Improved Effective-Potential Monte Carlo Theory

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The free energy of a quantum crystal with large zero-point motion, calculated using the effective-potential Monte Carlo (EPMC) method, is deficient at zero temperature because of the omission of cubic terms in the potential. We propose an improved effective-potential theory which includes a perturbative cubic correction. From the many possible forms of this correction, consistency requirements indicate a unique one. We show that, for a model of neon, this correction leads to superior results, and that the EPMC method's speed and ease of computation are preserved.

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The effective-potential method is a variational technique based on the path-integral representation of the partition function. The variations result in reducing the quantum partition function to one of classical form with an effective potential incorporating the quantum effects. This method has been successfully applied in many fields of condensed matter theory, including quantum solids [1–3], ferroelectrics [4], dynamic correlations [5], and transition state theory and reaction rates [6]. When the classical partition function is evaluated by Monte Carlo simulation, we call this the effective-potential Monte Carlo (EPMC) method [1].

In the EPMC method, all classical effects are integrated exactly by the classical Monte Carlo simulation. The purely quantum fluctuations of the atoms are taken into account by smearing the potential, which represents the sampling of the surrounding neighborhood due to quantum fluctuations. This smearing is even (in fact, Gaussian), with the effect that odd terms in the potential do not contribute. The first such missing term is the cubic term in the expansion of the potential, which, in perturbation theory, is part of the leading order anharmonic correction to the harmonic free energy [7]. Thus, EPMC theory is missing a potentially important contribution to the free energy.

This situation is reminiscent of problems with the first order self-consistent phonon theory (SC1) [8]. SC1 theory, like EPMC theory, simulates particle fluctuations by Gaussian smearing of the potential. The only difference is that SC1 theory simulates all the fluctuations, not just the purely quantum ones. Therefore, SC1 theory has a problem similar to that with EPMC theory at zero temperature: cubic contributions to the free energy are not included. To remedy this omission in SC1 theory, the improved self-consistent phonon theory (ISC) [9] was developed. ISC theory takes the cubic terms into account by perturbation theory, and it has been shown to be a very reliable theory at low and intermediate temperatures [10]; it is among the best lattice dynamical theories available.

The cubic term problem in EPMC theory only manifests itself at the lowest temperatures, unlike in SC1 theory where the problem persists at all temperatures. This is because what is meant by the cubic term is the cubic term in the expansion of the potential about *equilibrium*. In EPMC theory at zero degrees, the atoms in the classical Monte Carlo simulation are all at their equilibrium sites and, therefore, the cubic terms are not included. At finite temperature, however, the atoms do not remain at their equilibrium sites, but are displaced during the classical Monte Carlo simulation. Therefore, the cubic terms do contribute in a finite temperature EPMC simulation. In fact, EPMC theory is exact in the classical limit, so they must contribute more and more as the temperature increases. This is because the classical cubic terms are properly included. Thus, as the temperature approaches zero, the cubic terms unfortunately get "frozen out," and the way in which this happens is difficult to quantify. To remedy this problem, we proceed as follows, using some simple consistency requirements to guide us.

As a starting point, we look at the form of the EPMC trial potential V_0 [1] *after* the variations have been performed:

$$V_0(r) = f(\omega) + K(\bar{r}) + \tfrac{1}{2}(r_i - \bar{r}_i)K_{ij}(\bar{r})(r_j - \bar{r}_j).$$

Here $r = r(t)$ is a $3N$-dimensional coordinate, $\bar{r}$ is the average point on the path $r(t)$, K is the smeared potential, K_{ij} is the $3N \times 3N$ matrix of second derivatives of K (the quadratic force constants), and we assume the usual summation convention for repeated indices. $f(\omega)$ is a function of the normal mode frequencies given in [1], and its exact form is not important to this discussion.

Motivated by the form of V_0 and by the fact that it is the cubic terms that we want to include, we add to V_0 the term that is cubic in the Taylor expansion of $K(r)$ about $\bar{r}$.

