pi} = (2\pi)^{-M/2} \int d^M s e^{-[R(\vec{s}) + A(\vec{s})]} \prod_j \langle e^{i \vec{s}_{jj} \cdot \vec{x}_j} \tilde{f}(\vec{s}_{jj}) \rangle_0 \prod_{\substack{k,l \\ k < l}} \langle e^{i(\vec{s}_{kl} \cdot \vec{x}_k + \vec{s}_{lk} \cdot \vec{x}_l)} \tilde{f}(\vec{s}_{kl}, \vec{s}_{lk}) \rangle_0. \quad (2.15)$$

We now use

$$\vec{\nabla} e^{i \vec{s} \cdot \vec{x}} = i \vec{s} e^{i \vec{s} \cdot \vec{x}} \quad (2.16)$$

and require that *all gradient operations must be performed before averaging*. With this, all of the dependence on the transform variables can be set inside the angular brackets. Then by taking the inverse Fourier transform one obtains the exact result

$$A_{\Pi} = e^{[R(\vec{\nabla}) + A(\vec{\nabla})]} \prod_j \langle f(\vec{x}_j) \rangle_0 \prod_{\substack{k,l \\ k < l}} \langle f(\vec{x}_k, \vec{x}_l) \rangle_0, \quad (2.17)$$

where

$$R(\vec{\nabla}) = \sum'_{j,k} R_{jk}, \quad (2.18)$$

$$R_{jk} = k_B T \vec{\nabla}_{jj} \cdot \vec{K}_j^{-1} \cdot \vec{\nabla}_{jk}, \quad (2.19)$$

$$A(\vec{\nabla}) = \sum_j \sum_{\substack{k,l \\ k < l}}^{(j)} A_{jkl}, \quad (2.20)$$

$$\langle e^{iL} \rangle_0 = \exp \left[-\frac{1}{2} \langle (L - \langle L \rangle_0)^2 \rangle_0 + i \langle L \rangle_0 \right], \quad (2.10)$$

where L is any real linear function of the normal coordinates, i.e., the coordinates that diagonalize Φ_0 . When Φ_0 has the Einstein form given by Eq. (2.4), it is diagonal in the \vec{x}_i 's as given, so that the particle variables are essentially the normal coordinates. Equation (2.10) is a special property of harmonic averages that is valid both classically and quantum mechanically. For the classical averages considered here the proof of Eq. (2.10) is a straightforward exercise in completing the square and changing variables in integrals of exponentials of quadratic forms.

The average in Eq. (2.9) can be simplified to have the form $\langle e^{iL} \rangle_0$ by changing the order in which the integrating and averaging is done. By applying Eq. (2.10) to the resulting average, one obtains

and

$$A_{jkl} = k_B T \vec{\nabla}_{jk} \cdot \vec{K}_j^{-1} \cdot \vec{\nabla}_{jl}. \quad (2.21)$$

When $j \neq k$, the operator $\vec{\nabla}_{jk}$ operates on the variable \vec{x}_j in the function $f(\vec{x}_j, \vec{x}_k)$, while $\vec{\nabla}_{jj}$ operates on the \vec{x}_j in the function $f(\vec{x}_j)$. (If desired, one can avoid the requirement that the gradients be performed before the averaging is done by introducing another set of variables for the gradients to operate on, as was done in an earlier paper.¹) Equation (2.17) is equivalent to Eq. (1.1).

Note that the elementary operator A_{jkl} acts on a pair of two-particle functions that have one particle in common, so that A_{jkl} introduces a relationship between three particles. The elementary operator R_{jk} introduces a relationship between two particles; for it to be significant a non-trivial one-particle function must be associated with particle j .

B. Expansion

The CPE is obtained by expanding the exact result given by Eq. (2.17) in powers of a parameter λ that is in-

troduced as a multiplier of the operator $R(\vec{\nabla}) + A(\vec{\nabla})$. We refer to the number of factors of λ in a term, which equals the number of factors of A_{jkl} and R_{jk} , as the *order* of the term. The expansion is an expansion in the number of elementary relationships, or connections. The totality of all such elementary connections exactly corrects for the correlations neglected when the average of the product A_{Π} is approximated by the product of averages on the right-hand side of Eq. (2.17).

It follows from Eqs. (2.18) and (2.20) that

$$e^{\lambda[R(\vec{\nabla}) + A(\vec{\nabla})]} = \prod_{j',k'} \left[\sum_{m(j',k')} \frac{(\lambda R_{j'k'})^{m(j',k')}}{m(j',k')!} \right] \prod_j \prod_{\substack{k,l \\ k < l}}^{(j)} \left[\sum_{n(j,k,l)} \frac{(\lambda A_{jkl})^{n(j,k,l)}}{n(j,k,l)!} \right] \\ = \left[\cdots \sum_{m(\dots, \dots)} \cdots \right] \left[\cdots \sum_{n(\dots, \dots, \dots)} \cdots \right] \\ \times \left[\prod_{j',k'} \frac{(R_{j'k'})^{m(j',k')}}{m(j',k')!} \prod_j \prod_{\substack{k,l \\ k < l}}^{(j)} \frac{(A_{jkl})^{n(j,k,l)}}{n(j,k,l)!} \right] \lambda^p, \quad (2.23)$$

where there are $N(N-1)$ sums from zero to infinity over the different indices $m(j',k')$ and where there are $N(N-1)(N-2)/2$ sums from zero to infinity over the different indices $n(j,k,l)$. The order of a term is given by p , which is

$$p = \sum_{j',k'} m(j',k') + \sum_j \sum_{\substack{k,l \\ k < l}}^{(j)} n(j,k,l). \quad (2.24)$$

By inserting Eq. (2.23) into Eq. (2.17), one obtains the CPE

$$A_{\Pi} = \Pi_A (1 + \lambda S_1 + \lambda^2 S_2 + \cdots) |_{\lambda=1}. \quad (2.25)$$

Here S_p is the sum of all terms proportional to λ^p , and Π_A is the product of averages defined by

$$\Pi_A = \prod_j \langle f(\vec{x}_j) \rangle_0 \prod_{\substack{k,l \\ k < l}} \langle f(\vec{x}_k, \vec{x}_l) \rangle_0. \quad (2.26)$$

Each term in the CPE has the form

$$\frac{1}{\Pi_A} \prod_{j',k'} \frac{(R_{j'k'})^{m(j',k')}}{m(j',k')!} \prod_j \prod_{\substack{k,l \\ k < l}}^{(j)} \frac{(A_{jkl})^{n(j,k,l)}}{n(j,k,l)!} \prod_i \langle f(\vec{x}_i) \rangle_0 \prod_{\substack{m,n \\ m < n}} \langle f(\vec{x}_m, \vec{x}_n) \rangle_0. \quad (2.27)$$

Note that all averages $\langle f(\vec{x}_i) \rangle_0$ and $\langle f(\vec{x}_m, \vec{x}_n) \rangle_0$ that are not operated on by a $R_{j'k'}$ or A_{jkl} cancel with the corresponding average occurring in Π_A .

