Quantum corrections to the simulated properties of solids

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It is shown that a practical procedure for including both anharmonic and quantum effects in the calculation of the properties of solids is to combine classical molecular-dynamics simulations with quantum corrections obtained with the quasiharmonic approximation. The procedure is simple to implement and possesses an ordered set of anharmonic quantum corrections. It is tested by calculations on a Lennard-Jones model for solid Ar with nearest-neighbor interactions. The results obtained are competitive with the predictions of effective-potential Monte Carlo (EPMC) and are in very good agreement with path-integral Monte Carlo results, which were obtained with a constant-pressure algorithm that includes higher-order corrections to the Trotter expansion. The lowest-order perturbative correction to EPMC is shown to be the same as the cubic part of the anharmonic quantum correction. [S0163-1829(98)02302-9]

I. INTRODUCTION

Once the interatomic potentials are specified, equilibrium properties can in principle be obtained from the quantum-mechanical expression for the Helmholtz free energy,

$$F^Q = -\beta^{-1} \ln \mathrm{Tr}\, e^{-\beta H}, \qquad (1)$$

where H is the Hamiltonian and $\beta = 1/k_B T$. In most cases $\ln \mathrm{Tr}\, e^{-\beta H}$ can only be determined with the aid of approximations. Two characteristically different types of approximations are available. Statistical approximations, such as those given by Monte Carlo and molecular-dynamics techniques, are most useful at high temperatures where anharmonic effects dominate. Analytic approximations, such as the quasi-harmonic approximation, perturbation theory, and self-consistent phonon theory, are most successful at low temperatures where quantum effects dominate.

Classical simulations using Monte Carlo (MC) and molecular-dynamics (MD) techniques possess two desirable characteristics: one, their accuracy is limited only by the size of the statistical sample employed, and two, they are capable of giving reliable estimates for the errors inherent in the necessarily finite size of the sample. Quantum effects can be included with path-integral Monte Carlo (PIMC),[1–4] but the technique is very demanding of computational resources and requires taking the limit of infinite Trotter number, in addition to infinite sample size, before the results obtained are in principle exact.

The simplest analytic technique is the quasiharmonic approximation (QHA), which typically fails well below half the melting temperature. A well ordered sequence of corrections to the QHA can be obtained with perturbation theory,[5,6] but the resulting sequence diverges at high temperatures.[7] Self-consistent phonon theory at the first level of approximation

(SC1) fails at roughly the same temperatures as the QHA.[8] However, for many solids the improved self-consistent phonon approximation (ISC) gives excellent results right up to melting,[1,9] as does the uncorrelated factors approximation (UFA).[10]

Classical MC and MD simulations fully account for anharmonic effects, while the harmonic approximation easily and fully includes quantum effects. The problem is with the quantum-mechanical treatment of anharmonicity. To date the most practical statistical approach to the problem has been the effective potential Monte Carlo (EPMC) method,[11–14] which involves making both statistical and analytic approximations. Its extension by Acocella, Horton, and Cowley[14,15] through improved effective potential theory has been used successfully to study the difficult case of solid Ne in which anharmonic effects are large even near absolute zero. These techniques are less demanding computationally than PIMC, although calculations with them are certainly more involved than classical MC and MD simulations. A graphical comparison of the predictions of EPMC, UFA, ISC, SC1, QHA, and perturbation theory through orders λ^2 and λ^4 is given in Ref. 10.

An obvious way to include both quantum and anharmonic effects is to correct the results of purely classical MD (or MC) simulations with the difference between the quantum and classical behavior calculated in the QHA. We refer to this approach as simulations with harmonic quantum corrections (SHQC's). Berens, Mackay, White, and Wilson[16] used a similar approach to study liquid water. An ordered sequence of anharmonic quantum corrections to SHQC's can be obtained from the well understood results of perturbation theory. Since the difference between quantum and classical behavior disappears in the high-temperature limit, the high-temperature divergence of perturbation theory is avoided.

