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Uncorrelated-factors approximation and a comparison of theories for predicting thermal properties: A Lennard-Jones solid

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The equations for determining the free energy of a solid with two-body interactions in the uncorrelated-factors approximation (UFA) are derived from the correlated-factors theorem. A self-consistent choice of the parameters in the harmonic Hamiltonian causes the approximation to be accurate through second order. The specific heat, thermal expansion, and bulk modulus of an fcc Lennard-Jones solid with nearest-neighbor interactions only are calculated in the UFA and the results are compared with the predictions of lowest-order and improved self-consistent phonon theory (SC1 and ISC), perturbation theory through fourth order, and other approximations. The predictions of the UFA are in very good agreement with new classical Monte Carlo estimates and with recent effective potential Monte Carlo results. The calculational effort required in the UFA is similar to that in SC1, while the accuracy of the predictions is similar to that of ISC.

I. INTRODUCTION

A reasonable goal for solid-state theory is the ability to predict the thermodynamic properties of crystalline solids from a knowledge of the interatomic potentials at all temperatures from absolute zero to melting. Ideally, a single approximation that is computationally efficient and easily programmed should be able to account for both quantum and anharmonic effects. The purpose of this paper is to report the results of an application of the uncorrelated-factors approximation (UFA), which is one of the newer approaches to this problem, and to compare it with several competing approximations.

In Sec. II the equations for determining the free energy in the UFA are derived for a solid with two-body interactions. In Sec. III the equations are applied to an fcc Lennard-Jones solid with interactions between nearest neighbors only. The predictions of the UFA are then compared with the predictions of several other analytic approximations, new classical Monte Carlo (MC) estimates, and recent effective-potential Monte Carlo (EPMC) results.

The UFA is based on the correlated-factors theorem, which was proved in an earlier paper, where it was applied to the ϕ^4 model.[1] The UFA can be viewed as a generalization of an earlier approximation, the uncorrelated-pairs approximation,[2] in which only one of the two zeroing conditions was satisfied [i.e., Eq. (18) was satisfied but not Eq. (19)]. Even this lower order of approximation gave very good agreement with the experimental results for solid argon when a realistic potential was used.[3] Another approximation related to the UFA is the correlated-Einstein model (CEM),[4] in which both zeroing conditions were satisfied but a less general harmonic Hamiltonian of the Einstein type was used. The approximation (CPE3) obtained by adding third-order corrections to the CEM gave very good agreement with the classical MC estimates for both the Lennard-Jones and the hard-sphere solids.[5,6]

Quantum effects, which are most significant at low temperatures, are easily accounted for in approximations that utilize normal modes (or phonons). In addition to the UFA, the approximations of this type considered here are the quasiharmonic approximation (QHA), second-order perturbation theory (PT2),[7] fourth-order perturbation theory (PT4),[8,9] lowest-order self-consistent phonon theory (SC1),[10] and improved self-consistent phonon theory (ISC).[11,12] Of these only the UFA and ISC give accurate predictions for a Lennard-Jones solid from absolute zero to the estimated melting temperature.

Another type of approximation is based on independent sites, instead of normal modes. The cell cluster expansion (CCE),[13] the CEM, and the CPF3 are the approximations of this type considered here. Such approximations are quite effective in treating anharmonic effects, which are most significant at high temperatures, but they have difficulty with quantum effects. Only classical results are given. The UFA, ISC, CCE, and CPE3 results

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are in good agreement with the classical MC results.

Monte Carlo methods give statistical approximations. Classical MC in its computationally efficient and easily programmed form gives estimates for the averages of phase functions of small model systems but not for the free energy. Even though quantum effects are not included, classical MC is very useful for the testing of analytic approximations, since its accuracy is limited only by the size of the statistical sample used. A comparison with MC results gives a more meaningful test of an analytic approximation than a comparison with experimental results, since it is not affected by any uncertainty about the correct form for the interatomic potentials.