It is not difficult to determine the form of the low-order terms in the CPE. For example, the collection of all terms of order $p=1$ is

$$S_1 = k_B T \sum_{j,k} \frac{\langle \vec{\nabla}_j f(\vec{x}_j) \rangle_0 \cdot \vec{\mathbf{K}}_j^{-1} \cdot \langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_k) \rangle_0}{\langle f(\vec{x}_j) \rangle_0 \langle f(\vec{x}_j, \vec{x}_k) \rangle_0} + k_B T \sum_j \sum_{\substack{k,l \\ k < l}}^{(j)} \frac{\langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_k) \rangle_0 \cdot \vec{\mathbf{K}}_j^{-1} \cdot \langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_l) \rangle_0}{\langle f(\vec{x}_j, \vec{x}_k) \rangle_0 \langle f(\vec{x}_j, \vec{x}_l) \rangle_0}. \quad (2.28)$$

The second subscript on the gradients has now been omitted since it is clear which function is operated on.

C. Diagrams

Because of the complexity of the higher-order terms in the CPE, it is helpful to represent them by diagrams. Although the appropriate diagrams are visually similar to those used in the Ursell-Mayer type of cluster expansion, they are conceptually quite different.

where the primed product excludes factors with $j'=k'$ and the superscripted product excludes factors with either $k=j$ or $l=j$. By expanding in powers of λ and changing the order in which products and sums are taken, one obtains

A diagram contains points, circles, and bonds. Each *point* is identified by an integer from 1 through N and represents one of the particles in the system. A point may have a small *circle* drawn around it. A circle represents the average of a one-particle function that is operated on by at least one gradient operator. A *bond* is a line drawn between two points. A small gap must be left between the ends of the bond and the points. Bonds represent averages of two-particle functions. The number of bonds between a pair of points equals the number of gradient operators

that act on the two-particle function. It is convenient (but not necessary) to omit those points that are not associated with any circle or bond.

The concept of a *connection* is essential. Each bond must be connected either to a circle or to another bond at one and only one of its ends. A connection represents an operator R_{jk} or A_{jkl} . The total number of connections in a diagram equals the order p of the term represented by the diagram. The unconnected end of a bond is referred to as its free end.

A bond that is connected to a circle around point j and that has its free end at point k is associated with R_{jk} . A bond connected to a circle is referred to as a *ray*, and R_{jk} is referred to as a *ray operator*. Every circle must have at least one ray. A circle and all of the rays connected to it is referred to as a *star*. The diagram in Fig. 1(a) contains one star and the star has one ray. It represents the term

$$\frac{k_B T \langle \vec{\nabla}_m f(\vec{x}_m) \rangle_0 \cdot \vec{\mathbf{K}}_m^{-1} \cdot \langle \vec{\nabla}_m f(\vec{x}_m, \vec{x}_n) \rangle_0}{!! \langle f(\vec{x}_m) \rangle_0 \langle f(\vec{x}_m, \vec{x}_n) \rangle_0} \quad (2.29)$$

A bond between points j and k that is connected at

$$\frac{k_B T \quad k_B T \quad \langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_i) \rangle_0 \cdot \vec{\mathbf{K}}_j^{-1} \cdot \langle \vec{\nabla}_j \vec{\nabla}_k f(\vec{x}_j, \vec{x}_k) \rangle_0 \cdot \vec{\mathbf{K}}_k^{-1} \cdot \langle \vec{\nabla}_k f(x_k) \rangle_0}{!! \quad !! \quad \langle f(\vec{x}_j, \vec{x}_i) \rangle_0 \langle f(\vec{x}_j, \vec{x}_k) \rangle_0 \langle f(x_k) \rangle_0} \quad (2.31)$$

is represented by the diagram in Fig. 2(a).

When the distinction between a diagram and the term it represents is ignored, it follows that S_p , the sum of all terms of order p , is given by the sum of all diagrams in \mathcal{D} that contain p connections.

D. Generalizations

Exact results with the general form of Eq. (2.17) can be proved without either the restriction that Φ_0 is of the Einstein type or the restriction that the functions being averaged in A_{Π} are one- and two-particle functions. What is necessary is that the average is a harmonic average and that each function in the product of functions being averaged has a finite number of variables with the variables being linear functions of the normal coordinates of the approximate potential energy. However, when either or both of these restrictions is removed, the operator analogous to $R(\vec{\nabla}) + A(\vec{\nabla})$ becomes more complex and the expansion analogous to the CPE contains terms that are not represented by the diagrams described above.

For example, if the approximate potential energy Φ_0 was harmonic but contained terms proportional to $x_i^\alpha x_j^\beta$ with $i \neq j$, a normal-mode transformation would be required, and the operator analogous to $R(\vec{\nabla}) + A(\vec{\nabla})$ would connect averages $\langle f(\vec{x}_j) \rangle_0$ and $\langle f(\vec{x}_j, \vec{x}_k) \rangle_0$ that are not connected in the CPE. If three-particle functions $f(\vec{x}_i, \vec{x}_j, \vec{x}_k)$ were included in the product A_{Π} their Fourier transforms would be needed, and in analogy to the proof of Eq. (2.17) one would need transform variables \vec{s}_{ijk} with three subscripts. A diagrammatic representation of the expansion that results would require a new symbol to represent the average of a three-particle function.

point j to a bond between points j and l is associated with A_{jkl} . The pair of connected bonds will be referred to as an *angle*, and A_{jkl} will be called an *angle operator*. Since A_{jkl} only occurs in Eq. (2.21) with $k \neq l$ the free ends of the two bonds that form an angle must be at different points. The diagram in Fig. 1(b) contains one angle; it represents the term

$$\frac{k_B T \langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_i) \rangle_0 \cdot \vec{\mathbf{K}}_j^{-1} \cdot \langle \vec{\nabla}_j f(\vec{x}_j, \vec{x}_k) \rangle_0}{!! \langle f(\vec{x}_j, \vec{x}_i) \rangle_0 \langle f(\vec{x}_j, \vec{x}_k) \rangle_0} \quad (2.30)$$

Note that both gradient operators in each ray or angle operator operate on the same particle variable, which is the variable associated with the point where the connection occurs.

