Uncorrelated-pairs approximation for the free energy of a crystal

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An approximation for estimating the anharmonic contributions to the Helmholtz free energy F is derived as the lowest-order part of an expansion of F in powers of the harmonic pair-pair displacement correlation function. Readily evaluated formulas that are applicable to a perfect monoatomic crystal with periodic boundary conditions are given. When applied to the special case of a linear chain with nearest-neighbor interactions, these formulas become exact. The relationship of the theory developed to the cumulant expansion for F, to perturbation theory, and to self-consistent phonon theory is discussed.

I. INTRODUCTION

The equilibrium thermodynamic properties of a system can be determined from the Hamiltonian describing its microscopic structure with the aid of the partition-function formula for the Helmholtz free energy

$$F = -kT \ln Z. \tag{1.1}$$

Classically the partition function for a three-dimensional system of N particles is

$$Z = \int d^{3N}p \int d^{3N}q\, e^{-\beta H}, \tag{1.2}$$

where $\beta = 1/kT$. It will be assumed here that the Hamiltonian can be written

$$H = H_0 + \sum_p V_p, \tag{1.3}$$

where H_0 is a harmonic Hamiltonian and $H - H_0$ is a sum over all pairs of the anharmonic part of the potential energies of interaction for different pairs of particles. When H is of this form, the free energy can be written

$$F = F_0 - kT \ln \left\langle \prod_p e^{-\beta V_p} \right\rangle_0, \tag{1.4}$$

where

$$F_0 = -kT \ln Z_0. \tag{1.5}$$

Z_0 is the partition function formed with H_0 and the brackets indicate a harmonic average

$$\langle Q \rangle_0 = \int d^{3N}p \int d^{3N}q\, \frac{e^{-\beta H_0}}{Z_0} Q. \tag{1.6}$$

Equation (1.4) is exact. The main interest here will be with approximations to Eq. (1.4) where the average of the product is approximated by the product of averages:

$$-\frac{F - F_0}{kT} \approx \ln \prod_p \langle e^{-\beta V_p} \rangle_0 = \sum_p \ln \langle e^{-\beta V_p} \rangle_0. \tag{1.7}$$

Such approximations will be referred to as uncorrelated-pairs approximations (UPA).

To determine the validity of such approximations, two correlated-pairs expansions are derived in Sec. II. When applied to Eq. (1.4), the zeroth-order terms in these expansions give the UPA. The relative sizes of successive terms in the expansions are determined by the sizes of the harmonic pair-pair displacement correlation functions $\tilde{\Lambda}_{pp'}$. It is shown that in the case of a perfect monatomic lattice with periodic boundary conditions there are no contributions to F that depend linearly on the $\tilde{\Lambda}_{pp'}$, so that the UPA is accurate through first order. The relatively simple formulas for calculating the free energy in the UPA in this case are summarized in Sec. III.

It is shown in Sec. IV that, when applied to a linear chain with nearest-neighbor interactions only, the UPA yields Takahashi's exact solution for the free energy.[1] The relationship of the UPA to perturbation theory[2,3] and to self-consistent phonon theory[2,4,5] is discussed, and it is shown how the cumulant expansion[5,6] through second order can be obtained as an approximation to the second type of correlated-pairs expansion.

The UPA includes contributions from V_p, the anharmonic part of the pair potential, to all orders; it neglects the contribution of correlations in the anharmonic part of F. For comparison, self-consistent phonon theory in lowest order utilizes an optimized choice for the harmonic Hamiltonian, but includes explicit contributions to F through only first order in V_p. Actually, only contributions from "even" terms in the series representation of V_p are included. Perturbation theory and the so-called improved self-consistent phonon approximation[2,7] include explicit contributions from the cubic terms in the series representation of V_p through second order, and include the contribution to F of the correlations associated with these particular anharmonic terms. The Lennard-Jones Devonshire cell model[2,8] includes contributions from V_p to all orders, but neglects the contribution of correlations to the harmonic

part of F, as well as to the anharmonic part.

The accuracy of the UPA can be expected to depend on the temperatures and pressures being considered, the materials being studied, and the accuracy being sought. As a test of the UPA, it has been used to predict values for the specific heat, thermal expansion, bulk modulus, etc., for a simple model of solid Xe.[9] Temperatures near melting and pressures near zero were considered. The predictions obtained agree with the results of the Monte Carlo calculations of Klein and Hoover[10] to an amount that is of the order of (or less than) the statistical uncertainty in the Monte Carlo results. The agreement obtained with the Monte Carlo results appears to be generally better than that obtained with the improved self-consistent phonon approximation. Although statistical in nature, Monte Carlo results neglect neither correlations nor higher-order anharmonicity.

The theory presented is based on classical statistical mechanics, so that strictly speaking its validity is limited to high temperatures. However, by evaluating F_0 quantum mechanically and using the (classical) UPA to determine $F - F_0$, one should also be able to predict the low- and intermediate-temperature properties of the many crystals in which quantum effects are insignificant at the temperatures at which anharmonic effects are important.