To facilitate the comparison of the different approximations, calculations were performed on a Lennard-Jones model of solid Ar with nearest-neighbor interactions only. Since the Lennard-Jones potential is highly anharmonic[6] and since quantum effects are large in solid Ar, although less so than in Ne, the trends observed should have general significance. The SHQC approximation was tested in several ways. First, PIMC predictions were obtained for the zero pressure nearest-neighbor distance and internal energy. These were compared with SHQC predictions, and very good agreement was found. Second, perturbation theory was used to calculate the anharmonic quantum corrections in the lowest nonvanishing order, which is the λ^2 order. These anharmonic quantum corrections alter the results predicted by SHQC by only a few percent. Finally, the predictions obtained were compared with available EPMC results and were found to be competitive. Because of its relative simplicity, we conclude that for most predictions of thermodynamic properties classical MC or MD simulations with harmonic quantum corrections are a more efficient alternative to PIMC or EPMC calculations.

Perturbation theory is a useful tool for investigating the type of information that is included in different analytic approximation schemes. It is used here to study the difference between the exact free energy and that of EPMC in the low coupling approximation. It is found that the lowest-order correction to EPMC is the same as the cubic part of the λ^2 quantum correction to SHQC and is formally similar to the correction proposed in improved effective potential theory.[15]

II. QUANTUM CORRECTIONS

The exact Helmholtz free energy with all quantum and anharmonic effects included is F^Q, as given by Eq. (1). A monatomic solid of N atoms with a potential energy that is the sum of pair potentials is considered. The Hamiltonian is

$$H = K + \Phi, \qquad (2)$$

where K is the kinetic energy and

$$\Phi = \sum_{I<J} \phi(|\mathbf{R}_I - \mathbf{R}_J + \mathbf{u}_I - \mathbf{u}_J|). \qquad (3)$$

$\mathbf{u}_I = (u_{Ix}, u_{Iy}, u_{Iz})$ is the displacement of atom I from its lattice site $\mathbf{R}_I$. The harmonic approximation is based on Hamiltonians of the form

$$H_0 = K + V_2, \qquad (4)$$

where the harmonic potential energy function is

$$V_2 = \frac{1}{2} \sum_{I\alpha/J\gamma} \Phi_{I\alpha,J\gamma} u_{I\alpha} u_{J\gamma} = \sum_k \frac{1}{2} m \omega_k^2 |u_k|^2. \qquad (5)$$

$\Phi_{I\alpha,J\gamma}$ is a $3N$ by $3N$ matrix of force constants, the $3N$ normal mode displacements u_k are related to the atomic displacements $u_{I\alpha}$ by a linear transformation, and ω_k is the frequency of the kth normal mode. Quantum mechanically the quasiharmonic free energy is

$$F_0^Q = \beta^{-1} \sum_k \ln(2 \sinh f_k), \qquad (6)$$

where $f_k = \frac{1}{2} \beta \hbar \omega_k$. Classically it is

$$F_0^C = \beta^{-1} \sum_\kappa \ln(\beta \hbar \omega_k). \qquad (7)$$

Perturbation theory is based on an expansion of the potential energy in a power series of the displacements,

$$\Phi = V_{\text{stat}} + V_2 + [\lambda V_3 + \lambda^2 V_4 + \cdots]_{\lambda=1}, \qquad (8)$$

where λ is the ordering parameter. The cubic term is

$$V_3 = \sum_{klm} C_{klm} u_k u_l u_m. \qquad (9)$$

The quartic term V_4 contains products of four displacements, and so forth. There is no linear term, since it is assumed that the lattice sites $\mathbf{R}_I$ have been chosen to make it vanish. The constant term V_{stat} is the static contribution to the energy, that is, the energy of the system when every atom is at its lattice site and there is no vibrational motion. The frequencies ω_k and the coefficients C_{klm}, etc., were obtained by expanding Φ in a Taylor series. Other expansions can be used. The perturbation expansion for the free energy with all terms through order λ^2 included is

$$F^C = V_{\text{stat}} + F_0^C + F_3^C + \langle V_4 \rangle_0^C + \cdots \qquad (10)$$