Consider the set \mathcal{D} of all distinct diagrams that can be drawn with $n_S \geq 0$ stars and $n_A \geq 0$ angles. That there is a one-to-one correspondence between the diagrams in \mathcal{D} and the terms in the CPE follows from the fact that the above descriptions of angles, stars, rays, connections, etc., suggests a prescription for associating a distinct diagram with each term and vice versa. For example, the term

III. CEM

A. True potential energy; lattice sites

We consider systems with a true potential energy of the form

$$\Phi = \sum_{\substack{i,j \\ i < j}} \phi_{ij}(|\vec{\mathbf{R}}_i + \vec{x}_i - \vec{\mathbf{R}}_j - \vec{x}_j|), \quad (3.1)$$

where $\vec{\mathbf{R}}_i$ is the position of the i th lattice site relative to a common origin. There is often a natural choice for the N vectors $\vec{\mathbf{R}}_i$, but in principle they are arbitrary. Presumably, this arbitrariness can be removed by requiring that

$$\vec{\Gamma}_i = \vec{0} \quad (3.2)$$

for all i . Note that to specify the point where the potential energy of the i th Einstein oscillator is at a minimum one must specify both $\vec{\mathbf{R}}_i$ and $\vec{\Gamma}_i$. It follows from Eq. (2.5) that requiring that $\vec{\Gamma}_i = \vec{0}$ is equivalent to requiring that $\vec{\mathbf{R}}_i$ be chosen so that the Einstein-oscillator value for the average displacements $\langle \vec{x}_i \rangle_0$ is zero.

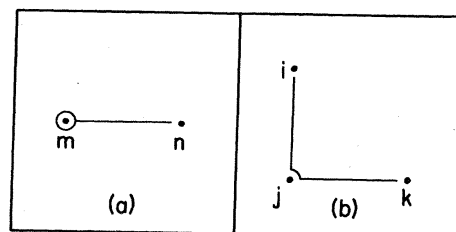


FIG. 1. Diagrams of first-order terms.

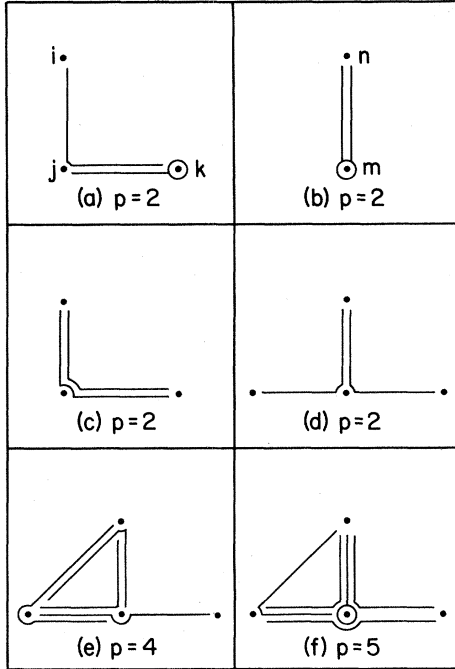


FIG. 2. Some diagrams of terms of order p that are zeroed by the zeroing conditions.

B. Choice of two-particle functions; free energy

The CEM expression for F is obtained by approximating the average on the right-hand side of Eq. (1.6) with the zeroth-order term in the CPE and choosing the constants \vec{K}_i and $\vec{\Gamma}_i$ in the Einstein potential Φ_0 so that all first- and second-order terms vanish. Since the true potential Φ appears in the exact expression for F , Eq. (1.3), the approximate potential Φ_0 must in a sense be “added in” and “subtracted out.”

Ideally, the subtracting out can be done entirely through the two-particle functions. To do so one must replace the single sum in Eq. (2.4) for Φ_0 by a double sum, which we do by expressing \vec{K}_i and $\vec{\Gamma}_i$ as sums of two-particle constants:

$$\vec{K}_i = \sum_j \vec{k}_{ij}, \quad (3.3)$$

$$\vec{\Gamma}_i = \sum_j \vec{\gamma}_{ij}. \quad (3.4)$$

Note that for generality the constants \vec{k}_{ii} and $\vec{\gamma}_{ii}$, which are one-particle constants, have been included. Ideally they will not be needed. By substituting Eqs. (3.3) and (3.4) into Eq. (2.4) for Φ_0 and rearranging terms, one obtains

$$\Phi_0 = \sum_{\substack{i,j \\ i < j}} \phi_{ij}^0 + \sum_k \psi_k, \quad (3.5)$$

where for $i < j$

$$\phi_{ij}^0 = \frac{1}{2} \vec{x}_i \cdot \vec{k}_{ij} \cdot \vec{x}_i + \frac{1}{2} \vec{x}_j \cdot \vec{k}_{ji} \cdot \vec{x}_j - \vec{\gamma}_{ij} \cdot \vec{x}_i - \vec{\gamma}_{ji} \cdot \vec{x}_j, \quad (3.6)$$

and where

$$\psi_i = \frac{1}{2} \vec{x}_i \cdot \vec{k}_{ii} \cdot \vec{x}_i - \vec{\gamma}_{ii} \cdot \vec{x}_i. \quad (3.7)$$

Equations (3.3) and (3.4) will be referred to as *self-consistency conditions*, since they must be satisfied for the subtracted-out potentials ϕ_{ij}^0 and ψ_i to exactly cancel the added-in potential Φ_0 that is implied by the angular brackets in Eqs. (1.6) and (1.2).