II. CORRELATED-PAIRS EXPANSIONS

A. Notation

Let $\vec{q}_{\vec{A}}$ designate the displacement of particle $\vec{A}$ relative to its reference position, and let the vector $\vec{A}$ both identify the particles and specify their reference positions relative to the origin of the coordinate system. Let the pair-displacement $\vec{q}_p$ be the difference between the particle displacements $\vec{q}_{\vec{A}}$ and $\vec{q}_{\vec{A}'}$ of the pair of particles labeled by p; that is,

$$\vec{q}_p = \vec{q}_{\vec{A}'} - \vec{q}_{\vec{A}}. \tag{2.1}$$

Consider a system with N particles so that there are

$$M = \tfrac{1}{2}N(N-1) \tag{2.2}$$

different pairs. Sums (or products) over the sets $\{\vec{A}\}$, $\{\vec{A}'\}$, etc., are sums (or products) of N quantities, while sums (or products) over the sets $\{p\}$, $\{p'\}$, etc., are sums (or products) of M quantities.

B. A useful result

Consider harmonic averages of products of functions of the individual pair displacments $\vec{q}_p$. By using the properties of the Dirac δ function and the representation for it that arises from the theory of Fourier transforms, one can show that

$$\begin{aligned}\left\langle \prod_p f_p(\vec{q}_p) \right\rangle_0 &= \left\langle \prod_p \int d^3y_p\, \delta(\vec{q}_p - \vec{y}_p) f_p(\vec{y}_p) \right\rangle_0 \\ &= \left\langle \prod_p \int d^3y_p \left((2\pi)^{-3} \int d^3s_p e^{i\vec{s}_p\cdot(\vec{q}_p - \vec{y}_p)} \right) f_p(\vec{y}_p) \right\rangle_0 \\ &= \int d^{3M}s \left\langle \prod_p e^{i\vec{s}_p\cdot\vec{q}_p} \right\rangle_0 \left(\prod_p (2\pi)^{-3} \int d^3y_p e^{-i\vec{s}_p\cdot\vec{y}_p} f_p(\vec{y}_p) \right),\end{aligned} \tag{2.3}$$

where the fact that only the pair displacements $\vec{q}_p$ are affected by the averaging has been used. Note that the symbols $\prod$ indicate products of only those subscripted quantities that are contained within the same brackets.

The exponential averaging theorem, which is crucial to the theory of the Debye-Waller factor, states that[11]

$$\langle e^{iL} \rangle_0 = e^{-(1/2)\langle L^2 \rangle_0}, \tag{2.4}$$

where L is any real linear function of the normal coordinates of the harmonic Hamiltonian H_0. Since the pair displacements $\vec{q}_p$ are linear functions of the particle displacements $\vec{q}_{\vec{A}}$, which are linearly related to the normal coordinates, it follows that

$$\begin{aligned}\left\langle \prod_p e^{i\vec{s}_p\cdot\vec{q}_p} \right\rangle_0 &= \left\langle \exp\left(i \sum_p \vec{s}_p \cdot \vec{q}_p \right) \right\rangle_0 \\ &= \exp\left(-\frac{1}{2} \sum_{pp'} \vec{s}_p \cdot \vec{\Lambda}_{pp'} \cdot \vec{s}_{p'} \right) \\ &= \exp\left(-\frac{1}{2} \sum_{pp'}{}' \vec{s}_p \cdot \vec{\Lambda}_{pp'} \cdot \vec{s}_{p'} \right) \\ &\quad \times \left(\prod_p e^{-(1/2)\vec{s}_p\cdot\vec{\Lambda}_p\cdot\vec{s}_p} \right),\end{aligned} \tag{2.5}$$

where the prime on the sum indicates that terms with $p = p'$ are excluded. The harmonic pair-pair displacement correlation function for pairs p and p' is given by the second rank tensor

$$\vec{\Lambda}_{pp'} = \langle \vec{q}_p \vec{q}_{p'} \rangle_0. \tag{2.6}$$

The harmonic pair-displacement autocorrelation function is

$$\vec{\Lambda}_p = \vec{\Lambda}_{pp} = \langle \vec{q}_p \vec{q}_p \rangle_0 . \tag{2.7}$$

By using Eq. (2.5) in Eq. (2.3) and

$$\vec{S} = -i\nabla e^{i\vec{s}\cdot\vec{x}}\big|_{\vec{x}=0}, \tag{2.8}$$

one obtains the following useful result:

$$\left\langle \prod_p f_p \right\rangle_0 = \int d^{3M}s \exp\left(-\frac{1}{2}\sum_{pp'}{}' \vec{s}_p \cdot \vec{\Lambda}_{pp'} \cdot \vec{s}_{p'}\right)\left(\prod_p (2\pi)^{-3} \int d^3y_p\, e^{-(1/2)\vec{s}_p\cdot\vec{\Lambda}_p\cdot\vec{s}_p}\, e^{-i\vec{s}_p\cdot\vec{y}_p} f_p(\vec{y}_p)\right)$$

$$= \exp\left(\frac{1}{2}\sum_{pp'}{}' W_{pp'}\right)\left(\prod_p \langle f_p \rangle_{\vec{x}(p)}\right)\Big|_{\vec{x}=0} . \tag{2.9}$$