To test the ability to predict quantum as well as anharmonic effects, comparisons are made with some recent EPMC results.[14,15] This and other quantum extensions of classical MC are still under development and have some limitations. For example, an EPMC calculation takes about a half hour on a Cray-YMP. Reported times for a path integral Monte Carlo (PIMC) calculation are even longer.[16] In contrast, calculations with the analytic approximations typically take about a minute on a personal computer with an Intel 486 CPU. The analytic approximations give the free energy, volume coefficient of thermal expansion, and bulk modulus; to date there are no published EPMC or PIMC values for these properties.

II. UNCORRELATED-FACTORS APPROXIMATION

In this section we derive the equations that give the free energy of solids with two-body interactions in the UFA. The result is Eq. (23). The derivation starts with the correlated-factors theorem which states that the harmonic average of a product of factors $f_p(\mathbf{q}_p)$ is given exactly by[1]

$$\left\langle \prod_p f_p(\mathbf{q}_p) \right\rangle_0 = \left[e^{W} \prod_p \langle f_p(\mathbf{q}_p+\mathbf{x}_p)\rangle_0 \right] \Bigg|_{x=0} , \tag{1}$$

which is equivalent to Eq. (31) of Ref. 1. The validity of the theorem requires (a) that the arguments $\mathbf{q}_p$ of the factors are linear functions of the canonical coordinates and (b) that the harmonic Hamiltonian is a sum of linear and quadratic functions of the canonical coordinates. The theorem is valid both classically and quantum mechanically. The correlations neglected in the product of averages on the right are accounted for by the differential operator e^W. Specific forms for f_p, $\mathbf{q}_p$, and W are given below.

To apply the theorem to the determination of the Helmholtz free energy F one uses the relationship

$$F=F_0-\frac{1}{\beta}\ln\langle e^{-\beta(H-H_0)}\rangle_0 , \tag{2}$$

which is exact classically, but not quantum mechanically. Here, $\beta=1/k_BT$. With two-body interactions the true Hamiltonian for the system is

$$H=\sum_i \frac{|\mathbf{p}_i|^2}{2m_i}+\sum_{j<k}\phi_{jk}(|\mathbf{R}_j-\mathbf{R}_k+\mathbf{u}_j-\mathbf{u}_k|) , \tag{3}$$

where the canonical coordinates are the components of the displacements $\mathbf{u}_i$ of the particles from their lattice sites $\mathbf{R}_i$. The potential for the pair of particles j and k is $\phi_{jk}(r)$, and $\mathbf{p}_i$ is the momentum of particle i. Both F_0 and the canonical average $\langle \cdots \rangle_0$ are formed with a harmonic Hamiltonian H_0. To make the harmonic potential energy a sum of pair terms, like the true potential energy, the harmonic Hamiltonian is chosen to be

$$H_0=\sum_i \frac{|\mathbf{p}_i|^2}{2m_i}+\sum_{j<k}\left[\frac{1}{2}\sum_{\alpha=1}^{3}\sum_{\gamma=1}^{3}(u_j^\alpha-u_k^\alpha)\phi_{jk}^{\alpha\gamma}(u_j^\gamma-u_k^\gamma) - \sum_{\alpha=1}^{3}\Gamma_{jk}^{\alpha}(u_j^\alpha-u_k^\alpha)\right] , \tag{4}$$

where the superscripts α and γ label different Cartesian components. The six components of the symmetric tensor $\phi_{jk}^{\alpha\gamma}$ (or $\boldsymbol{\phi}_{jk}$) and the three components of the vector Γ_{jk}^{α} (or $\boldsymbol{\Gamma}_{jk}$) are adjustable parameters. The difference $H-H_0$ can now be written as a sum of terms,

$$H-H_0=\sum_{j<k}\{\phi_{jk}(|\mathbf{R}_j-\mathbf{R}_k+\mathbf{u}_j-\mathbf{u}_k|) - [\tfrac{1}{2}(\mathbf{u}_j-\mathbf{u}_k)\cdot\boldsymbol{\phi}_{jk}\cdot(\mathbf{u}_j-\mathbf{u}_k) - \boldsymbol{\Gamma}_{jk}\cdot(\mathbf{u}_j-\mathbf{u}_k)]\} , \tag{5}$$