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We find the correction ΔF to the free energy by treating this term as a perturbation to the quadratic potential V_0, and so restrict $\bar{r}$ to the equilibrium positions. Of course, we get exactly the same expression as in ISC theory [9], except that we use EPMC frequencies, eigenvectors, and smearing:

$$\Delta F = \frac{-\hbar^2}{3NM^3}\sum_{123}\frac{\Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)}{\omega_1\omega_2\omega_3}|\psi_{123}|^2 W_{123},$$

$$W_{123} = \frac{n_1n_2+n_2n_3+n_3n_1+n_1+n_2+n_3+1}{\omega_1+\omega_2+\omega_3} + \frac{3(n_2n_3+n_3n_1-n_1n_2+n_3)}{\omega_1+\omega_2-\omega_3},$$

$$\psi_{123} = \sum_\rho e^{i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\cdot\mathbf{R}_\rho/2} S_\alpha(1)\,S_\beta(2)\,S_\gamma(3)\langle\phi_{\alpha\beta\gamma}(\mathbf{R}_\rho)\rangle,$$

$$S_\alpha(1) = \sin(\mathbf{q}_1\cdot\mathbf{R}_\rho/2)\,e_\alpha(\mathbf{q}_1 j_1). \quad (1)$$

Here, $\mathbf{q}$ is a wave vector in the first Brillouin zone, $n = (e^{\beta\hbar\omega}-1)^{-1}$ is the average occupation number, $\langle\phi_{\alpha\beta\gamma}\rangle$ are the smeared third derivatives, and e and ω are the normal mode vectors and frequencies. More details can be found in [9].

However, if we used this ΔF, we would include the full quantum mechanical cubic contribution to the free energy, which is already included by EPMC theory at high temperatures. To avoid this double counting, the cubic correction that we add to the EPMC free energy must vanish in the classical limit. There are many ways this can be accomplished, but we must do this in a manner consistent with EPMC theory. This is done by including only the purely quantum contributions to the cubic correction; that is, by subtracting the classical limit from the full cubic ΔF. This is our first consistency requirement.

While this prescription is in the spirit of EPMC theory, it is still not unique; there are different classical limits we can use. For example, we can take the classical limit of the smearing in $\langle\phi_{\alpha\beta\gamma}\rangle$, or of the frequencies ω, or of n, or take any combination of these. Again, we wish to avoid double counting. At low, but finite, temperatures, the cubic term is accounted for by the new correction ΔF, but also partially by the Monte Carlo simulation. The latter must be removed. Since the partition function in EPMC theory is of classical form, we know that classical perturbation theory is valid at very low temperatures, and we therefore subtract the classical-perturbation-theory cubic contribution. We find that this is equivalent to taking the classical limit of the occupation numbers only. Hence, we have

$$\Delta F_{\rm cl} = -\frac{4}{3NM^3\beta^2}\sum_{123}\frac{\Delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)}{\omega_1^2\omega_2^2\omega_3^2}|\psi_{123}|^2, \quad (2)$$

where ω and ψ mean the same as in Eq. (1), and the cubic correction to the EPMC free energy is $\Delta F - \Delta F_{\rm cl}$. Recalling the EPMC equations from Ref. [1], what we have, for the equations of our new theory, is

$$Z = e^{-\beta(\Delta F-\Delta F_{\rm cl})}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} \times\int d^{3N}R\, e^{-\beta V_{\rm eff}(R)},$$

$$V_{\rm eff}(R) = K(R) - \frac{m\alpha_a f_a^2}{\beta^2\hbar^2} + \frac{1}{\beta}\sum_a \ln\left(\frac{\sinh f_a}{f_a}\right),$$

$$K(R) = \frac{1}{2}\sum_I\sum_{J\neq I}\int d^3x\,\frac{e^{-\mathbf{x}^T[D^{IJ}]^{-1}\mathbf{x}}}{(\pi^3\det D^{IJ})^{1/2}} \times\phi(\mathbf{R}_I-\mathbf{R}_J+\mathbf{x}),$$

$$(D^{IJ})_{\alpha\beta} = (U_{I\alpha,a}-U_{J\alpha,a})\,\alpha_a(U_{I\beta,a}-U_{J\beta,a}),$$

$$\alpha_a = \frac{\beta\hbar^2}{2mf_a}\left(\coth f_a - \frac{1}{f_a}\right),$$

$$f_a = \frac{\beta\hbar\omega_a}{2},$$

$$U_{ai}^T K_{ij} U_{jb} = m\omega_a^2\delta_{ab},$$

$$K_{I\alpha,J\beta} = \frac{\partial^2 K(R)}{\partial R_{I\alpha}\partial R_{J\beta}}. \quad (3)$$

We call this the improved effective-potential Monte Carlo (IEP) theory.