Here, the dependence of f_p on the variables affected by the averaging is not explicitly indicated. The operator $W_{pp'}$ is

$$W_{pp'} = \nabla_p \cdot \vec{\Lambda}_{pp'} \cdot \nabla_{p'} , \tag{2.10}$$

where ∇_p indicates a differentiation with respect to $\vec{x}(p)$ and similarly for $\nabla_{p'}$. The $\vec{x}=0$ at the end of Eq. (2.9) indicates that the variables $\vec{x}(p)$ for all pairs are to be set to zero after the indicated differentiations have been carried out. $\vec{x}(p)$ is the independent variable of the function

$$\langle f_p \rangle_{\vec{x}(p)} = (2\pi)^{-3} \int d^3y_p \int d^3s_p\, e^{-(1/2)\vec{s}_p\cdot\vec{\Lambda}_p\cdot\vec{s}_p}\, e^{-i\vec{s}_p\cdot[\vec{y}_p - \vec{x}(p)]} f_p(\vec{y}_p)$$

$$= \int d^3y_p\, P_0(\vec{y}_p - \vec{x}(p))\, f_p(\vec{y}_p)$$

$$= \int d^3q_p\, P_0(\vec{q}_p)\, f_p(\vec{q}_p + \vec{x}(p)). \tag{2.11}$$

$P_0(\vec{q}_p)$ is the harmonic probability density for the pair displacement $\vec{q}_p$

$$P_0(\vec{q}_p) = (8\pi^3 \det\Lambda_p)^{-1/2} \exp(-\tfrac{1}{2}\vec{q}_p \cdot \vec{\Lambda}_p^{-1} \cdot \vec{q}_p). \tag{2.12}$$

$\vec{\Lambda}_{pp'}^{-1}$ is the matrix inverse of $\vec{\Lambda}_{pp'}$, and $\det\Lambda_{pp'}$ is the determinant of $\vec{\Lambda}_{pp'}$.

Note that $\langle f_p \rangle_{\vec{x}(p)}$ reduces to the equilibrium average $\langle f_p \rangle_0$ when $\vec{x}(p)=0$, as is suggested by the notation. Both the operator $W_{pp'}$ and the smeared functions $\langle f_p \rangle_{\vec{x}(p)}$ have been used by Choquard,[5] who also discusses expansions that are similar in some aspects to those derived below (see his[5] Sec. 4.4).

C. Expansions

The *first type of correlated pairs expansion* is a cumulant type of expansion.[6] It can be obtained by expanding the exact result, Eq. (2.9), in powers of an artificially introduced parameter λ as follows:

$$\ln\left\langle \prod_p f_p \right\rangle_0 = \ln\left[\exp\left(\frac{1}{2}\lambda \sum_{pp'}{}' W_{pp'}\right)\left(\prod_p \langle f_p \rangle_{\vec{x}(p)}\right)\right]\Big|_{\substack{\lambda=1 \\ \vec{x}=0}}$$

$$= \left[\ln\left(\prod_p \langle f_p \rangle_{\vec{x}(p)}\right) + \left(\prod_p \langle f_p \rangle_{\vec{x}(p)}\right)^{-1}\left(\frac{1}{2}\sum_{pp'}{}' W_{pp'}\right)\left(\prod_p \langle f_p \rangle_{\vec{x}(p)}\right) + \cdots\right]\Big|_{\vec{x}=0}$$

$$= \sum_p \ln\langle f_p \rangle_0 + \frac{1}{2}\sum_{pp'}{}' (\nabla_p \ln\langle f_p \rangle_{\vec{x}(p)}) \cdot \vec{\Lambda}_{pp'} \cdot (\nabla_{p'} \ln\langle f_{p'} \rangle_{\vec{x}(p')})\,|_{\vec{x}=0} + \cdots . \tag{2.13}$$

The primes on the sums indicate that terms with $p=p'$ are excluded.

Another way to proceed is to expand in powers of $(e^W - 1)$, a procedure that is suggested by the Ursell-Mayer cluster expansion.[12] It is convenient to first replace the sum over all pairs of pairs with a sum over all distinct pairs of pairs. If one lets the pair index p take on all integer values from 1 through M, one has

$$\exp\left(\frac{1}{2}\sum_{pp'}{}' W_{pp'}\right) = \exp\left(\sum_{p>p'} W_{pp'}\right) = \prod_{p>p'} e^{W_{pp'}} . \tag{2.14}$$

By using this and expanding in powers of an artificially introduced parameter λ, one obtains the *second type of correlated-pairs expansion*

$$\ln\left\langle \prod_p f_p \right\rangle_0 = \ln\left[\left(\prod_{p>p'} [\lambda(e^{W_{pp'}}-1)+1]\right)\left(\prod_p \langle f_p\rangle_{\vec{x}(p)}\right)\right]\Big|_{\substack{\lambda=1\\ \vec{x}=0}}$$

$$= \sum_p \ln\langle f_p\rangle_0 + \sum_{p>p'} (\langle f_p\rangle_0\langle f_{p'}\rangle_0)^{-1}(e^{W_{pp'}}-1)\langle f_p\rangle_{\vec{x}(p)}\langle f_{p'}\rangle_{\vec{x}(p')}\Big|_{\vec{x}=0} + \cdots . \tag{2.15}$$

Here, all factors of $\langle f_p\rangle_0$ that are common to both the numerator and denominator have been cancelled.