By substituting Eqs. (3.1) and (3.5) into Eq. (1.2) for the Helmholtz free energy, one obtains

$$F = F_0 - \beta^{-1} \ln \left\langle \prod_j e^{\beta \psi_j} \prod_{\substack{k,l \\ k < l}} e^{-\beta \Delta \phi_{kl}} \right\rangle_0, \quad (3.8)$$

where

$$\Delta \phi_{kl} = \phi_{kl}(\vec{R}_k + \vec{x}_k - \vec{R}_l - \vec{x}_l) - \phi_{kl}^0. \quad (3.9)$$

The average in Eq. (3.8) can be expanded in a CPE by letting

$$f(\vec{x}_j) = e^{\beta \psi_j} \quad (3.10)$$

and

$$f(\vec{x}_k, \vec{x}_l) = e^{-\beta \Delta \phi_{kl}}. \quad (3.11)$$

Then, by neglecting all terms in the CPE of order $p > 0$, one obtains

$$F = F_0 - \beta^{-1} \sum_j \ln \langle e^{\beta \psi_j} \rangle_0 - \beta^{-1} \sum_{\substack{k,l \\ k < l}} \ln \langle e^{-\beta \Delta \phi_{kl}} \rangle_0. \quad (3.12)$$

This is the basic formula for the free energy in the CEM. Note that if

$$\vec{k}_{ii} = \vec{0} \quad (3.13)$$

and

$$\vec{\gamma}_{ii} = \vec{0},$$

the one-particle quantities \vec{k}_{ii} , $\vec{\gamma}_{ii}$, ψ_j , $\langle \exp(\beta \psi_j) \rangle_0$, etc., would not need to be considered.

C. Zeroing conditions

The sums S_1 and S_2 in Eq. (2.25) contain all first- and second-order terms in the CPE. Most of the terms in S_1 and S_2 can be made to vanish by causing the following two-particle averages to vanish:

$$\langle \vec{\nabla}_i e^{-\beta \Delta \phi_{ij}} \rangle_0 = \vec{0}, \quad (3.14)$$

$$\langle \vec{\nabla}_i \vec{\nabla}_i e^{-\beta \Delta \phi_{ij}} \rangle_0 = \vec{0}. \quad (3.15)$$

Equations (3.14) and (3.15) will be referred to as *zeroing conditions*. They are to be satisfied both with $i < j$ and with $i > j$. Note that $\Delta \phi_{ij} = \Delta \phi_{ji}$; see Eq. (2.2). All of the gradients in the above operate on the variable \vec{x}_i and $\vec{\nabla}_i \vec{\nabla}_i$ is equivalent to $\partial^2 / \partial x_i^\alpha \partial x_i^\beta$.

The $N(N-1)$ vector conditions (3.14) and the $N(N-1)$ tensor conditions (3.15) are to be satisfied by the choice of the $N(N-1)$ vectors $\vec{\gamma}_{ij}$ and the $N(N-1)$ tensors \vec{k}_{ij} with $i \neq j$. Since the $\vec{\gamma}_{ij}$'s and \vec{k}_{ij} 's occur both ex-

licitly in $\Delta\phi_{ij}$ and implicitly in the averaging (because of the self-consistency conditions), satisfying the zeroing conditions is a problem of the familiar self-consistent type. The zeroing conditions are to be satisfied with the one-particle constants $\vec{\gamma}_{ii}$ and \vec{k}_{ii} as small as possible. Ideally Eqs. (3.13) can be satisfied, so that one-particle quantities are not needed.

If a diagram contains a single bond, that is, if there are two points i and j with exactly one bond between them, then the term in the CPE represented by the diagram contains either the factor $\langle \vec{\nabla}_i \exp(-\beta\Delta\phi_{ij}) \rangle_0$ or the factor $\langle \vec{\nabla}_j \exp(-\beta\Delta\phi_{ij}) \rangle_0$. Similarly, if a diagram contains a double bond between i and j and the free ends of both bonds are at point j , then the term represented contains the factor $\langle \vec{\nabla}_i \vec{\nabla}_j \exp(-\beta\Delta\phi_{ij}) \rangle_0$. Satisfying the zeroing conditions causes all such factors to vanish. Hence satisfying the zeroing conditions causes all terms to vanish that are represented either by a diagram with one or more single bonds or by a diagram with one or more double bonds with free ends at the same point.

For example, the diagrams in Figs. 1 and 2 represent terms that vanish when the zeroing conditions are satisfied. Also, any diagram that contains at least one cluster with either a single bond or a double bond with free ends at the same point represents a term that vanishes, and this is independent of the number or complexity of any other clusters in the diagram.

The diagrams in Fig. 3 represent some terms of low order that are not zeroed when conditions (3.14) and (3.15) are satisfied. The diagram in Fig. 3(a) represents the only type of terms of order $p=2$ or 1 that cannot be zeroed by the zeroing conditions. For the CEM approximation for F to be accurate through order $p=2$, all terms of the type represented by Fig. 3(a) must vanish for reasons other than the zeroing conditions. Such terms do vanish either when Eqs. (3.13) are satisfied or when

$$\vec{\gamma}_{ii} = \vec{\Gamma}_i = \vec{0}. \quad (3.16)$$

When Eqs. (3.13) are satisfied, one need not even consider diagrams with circles since they represent averages of one-particle functions. When Eqs. (3.16) are satisfied, the factors $\langle \vec{\nabla}_i \exp(\beta\psi_i) \rangle_0$ and $\langle \vec{\nabla}_j \exp(\beta\psi_j) \rangle_0$ represented by the circles in Fig. 3(a) vanish, since each factor reduces to the integral of an odd function over a symmetric interval [see Eq. (3.20)].

D. Phase-function averages

The macroscopic potential energy, the potential contribution to the pressure, and other properties of interest are given by averages of sums of two-particle phase functions. These averages have the form

$$\langle P_2 \rangle = \left\langle \sum_{\substack{m,n \\ m < n}} p_{mn}(\vec{x}_m, \vec{x}_n) \right\rangle, \quad (3.17)$$

where the averaging is done with the true potential energy Φ . When Φ_0 and Φ are given by Eqs. (3.5) and (3.1), it follows that

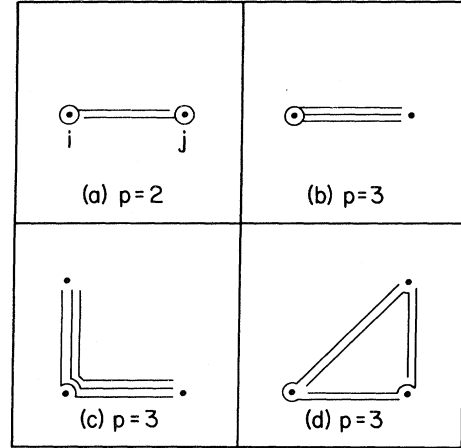


FIG. 3. Some diagrams of terms of order p that are not zeroed by the zeroing conditions.

$$\langle P_2 \rangle = \sum_{\substack{m,n \\ m < n}} \frac{\left\langle p_{mn} \prod_j e^{\beta\psi_j} \prod_{\substack{k,l \\ k < l}} e^{-\beta\Delta\phi_{kl}} \right\rangle_0}{\left\langle \prod_j e^{\beta\psi_j} \prod_{\substack{k,l \\ k < l}} e^{-\beta\Delta\phi_{kl}} \right\rangle_0}. \quad (3.18)$$

