

AN INTRODUCTION TO PATH INTEGRAL MONTE CARLO FOR CONDENSED PHASES

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Path Integral Monte Carlo (PIMC) is currently the most successful method for simulating quantum systems at nonzero temperatures. As its name suggests, it is the combination of the path integral formulation of quantum mechanics, devised by Feynmann [1], and the familiar Metropolis Monte Carlo method [2] more commonly used in simulations of classical systems. Such a combination of approaches might be regarded as conceptually or practically difficult, but fortunately this is not the case. In practice it proves to be no more difficult to implement than an ordinary Monte Carlo simulation. Conceptually, the difficulties arise more from unfamiliarity with the approach than with physical principles. Our purpose in presenting this article is to provide a pedagogic introduction to PIMC which will serve as a starting point for newcomers to the subject. The minimum of mathematics necessary to give a self-consistent introduction will be presented. We hope that the essential simplicity of the method will become manifest.

In its original formulation the PIMC method does not provide information on the dynamical aspects of the system being simulated, but it is extremely useful when it comes to providing structural and thermodynamic information. With respect to time dependence it is inferior to the gaussian wavepacket methods [3] and the discrete wavepacket methods [4]. However it has some advantages of its own. The method is rigorous, and we have found it to be easily adaptable to many-particle systems (without exchange). Gaussian wavepackets are not yet sufficiently accurate [5], while discrete wavepackets presently appear to require too much computer memory for practical simulations. The interpretation of the physical properties of the system is another advantage. It is difficult, for example, to define the temperature in a system of gaussian wavepackets [5], (presumably the problem is worse in systems of discrete wavepackets), whereas it is an explicit parameter in PIMC. Also, the delocalisation of the quantum particles is easily dealt with in PIMC, but in wavepacket methods, the break-up of the scattered wavepackets is problematical.

1 The Propagator

We begin with the simple case of a single particle moving in one dimension and consider the concept of a propagator. Suppose we wish to solve the time dependent Schroedinger equation (in which the Hamiltonian operator H is *not* an explicit function of time and \hbar is Planck's constant; $h/2\pi$.)

$$H\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (1)$$

given that the solution $\psi = \psi(x, 0)$ is known at time $t=0$. A possible solution is provided by the following integral:

$$\psi(x, t) = \int G(\xi, 0; x, t) \psi(\xi, 0) d\xi \quad (2)$$

In which the function G (the Green's function) is known as a propagator, since a knowledge of the initial state of the wavefunction $\psi(\xi, 0)$, and the function G allows us to propagate the wavefunction through time, thus providing a solution of the Schroedinger equation at a later time t . Obtaining the form of the function G , is therefore formally equivalent to solving the time dependent Schroedinger equation. Clearly, this is not the only way the equation could be solved, but the concept of a propagator is central to the Feynmann formulation of quantum mechanics, and it is to that formulation that we look to guide us to the correct form of the function G in difficult cases. For the simple case being considered here however, we write the function G directly as (see Appendix):

$$G(\xi, 0; x, t) = \sum_n \phi_n^*(\xi) \phi_n(x) \exp(-i\hbar^{-1} E_n t) \quad (3)$$

in which the functions ϕ_n are the eigenfunctions of the operator H and E_n are the corresponding eigenvalues. Thus, provided we can solve the time independent Schroedinger equation for the operator H we have, through G , the solution to the more difficult problem of the propagation of a wavefunction ψ through time.

A simple example of the use of a Green's function, and one which is of particular relevance to PIMC (see below), is the propagation of a free-particle wavefunction (i.e one moving in a constant potential V_o). The eigenfunctions for the Hamiltonian appropriate to this case have the form:

$$\phi_p(x) = (2\pi\hbar)^{-1/4} \exp(-i\hbar^{-1} p x) \quad (4)$$

In which $p^2 = 2m(E_p - V_o)$, p is the momentum and E_p the energy. Using this form of eigenfunction, the Green's function may be written as:

$$G(\xi, 0; x, t) = (2\pi\hbar)^{-1/2} \int \exp(-i\hbar^{-1} [(p^2/2m)t + p(\xi - x) + tV_o]) dp \quad (5)$$