III. UNCORRELATED-PAIRS APPROXIMATION

A. Hamiltonian

Consider a perfect monatomic lattice with periodic boundary conditions, so that the mass m is the same for all particles (i.e., is independent of $\vec{A}$) and the vectors $\vec{A}$ can be considered to be lattice translation vectors. One can then specify a pair of particles p by giving two vectors $\vec{A}, \vec{B}$, where the first vector identifies one of the particles and the second vector gives the lattice translation vector from it to the other particle. That is, let

$$\vec{q}_p = \vec{q}_{\vec{A}\vec{B}} = \vec{q}_{\vec{A}+\vec{B}} - \vec{q}_{\vec{A}} . \tag{3.1}$$

With this notation, a sum over the set $\{p\}$ is such that

$$\sum_p = \sum_{\vec{A}\vec{B}\,(B_x>0)} = \frac{1}{2}\sum_{\vec{A}\vec{B}}' , \tag{3.2}$$

and similarly for a product. The restriction $B_x>0$ suggests one way to avoid a double counting of the pairs, the factor of $\frac{1}{2}$ is to correct for a double counting, and the prime indicates that $\vec{B}=0$ is excluded from the sum (or product).

Consider Hamiltonians of the form

$$H = H(\Gamma) = H_0 + \frac{1}{2}\sum_{\vec{A}\vec{B}}' V_{\vec{A}\vec{B}}(\Gamma), \tag{3.3}$$

where

$$H_0 = \frac{1}{2m}\sum_{\vec{A}} |\vec{P}_{\vec{A}}|^2 + \frac{1}{4}\sum_{\vec{A}\vec{B}}' \vec{q}_{\vec{A}\vec{B}} \cdot \vec{\phi}_{\vec{B}} \cdot \vec{q}_{\vec{A}\vec{B}} \tag{3.4}$$

and

$$V_p = V_{\vec{A}\vec{B}}(\Gamma) = \phi(|\vec{B}+\vec{q}_{\vec{A}\vec{B}}|) - \tfrac{1}{2}\vec{q}_{\vec{A}\vec{B}} \cdot \vec{\phi}_{\vec{B}} \cdot \vec{q}_{\vec{A}\vec{B}} + \vec{\Gamma}_{\vec{B}} \cdot \vec{q}_{\vec{A}\vec{B}} . \tag{3.5}$$

Here, $\phi(r)$ is the potential energy of interaction of a pair of particles a distance r apart. The force constants $\vec{\phi}_{\vec{B}}$ determine the quadratic contribution to the potential energy, which is subtracted from the pair potentials to form the harmonic Hamiltonian H_0.

B. Constants $\vec{\Gamma}_{\vec{B}}$

As is shown below, the Hamiltonian $H(\Gamma)$ and the exact value for F predicted by it are independent of the constant vectors $\vec{\Gamma}_{\vec{B}}$, and the exact average of the $\vec{q}_{\vec{A}\vec{B}}$ formed with the exact distribution function $Z^{-1}\exp[-\beta H(\Gamma)]$ is zero

$$\langle \vec{q}_{\vec{A}\vec{B}} \rangle = 0. \tag{3.6}$$

However, in the UPA the value of F does depend on the $\vec{\Gamma}_{\vec{B}}$ and the value of $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ does not necessarily equal zero. This suggests that the $\vec{\Gamma}_{\vec{B}}$ be chosen so that the UPA value for $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ vanishes.

It follows from Eq. (3.1) and the translational invariance of the lattice that

$$\sum_{\vec{A}} \vec{q}_{\vec{A}\vec{B}} = \sum_{\vec{A}} \vec{q}_{\vec{A}+\vec{B}} - \sum_{\vec{A}} \vec{q}_{\vec{A}} = 0. \tag{3.7}$$

From this it follows that for all choices of the $\vec{\Gamma}_{\vec{B}}$ one has

$$\sum_{\vec{A}\vec{B}}' \vec{\Gamma}_{\vec{B}} \cdot \vec{q}_{\vec{A}\vec{B}} = \sum_{\vec{B}\,(\neq 0)} \vec{\Gamma}_{\vec{B}} \cdot \sum_{\vec{A}} \vec{q}_{\vec{A}\vec{B}} = 0, \tag{3.8}$$

so that $H(\Gamma)$ is indeed independent of the $\vec{\Gamma}_{\vec{B}}$. Equation (3.6) follows from Eq. (3.7) and the translational invariance of the lattice which causes the averages $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ to be independent of $\vec{A}$.

A definition is needed for the average $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ when an approximate expression for F is used. When H has the form given in Eq. (3.3), it follows from Eqs. (1.1) and (1.2) that

$$\frac{1}{2}\sum_{\vec{A}} \langle \vec{q}_{\vec{A}\vec{B}} \rangle = \frac{\partial F}{\partial \vec{\Gamma}_{\vec{B}}} . \tag{3.9}$$

Since $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ is independent of $\vec{A}$ (even in the UPA), one can define the approximate $\langle \vec{q}_{\vec{A}\vec{B}} \rangle$ as the value given by Eq. (3.9) when the approximate expression for F is used. This leads to the following criterion for choosing the $\vec{\Gamma}_{\vec{B}}$: Choose the $\vec{\Gamma}_{\vec{B}}$ so that

$$\frac{\partial F}{\partial \vec{\Gamma}_{\vec{B}}} = 0, \tag{3.10}$$

where F is evaluated in the approximation being considered.