A CEM approximation for $\langle P_2 \rangle$ can be obtained by approximating the averages on the right-hand side of Eq. (3.18) with the zeroth-order term in a CPE and by choosing the constants \vec{k}_{ij} and $\vec{\gamma}_{ij}$ so that the self-consistency and zeroing conditions are satisfied. The zeroth-order term in the CPE approximates the average of a product by the product of the averages. When all averages that occur in both a numerator and denominator are cancelled, one obtains

$$\langle P_2 \rangle = \sum_{\substack{m,n \\ m < n}} \frac{\langle p_{mn} e^{-\beta\Delta\phi_{mn}} \rangle_0}{\langle e^{-\beta\Delta\phi_{mn}} \rangle_0}. \quad (3.19)$$

When Eqs. (3.13) are satisfied, so that one-particle quantities need not be considered, the above approximation is accurate through second order. Note that when approximating the average in Eq. (3.18) involving p_{mn} the zeroing conditions do not zero terms that are represented by diagrams with a single or double bond between the specific points m and n . Nevertheless, there is no way that one can draw a diagram with one or two angles (but no stars) that does not have at least a single or a double bond between points other than m and n . Because of these additional bonds, all first- and second-order terms vanish when Eqs. (3.13) are satisfied.

When one-particle terms are included, the CPE of Eq. (3.18) will contain terms of both first and second order that are not zeroed by the zeroing conditions. Examples of such terms are represented by the diagrams in Figs. 1(a) and 2(b). The difficulty is that the factors $\langle \vec{\nabla}_m p_{mn} \exp(-\beta\Delta\phi_{mn}) \rangle_0$ and $\langle \vec{\nabla}_m \vec{\nabla}_m p_{mn} \times \exp(-\beta\Delta\phi_{mn}) \rangle_0$ that are represented by the bonds in Figs. 1(a) and 2(b) are not zeroed by conditions (3.14) and

(3.15). (The same argument applies when the labels m and n are exchanged in the diagrams.) When Eqs. (3.16) are satisfied, all terms of the type represented by Fig. 1(a) will vanish, but some terms of the type represented by Fig. 2(b) will not vanish. Thus when Eqs. (3.16) are satisfied the CEM approximation for phase-function averages is only accurate through first order.

E. Explicit formulas

Since it greatly simplifies the formulas to be given, we assume here that the lattice sites have been chosen so that

$$\langle f(\vec{x}_i, \vec{x}_j) \rangle_0 = c_i c_j \int d^3 x_i \int d^3 x_j e^{-(\beta/2)(\vec{x}_i \cdot \vec{K}_i \cdot \vec{x}_i + \vec{x}_j \cdot \vec{K}_j \cdot \vec{x}_j)} f(\vec{x}_i, \vec{x}_j). \quad (3.22)$$

By performing an integration by parts, the zeroing condition given by Eq. (3.14) can be simplified as follows:

$$\begin{aligned} \langle \vec{\nabla}_i e^{-\beta \Delta \phi_{ij}} \rangle_0 &= -c_i c_j \int d^3 x_i \int d^3 x_j (\vec{\nabla}_i e^{-(\beta/2)(\vec{x}_i \cdot \vec{K}_i \cdot \vec{x}_i + \vec{x}_j \cdot \vec{K}_j \cdot \vec{x}_j)}) e^{-\beta \Delta \phi_{ij}} \\ &= \beta \vec{K}_i \cdot \langle \vec{x}_i e^{-\beta \Delta \phi_{ij}} \rangle_0 = \vec{0}. \end{aligned} \quad (3.23)$$

Since \vec{K}_i is assumed to have nonzero eigenvalues and since $\langle \exp(-\beta \nabla \phi_{ij}) \rangle_0$ is nonzero, this is equivalent to

$$\frac{\langle \vec{x}_i e^{-\beta \Delta \phi_{ij}} \rangle_0}{\langle e^{-\beta \Delta \phi_{ij}} \rangle_0} = \vec{0}. \quad (3.24)$$

If the assumption $\vec{\Gamma}_i = \vec{0}$ had not been made, the term on the right-hand side of Eq. (3.24) would have been $\vec{K}_i^{-1} \cdot \vec{\Gamma}_i$, which equals $\langle \vec{x}_i \rangle_0$.

The zeroing condition given by Eq. (3.15) can be simplified as follows:

$$\left\langle \frac{\partial^2}{\partial x_i^\alpha \partial x_j^\gamma} e^{-\beta \Delta \phi_{ij}} \right\rangle_0 = -\beta \langle [(\vec{K}_i)^\alpha \gamma - \beta (\vec{K}_i \cdot \vec{x}_i)^\alpha (\vec{K}_i \cdot \vec{x}_i)^\gamma] e^{-\beta \Delta \phi_{ij}} \rangle_0 = 0. \quad (3.25)$$

Multiplying by $(\vec{K}_i^{-1})^{\mu\alpha} (\vec{K}_i^{-1})^{\nu\gamma}$ and summing over α and γ , this can be rearranged as

$$\frac{\langle x_i^\mu x_j^\nu e^{-\beta \Delta \phi_{ij}} \rangle_0}{\langle e^{-\beta \Delta \phi_{ij}} \rangle_0} = \beta^{-1} (\vec{K}_i^{-1})^{\mu\nu}. \quad (3.26)$$

F. Interpretation of zeroing conditions

The zeroing conditions can be interpreted as a requirement that the Einstein oscillator values for the average and mean-square displacements of a particle equal the corresponding CEM values. The zeroing conditions, Eqs. (3.14) and (3.15), reduce to Eqs. (3.24) and (3.26), which can be rewritten with the aid of Eqs. (2.5) and (2.6) and $\vec{\Gamma}_i = 0$ as

$$\langle \vec{x}_i \rangle_0 = \frac{\langle \vec{x}_i e^{-\beta \Delta \phi_{ij}} \rangle_0}{\langle e^{-\beta \Delta \phi_{ij}} \rangle_0} \quad (3.27)$$

and

$$\langle x_i^\mu x_j^\nu \rangle_0 = \frac{\langle x_i^\mu x_j^\nu e^{-\beta \Delta \phi_{ij}} \rangle_0}{\langle e^{-\beta \Delta \phi_{ij}} \rangle_0}. \quad (3.28)$$

The modulated averages on the right-hand side of the above have the same form as the CEM approximation for

$\vec{\Gamma}_i = \vec{0}$ [see Eq. (3.2)]. It then follows from Eqs. (2.3) and (2.4) that the harmonic average of a general one-particle function is given by

$$\langle f(\vec{x}_i) \rangle_0 = c_i \int d^3 x_i e^{-(\beta/2) \vec{x}_i \cdot \vec{K}_i \cdot \vec{x}_i} f(\vec{x}_i), \quad (3.20)$$

where

$$c_i = [|\vec{K}_i| / (2\pi k_B T)^3]^{1/2} \quad (3.21)$$

and $|\vec{K}_i|$ is the determinant of \vec{K}_i . The harmonic average of a general two-particle function is given by

averages of two-particle phase functions. See Eq. (3.19). Although \vec{x}_i and $x_i^\mu x_j^\nu$ are one-particle functions, it is reasonable to interpret these averages as "CEM averages" or equivalently as averages "evaluated through second order in the CPE."