and the Boltzmann factor in Eq. (2) can be written as a product of factors,

$$e^{-\beta(H-H_0)}=\prod_{j<k} f_{jk} . \tag{6}$$

Since the canonical coordinates in the factor f_{jk} appear in the linear combination $\mathbf{u}_j-\mathbf{u}_k$, we consider the arguments of f_{jk} to be the three components of

$$\mathbf{q}_p=\mathbf{u}_j-\mathbf{u}_k . \tag{7}$$

$\mathbf{q}_p$ is referred to as a *pair displacement*. The different values for p must be put into one to one correspondence with the $N(N-1)/2$ different combinations of j and k with $1\le j<k\le N$, where N is the number of particles. By using p to label the different factors and by setting $\mathbf{R}_j-\mathbf{R}_k=\mathbf{R}_p$, the average of the Boltzmann factor in Eq. (2) becomes

$$\langle e^{-\beta(H-H_0)}\rangle_0=\left\langle \prod_p f_p(\mathbf{q}_p)\right\rangle_0 , \tag{8}$$

where

$$f_p(\mathbf{q}_p)=e^{-\beta\Delta\phi_p} \tag{9}$$

and

$$\Delta\phi_p=\phi_p(|\mathbf{R}_p+\mathbf{q}_p|)-(\tfrac{1}{2}\mathbf{q}_p\cdot\boldsymbol{\phi}_p\cdot\mathbf{q}_p-\boldsymbol{\Gamma}_p\cdot\mathbf{q}_p) . \tag{10}$$

The correlated-factors theorem can be applied to the product on the right-hand side of Eq. (8).

For solids with two-body interactions the operator W is

$$W={\sum_{pp'}}' W_{pp'} , \tag{11}$$

where the prime on the sum indicates that terms with

$p=p'$ are excluded from the sum, and

$$W_{pp'}=\tfrac{1}{2}\boldsymbol{\nabla}_p\cdot\boldsymbol{\Lambda}_{pp'}\cdot\boldsymbol{\nabla}_{p'}\ . \tag{12}$$

Equations (11) and (12) are equivalent to Eq. (32) of Ref. 1. The components of the *pair-pair-correlation tensor* $\boldsymbol{\Lambda}_{pp}$ are

$$\Lambda_{pp'}^{\alpha\gamma}=\langle(q_p^\alpha-\langle q_p^\alpha\rangle_0)(q_{p'}^\gamma-\langle q_{p'}^\gamma\rangle_0)\rangle_0\ . \tag{13}$$

Note that, since the pair displacements are functions of the canonical coordinates u_i^α and since it is the canonical coordinates that are harmonically averaged, $\Lambda_{pp'}^{\alpha\gamma}$ is not a function of either q_p^α or $q_{p'}^\gamma$. The gradients in W represent differentiations with respect the variables $\mathbf{x}_p$ in Eq. (1). Each $\mathbf{x}_p$ is added to the corresponding $\mathbf{q}_p$ in $f_p(\mathbf{q}_p)$ before the averaging is done and is set to zero after the differentiations have been performed. Once it is clear what the operator W operates on, it is convenient to rewrite the correlated-factors theorem, Eq. (1), as

$$\left\langle\prod_p f_p(\mathbf{q}_p)\right\rangle_0=\exp\left[\sum_{pp'}{}'\,W_{pp'}\right]\prod_{p''}\langle f_{p''}(\mathbf{q}_{p''})\rangle_0\ , \tag{14}$$

where $\boldsymbol{\nabla}_p$ is interpreted as $\partial/\partial\mathbf{q}_p$ and the factors $f_p(\mathbf{q}_p)$ are differentiated *before* the averaging is done.