This is the classical expansion. The quantum-mechanical expansion has the same form but with the superscript C replaced by Q. The brackets $\langle \cdots \rangle_0^C$ and $\langle \cdots \rangle_0^Q$ designate classical and quantum harmonic averages, respectively. The cubic terms F_3^C and F_3^Q and the quartic terms $\langle V_4 \rangle_0^C$ and $\langle V_4 \rangle_0^Q$ are of order λ^2. The classical and quantum-mechanical quasiharmonic free energies F_0^Q and F_0^C are given in Eqs. (6) and (7).

For the study of quantum corrections it is convenient to write F^Q as

$$F^Q = F^C + (F^Q - F^C). \qquad (11)$$

where F^C is the classical free energy, and the quantity in parenthesis is the exact expression for the quantum corrections. Derivatives of F^C can be estimated with classical simulations, and F^C itself can be obtained by thermodynamic integration. Substituting the classical and quantum perturbation expansions into the quantity in parenthesis in Eq. (11) gives

$$F^Q = F^C + (F_0^Q - F_0^C) + (F_3^Q - F_3^C) + (\langle V_4 \rangle_0^Q - \langle V_4 \rangle_0^C) + \cdots, \qquad (12)$$

which includes all corrections through order λ^2. This can be rewritten as

$$F^Q = F_{\text{SHQC}} + F_{\text{AQC}} + \cdots, \qquad (13)$$

where the classical free energy with *harmonic* quantum corrections is

$$F_{\text{SHQC}} = F^C + (F_0^Q - F_0^C), \qquad (14)$$

and the λ^2 *anharmonic* quantum corrections are

$$F_{\text{AQC}} = (F_3^Q - F_3^C) + (\langle V_4 \rangle_0^Q - \langle V_4 \rangle_0^C). \qquad (15)$$

III. EFFECTIVE POTENTIAL APPROXIMATION

The effective potential method is based on a variational approximation to the path integral representation of the exact free energy F^Q. The result is[13]

$$F_{EP} = -\beta^{-1} \ln\left[\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} \int d^{3N}u\, e^{-\beta V_{eff}} \right], \quad (16)$$

which has the form of a classical free energy with the potential energy replaced by the effective potential

$$V_{eff} = \langle \Phi \rangle_0^D - \sum_k \frac{1}{4} m\omega_k^2 \alpha_k + \frac{1}{\beta} \sum_k \ln(\sinh f_k / f_k), \quad (17)$$

where

$$\alpha_k = \frac{\hbar \coth f_k}{m\omega_k} - \frac{2}{\beta m\omega_k^2} = 2(\langle u_k^2\rangle_0^Q - \langle u_k^2\rangle_0^C), \quad (18)$$

where $\langle u_k^2\rangle_0^Q$ and $\langle u_k^2\rangle_0^C$ are the quantum and classical harmonic mean-square displacements of the kth normal mode. $\langle\Phi\rangle_0^D$ is the smeared potential energy. Smeared quantities are the functions of the $u_{I\alpha}$ defined by

$$\langle f\rangle_0^D = \int d^{3N}x \frac{\exp\left(-\beta\sum_{I\alpha J\gamma} d_{I\alpha,J\gamma}^{-1} x_{I\alpha} x_{J\gamma}\right)}{\sqrt{\pi^{3N}\|d_{I\alpha,J\gamma}\|}}$$
$$\times f(\cdots, u_{I\alpha}+x_{I\alpha}, \cdots), \quad (19)$$

where $f(\cdots, u_{I\alpha}+x_{I\alpha}, \cdots)$ is some function of the atomic displacements $u_{I\alpha}$ that has had each $u_{I\alpha}$ replaced by $u_{I\alpha} + x_{I\alpha}$. The $3N$ by $3N$ matrix $d_{I\alpha,J\gamma}^{-1}$ is the inverse of

$$d_{I\alpha,J\gamma} = 2(\langle u_{I\alpha}u_{J\gamma}\rangle_0^Q - \langle u_{I\alpha}u_{J\gamma}\rangle_0^C), \quad (20)$$

and $\|d_{I\alpha,J\gamma}\|$ is its determinant. Equations (16) through (20) are equivalent to Eqs. (19) of Ref. 13, where the displacements $\mathbf{u}_I$ are represented by $\mathbf{R}_I$. When the potential energy is a sum of pair potentials, as in Eq. (3), the smeared potential energy can be reduced to the more easily evaluated quantity $K(\mathbf{R})$ defined in Ref. 13.