Since there are only two constants $\vec{\Gamma}_i$ and \vec{K}_i for each particle i in the Einstein potential Φ_0 , it may seem surprising that Eqs. (3.27) and (3.28) can be satisfied for every choice of i and j except $i=j$. The additional degrees of freedom that are needed come from the arbitrariness in the manner in which a sum of one-particle functions can be rewritten as a sum of two-particle functions.

G. Cubic monatomic crystals

So far the development of the CEM has only assumed that the system being studied is a solid. That is, that the probability of a particle migrating through the system is negligible, so that the particles can be associated with sites that are fixed in space. It has not been required either that the system has the symmetry of a crystal or that the particles are identical. Here we restrict ourselves to systems of identical particles whose average positions form a cubic Bravais lattice.

These restrictions allow one to assume that

$$\vec{\Gamma}_i = \vec{\gamma}_{ii} = \vec{0}, \quad (3.29)$$

$$\vec{\mathbf{K}}_i = K\vec{\mathbf{I}}, \quad (3.30)$$

and

$$\vec{\mathbf{k}}_{ii} = k\vec{\mathbf{I}}, \quad (3.31)$$

where $\vec{\mathbf{I}}$ is the unit tensor (matrix) and the constant K and k are the same for all particles. One can also assume that for $i \neq j$

$$\vec{\gamma}_{ij} = -\vec{\gamma}_{ji} = (0, 0, \gamma_{ij}) \quad (3.32)$$

and

$$\vec{\mathbf{k}}_{ij} = \vec{\mathbf{k}}_{ji} = \begin{pmatrix} k_{ij}^{xx} & 0 & 0 \\ 0 & k_{ij}^{yy} & 0 \\ 0 & 0 & k_{ij}^{zz} \end{pmatrix}, \quad (3.33)$$

where $k_{ij}^{xx} = k_{ij}^{yy} \neq k_{ij}^{zz}$ in the coordinate system with the z axis parallel to the lattice vector $\vec{\mathbf{R}}_i - \vec{\mathbf{R}}_j$.

The self-consistency condition (3.3) can be simplified by taking the trace, which gives

$$K = k + \frac{1}{3} \sum_{\substack{j \\ j \neq i}} (2k_{ij}^{xx} + k_{ij}^{zz}). \quad (3.34)$$

The self-consistency condition (3.4) is automatically satisfied by assumptions (3.29) and (3.32).

The zeroing conditions (3.23) and (3.25) can be simplified by changing variables from $\vec{\mathbf{x}}_i$ and $\vec{\mathbf{x}}_j$ to $\vec{\mathbf{t}}$ and $\vec{\mathbf{r}}$, where

$$\vec{\mathbf{t}} = (\vec{\mathbf{x}}_i + \vec{\mathbf{x}}_j)/2 \quad (3.35)$$

and

$$\vec{\mathbf{r}} = \vec{\mathbf{x}}_i - \vec{\mathbf{x}}_j, \quad (3.36)$$

and then performing the $\vec{\mathbf{t}}$ integration. This gives

$$\int d^3r \vec{\mathbf{r}} e^{-\beta\phi(\rho)} e^{-\beta[(1/4)\vec{\mathbf{r}} \cdot \vec{\mathbf{K}}_{ij} \cdot \vec{\mathbf{r}} + \vec{\gamma}_{ij} \cdot \vec{\mathbf{r}}]} = \vec{0} \quad (3.37)$$

and

$$\int d^3r [(2/K)\delta^{\alpha\gamma} - (\vec{\mathbf{K}}_{ij}^{-1})^{\alpha\gamma} - (\beta/2)r^\alpha r^\gamma] \times e^{-\beta\phi(\rho)} e^{-\beta[(1/4)\vec{\mathbf{r}} \cdot \vec{\mathbf{K}}_{ij} \cdot \vec{\mathbf{r}} + \vec{\gamma}_{ij} \cdot \vec{\mathbf{r}}]} = 0, \quad (3.38)$$

where

$$\vec{\mathbf{K}}_{ij} = \vec{\mathbf{K}}_i - \vec{\mathbf{k}}_{ij} \quad (3.39)$$

and

$$\rho = |\vec{\mathbf{R}}_i - \vec{\mathbf{R}}_j + \vec{\mathbf{r}}|. \quad (3.40)$$

The two-particle averages needed in Eq. (3.12) are given by

$$\langle e^{-\beta\Delta\phi_{ij}} \rangle_0 = \left[\frac{\beta}{4\pi} \right]^{3/2} \frac{K^3}{K_{ij}^{xx} [K_{ij}^{zz}]^{1/2}} \times \int d^3r e^{-\beta\phi(\rho)} e^{-\beta[(1/4)\vec{\mathbf{r}} \cdot \vec{\mathbf{K}}_{ij} \cdot \vec{\mathbf{r}} + \vec{\gamma}_{ij} \cdot \vec{\mathbf{r}}]}, \quad (3.41)$$

where

$$K_{ij}^{xx} = K - k_{ij}^{xx}, \quad (3.42)$$

and

$$K_{ij}^{zz} = K - k_{ij}^{zz}. \quad (3.43)$$

Note that only three-dimensional integrals need to be evaluated. For a fcc crystal with interactions between nearest neighbors only, Eqs. (3.37) and (3.38) need to be satisfied for only one bond, because of the high symmetry of the structure. Also, Eq. (3.41) needs to be evaluated only once. In the Appendix Eqs. (3.37), (3.38), and (3.41) are expressed in terms of one-dimensional integrals.