Our guiding principle in formulating IEP theory was to retain the basic speed and elegance of EPMC theory while correcting its deficiencies at the lowest temperatures. One might argue that this should have been done consistently by treating the cubic term variationally. However, the improvement of SC1 theory by ISC theory was also not consistent. Just as ISC theory nevertheless gave a reliable approximation to the complete theory at low temperatures, so too will IEP theory be a significant improvement over EPMC theory. We would also like to point out that using SC1 frequencies, eigenvectors, and smearing in Eqs. (1) and (2) makes virtually no difference in the results. The cubic correction is very insensitive to such changes.

Although ISC theory is very reliable at low temperatures, it breaks down at higher temperatures since it involves perturbation terms. And although EPMC theory is exact at high temperatures, at lower temperatures it is forced to reduce to SC1 theory. From the structure of Eqs. (1)–(3), IEP theory reduces to ISC theory at lower temperatures and, just like EPMC theory, it is exact at high temperatures. In fact, in the classical limit, the correction to the EPMC free energy is $\Delta F - \Delta F_{\rm cl} = O(\hbar^4)$. This is the best theory available, rivaling path-integral Monte Carlo [11] (which is exact, in principle) in accuracy, and yet being orders of magnitude faster.

To illustrate the improvement provided by IEP theory over EPMC theory, we have applied IEP theory to a nearest-neighbor Lennard-Jones model of neon. The potential used was

$$\phi(\mathbf{x}) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

where $r = |\mathbf{x}|$, $\epsilon = 72.09 \times 10^{-16}$ erg, and $\sigma = 2.7012 \times 10^{-8}$ cm. This is exactly the same model as was used in [1]. The addition of the cubic correction alters the expressions used for the physical quantities we have calculated. For example, the energy is given by

$$E = -\frac{\partial}{\partial\beta}\ln Z = (\Delta F - \Delta F_{\rm cl}) + \beta\frac{\partial}{\partial\beta}(\Delta F - \Delta F_{\rm cl}) + \frac{3N}{2\beta} + \langle V_{\rm eff}\rangle + \left\langle \frac{\partial}{\partial\beta} V_{\rm eff}\right\rangle .$$

The contributions from the cubic correction were calculated at equilibrium and the derivatives were obtained numerically. The Monte Carlo part of the calculation was done in the same way as in [1], where explicit expressions are written out, except that the smearing used a three-point Gauss-Hermite integration instead of a six-point integration. The difference was negligible compared to the cubic correction. To properly cancel the cubic terms from the Monte Carlo simulation, we also used a three-point smearing in calculating $\Delta F_{\rm cl}$. Also, as in [1], we used the low-coupling approximation (LCA). The validity of this approximation is currently being explored, and we will report on this soon. Notice that the cubic correction is only worked out once, at equilibrium, so that only a few minutes are needed to find it, compared to the several hours needed for the Monte Carlo simulation. Thus, an IEP simulation essentially requires the same amount of machine time as an EPMC simulation.

In the figures, the solid circles are the new IEP points. The open triangles are EPMC results taken from [1], the open squares are ISC results, and the open circles are path-integral Monte Carlo (PIMC) results taken from [2]. PIMC theory is exact, in principle, and it is these results that we wish to reproduce. The error bars are too small to be shown for the EPMC and IEP results. The size of the error bars for the PIMC points are exactly the size of the open circles. We also note that neon melts at approximately $0.5\epsilon/k$.

In Fig. 1, we are struck by the improvement made by IEP theory over EPMC theory. The IEP points reproduce the PIMC results. We also see that we have succeeded in what we originally set out to do: the IEP results interpolate smoothly between the EPMC results at high temperatures and the ISC results at low temperatures. Note that even near melting, the new cubic correction is not negligible. Also recall that ISC theory is an excellent low temperature theory, and it is encouraging to see the IEP results follow it closely at low temperatures, whereas at high temperatures, as expected, the ISC results begin to diverge from the correct results.

In Fig. 2, we again observe that IEP theory interpolates smoothly between EPMC theory at high temperatures and ISC theory at low temperatures. If neon did not melt at such a low temperature, the thermal expansion would flatten out and become constant. Clearly the ISC results would be too low.