The UFA is obtained by expanding the exponential operator in the correlated-factors theorem. First, the logarithm of the right-hand side of Eq. (14) is expanded in powers of an ordering parameter λ:

$$\ln\left[\exp\left[\lambda\sum_{pp'}{}'\,W_{pp'}\right]\prod_p\langle f_p(\mathbf{q}_p)\rangle_0\right]=\sum_p\ln\langle f_p(\mathbf{q}_p)\rangle_0+\lambda Z_1+\tfrac{1}{2}\lambda^2 Z_2+\cdots\ . \tag{15}$$

Then, the adjustable parameters $\boldsymbol{\phi}_p$ and $\boldsymbol{\Gamma}_p$ in the harmonic Hamiltonian are chosen so that the coefficients of λ and λ^2 vanish. Terms of order λ^3 and higher are neglected. Finally, λ is set equal to one. The coefficient of λ in the expansion is

$$Z_1=\frac{\left[\sum_{pp'}{}'\,W_{pp'}\right]\prod_{p''}\langle f_{p''}(\mathbf{q}_{p''})\rangle_0}{\prod_{p''}\langle f_{p''}(\mathbf{q}_{p''})\rangle_0}=\sum_{pp'}{}'\,\frac{\langle\boldsymbol{\nabla}_p f_p(\mathbf{q}_p)\rangle_0\cdot\boldsymbol{\Lambda}_{pp'}\cdot\langle\boldsymbol{\nabla}_{p'}f_{p'}(\mathbf{q}_{p'})\rangle_0}{2\langle f_p(\mathbf{q}_p)\rangle_0\langle f_{p'}(\mathbf{q}_{p'})\rangle_0}\ , \tag{16}$$

where cancellations of identical averages between the numerator and denominator give the result on the right. The coefficient of λ^2 is

$$Z_2=\frac{\left[\sum_{pp'}{}'\,W'_{pp'}\right]\left[\sum_{\hat{p}\hat{p}''}W'_{\hat{p}\hat{p}'}\right]\prod_{p''}\langle f_{p''}(\mathbf{q}_{p''})\rangle_0}{\prod_{p''}\langle f_{p''}(\mathbf{q}_{p''})\rangle_0}-Z_1^2\ . \tag{17}$$

When the subscripts p, p', $\hat{p}$, and $\hat{p}'$ on the operators $W_{pp'}$ and $W_{\hat{p}\hat{p}'}$ in Z_2 are all different, there are averages in the numerator of the types $\langle f_p(\mathbf{q}_p)\rangle_0$ and $\langle\boldsymbol{\nabla}_p f_p(\mathbf{q}_p)\rangle_0$. Averages of the first type cancel between numerator and denominator. When one of the subscripts on $W_{pp'}$ equals one of the subscripts on $W_{\hat{p}\hat{p}'}$, averages of the type $\langle\nabla_p^\alpha\nabla_p^\gamma f_p(\mathbf{q}_p)\rangle_0$ also arise. Since $p\neq p'$ and $\hat{p}\neq\hat{p}'$, there are no averages with three or more gradients in them. Thus, both the coefficients Z_1 and Z_2 vanish when $\boldsymbol{\phi}_p$ and $\boldsymbol{\Gamma}_p$ are chosen so that

$$\langle\boldsymbol{\nabla}_p f_p(\mathbf{q}_p)\rangle_0=0 \tag{18}$$

and

$$\langle\nabla_p^\alpha\nabla_p^\gamma f_p(\mathbf{q}_p)\rangle_0=0\ . \tag{19}$$