When the crystal is not cubic and monatomic, a transformation more complicated than Eqs. (3.35) and (3.36) is needed to reduce the averages to three-dimensional integrals. Nevertheless, the possibility of reducing the integrals requiring numerical integration to three-dimensional integrals depends on the fact that each average associated with the bond between i and j contains a product of a polynomial, a Gaussian, and a general function of $\vec{\mathbf{r}} = \vec{\mathbf{x}}_i - \vec{\mathbf{x}}_j$. With two-particle potentials this will be true for terms of all orders in the CPE.

IV. NUMERICAL TESTS

The CEM was tested by comparing the predictions it makes with MC results for two different systems. Presumably, the MC results are exact except for statistical errors. The numerical procedures used to obtain the CEM values in Tables I and II have been sufficiently tested so that we are confident they are accurate through the number of significant figures given.

A. Lennard-Jones potential

We first considered a model for a fcc crystal in which a Lennard-Jones potential acts between nearest neighbors only. The true two-particle potential is

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (4.1)$$

It was found that the self-consistency and zeroing conditions could be satisfied with $\vec{\mathbf{k}}_{ii} = \vec{0}$ and $\vec{\gamma}_{ii} = \vec{0}$ [see Eq. (3.13)], so that one-particle quantities need not be considered. [$\vec{\mathbf{k}}_{ii} = \vec{0}$ implies that $k = 0$ in Eq. (3.32).]

Predictions for the pressure P , the average potential energy $\langle \Phi \rangle = U - \frac{3}{2}Nk_B T$, the constant volume heat capacity C_V , the isothermal bulk modulus B_T , the linear coefficient of thermal expansion α , and the Grüneisen parameter $\gamma = 3\alpha B_T B / C_V$ were obtained by numerically differentiating the free energy F as given by Eq. (3.12). P and $\langle \Phi \rangle$ were also obtained by using Eq. (3.19) and the appropriate two-particle phase functions. The values of P and $\langle \Phi \rangle$ obtained by the two methods are equal to the number of significant figures given in the table.

The results for the temperature $T = 0.48265\epsilon/k_B$ and lattice constant $a = 1.65169\sigma$ are given in Table I. A model for solid xenon is obtained by setting $\epsilon/k_B = 331.5$ K and $\sigma = 3.847$ Å. With these values the above tempera-

TABLE I. Results for a Lennard-Jones potential at $T=0.48265 \epsilon/k_B$ and $a=1.65169\sigma$.

	CEM	UPA	CCM	CM	ISC	MC
$\langle \Phi \rangle / Nk_B T$	-10.528		-10.607	-10.621		-10.583 ± 0.003 ^a -10.59 ± 0.01 ^b
$PV / Nk_B T$	0.383	0.701	0.390	0.655		0.402 ± 0.015 ^a 0.358 ± 0.02 ^b
C_v / Nk_B	2.782 (4.2%) (0.1%)	2.791 (4.5%) (0.4%)	2.646 (-0.9%) (-4.8%)	2.621 (-1.8%) (-5.7%)	2.62 (-1.9%) (-5.8%)	2.67 ± 0.03 ^a 2.78 ± 0.05 ^b
$B_T V / Nk_B T$	42.31 (-2.1%) (7.3%)	40.69 (-5.9%) (3.2%)	~38.7 (-10.5%) (-1.9%)		41.0 (-5.2%) (4.0%)	43.24 ± 0.99 ^a 39.43 ^b
γ	2.806 (-1.5%) (-5.5%)	2.978 (4.5%) (0.3%)	2.876(0.9%) (3.2%)	3.001 (5.3%) (1.0%)	2.70 (-5.3%) (-9.1%)	2.85 ± 0.03 ^a 2.97 ± 0.05 ^b
$3\alpha T$	0.1845 (4.8%) (-11.7%)	0.2042 (16.0%) (-2.3%)			0.173 (-1.7%) (-17.2%)	0.176 ^a 0.209 ^b

^aCowley, in Ref. 5.^bKlein, in Ref. 6.

ture and lattice constant become 160 K and 6.35406 Å, respectively. The experimental melting temperature of xenon is 161 K.

Also included in Table I are the predictions of the UPA obtained by Hardy and Jones,² the predictions of the CCM, and the CM obtained by Westera and Cowley,³ the predictions of improved self-consistent phonon theory (ISC) obtained by Goldman, Horton, and Klein,⁴ and the MC predictions of Cowley⁵ and of Klein and Hoover.⁶ The percentages given indicate the difference between the various approximate values and the MC value given on the same line in the table. The recent results of Cowley are likely to be the more accurate of the two sets of MC values. The information in the table does not indicate that any one of the approximations is strongly superior to the others, although it could be argued that the CCM, UPA, and CEM values are slightly more accurate than the CM and ISC values.

B. Soft-core potential

For our second test we compared the predictions of the CEM with the high-quality MC results of Hoover *et al.*⁷ for a fcc crystal with the soft-core potential given by

$$\phi(r) = \epsilon \left(\frac{\sigma}{r} \right)^{12}. \quad (4.2)$$

In principle this interaction extends to all neighbors, but it is only significant for near neighbors. The CEM values for $PV/Nk_B T$ that are given in Table II were obtained by numerically differentiating the free energy F . The significance of the dimensionless parameter $(\sigma/R_0)^3(\epsilon/k_B T)^{1/4}$ is discussed in Ref. 7.

For the soft-core potential the self-consistency and zeroing conditions could not be satisfied with $\vec{\gamma}_{ii} = 0$ and $\vec{k}_{ii} = 0$, so that one-particle terms had to be included in Eq. (3.12) for F . The values of $\vec{\gamma}_{ij}$ and \vec{k}_{ij} were determined by satisfying the self-consistency and zeroing conditions with $\vec{\gamma}_{ii} = \vec{\Gamma}_i = 0$ and with the ratio

$$\left| \frac{k}{K-k} \right| \quad (4.3)$$

minimized. The constants K and k are defined by Eqs. (3.28) and (3.29). It was found that only pairs of particles up through third neighbors had to be treated exactly in order to obtain predictions that are accurate to the number of significant figures given.

TABLE II. Results for $PV/Nk_B T$ for a soft-core potential. R_0 is the nearest-neighbor distance.

