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Comparative study of a model quantum solid using quantum Monte Carlo, the effective potential, and improved self-consistent theories

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We have used the quantum Monte Carlo formalism to calculate the volume, pressure, and energy at three temperatures for a nearest-neighbor Lennard-Jones solid, with parameters appropriate to solid neon. The purpose is to provide accurate test data for a system with substantial quantum effects. The results are compared with the predictions of the effective potential and improved self-consistent theories. The agreement of all three techniques is good. The effective-potential method results agree better with the quantum Monte Carlo results at high temperatures, and those of the improved self-consistent method agree better with the quantum Monte Carlo results at low temperatures. The relationship between the three theories is discussed. We show that at zero degrees the effective-potential method is equivalent to first-order self-consistent theory.

I. INTRODUCTION

The main purpose of this paper is to present accurate quantum Monte Carlo (QMC) calculations of the volume, pressure, and energy as functions of temperature, for a more-or-less realistic model of a solid showing substantial quantum mechanical effects. Specifically, we use a nearest-neighbor Lennard-Jones model of a face-centered-cubic crystal, with the atomic mass and the potential parameters chosen to reproduce the neon isotope 22. We have previously reported QMC results for a linear chain[1] as well as some preliminary three-dimensional calculations for a more classical material, argon.[2] We use our QMC results to test an alternative method of calculation, the effective-potential–Monte Carlo formalism (EPMC).[3–7] In this method, the path-integral version of the partition function is approximated by means of a trial, quadratic, action. When the parameters in the trial action are chosen to minimize the expectation value of the free energy, the partition function is obtained in classical form but with an effective potential. We have shown[8,9] that the use of this effective potential in a classical Monte Carlo calculation yields thermodynamic properties for the heavier inert-gas solids which agree closely at high temperatures with classical Monte Carlo results, at low temperatures with anharmonic perturbation theory, and succeed in interpolating smoothly between the two. For the lighter materials, neon and helium, the classical calculation is not relevant at any temperature (at least at zero pressure), and the anharmonic perturbation theory does not converge even at zero degrees. The present QMC calculation was carried out to provide good quality numbers to compare with the EPMC results. In our earlier work[9] we made a limited comparison of EPMC results with one of the best of the lattice dynamical theories, the improved self-consistent theory (ISC),[10] and this proved informative. We have, therefore, extended the earlier ISC calculations and present those results here also. In the next section we discuss the three techniques and the relationship between them. To this end we have made the notation used in the various methods as similar as possible. The numerical results are presented in Sec. III and discussed in Sec. IV.

II. FORMALISM

All three formalisms used here can be based in the path-integral form of the partition function

$$Z = e^{-\beta F} = \int \prod_{i=1}^{N} \mathcal{D}\mathbf{r}_i(\tau) e^{-S[\mathbf{r}(\tau)]/\hbar},$$

where $\mathbf{r}(\tau) \equiv \mathbf{r}_1(\tau), \mathbf{r}_2(\tau), \ldots, \mathbf{r}_N(\tau)$, $\beta = 1/k_B T$, and N is the number of atoms. The action S is

$$S[\mathbf{r}(\tau)] = \int_0^{\beta\hbar} \left(\sum_{i=1}^{N} \frac{1}{2} m \dot{\mathbf{r}}_i^2(\tau) + V[\mathbf{r}(\tau)] \right) d\tau,$$

where $V(\mathbf{r})$ is the potential. The integration variable τ has the dimension of time. The path integral is over all paths $\mathbf{r}(\tau)$ with the same end point and beginning point, and then over all beginning points. We neglect any effects arising from the indistinguishability of the particles.

In QMC the integration over τ is approximated by a summation over a discrete set of M values of τ.[1,11] We shall refer to M as the Trotter number. The calculation of thermodynamic averages such as the energy and the pressure can then be set up in the form of a classical Monte Carlo calculation but for a system of $N \times M$ particles, representing the positions of the N actual particles at the M values of τ. Provided the Trotter number can be made large enough, the results should be exact within the usual statistical uncertainties of a Monte Carlo simulation, and we seem to be able to achieve this. In principle, it should be possible to calculate other thermodynamic quantities including the heat capacity. However, this is obtained as the fluctuation of the energy and even in a classical calculation it is substantially more difficult to calculate accurately. We find that with the presently available computer power we cannot obtain any meaningful convergence for the heat capacity.