These are referred to as the *zeroing conditions.* With the aid of Eqs. (9) and (10), they can be reexpressed as

$$\Gamma_p^\alpha=\langle G_p^\alpha(\mathbf{q}_p)e^{-\beta\Delta\phi_p}\rangle_0/\langle e^{-\beta\Delta\phi_p}\rangle_0 \tag{20}$$

and

$$\phi_p^{\alpha\gamma}=\left\langle\left[\frac{\partial^2\phi_p(|\mathbf{R}_p+\mathbf{q}_p|)}{\partial q_p^\alpha\partial q_p^\gamma}-\beta[G_p^\alpha(\mathbf{q}_p)-\Gamma_p^\alpha][G_p^\gamma(\mathbf{q}_p)-\Gamma_p^\gamma]\right]\frac{e^{-\beta\Delta\phi_p}}{\langle e^{-\beta\Delta\phi_p}\rangle_0}\right\rangle_0\ , \tag{21}$$

where

$$G_p^\alpha(\mathbf{q}_p)=-[\partial\phi_p(|\mathbf{R}_p+\mathbf{q}_p|)/\partial q_p^\alpha]-\sum_\gamma\phi_p^{\alpha\gamma}q_p^\gamma\ . \tag{22}$$

In addition to the explicit dependence on $\boldsymbol{\Gamma}_p$ and $\boldsymbol{\phi}_p$, Eqs. (20) and (21) depend on $\boldsymbol{\Gamma}_p$ and $\boldsymbol{\phi}_p$ implicitly through $\Delta\phi_p$ and the harmonic averaging. They have a form that can be easily iterated to produce self-consistent values for $\boldsymbol{\Gamma}_p$ and $\boldsymbol{\phi}_p$.

By combining Eqs. (2), (8), and (14) with the above expansion, the free energy becomes

$$F\approx F_0-\frac{1}{\beta}\sum_p\ln\langle e^{-\beta\Delta\phi_p}\rangle_0=F_{\mathrm{UFA}}\ , \tag{23}$$

where this defines F_{UFA}. When the zeroing conditions are satisfied this approximate free energy is accurate through second order in λ. It is referred to as the uncorrelated-factors approximation, since it allows the factors in Eq. (8) to be treated as statistically uncorrelated random variables.[17]

Both classically and quantum mechanically harmonic averages like those in Eqs. (20), (21), and (23), which are functions of a single pair coordinate, can be reduced to three-dimensional integrals of the form[18]

$$\langle g(\mathbf{q}_p)\rangle_0=\int d^3q_p\,\frac{\exp[-\tfrac{1}{2}(\mathbf{q}_p-\langle\mathbf{q}_p\rangle_0)\cdot\boldsymbol{\Lambda}_{pp}^{-1}\cdot(\mathbf{q}_p-\langle\mathbf{q}_p\rangle_0)]}{\sqrt{(2\pi)^3\|\boldsymbol{\Lambda}_{pp}\|}}\,g(\mathbf{q}_p)\ , \tag{24}$$

where Λ_{pp}^{-1} is the inverse of the 3×3 matrix Λ_{pp}. The *pair-autocorrelation tensor* Λ_{pp} is given by Eq. (13) with $p=p'$ and $\|\Lambda_{pp}\|$ is its determinant. The harmonic contribution to the free energy F_0 can be evaluated either classically or quantum mechanically. To be consistent with Eq. (2) not being quantum mechanically exact, the anharmonic contribution $F_{\text{UFA}}-F_0$ should be evaluated classically, even when the quantum form of F_0 is used. This means that classical statistical mechanics is used to determine Λ_{pp} and $\langle \mathbf{q}_p \rangle_0$.

III. CALCULATIONS AND RESULTS

The equations that must be satisfied to determine the free energy in the UFA are (20), (21), and (23). We consider an fcc Lennard-Jones solid with interactions between nearest neighbor only, which is a standard test case. The form of the potential is