C. Free energy

The UPA for F is obtained by setting

$$f_p = \exp[-\beta V_{\vec{A}\vec{B}}(\Gamma)] \tag{3.11}$$

in the correlated-pairs expansion (2.13) or (2.15), keeping only the zeroth-order terms, using property

(3.2), and substituting into Eq. (1.4). One obtains

$$F - F_0 = -\tfrac{1}{2}kT \sum_{\vec{A}\vec{B}}{}' \ln\langle \exp[-\beta V_{\vec{A}\vec{B}}(\Gamma)]\rangle_0$$
$$= -\tfrac{1}{2}NkT \sum_{\vec{B}(\neq 0)} \ln\left[(8\pi^3 \det\Lambda_{\vec{B}})^{-1/2} \int d^3q \times \exp\left(\frac{-E_{\vec{B}}(\vec{q})}{kT}\right)\right], \quad (3.12)$$

where

$$E_{\vec{B}}(\vec{q}) = \phi(|\vec{B}+\vec{q}|) + \tfrac{1}{2}\vec{q}\circ(kT\vec{\Lambda}_{\vec{B}}^{-1} - \vec{\phi}_{\vec{B}})\cdot\vec{q} + \vec{\Gamma}_{\vec{B}}\circ\vec{q}. \quad (3.13)$$

It follows from this and the above criterion that the $\vec{\Gamma}_{\vec{B}}$ are determined by

$$\int d^3q\, \vec{q} \exp\left(\frac{-\vec{E}_{\vec{B}}(\vec{q})}{kT}\right) = 0. \quad (3.14)$$

Because of the translational invariance of the lattice, the pair autocorrelation functions $\vec{\Lambda}_p$ depends on only the relative positions of the particles in the pair. Thus, only a single subscript is needed. It can be shown that[13]

$$\vec{\Lambda}_p = \vec{\Lambda}_{\vec{B}} = \frac{kTv_c}{8\pi^3}\int d^3k \sum_{n=1}^{3} \frac{\vec{e}_{\vec{k}n}\vec{e}_{\vec{k}n}(1-\cos\vec{k}\circ\vec{B})}{\frac{1}{2}m\omega_{\vec{k}n}^2}; \quad (3.15)$$

where $\omega_{\vec{k}n}^2$ and $\vec{e}_{\vec{k}n}$ are the eigenvalues and eigenvectors of the dynamical matrix[14]

$$\vec{D}(\vec{k}) = \frac{1}{m}\sum_{\vec{B}(\neq 0)} \vec{\phi}_{\vec{B}}(1-\cos\vec{k}\circ\vec{B}). \quad (3.16)$$

The different normal modes are labeled by the wave vector $\vec{k}$, the polarization index n, and v_c is the volume of a unit cell. The classical (quasi) harmonic contribution to F is

$$F_0 = 3NkT\left(-\ln(2\pi kT) + \frac{v_c}{8\pi^3}\int d^3k\, \frac{1}{3}\sum_{n=1}^{3} \ln\omega_{\vec{k}n}\right). \quad (3.17)$$

D. Discussion

The anharmonic contributions to the free energy in the UPA are determined by harmonic averages of Boltzmann factors that are formed with the anharmonic pair potentials. Contributions only exist for those types of pairs for which there is an anharmonic contribution to the total potential energy. For the case of a face-centered cubic lattice with nearest-neighbor interactions only, there are only 12 such types of pairs, i.e., only 12 vectors $\vec{B}$ in the sum in Eq. (3.12). Because of the symmetry of the lattice, all 12 types contribute equally, so that only one integration over $\vec{q}$ space and one integration over $\vec{k}$ space is required to determine the anharmonic contribution to F.

The validity of the UPA does not require that the harmonic part of the potential energy be a sum of contributions from different pairs as in Eq. (3.4). For example, to include contributions to the harmonic Hamiltonian from a three-body potential would only require that the formula for calculating the dynamical matrix be appropriately generalized.

The UPA for F is accurate through first order in the pair-pair displacement correlation function $\vec{\Lambda}_{pp'}$, since the terms in the correlated-pairs expansion (2.13) that are of first order in $\vec{\Lambda}_{pp'}$ all vanish. To see this note that

$$\nabla \ln\langle e^{-\beta V_p}\rangle_{\vec{x}(p)}\big|_{\vec{x}=0} = \langle e^{-\beta V_p}\rangle_0^{-1}\vec{\Lambda}_p^{-1}\cdot\langle \vec{q}_p e^{-\beta V_p}\rangle_0 = 0, \quad (3.18)$$

where the first equality follows from Eqs. (2.11) and (2.12) and the last equality follows from Eq. (3.14), which in turn follows from the criterion for choosing the constants $\vec{\Gamma}_{\vec{B}}$.

The constants $\vec{\Gamma}_{\vec{B}}$ determine the size of the linear term in the anharmonic pair potential $V_{\vec{A}\vec{B}}(\Gamma)$. These linear terms are of great importance in the UPA, even though they make no contribution in the exact expression for F. As can be seen from Eq. (3.12), the UPA relates the anharmonic part of F to a sum of contributions from different pairs. Each contribution has the form of the configurational contribution to the free energy of a diatomic molecule (plus a harmonic correction term proportional to $\ln 8\pi^3 \det\Lambda_{\vec{B}}$). In the UPA the presence of other atoms in the lattice is accounted for by the modifications to the linear and the harmonic terms in the potential energy function for the hypothetical diatomic molecule. For a diatomic molecule with an asymmetric potential the mean distance between the atoms is a function of temperature. The direction of the vector connecting the two atoms is random. For a lattice the mean displacement vector connecting a pair of atoms is fixed by the boundary conditions and the lattice symmetry independent of the form of the potential. The forces that keep the mean displacement fixed result from the interactions of the pair of atoms with the other atoms in the lattice. In the UPA these forces are accounted for by the linear term in $V_{\vec{A}\vec{B}}(\Gamma)$.