An alternative approach to finding the heat capacity is to calculate the temperature derivative of the energy,[2] but the numerical differentiation itself introduces errors. In a recent preprint, Cuccoli *et al.*[12] have presented QMC values for the specific heat of a Lennard-Jones model of a face-centered cubic crystal, with atomic mass and potential parameters chosen to represent Ar. For this case, quantum effects are much smaller and yet QMC results for C_v could only be obtained by ignoring certain, so-called, outlying values due to slow convergence of the fluctuation formula. At the largest Trotter number and the lowest temperature, their standard deviation is over twice as large as the specific heat itself. This agrees with our results. At higher temperatures and lower Trotter numbers, their results are much more acceptable. They have also applied a correction for the small Trotter numbers, based on a harmonic calculation, which seems extremely promising. Of course, Ne with its much larger quantum effects represents a more stringent test of the applicable theories. For these reasons we have not tried to calculate the specific heat by the QMC method in this work.

In the self-consistent phonon and effective potential methods the action is approximated by a trial form. The parameters of the trial action are determined by a variational method based on the inequality[3]

$$F < F_0 + \frac{1}{\beta}\langle S - S_0 \rangle_0. \tag{1}$$

The final subscript 0 indicates that the average is weighted by the trial action. If the trial action differs from the true action only in the potential energy, this reduces to the more familiar inequality

$$F < F_0 + \langle V - V_0 \rangle_0. \tag{2}$$

To obtain the first-order self-consistent phonon approximation (SC1) we use a trial action

$$S_0[\mathbf{r}(\tau)] = \int_0^{\beta\hbar} \left(\sum_{i=1}^{N} \frac{1}{2} m \dot{\mathbf{r}}_i^2(\tau) + \frac{1}{2} \sum_{ij}^{N} \sum_{\alpha\beta} \phi_{\alpha\beta}(ij) u_\alpha(i,\tau) u_\beta(j,\tau) \right) d\tau,$$

where $u_\alpha(i,\tau)$ is the α component of the displacement of the ith atom from its equilibrium position at time τ. The force constants $\phi_{\alpha\beta}(ij)$ are independent of τ and show the periodicity of the lattice. In consequence, the trial action can be diagonalized by a standard transformation to phonon coordinates, and the right-hand side of Eq. (2) evaluated as

$$\begin{aligned} F_{\mathrm{SC1}} &= F_0 + \langle V - V_0 \rangle_{\mathrm{SC1}} \\ &= \frac{1}{\beta} \sum_{\mathbf{q}j} \ln 2 \sinh(f_{\mathbf{q}j}) + \langle V \rangle_{\mathrm{SC1}} \\ &\quad - \frac{1}{2\beta} \sum_{\mathbf{q}j} f_{\mathbf{q}j} \coth(f_{\mathbf{q}j}), \end{aligned} \tag{3}$$

where

$$f_{\mathbf{q}j} = \tfrac{1}{2}\hbar\beta\omega_{\mathbf{q}j}$$

and the sum over $\mathbf{q}j$ is over the normal modes. When the force constants are chosen to minimize this expression they turn out to be the second derivatives of the true potential, averaged, or smeared, over the pair distribution calculated from the trial force constants. In many cases the potential can be written as a sum of pair contributions. The average of any function $A(\mathbf{r}_{ij})$ which depends on the separation of a pair of atoms can be put in the form

$$\langle A(\mathbf{r}_{ij}) \rangle_{\mathrm{SC1}} = [(2\pi^3) \det \underline{D}]^{-1/2} \int A(\mathbf{R}_{ij} + \mathbf{u}) \exp\left(-\frac{1}{2} \sum_{\alpha\beta} u_\alpha [\underline{D}^{-1}]_{\alpha\beta} u_\beta \right) d^3u, \tag{4}$$

where

$$D_{\alpha\beta} = \frac{\hbar}{mN} \sum_{\mathbf{q}j} e_\alpha(\mathbf{q}j) e_\beta(\mathbf{q}j)(1 - \cos \mathbf{q} \cdot \mathbf{R}_{ij}) \coth(f_{\mathbf{q}j})/\omega_{\mathbf{q}j}.$$