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}] \ . \qquad (25)$$

Since the potential acts between nearest neighbors only, calculations are needed only for pairs that are nearest neighbors. Because of the symmetry of the lattice, scalar properties have the same value for all nearest neighbors, and vector and tensor properties can be determined for all nearest neighbors by symmetry transformations of the properties for one particular pair. Also, because of the symmetry of the lattice, $\langle q_p^{\alpha} \rangle_0 = 0$. With one atom per unit cell the components of the pair-autocorrelation tensor are

$$\Lambda_{pp}^{\alpha\gamma}=\langle q_p^{\alpha} q_p^{\gamma} \rangle_0 = \frac{k_B T}{N} \sum_{\mathbf{k}n} \frac{2 e_{\mathbf{k}n}^{\alpha} e_{\mathbf{k}n}^{\gamma} (1-\cos \mathbf{k}\cdot\mathbf{R}_p)}{m\omega_{\mathbf{k}n}^2} \ , \qquad (26)$$

where $e_{\mathbf{k}n}$ and $m\omega_{\mathbf{k}s}^2$ are the eigenvectors and eigenvalues of the dynamical matrix for the normal mode with wave vector **k** and polarization index n. The sum is over the **k** vectors in the first Brillouin zone and the three values for n. The integrals in Eq. (24) are done by changing to cylindrical coordinates and doing the angle integration analytically, which give rise to modified Bessel functions. The remaining two integrations are done numerically.

The approximate free energy for N particles is

$$\beta F_{\text{UFA}} = \sum_{\mathbf{k}n} \ln[2\sinh(\tfrac{1}{2}\beta\hbar\omega_{\mathbf{k}n})] - 6N \ln\langle e^{-\beta\Delta\phi_p} \rangle_0 \ , \qquad (27)$$

where the quantum-mechanical form of F_0 is given and $6N$ is the number of nearest-neighbor pairs. The constant-volume specific heat per particle c_V, the volume coefficient of thermal expansion α_V, and the isothermal bulk modulus B_T were obtained by numerically differentiating the approximate free energy.

In Figs. 1 and 2 the quantum-mechanical values for the specific heat c_V and the equilibrium nearest-neighbor separation R_{nn} are given as function of the temperature T. The magnitude of quantum effects is determined by the de Boer parameter

$$\alpha_{dB} = \hbar/(\sigma\sqrt{m\varepsilon}) \ , \qquad (28)$$

where m is the mass of an atom. A value of $\alpha_{dB}=0.02551$ was used. It was calculated with $2^{1/6}\sigma = 3.709\times 10^{-8}$ cm and $\varepsilon = 235.95\times 10^{-16}$ ergs, which are the recommended values for a model of solid argon.[19] The values for the different approximations are for the volume V that causes the pressure to vanish in the approximation considered and for the limit $N=\infty$. For comparison the EPMC values and their error estimates are included.[14] Note that quantum effects are neglected in the anharmonic contributions to the UFA results, but not in the other results presented.

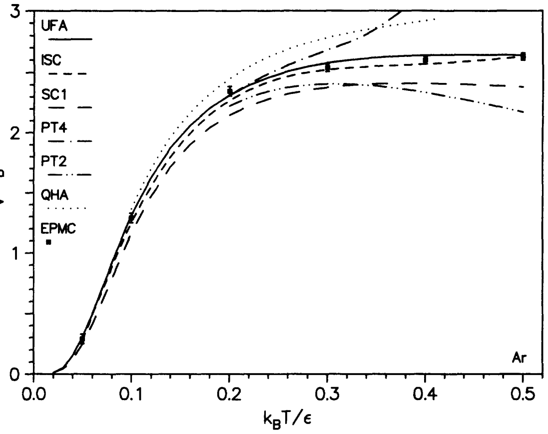

FIG. 1. Zero-pressure constant-volume specific heat per particle versus temperature for an fcc Lennard-Jones nearest-neighbor solid for a model of Ar. $\alpha_{dB}=0.025\,51$.

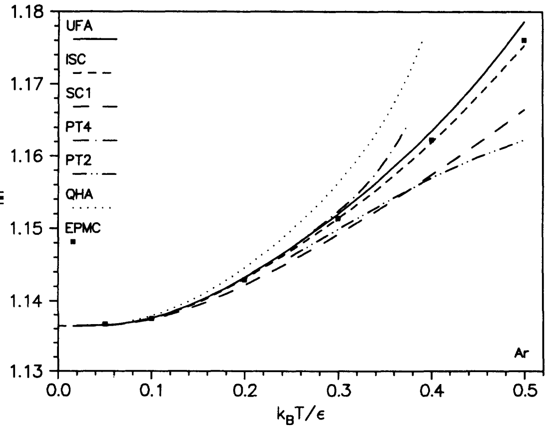

FIG. 2. Zero-pressure nearest-neighbor separation versus temperature for a Lennard-Jones nearest-neighbor solid. $\alpha_{dB}=0.025\,51$.