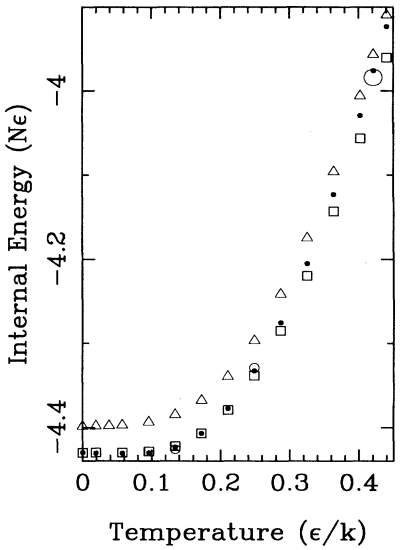

FIG. 1. Internal energy at zero pressure vs temperature. Solid circles correspond to IEP, open triangles to EPMC, open squares to ISC, and open circles to PIMC. Note the PIMC point near $T = 0.14$.

We can see from Fig. 3 that IEP theory again follows ISC theory at low temperatures and reduces to EPMC theory at high temperatures, whereas ISC theory again diverges at high temperatures.

There is one point, concerning the LCA, which has not yet been addressed. In this approximation, the frequency-dependent terms in the effective potential (the phonon terms) are constant and are evaluated at equilibrium. In an exact-EPMC calculation, the phonon terms are not con-

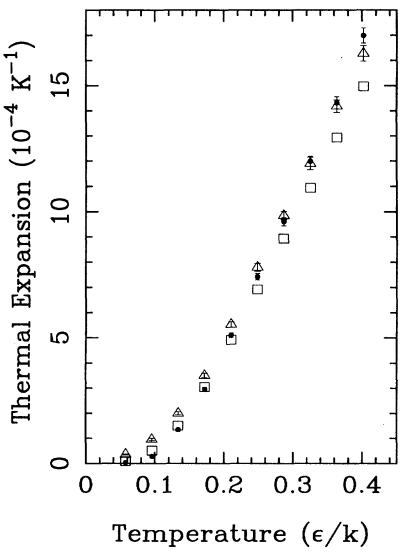

FIG. 2. Thermal expansion at zero pressure vs temperature. Symbols as in Fig. 1.

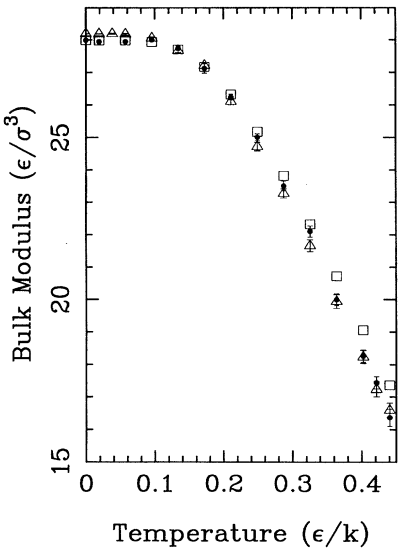

FIG. 3. Isothermal bulk modulus at zero pressure vs temperature. Symbols as in Fig. 1.

stant and the frequencies are evaluated at every configuration R. Thus, as we have already emphasized, at finite temperature the cubic terms in an exact-EPMC simulation partially contribute to both the smeared potential and the phonon terms, whereas, in an LCA-EPMC simulation, they partially contribute to the smeared potential, which is configuration dependent, but not to the phonon terms, which are constant. Thus, the new cubic correction (IEP theory) is expected to be much more important in an LCA-EPMC simulation than in an exact-EPMC simulation. And since the LCA is crucial to EPMC simulations, our cubic correction is crucial to the EPMC approach. We will soon verify these speculations in our investigation of the validity of the LCA, where an exact-EPMC calculation for this same model will be presented.

Finally, it is worthwhile comparing the time required for an IEP calculation with that for a PIMC calculation. For the IEP results shown here, we made 8×10^6 Monte Carlo moves in 16 h on a Sparcstation 10. This is orders of magnitude faster than what would have been required for the corresponding PIMC points to reach the same accuracy. Each PIMC point took over 10 h on a Cray YMP [2], which would correspond to about 200 h on a Sparcstation 10. Since the error bars on the IEP points are about 10 times smaller, the PIMC simulation would need to run 100 times longer to achieve the same statistical accuracy. If we generously allow that a PIMC simulation could become 10 times faster in the near future, it would still be 100 times slower than an IEP simulation.

We believe that IEP theory is the best theory available for calculating the thermodynamics of those quantum crystals for which nuclear exchange can be neglected. It is exact in the high temperature limit and reduces to ISC theory in the low temperature limit. It is a significant improvement over EPMC theory, reproduces PIMC results well, and is orders of magnitude faster than the PIMC method. It is, therefore, the method of choice.

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