$\mathbf{R}_{ij}$ is the equilibrium separation of atoms i and j, and the sum over $\mathbf{q}j$ is over the normal modes with wave vectors $\mathbf{q}$, angular frequencies $\omega(\mathbf{q}j)$, and polarization vectors $\mathbf{e}(\mathbf{q}j)$. The averages of both the potential energy and the force constants can be put in the form of Eq. (4).

The SC1 scheme is very simple to program and gives a vivid picture of the physics. Unfortunately, it is not reliable in practice. Too much is left out. Samathiyakanit and Glyde[13] have shown how the procedure can be extended to higher accuracy within the path-integral formalism. However, in practice useful extensions to the theory have been made within the framework of perturbation theory. The SC1 theory corresponds to a summation of all first-order free-energy diagrams and all ring diagrams with first-order inserts, iterated to self-consistency. The lowest order diagram which is omitted is of second order, with two cubic vertices. This diagram is often comparable with the largest of the diagrams included. The ISC scheme[10] includes this diagram in a non-self-consistent way. This procedure has been successful in many applications, but it is difficult to estimate its reliability for Ne, where there are no perturbation theory results guide us.

The effective potential formalism also introduces a quadratic trial action. However, attention is focused on the average point of a particle in its path:

$$\bar{\mathbf{r}}_i = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} \mathbf{r}_i(\tau)d\tau.$$

The displacements $u_\alpha(i,\tau)$ are now measured from the average point on the path, and the trial action also contains a term looking like a potential evaluated at the average point:

$$S_0[\mathbf{r}(\tau)] = \int_0^{\beta\hbar} \left(\sum_{i=1}^{N} \frac{1}{2} m\dot{\mathbf{r}}_i^2(\tau) + W(\bar{\mathbf{r}}) + \frac{1}{2}\sum_{i,j=1}^{N} \sum_{\alpha\beta} \phi_{\alpha\beta}(ij,\bar{\mathbf{r}}) u_\alpha(i,\tau) u_\beta(j,\tau) \right) d\tau.$$

The path integral is now regarded as an integral over all paths with a given average value, followed by an integration over the average values. It has been shown[4,6] that when the integral over all paths with a given average has been performed, the value of $W(\bar{\mathbf{r}})$ which minimizes the right-hand side of Eq. (2) also has the effect of making $\langle S - S_0 \rangle_0$ disappear. The partition function Z_0 then has the appearance of a classical partition function with the potential replaced by an effective potential

$$Z_0 = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} \int e^{-V_{\text{eff}}(\bar{\mathbf{r}})} \prod_{i=1}^{N} d^3\bar{\mathbf{r}}_i .$$

It is convenient to add and subtract the true potential so that the effective potential can be written

$$V_{\text{eff}}(\bar{\mathbf{r}}) = V(\bar{\mathbf{r}}) + \Delta V(\bar{\mathbf{r}}),$$

where

$$\Delta V(\bar{\mathbf{r}}) = K(\bar{\mathbf{r}}) - V(\bar{\mathbf{r}}) - \frac{1}{2\beta}\sum_s (f_s \coth f_s - 1) + \frac{1}{\beta}\sum_s \ln\left(\frac{\sinh f_s}{f_s}\right). \tag{5}$$

The sums are over the $3N$ normal modes of the trial action, labeled by an index s. $K(\bar{\mathbf{r}})$ is a smeared potential. However, the smearing represents only the blurring of the particle paths due to quantum mechanical fluctuations and disappears in the classical limit. There is some similarity between the expression for ΔV and the SC1 free energy given by Eq. (3). In fact, the terms in Eq. (5) correspond to the differences between the quantum mechanical and classical values of the terms in Eq. (3), with the proviso that the nature of the smearing is different in the SC1 and effective potential cases. Finally, the force constants are found, from the variational principle, to be the smeared values of the second derivatives of the actual potential.