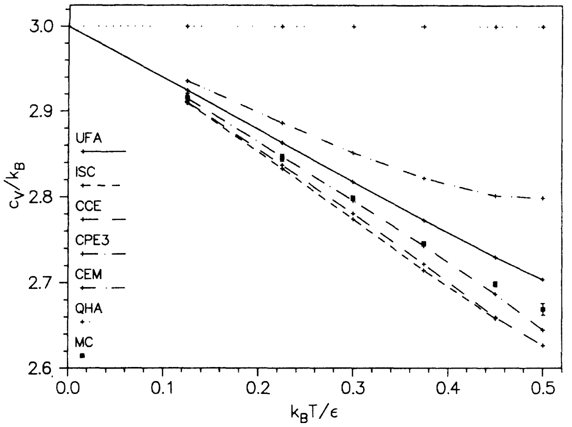

FIG. 3. Classical constant-volume specific heat per particle versus temperature for an fcc Lennard-Jones nearest-neighbor solid.

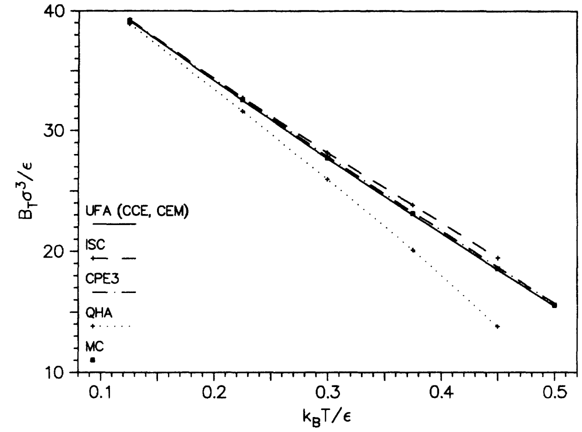

FIG. 5. Classical isothermal bulk modulus versus temperature for an fcc Lennard-Jones nearest-neighbor solid.

In Figs. 3 through 5 the classical values of c_V, α_V, and B_T are given as functions of the temperature T for the limit $N=\infty$. Note the relatively small range of values on the vertical axis of Fig. 3. The CCE and CEM values for B_T are not given since they would be almost indistinguishable on the graph from the UFA values. The lines between the crosses in Figs. 3 through 5 are guides to the eye. At each of the six temperatures for which results are given, the same volume was used for all approximations. The values used, which are given in Ref. 20, are those that cause the pressure P to vanish in the CCE. At $k_BT/\varepsilon=0.5$, where the difference from zero is greatest, the UFA value for $P\sigma^3/\varepsilon$ is 0.064 and the MC value is 0.018. For comparison $P\sigma^3/\varepsilon=0.0015$ at one atmosphere.

The classical MC estimates included are for a system of 108 particles with periodic boundary conditions. Each data point was obtained with a simple of 10^6 steps per particle. No extrapolation to the thermodynamic limit was made. The estimates are consistent with earlier MC results,[20] but since they involve a larger sample the estimated errors are smaller. Error bars representing one standard deviation are included where they can be seen beyond the plotting symbols.