The important consequences of criterion Eq. (3.10) for choosing the constants $\vec{\Gamma}_{\vec{B}}$ are the following: It causes the mean displacement vector connecting a pair of atoms to be consistent with the boundary conditions and the lattice symmetry. It causes the terms of first order in the $\vec{\Lambda}_{pp'}$ in the correlated-pairs expansion for F to vanish. It causes F to have the correct dependence on the strength of the external forces for a linear chain

(as is shown in Sec. IV), and it causes there to be no terms in the second-order perturbation-theory expansion of the UPA for F that are not also in the complete perturbation-theory expansion for F.

If one makes the usual assumption that the pair potential $\phi(r)$ vanishes as $r \to \infty$, the convergence of the integral in Eq. (3.12) requires that

$$\vec{\mathbf{r}} \cdot (kT\vec{\Lambda}_{\vec{B}}^{-1} - \vec{\phi}_{\vec{B}}) \cdot \vec{\mathbf{r}} > 0 \tag{3.19}$$

for all vectors $\vec{\mathbf{r}}$. It follows from Eq. (3.15) that this requirement is actually independent of T. Essentially, Eq. (3.19) is a restriction on the force constants $\vec{\phi}_{\vec{B}}$, since they determine the autocorrelation function $\vec{\Lambda}_{\vec{B}}$, and thus its inverse $\vec{\Lambda}_{\vec{B}}^{-1}$.

IV. RELATIONSHIP TO OTHER THEORIES

A. Linear chain

When applied to a linear chain with nearest-neighbor interactions only, the UPA for the free energy is exact in the limit of large N. The approximations based on the cumulant expansion, on perturbation theory, and on self-consistent phonon theory do not possess this property.

For this problem the Hamiltonian is

$$H(\Gamma) = H_0 + \sum_{i=1}^{N} V_i(\Gamma), \tag{4.1}$$

where

$$H_0 = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \tfrac{1}{2}\phi_2 \bar{q}_i^2 \right), \tag{4.2}$$

and

$$V_i(\Gamma) = \phi(a + \bar{q}_i) - \tfrac{1}{2}\phi_2 \bar{q}_i^2 + \Gamma \bar{q}_i . \tag{4.3}$$

Here, $\bar{q}_i = q_{i+1} - q_i$ is the pair displacement for neighboring particles, and q_i and p_i are the particle displacement and momentum of the ith particle. The distance between the reference positions of neighboring particles is a, and periodic boundary conditions are obtained by letting $q_{N+1} = q_1$. The normal mode frequencies of H_0 are[15]

$$\omega_k = (2\phi_2/m)^{1/2}(1 - \cos ka)^{1/2} . \tag{4.4}$$

The correlation functions are

$$\Lambda_i = \langle \bar{q}_i^2 \rangle_0 = (kT/\phi_2)(1 - N^{-1}), \tag{4.5}$$

and for $i \neq j$

$$\Lambda_{ij} = \langle \bar{q}_i \bar{q}_j \rangle_0 = -kT/N\phi_2 , \tag{4.6}$$

which is independent of the values of i and j.

By substituting the above results into Eqs. (3.12) and (3.17) after they have been altered to apply to a linear chain, one obtains

$$-\frac{F - F_0}{kT} = N \ln\left[\left(\frac{\phi_2}{2\pi kT} \right)^{1/2} \times \int d\bar{q} \exp\left(\frac{-[\phi(a+\bar{q}) + \Gamma\bar{q}]}{kT} \right) \right], \tag{4.7}$$

where $kT\Lambda_i^{-1}$ cancels with ϕ_2 in the integral, and

$$\frac{-F_0}{kT} = N \ln(2\pi kT) - N \ln\left(\frac{\phi_2}{m} \right)^{1/2} - \tfrac{1}{2} N \left(N^{-1} \sum_{k(\neq 0)} \ln 2(1 - \cos ka) \right). \tag{4.8}$$

The term in the second set of large parentheses in Eq. (4.8) becomes an integral that vanishes in the limit $N \to \infty$. When applied to a linear chain Eq. (3.10) reduces to

$$\int d\bar{q}\, \bar{q} \exp\{-[\phi(a+\bar{q}) + \Gamma\bar{q}]\} = 0 . \tag{4.9}$$

It can be shown that if Γ satisfies condition (4.9), then all terms in the correlated-pairs expansion of F that are of first or higher order in the Λ_{ij} vanish in the limit $N \to \infty$, so that the UPA becomes exact.