Equation (16) has a form that allows the properties of solids to be determined with classical Monte Carlo techniques. In principle, the variational choice for the harmonic force constants should be done in such a way that the normal-mode transformation and the associated frequencies ω_k are functions of the atomic displacements, but this requires a separate normal-mode transformation for every configuration sampled. To avoid the computational complexity that would result, the harmonic force constants are usually chosen so that the transformation and frequencies are independent of the displacements. Such choices are referred to as low coupling approximations (LCA).[13,14,17,18] When a LCA is made, several of the quantities involving the frequencies can be taken outside of the integral in Eq. (16). By doing this and rearranging terms, the effective-potential approximation to the free energy becomes

$$F_{EP} = F_0^Q - \beta^{-1} \ln\langle e^{-\beta\langle\Phi-V_2\rangle_0^D}\rangle_0^C. \quad (21)$$

That is, effective-potential theory in the LCA expresses the free energy as a sum of a fully quantum-mechanical harmonic part plus an anharmonic part that becomes exact in the high-temperature limit.

The classical harmonic average on the right-hand side of Eq. (21) can be expanded with the aid Eq. (8) and the cumulant expansion,

$$\ln\langle e^{-X}\rangle = -\langle X\rangle + \tfrac{1}{2}(\langle X^2\rangle - \langle X\rangle^2) + \cdots . \quad (22)$$

By setting $X = \langle\Phi - V_{stat} - V_2\rangle_0^D$ it follows through order λ^2 that

$$F_{EP} = F_0^Q + V_{stat} + \langle\langle V_3+V_4\rangle_0^D\rangle_0^C$$
$$-\frac{\beta}{2}[\langle(\langle V_3\rangle_0^D)^2\rangle_0^C - (\langle\langle V_3\rangle_0^D\rangle_0^C)^2] + \cdots . \quad (23)$$

The classical harmonic average of a smeared function can be shown to be equal to the quantum harmonic average of the function without smearing. Specifically,

$$\langle\langle V_4\rangle_0^D\rangle_0^C = \langle V_4\rangle_0^Q, \quad (24)$$

and similarly for V_3. Since $\langle V_3\rangle_0^Q = 0$, the double average $\langle\langle V_3\rangle_0^D\rangle_0^C$ vanishes. For lattices in which every site is a center of inversion it can be shown that

$$-\frac{\beta}{2}\langle(\langle V_3\rangle_0^D)^2\rangle_0^C = -\frac{\beta}{2}\langle V_3^2\rangle_0^C = F_3^C. \quad (25)$$

This somewhat surprising result states that the λ^2 contribution of V_3 is simply the *classical* perturbation term F_3^C in Eq. (10). By combining these results it follows through order λ^2 that

$$F_{EP} = V_{stat} + F_0^Q + \langle V_4\rangle_0^Q + F_3^C + \cdots . \quad (26)$$

Subtracting this from the perturbation expansion for F^Q and including all terms through order λ^2 gives

$$F^Q = F_{EP} + (F_3^Q - F_3^C) + \cdots . \quad (27)$$

Thus, the λ^2 correction to the effective-potential free energy is the same as the cubic part of the anharmonic quantum correction to F_{SHQC}.