This formalism is still too complicated to be applied exactly. In particular, at a general value of $\bar{\mathbf{r}}$, the force constants do not have the periodicity of the lattice, and a $3N \times 3N$ matrix would need to be diagonalized to give the frequencies. Since the correction term disappears in the high-temperature limit while at low temperatures the atoms remain close to their equilibrium positions, we make the approximation of evaluating the force constants and frequencies at the equilibrium positions. For a pair potential the averages, of the potential and of the force constants, then take a form identical with Eq. (4), except that the quantities $D_{\alpha\beta}$ are given by

$$D_{\alpha\beta} = \frac{\hbar}{mN}\sum_{\mathbf{q}j} e_\alpha(\mathbf{q}j) e_\beta(\mathbf{q}j)(1 - \cos\mathbf{q}\cdot\mathbf{R}_{ij})[\coth(f_{\mathbf{q}j}) - 1/f_{\mathbf{q}j}]/\omega_{\mathbf{q}j}.$$

In addition, in all applications of the method so far, the smeared quantities have been evaluated by series expansion in powers of a quantum renormalization parameter, essentially in powers of the elements of $\underline{D}$. The details have been given elsewhere.[5,7–9] In a first-order EPMC theory the expansion is truncated at the first term. In this case, the bare quasiharmonic frequencies are used in the calculation of the effective potential. In a second- or higher-order theory, the frequencies must be calculated self-consistently, since the renormalization factor itself depends on the frequencies. We can carry out a completely self-consistent second-order theory. The equations clearly simplify drastically at zero degrees. At this temperature we can obtain an approximate third-order theory.

As the temperature goes to zero, the free energy in the effective potential method is given entirely by the value of the effective potential itself. Furthermore, the values of the functions $D_{\alpha\beta}$ are equal to the SC1 values, and the effective potential is equal to the SC1 free energy. Also, note that the effective potential V_{eff} is expressed in terms of the actual potential $V(\mathbf{r})$ plus a correction, and the trial action is involved only in the calculation of this correction. As the temperature increases the whole of the correction term in Eq. (5) goes to zero and we are left with an exact classical expression for the partition function.

III. CALCULATIONS

In all of our calculations we have used the same nearest-neighbor Lennard-Jones potential on which our earlier work[9] was based, i.e., we used $m = 21.9914$, $\epsilon = 72.09 \times 10^{-16}$ ergs, $\sigma = 2.7012$ Å. We believe that the use of this model potential with parameters determined by properties of the solid at $T = 0$ K is preferable to the use of a two-body potential with parameters based on gas properties,[12] since it contains some compensation for the omitted many-body forces. In the figures and tables the calculated thermodynamic properties are expressed in terms of the Lennard-Jones parameters, e.g., the nearest-neighbor distance is expressed in terms of σ.

For the effective potential and ISC formalisms we have found the zero-pressure atomic spacing as a function of temperature, and have calculated the internal energy and heat capacity at that spacing. In the effective potential calculations we did not use the most general form for the force constants but made the assumption

$$\phi_{\alpha\beta}(ij,\bar{\mathbf{r}}) = \Omega(ij,\bar{\mathbf{r}})\delta_{\alpha\beta}.$$

Cuccoli *et al.* have used a more general form,[12] but the advantage of the simpler version used here is that we can solve the self-consistent equations to higher order more easily. The effective potential calculations are done with 108 atoms and 4.2 million configurations in the Monte Carlo simulations. The main reason for repeating the earlier ISC calculations was to obtain values for the internal energy. The results are shown in Figs. 1 and 2. Since the QMC calculation is much more time consuming we did not try to zero the pressure in that case, but instead used the spacings calculated by the second-order effective potential method. We expected that the pressures would then be small, and that turned out to be the case, though except at the highest temperature they are statistically not zero. We performed QMC runs for 32 and 108 atom samples, at three temperatures, 7, 13, and 22 K. In the reduced units ϵ/k_B these are 0.134, 0.249, and 0.421, respectively. We used a variety of Trotter numbers, ranging from 10 to 40, and in each case used a large enough value that the results were converged to within the statistical uncertainties. The number of single particle moves attempted in a run varied from 13 to 40 million. Table I gives a summary of our QMC results.