In order to compare the above results with Takahashi's exact solution, an expression is needed for the force f, exerted on the ends of the chain which is the analog of pressure. The analog of volume is the length $\bar{l} = Na$, so that

$$f = -\left(\frac{\partial F}{\partial l} \right)_T = -\left[\int d\bar{q} \exp\left(\frac{-[\phi(a+\bar{q}) + \Gamma\bar{q}]}{kT} \right) \right]^{-1} \times \int d\bar{q} \exp\left(\frac{-[\phi(a+\bar{q}) + \Gamma\bar{q}]}{kT} \right) \phi'(a+\bar{q}), \tag{4.10}$$

where the prime indicates a derivative. Note that for reasonable potentials $\phi(r)$ and $\Gamma > 0$ one has

$$0 = \int d\bar{q} \left(\frac{de^{-[\phi(a+\bar{q}) + \Gamma\bar{q}]/kT}}{d\bar{q}} \right) = \frac{-1}{kT} \int d\bar{q} \exp\left(\frac{-[\phi(a+\bar{q}) + \Gamma\bar{q}]}{kT} \right) \times [\phi'(a+\bar{q}) + \Gamma]. \tag{4.11}$$

These two results combine to give

$$f = \Gamma . \tag{4.12}$$

By combining and simplifying Eqs. (4.7) and (4.8), by introducing the Gibbs free energy $G = F + fl$ with $l = Na$, and by changing to the variable $r = a + \bar{q}$, one can show that

$$\frac{-G}{kT} = \tfrac{1}{2} N \ln(2\pi m kT) + N \ln \int dr \exp\left(\frac{-[\phi(r) + fr]}{kT} \right). \tag{4.13}$$

This is Takahashi's exact solution for the linear-chain problem.[1]

B. Cumulant expansion of F

The cumulant expansion for F through second order in the anharmonicity can be obtained as an approximation to the second type of correlated-pairs expansion, which has the form

$$-\frac{F-F_0}{kT}=\sum_p\langle e^{-\beta V_p}\rangle_0+\sum_{p>p'}(\langle e^{-\beta V_p}\rangle_0\langle e^{-\beta V_{p'}}\rangle_0)^{-1}\times(e^{W_{pp'}}-1)\langle e^{-\beta V_p}\rangle_{\vec{x}(p)}\times\langle e^{-\beta V_{p'}}\rangle_{\vec{x}(p')}\big|_{\vec{x}=0}+\cdots. \tag{4.14}$$

By expanding the Boltzmann factors $e^{-\beta V_p}$ in powers of $(-\beta V_p)$ and keeping terms through second order, one obtains

$$-\frac{F-F_0}{kT}=\sum_p[-\beta\langle V_p\rangle_0+\tfrac{1}{2}\beta^2(\langle V_p^2\rangle_0-\langle V_p\rangle_0)+\cdots]+\beta^2\sum_{p>p'}(e^{W_{pp'}}-1)\langle V_p\rangle_{\vec{x}(p)}\langle V_{p'}\rangle_{\vec{x}(p')}\big|_{\vec{x}=0}+\cdots. \tag{4.15}$$

This is the cumulant expansion for F through second order. It can also be obtained by using the techniques in Sec. II to expand $\ln\langle\exp(-\lambda\beta\sum_p V_p)\rangle_0$ in power of λ. Note that any nonintegrable infinities in V_p, such as can occur when the positions of the two particles in a pair coincide, cause convergence difficulties in the cumulant expansion but not in the correlated-pairs expansions, since $e^{-\beta V_p}\to 0$ as $V_p\to\infty$.

To bring Eq. (4.15) into closer correspondence with the results of Choquard,[5] one needs the identity

$$\langle U_pV_p\rangle_0=e^{\nabla_p\cdot\vec{\Lambda}_p\cdot\nabla_p'}\langle U_p\rangle_{\vec{x}(p)}\langle V_p\rangle_{\vec{x}'(p)}\big|_{\vec{x}=0}, \tag{4.16}$$

where ∇_p' operates on $\vec{x}'(p)$. This can be proved by setting $f_p=U_pV_p$ for one pair and $f_p=1$ for all other pairs in Eq. (2.9), making a change of integration variable, etc. By setting $U_p=V_p$, substituting Eq. (4.16) into Eq. (4.15), and using Eqs. (2.7) and (2.10), the cumulant expansion for F becomes

$$-\frac{F-F_0}{kT}=-\beta\sum_p\langle V_p\rangle_0+\tfrac{1}{2}\beta^2\sum_{pp'}(e^{\nabla_p\cdot\vec{\Lambda}_{pp'}\cdot\nabla_{p'}'}-1)\times\langle V_p\rangle_{\vec{x}(p)}\langle V_{p'}\rangle_{\vec{x}'(p')}\big|_{\vec{x}=0}+\cdots, \tag{4.17}$$

where the double sum is over all values of both p and p' without restriction.