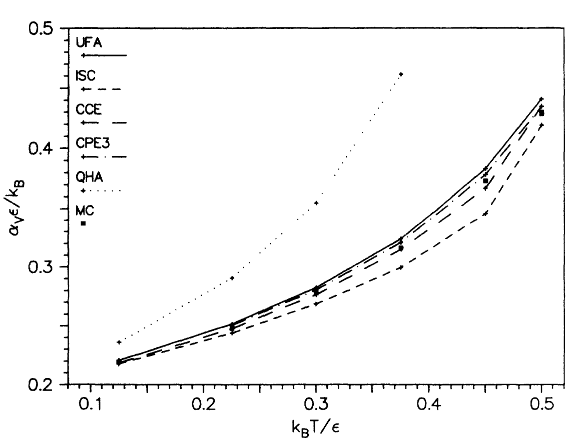

FIG. 4. Classical volume coefficient of thermal expansion versus temperature for an fcc Lennard-Jones nearest-neighbor solid.

IV. CONCLUSIONS AND DISCUSSION

It is clear from Figs. 1 and 2 that only the UFA and ISC are accurate at all temperatures from absolute zero to $k_BT/\varepsilon=0.5$. For comparison k_BT/ε equals 0.49 at the experimental atmospheric-pressure melting temperature of argon, which is 83.8 K. The curves labeled QHA, PT2, and PT4 suggest that the perturbation theory expansion is not converging for this potential, although the convergence is much better for the Morse and Rydberg potentials.[9] The neglect of quantum effect in the anharmonic part of the UFA is not likely to be significant for the value of the de Boer parameter used here, but it is expected that it would be significant for a model of solid neon. The inclusion of these neglected quantum effects is planned for a future publication. It is clear from Figs. 3 through 5 that the CCE and CPE3 are the most accurate of the approximations based on independent sites.

It is convenient to introduce the concept of *layer of approximation* as distinct from order of approximation. A higher layer of approximation is to be associated with an additional set of equations to be evaluation, while the order of an approximation is associated with accuracy through a particular power of some ordering parameter, such as the λ introduced in Sec. II. For example, in perturbation theory the potential energy is expanded in powers of the displacements of the particles from their lattice sites, and the cubic terms are considered to be of order λ, the quartic terms are associated to be of order λ^2, etc. The QHA is the first layer of approximation, PT2 is the second layer of approximation, and PT4 is the third layer approximation. For the symmetric structure considered here the contributions of order λ and λ^3 vanish, so that there are no additional sets of equations to be evaluated in these orders. In self-consistent phonon theory the first layer approximation is SC1 and the second layer is ISC. The additional set of equations to be evaluated in ISC is very similar to the additional set in PT2. Only a leading second-order contribution from Choquard's full second-order self-consistent theory is retained in ISC.[12,21]

The UFA is the first layer of approximation in the expansion discussed in Sec. II. An important conclusion of this paper is that this first layer of approximation has the same level of accuracy as the second layer of self-consistent phonon theory. This is significant, since the equations in the UFA are quite similar to those in the first layer of self-consistent phonon theory. Specifically, Eqs. (21), and (23) for the UFA are replaced in SC1 by

$$\phi_p^{\alpha\gamma} = \left\langle \frac{\partial^2 \phi_p(|\mathbf{R}_p + \mathbf{q}_p|)}{\partial q_p^{\alpha} \partial q_p^{\gamma}} \right\rangle_0 , \tag{29}$$

and

$$F \approx F_0 + \sum_p \langle \Delta\phi_p \rangle_0 = F_{\text{SC1}} , \tag{30}$$

respectively. The same FORTRAN program was used to produce both the UFA and SC1 results presented here, and there are only 22 lines of code that differ for the two approximations.

Finally, it should be mentioned that CPE3 is the second layer of approximation in the expansion in which the CEM is the first layer. The improved accuracy obtained by going from the CEM to CPE3 seen in Fig. 3, and the close relationship of the CEM to the UFA suggests that the second layer of approximation that corrects the UFA could significantly improve the UFA, if such an improvement becomes desirable. The second layer of approximation would be obtained by evaluating the terms of order λ^3 in the expansion in Eq. (15).

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[18] Equation (13) follows from Eq. (28) of Ref. 1 by doing the integral over k_{Ii} and changing to the notation used in this paper.

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