The best QMC results, i.e., those for 108 atoms and with the highest Trotter numbers, for the three temperatures, are plotted in the figures and are also compared in Table II with effective potential and ISC values. The ISC numbers in the table were calculated around the same atomic spacings used in the other calculations, as opposed to the results shown in the figures, which are at the

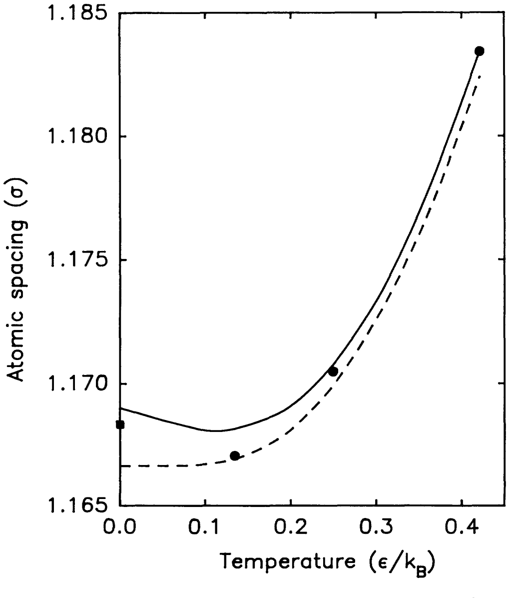

FIG. 1. Nearest-neighbor distance in Ne^{22}, expressed in units of the hard sphere radius σ. Circles are QMC results, dashed line is ISC, and solid line is second-order EPMC. The square at 0 K is the third-order effective potential result

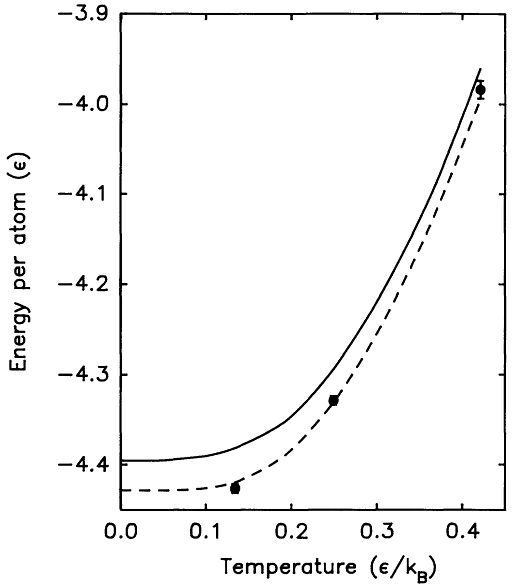

FIG. 2. Internal energy per atom in Ne^{22}, in units of the well-depth ϵ. Circles are QMC results, dashed line is ISC, and solid line is second-order EPMC.

TABLE I. Summary of QMC results.

Temperature (ϵ/k)	Spacing (σ)	Number of atoms	Trotter number	Millions of configs.	Pressure (ϵ/σ^3)	Energy (ϵ)
0.134	1.168 16	32	30	12	-0.10 ± 0.01	-4.434 ± 0.008
0.134	1.168 16	32	40	30	-0.10 ± 0.01	-4.435 ± 0.006
0.134	1.168 16	108	30	13	-0.08 ± 0.01	-4.426 ± 0.005
0.249	1.170 75	32	15	17	-0.06 ± 0.02	-4.340 ± 0.005
0.249	1.170 75	32	30	23	-0.06 ± 0.02	-4.340 ± 0.009
0.249	1.170 75	108	20	26	-0.02 ± 0.01	-4.329 ± 0.005
0.421	1.1834	32	10	20	-0.08 ± 0.02	-4.012 ± 0.007
0.421	1.1834	32	20	25	-0.09 ± 0.03	-4.016 ± 0.01
0.421	1.1834	108	10	14	0.01 ± 0.02	-3.984 ± 0.006

ISC equilibrium spacings. The difference is quite small and does not show in the figures. In order to plot nearest-neighbor distances for QMC in Fig. 1 we have assumed ISC values for the compressibility in order to convert the QMC pressures into changes of spacings. Again, this is a small correction and should be accurate.