Effective potential calculations usually do not use a Taylor series expansion of Φ to determine the normal-mode transformation, frequencies, and coefficients C_{klm}. Except for the method used to determine these quantities, the correction $(F_3^Q - F_3^C)$ in Eq. (27) is the same as that introduced in the improved effective potential method.[15]

IV. CALCULATIONS AND RESULTS

An fcc solid with a Lennard-Jones 6-12 potential acting between nearest neighbors only was used to test the theory. The dimensional parameters for the model are Boltzmann's constant k_B, Planck's constant $\hbar$, the mass m, the depth of the potential well ε, and the core diameter σ. The minimum of the potential is at $R_0 = 2^{1/6}\sigma$. The dimensionless quantities used in the calculation are the de Boer parameter $\alpha = \hbar/\sqrt{m\varepsilon\sigma^2}$, the reduced temperature $k_B T/\varepsilon$, and the reduced nearest-neighbor distance R_{nn}/σ. The dimensionless

forms for the internal energy and heat capacity are $U/N\varepsilon$ and C_V/Nk_B. The value used for the de Boer parameter is $\alpha = 0.025\,51$, which is appropriate when modeling solid Ar.[11] All results were obtained for a cubic system of $N = 108$ atoms with periodic boundary conditions. The small number of atoms is partially accounted for in the MD, QHA, and SHQC results by dividing the vibrational contributions by $N-1$, while the static contributions are divided by N. For example,

$$U/N\varepsilon = \frac{U_{\text{vib}}}{(N-1)\varepsilon} + \frac{V_{\text{stat}}}{N\varepsilon}. \qquad (28)$$

Similar results hold for the heat capacity, to which V_{stat} does not contribute, and for the free energy.

The PIMC simulations were carried out with a constant-pressure path-integral Monte Carlo technique that included the higher-order corrections to the Trotter expansion proposed by Li and Broughton.[19] These greatly improve the rate of convergence to the exact quantum limit. Constant-pressure PIMC simulations based on the primitive algorithm with no higher-order corrections have been described previously,[2,20] as have constant volume PIMC simulations that include higher-order corrections.[21] The method used here differs from these in that higher-order corrections were included in constant-pressure simulations.

The PIMC results in the figures and the table were obtained with a Trotter number of 8, except at $k_B T = 0.05\varepsilon$ where a Trotter number of 16 was used. The heat capacity was not calculated because of the large statistical errors that occur in PIMC evaluations of the fluctuation formula for C_V.[17]

The SHQC predictions were obtained by combining the MD results of Lacks and Shukla[22] with quantum corrections obtained with the QHA. These MD results, which were obtained by thermodynamic integration, were reduced to a parametrized expression for the temperature and volume dependence of the free energy. This expression was then used to obtain the predicted zero pressure nearest-neighbor distance R_{nn}, internal energy U, and heat capacity C_V.
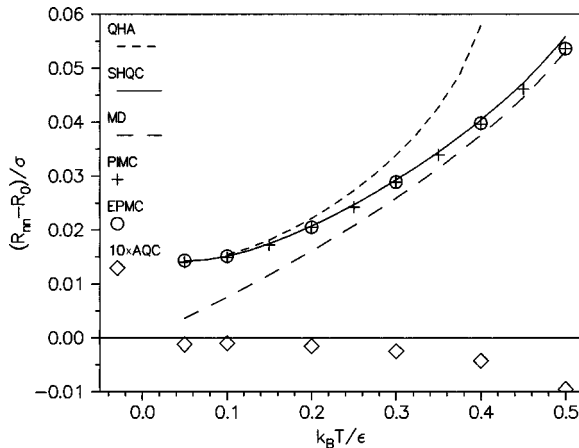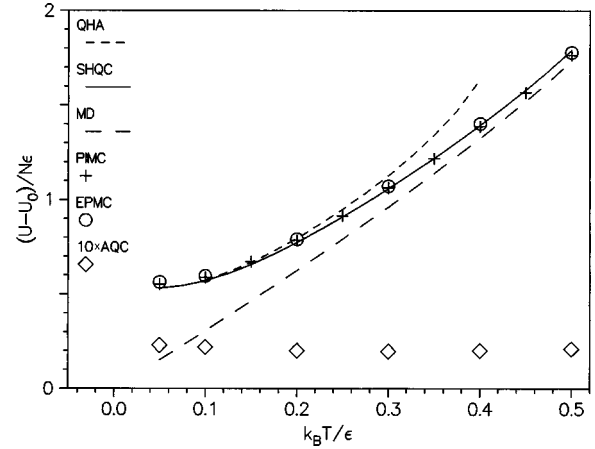