$(\sigma/R_0)^3(\epsilon/k_B T)^{1/4}$	CEM	correlated cell	CM	MC
0.74	13.47 (-3.2%)			13.91
0.80	16.32 (-1.2%)	16.53 (0.1%)	16.12 (-2.4%)	16.51
0.844				Melting
0.90	22.52 (-0.1%)	22.56	22.34 (-0.9%)	22.55
1.00	31.01 (0.1%)	30.98	30.85 (-0.5%)	30.99
1.20	57.21 (0.1%)	57.15	57.09 (-0.1%)	57.16

We also calculated $PV/Nk_B T$ with the aid of Eq. (3.19) and the appropriate two-particle phase function. The results obtained were significantly less accurate than those obtained by differentiating F . This is not surprising since the phase-function approach is only good through first order when one-particle terms are included (see Sec. III D).

The results in the table indicate that the CEM gives accurate predictions up to and beyond the melting temperature (where the crystal phase becomes metastable) and that its accuracy improves as the temperature decreases. The simple cell-model values and the *correlated-cell* values in Table II are those of Hoover *et al.*⁷ The CEM values are slightly more accurate than the cell-model values and slightly less accurate than the correlated-cell values.

V. DISCUSSION

The comparison with MC results in Sec. IV indicates that accurate predictions of the equilibrium properties of solids at temperatures up through the melting point can be obtained with the CEM. The comparison is purely classical. It should be possible to account for quantum effects at intermediate temperatures by using an expansion in powers of \hbar .⁸ Nevertheless, the CEM cannot be expected to be accurate at the low temperatures where the vibrational behavior of solids is dominated by the long-wavelength acoustic modes.

The data in Table I do not indicate that any of the five approximations considered is strongly superior to the others. However, all five are much more accurate at high temperatures than either the quasiharmonic approximation with or without perturbation-theory corrections or the self-consistent phonon approximation without the corrections included in ISC. An idea of the error that results when these latter approximations are used can be seen in the work of Klein, Goldman, and Horton.⁹

The advantage of the CEM over the UPA, the CCM, and ISC is its relative simplicity. Unlike the UPA and ISC, the CEM does not require a transformation to normal coordinates. Such transformations lead to involved computations for complex solids, but they do make it possible to treat low-temperature quantum effects correctly. Also, with the CEM and two-particle potentials, integrals of no more than three dimensions need to be evaluated numerically. The six-dimensional real-space integrals of the CCM and the complex \vec{k} -space integrations of ISC are avoided.

Besides greater accuracy, the advantage of the CEM over the cell model is that corrections to it are simpler. For example, the CCM is a cell model plus low-order corrections obtained with an Ursell-Mayer-type cluster expansion. The difficulty with such expansions is that increasing the size of the clusters considered increases the dimensionality of the integrals to be evaluated. With the CEM and two-particle potentials, integrals of only three dimensions are needed independent of the order of the corrections.

It should be mentioned, however, that if higher-order terms are to be added to the CEM, the logarithm of the quantity on the right-hand side of Eq. (1.1) should be expanded in powers of λ , not the quantity itself. This allows

problems with the N dependence of the added terms to be avoided.

The CEM values in Table II are slightly less accurate than the correlated-cell values of Hoover *et al.*⁷ However, to the best of our knowledge the approximation used to obtain these values has not been developed into a generally applicable method with known expressions for higher-order corrections.

Finally, the work of Fixman¹⁰ and of Cowley and Barker¹¹ should be mentioned. Both of these papers, like the present one, use approximations involving the self-consistent determination of parameters in a theory that emphasizes particle coordinates, not normal-mode coordinates.

APPENDIX

The integrals in Sec. III G can be reduced to one-dimensional integrals by changing to the spherical coordinates

$$\vec{R} + \vec{r} = \vec{\rho} = (\rho, \theta, \phi), \quad (\text{A1})$$

where $\vec{R} = \vec{R}_i - \vec{R}_j$. After performing the angle integrations, Eq. (3.37) reduces to

$$\int_0^\infty d\rho \rho e^{-\beta I(\rho)} (2\rho Q_1^s - R Q_0^s) = 0, \quad (\text{A2})$$

where $R = |\vec{R}|$ and

$$I(\rho) = \phi(\rho) + \frac{1}{4} K_{ij}^{zz} (\rho - R)^2 + \gamma_{ij} (\rho - R). \quad (\text{A3})$$

The functions $Q_n^s(\rho)$ are defined by

$$Q_n^s = \frac{e^{-s(\bar{y} + s\Delta y/2)^2}}{(\Delta y)^n} \int_{s\bar{y} - \Delta y/2}^{s\bar{y} + \Delta y/2} dy (y - s\bar{y})^n e^{+sy^2}, \quad (\text{A4})$$

where $n = 0, 1, \text{ or } 2$ and

$$s = \begin{cases} +1 & \text{if } k_{ij}^{zz} > k_{ij}^{xx}, \\ -1 & \text{if } k_{ij}^{zz} < k_{ij}^{xx}, \end{cases} \quad (\text{A5})$$

$$\bar{y} = \left[\frac{\beta}{|K_{ij}^{zz} - K_{ij}^{xx}|} \right]^{1/2} \left(\frac{1}{2} K_{ij}^{zz} R - \gamma_{ij} \right), \quad (\text{A6})$$

and

$$\Delta y = (\beta |K_{ij}^{zz} - K_{ij}^{xx}|)^{1/2} \rho. \quad (\text{A7})$$

The Q_n^s is related to Dawson's integral when $s = +1$ and to the error function when $s = -1$. On many computers Dawson's integral and the error function are internal subroutines.¹²

Similarly, Eq. (3.38) reduces to the following two equations:

$$\int_0^\infty d\rho \rho e^{-\beta I(\rho)} \left[\left[\frac{2}{K} - \frac{1}{K_{ij}^{xx}} - \frac{\beta}{4} \rho^2 \right] Q_0^s + \beta \rho^2 Q_2^s \right] = 0 \quad (\text{A8})$$

and

$$\int_0^\infty d\rho \rho e^{-\beta I(\rho)} \left[\left[\frac{2}{K} - \frac{1}{K_{ij}^{zz}} - \frac{\beta}{2} R^2 \right] Q_0^s + 2\beta \rho (R Q_1^s - \rho Q_2^s) \right] = 0. \quad (\text{A9})$$

Equation (3.41) reduces to

$$\langle e^{-\beta \Delta \phi_{ij}} \rangle_0 = \frac{\beta K^3}{2K_{ij}^{xx}} \frac{1}{(\pi K_{ij}^{zz} | K_{ij}^{zz} - K_{ij}^{xx} |)^{1/2}} \times \int_0^\infty d\rho \rho e^{-\beta I(\rho)} Q_0^s. \quad (\text{A10})$$

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