C. Perturbation theory

The UPA for F contains contributions that are omitted in the perturbation theory approximation (PTA) and vice versa. To obtain the PTA for F, let

$$V_p=(\lambda V_p^{(3)}+\lambda^2V_p^{(4)})\big|_{\lambda=1}, \tag{4.18}$$

where $V_p^{(3)}$ and $V_p^{(4)}$ are cubic and quartic functions of the pair displacements, respectively. By substituting this into Eq. (4.17), expanding in powers of λ, keeping terms through order λ^2, and using $\langle V_p^{(3)}\rangle_0=0$, one obtains

$$-\frac{F-F_0}{kT}=-\beta\Big\langle\sum_p V_p^{(4)}\Big\rangle_0+\tfrac{1}{2}\beta^2\sum_{pp'}\Big(\sum_{n=1}^{\infty}\frac{1}{n!}(\nabla_p\cdot\vec{\Lambda}_{pp'}\cdot\nabla_{p'}')^n\Big)\times\langle V_p^{(3)}\rangle_{\vec{x}(p)}\langle V_{p'}^{(3)}\rangle_{\vec{x}'(p')}\big|_{\vec{x}=0}+\cdots, \tag{4.19}$$

where tne exponential operator has been expanded in a power series. Assume that

$$V_p^{(3)}=(1/3!)V_p^{\alpha\beta\gamma}q_p^{\alpha}q_p^{\beta}q_p^{\gamma}, \tag{4.20}$$

where the superscripts indicate the components of vectors and repeated superscripts are to be summed over. It follows from Eqs. (2.11) and (2.12) that

$$\nabla_p\langle f_p\rangle_{\vec{x}(p)}\big|_{\vec{x}=0}=\langle\nabla f_p\rangle_0, \tag{4.21}$$

where ∇f_p indicates the gradient of $f_p(\vec{q}_p)$. By using Eqs. (4.18) and (4.21) in Eq. (4.19) and the fact that harmonic averages of odd powers of $\vec{q}_p$ vanish, one obtains

$$-\frac{F-F_0}{kT}=-\beta\Big\langle\sum_p V_p^{(4)}\Big\rangle_0+\tfrac{1}{2}\beta^2\sum_{pp'}\frac{1}{3!}V_p^{\alpha\beta\gamma}V_{p'}^{\alpha'\beta'\gamma'}\times\Lambda_{pp'}^{\alpha\alpha'}\Lambda_{pp'}^{\beta\beta'}\Lambda_{pp'}^{\gamma\gamma'}+\cdots, \tag{4.22}$$

where the last term comes from the $n=3$ term in Eq. (4.19) and were Eqs. (2.6) and (2.7) and the independence of the constants $V^{\alpha\beta\gamma}$ from the order of the superscripts has been used. The contribution of the $n=1$ term from Eq. (4.19) vanishes for monatomic lattices. Equation (4.22) is equivalent to the classical PTA for F, provided that the anharmonic forces are derivable from pair potentials. Of course, since the usual PTA for F is obtained by making normal-mode transformations of the full cubic and quartic anharmonic potentials, it is not restricted by this provision.[2]

To obtain a result based on the UPA with which to compare the above PTA result, one needs an expansion for the constants $\vec{\Gamma}_p$ in powers of λ. Substitute

$$V_p(\Gamma)=[(\lambda V_p^{(3)}+\lambda^2V_p^{(4)})+(\vec{\Gamma}_p^{\,0}+\lambda\vec{\Gamma}_p'+\cdots)\cdot\vec{q}_p]\big|_{\lambda=1} \tag{4.23}$$

into the criterion for choosing $\vec{\Gamma}_p$, which is $\langle e^{-\beta V_p(\Gamma)} \vec{q}_p \rangle_0 = 0$. By expanding in powers of λ, one finds that $\vec{\Gamma}_p^0 = 0$ and that

$$\Gamma_p'^{\alpha} = -\tfrac{1}{2} V_p^{\alpha\beta\gamma} \Lambda_p^{\beta\gamma} . \tag{4.24}$$

When Eqs. (4.23) and (4.24) are substituted into the UPA for F, the results are expanded in powers of λ, and terms through order λ^2 are kept, one obtains

$$-\frac{F - F_0}{kT} = -\beta \left\langle \sum_p V_p^{(4)} \right\rangle_0 + \tfrac{1}{2}\beta^2 \sum_p \frac{1}{3!} V_p^{\alpha\beta\gamma} V_p^{\alpha'\beta'\gamma'} \Lambda_p^{\alpha\alpha'} \Lambda_p^{\beta\beta'} \Lambda_p^{\gamma\gamma'} . \tag{4.25}$$

This is the same as Eq. (4.22) except that there are no terms with $p \neq p'$.

Equations (4.22) and (4.25) follow from the PTA and the UPA, respectively. Thus, it follows that the two approximations differ: (a) by the existance of terms in the PTA that involve the coupling of the cubic anharmonic coefficients associated with different pairs; and (b) by the existance of terms in the UPA that are of higher order than λ^2 in the sense of Eq. (4.18).

D. Self-consistent phonon theory

Self-consistent phonon theory in its simplest form is a harmonic approximation in which the force constants $\vec{\phi}_{\vec{B}}$ in H_0 are chosen with the aid of a variational principle so as to minimize the error made in the estimate for F. The resulting formula for the force constants is[4]

$$\vec{\phi}_{\vec{B}} = \langle \nabla\nabla\phi(|\vec{B} + \vec{x}|) \rangle_0 . \tag{4.26}$$

The averaging depends on the values of the $\vec{\phi}_{\vec{B}}$, so that the $\vec{\phi}_{\vec{B}}$ must be determined self-consistently. There is nothing to prevent the above choice for the $\vec{\phi}_{\vec{B}}$ from being used in the UPA.

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[12] See, e.g., K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), Chap. 14.

[13] See Eq. (1-82) in Ref. 5.

[14] See Eq. (1-31) in Ref. 5.

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