IV. DISCUSSION

The three numerical techniques we have used all yield remarkably similar results. This overall agreement gives us confidence that the statistical uncertainties which we estimate for QMC by the usual type of method are in fact a good indication of the reliability of those results. We can then gauge the other techniques by their agreement with QMC theory. Our results are presented in Tables I and II and in Fig. 1 for the nearest-neighbor distances and Fig. 2 for the energies. We draw attention to the highly expanded scale of both figures. At the lowest temperature, the ISC results lie within the statistical uncertainties of QMC. The energy remains accurate at all temperatures, but at the highest temperature the ISC pressure becomes inaccurate. This is all very plausible. ISC improves on the first-order self-consistent theory (SC1) in an *ad hoc* fashion. It is gratifying that it agrees as well as it does, and not disturbing that deviations appear at higher temperatures.

The EPMC method is designed to pass smoothly into an exact classical calculation at high temperatures, and the agreement with QMC is best at 22 K, and worst at 7 K. Note that at 22 K neon is still a long way from being classical. We believe that at zero degrees the physical content of the effective potential method is identical with SC1, any differences in numerical results arising from the different treatment of the smearing, i.e., truncated series expansion as opposed to numerical integration. The rise in the lattice spacing at low temperatures is certainly an artifact of the expansion procedure. As we have previously noted,[9] the rise is less in the second-order theory than in the first-order theory, and the third-order point we can calculate at $T = 0$ K shows almost no rise. We have plotted this single third-order point in Fig. 1. At finite temperatures, the use of the effective potential in a Monte Carlo simulation transcends SC1, and, as we have said, it becomes exact both at the classical limit, and in the first correction term in the Wigner expansion.[14] Already at 7 K the effective potential value of the heat capacity is much better than the SC1 value.

The relative cost of the calculations is pertinent information when the choice of method is being made. The QMC calculations described here required approximately 40 h of time on a Cray-YMP computer, the EPMC calculations at the same three temperatures used about 30 min, and the ISC calculations were done on a Hewlett-Packard minicomputer but would have occupied the Cray for a few seconds. The EPMC and ISC calculations yield values for the heat capacity, which we were not able to get from QMC calculations, and ISC theory also gave the entropy and compressibility.

To summarize, it is clear that for a quantum solid like Ne, thermal and elastic properties can be obtained

TABLE II. Calculated values of the pressure (units of σ/ϵ^3) and energy (units of ϵ)

		QMC	Second-order eff. pot.	ISC
t=0.134	Pressure	-0.08 ± 0.01	-0.002 ± 0.002	-0.0854
	Energy	-4.426 ± 0.005	-4.381 ± 0.0004	-4.4188
t=0.249	Pressure	-0.02 ± 0.01	0.000 ± 0.003	-0.0548
	Energy	-4.329 ± 0.005	-4.294 ± 0.001	-4.3297
t=0.421	Pressure	0.01 ± 0.02	0.009 ± 0.005	-0.0454
	Energy	-3.984 ± 0.01	-3.961 ± 0.001	-3.9882

cheaply and accurately using ISC theory, with some small inaccuracies near melting. The EPMC theory is at the limit of its usefulness here. For even more pronounced quantum solids, such as He, a different evaluation of the effective potential, not using a series expansion, is required and this seems feasible. The QMC approach is very accurate but correspondingly expensive in computer time. The currently available computer codes will require substantial improvement to bring reliable calculation of fluctuation terms within reach. Several of us are planning to address this problem presently.

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