FIG. 2. Dimensionless internal energy $U/N\varepsilon$ minus $U_0/N\varepsilon = -6$ vs temperature at zero pressure, and 10 times the anharmonic quantum correction to $U/N\varepsilon$ obtained from F_{AQC}.

The standard formulas of perturbation theory[5] were used to calculate the λ^2 anharmonic quantum corrections. Since U and C_V depend linearly on the free energy, substituting the free energy correction F_{AQC} into the thermodynamic formulas that relate U and C_V to the free energy gives additive corrections. Obtaining additive corrections to the zero pressure nearest-neighbor distance is more involved. Since the thermodynamic formula for pressure is $P = -(\partial F/\partial V)_T$ and since the volume V is proportional to the cube of R_{nn}, it follows that $(\partial F/\partial R_{nn})_T = 0$ when $P = 0$. Let R_1 and R_2 represent the zero pressure values of R_{nn} when the free energy is taken to be $F_1 = F_{\text{SHQC}}$ and $F_2 = F_1 + F_{\text{AQC}}$, respectively. It then follows that $\partial F_1(R_1)/\partial R_{nn} = 0$ and that

$$\frac{\partial F_2(R_2)}{\partial R_{nn}} = \frac{\partial F_2(R_1)}{\partial R_{nn}} + \frac{\partial^2 F_2(R_1)}{\partial R_{nn}^2}(R_2 - R_1) + \cdots = 0. \qquad (29)$$

By approximating F_2 by F_1 in the second derivative term, by neglecting higher powers of $(R_2 - R_1)$, and by solving for $(R_2 - R_1)$ it follows that

$$(R_2 - R_1) \approx \frac{\partial F_{\text{AQC}}(R_1)/\partial R_{nn}}{\partial^2 F_{\text{SHQC}}(R_1)/\partial R_{nn}^2}. \qquad (30)$$

FIG. 1. Dimensionless nearest-neighbor distance R_{nn}/σ minus $R_0/\sigma = 2^{1/2}$ vs temperature at zero pressure, and 10 times the anharmonic quantum corrections (AQC) to R_{nn}/σ obtained from F_{AQC}.
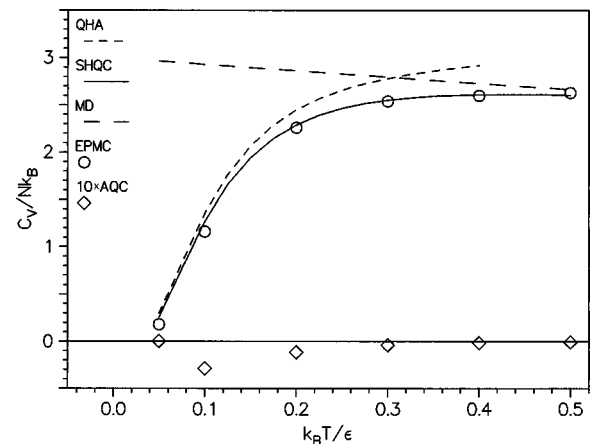

FIG. 3. Dimensionless heat capacity C_V/Nk_B vs temperature at zero pressure, and 10 times the anharmonic quantum corrections to C_V/Nk_B obtained from F_{AQC}.

TABLE I. Predictions for the zero-pressure nearest-neighbor distance R_{nn}, the internal energy U, and the heat capacity C_V. The minimum static potential energy $U_0 = -6N\varepsilon$ occurs when $R_{nn} = R_0 = 2^{1/2}\sigma$. The $+AQC$ predictions were obtained by adding the corrections obtained from F_{AQC} to the SHQC predictions. The 2nd order EPMC values are from Ref. 11.

$k_B T/\varepsilon$		0.05	0.10	0.20	0.30	0.40	0.50
$(R_{nn} - R_0)/\sigma$	SHQC	0.0142	0.0152	0.0208	0.0293	0.0404	0.0558
	$+$AQC	0.0141	0.0151	0.0206	0.0291	0.0400	0.0549
	PIMC	0.0141	0.0150	0.0205	0.0289	0.0396	0.0536
$(U - U_0)/N\varepsilon$	SHQC	0.532	0.571	0.773	1.059	1.394	1.790
	$+$AQC	0.555	0.593	0.793	1.079	1.414	1.811
	PIMC	0.553	0.588	0.784	1.063	1.387	1.765
C_V/Nk_B	SHQC	0.25	1.27	2.29	2.55	2.61	2.60
	$+$AQC	0.25	1.24	2.28	2.55	2.61	2.60
	EPMC	0.18	1.16	2.26	2.54	2.60	2.63

This is the approximation used to estimate the anharmonic quantum corrections to R_{nn} at zero pressure.

The results of our calculations are presented in Figs. 1, 2, and 3. To illustrate the effects of anharmonicity and quantum mechanics, fully anharmonic MD predictions and fully quantum-mechanical QHA predictions are also included, as are the 2nd-order EPMC predictions for Ar of Liu, Horton, and Cowley.[11] The values plotted are all for the nearest-neighbor distance that leads to zero pressure in the indicated approximation. The anharmonic quantum corrections obtained from F_{AQC} are also given. So that they can be clearly seen, they were multiplied by 10 before being plotted.

The anharmonic quantum correction to U does not tend to zero at high temperature. This results from the fact that the quartic part of the correction to U, which arises from the term $(\langle V_4 \rangle_0^Q - \langle V_4 \rangle_0^C)$ in Eq. (15), tends to a constant value in the limit of high temperatures when R_{nn} is fixed (while the total internal energy tends to infinity). The cubic part of the correction to U, which arises from the term $(F_3^Q - F_3^C)$, and both the cubic and quartic parts of the correction to C_V tend to zero at high temperatures. Also, the cubic and quartic parts of the correction to C_V tend to zero in the limit of low temperatures.

For the Lennard-Jones system considered the quartic part of the corrections to both U and C_V have roughly twice the magnitude of the cubic parts and have the opposite sign. Thus, since the λ^2 correction to the EPMC free energy is the same as the cubic part of the correction F_{AQC}, the correction to an EPMC prediction can be expected to have roughly the same magnitude as the anharmonic quantum corrections to a SHQC prediction.

There is very good agreement between the solid lines representing the SHQC results in the figures, the crosses representing the PIMC results, and the open circles representing the EPMC results. The most significant disagreements are for the zero pressure value of R_{nn} at high temperatures and for C_V at low temperatures. To put these disagreements in perspective, note that at $k_B T = 0.05\varepsilon$ the heat capacity in the thermodynamic limit of $N = \infty$ is roughly 8% larger than it is in a system of $N = 108$ atoms, as estimated with the QHA. The quantitative effect of adding the anharmonic quantum corrections obtained from F_{AQC} to the SHQC results can be seen in Table I.

A calculation of anharmonic quantum corrections can be used both to improve the accuracy of SHQC predictions and to test their accuracy. The type of solid for which SHQC is not satisfactory is one in which the interplay between anharmonicity and quantum effects is characteristically greater than in solid Ar. Solid Ne is such a system. The warning that the SHQC approach does not work for Ne is indicated by the unphysical results obtained in the perturbative calculation of the anharmonic corrections.

We conclude that a classical MC or MD simulation with harmonic quantum corrections would usually be preferable to a PIMC or EPMC calculation, because of its computational efficiency and conceptual simplicity. Nevertheless, it appears that the search for a simple and efficient method for determining the properties of all types of solids that is accurate from absolute zero to the melting temperature is not yet over.

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