In which the sum has been replaced by an integral to exploit the infinitesimal differences between the possible eigenvalues. Performing this integration leads to:

$$G(\xi, 0; x, t) = (m/2\pi i\hbar t)^{1/2} \exp((im/2\hbar t)[(\xi - x)^2 - 2t^2 V_o/m]) \quad (6)$$

From which it is important to note that the Green's function is a Gaussian in terms of the spatial coordinates. In practice one may now use this function to propagate a given starting wavefunction, and derive the time evolution. However it is not the purpose of this note to solve problems of this nature. What is of interest is the case where the potential is a function rather than a simple constant. In this circumstance the Green's function cannot, in general, be obtained in closed form, but we can use Feynman's path integral approach to derive an acceptable approximation to the correct solution, which can be made as accurate as desired.

Consider the space-time diagram for the propagation of a particle in one-dimensional space (Figure 1). The particle moves from point A at time zero to point B at time t.

According to the tenets of quantum theory we cannot know what path the particle follows with certainty; we can only make probabilistic statements about where the particle is likely to be at a given time. Neither can we perform any experiment to reveal its position, since this will disrupt the process of propagation. However, the path integral theory provides a way of analysing the propagation from point (A;0) to point (B;t) through consideration of the intermediate points on the trajectory. Basically, the theory postulates that all possible trajectories starting at (A;0) and ending at (B;t) are equally admissible. The probability amplitude of arrival at B arises from a sum (or integral) over all the possible paths. Most of the possible paths cancel each other through their different phase factors (destructive interference); only those paths close to the classical trajectory will effectively contribute to the propagation process. In the classical limit there is no significant contribution from any but the classical trajectory. On the atomic scale however one cannot specify the path followed with such certainty.

If we consider a point in time t_c between 0 and t (Figure 1) then we understand that the moving particle can cross the line t_c at *any* position (e.g. $x_{c'}$, $x_{c''}$ etc.). If we choose a point along this line ($x_{c'}$ say), then we can describe the propagator from point A to $x_{c'}$ quite simply as $G(A, 0; x_{c'}, t_c)$. Similarly the propagator from $x_{c'}$ to B is $G(x_{c'}, t_c; B, t)$. In Feynman's formulation, the propagator from A to B *via* $x_{c'}$ is the product $G(A, 0; x_{c'}, t_c)G(x_{c'}, t_c; B, t)$. (This is because the arrival of the particle at $x_{c'}$ from A has a probability amplitude proportional to $G(A, 0; x_{c'}, t_c)$ and the arrival at B from $x_{c'}$ has a probability amplitude proportional to $G(x_{c'}, t_c; B, t)$, thus the probability amplitude of both events occurring in sequence is proportional to the product [1]). To get the correct description of the complete propagator from A to B we must reconstruct all the possible paths in between, that is we must consider all arrivals along the line t_c from A and all the departures from t_c to B. In other words the propagator $G(A, 0; B, t)$ is given by:

$$G(A, 0; B, t) = \int G(A, 0; x_c, t_c)G(x_c, t_c; B, t)dx_c \quad (7)$$

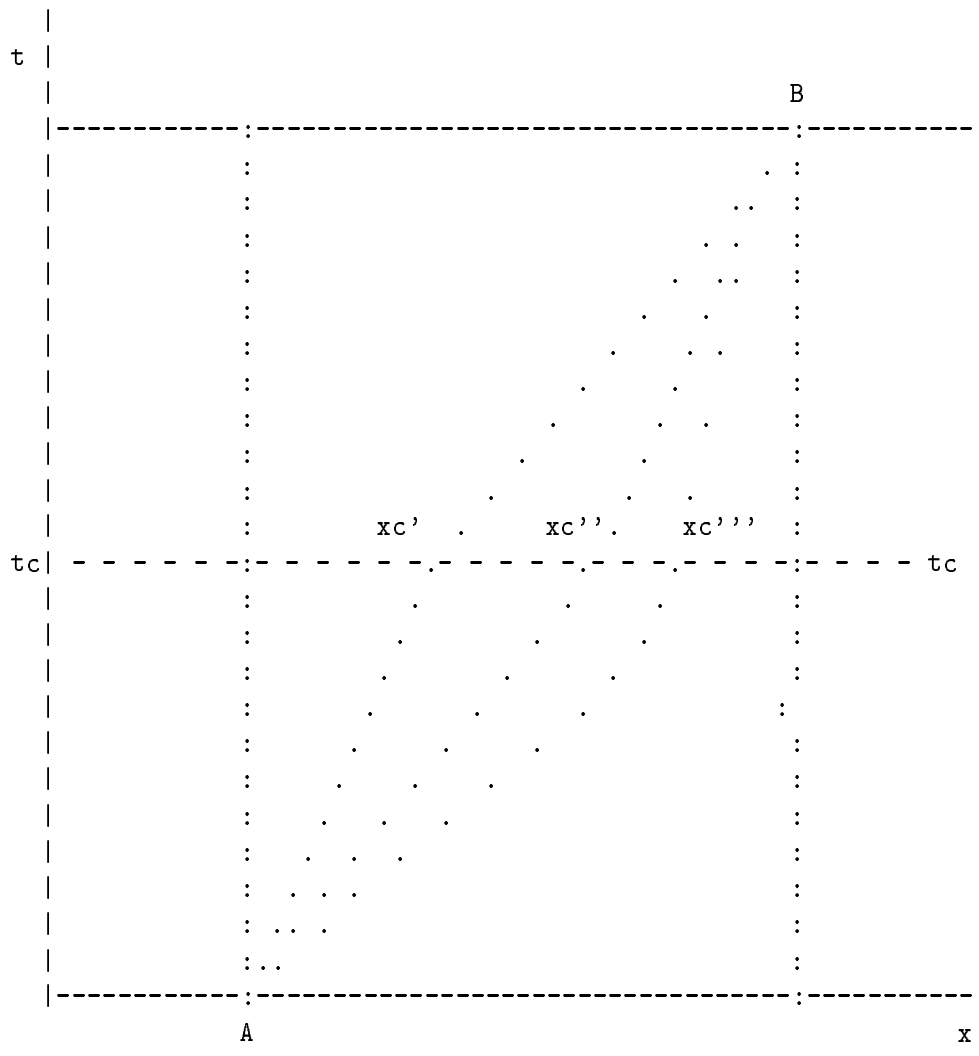


FIGURE 1

In this decomposition of the propagator we have considered only one partition of the time interval $[0, t]$. Clearly, we may consider any number of partitions, and by a similar process expand the propagator to:

$$G(A, 0; B, t) = \int \dots \int [\prod_{j=0}^{P-1} G(x_j, t_j; x_{j+1}, t_{j+1} - t_j)] \prod_{j=1}^{P-1} dx_j \quad (8)$$

Where $x_0 = A$, $x_P = B$, $t_0 = 0$ and $t_P = t$. This equation describes the partition of the interval $[0, t]$ into P sub-intervals. (Note the presence of the product of Green's functions within the above expression.)

The purpose of performing such a decomposition of the propagator is to be able to deal with more complicated potential energy functions, because we may now assume that the division of the time interval $[0, t]$ is such that over each sub-interval, the potential energy function hardly varies and we may treat it as a constant (i.e. $V(x) = V(x_i)$ over $[x_{i-1}, x_i]$). Therefore, using these assumptions we can write the propagator for the cases with more complicated potential functions as:

$$G(A, 0; B, t) = (m/2\pi i \hbar (t/P))^{P/2} \int \dots \int \exp((im/2\hbar(t/P)) \sum_{j=1}^P [(x_j - x_{j-1})^2 - 2(t/P)^2 V(x_j)/m]) dx_1 \dots dx_{P-1} \quad (9)$$

In which the propagator appropriate to the case of a constant potential (i.e. a Gaussian, see p.2) has been used for each sub-interval. This description is formally exact in the limit as P tends to infinity. Thus we see how the application of Feynman's path integral method has allowed us sufficient insight into this rather difficult problem to provide an acceptable description of the propagator. Later, we shall make use of this approximation of the trajectory by finite sub-intervals. It is commonly called the short time approximation.

2 Statistical Mechanics

When a particle is in a quantum state ϕ_n , the probability density of the particle at a point x is given by the product $\phi_n^*(x)\phi_n(x)$. However, in a system at a finite temperature, this is merely one of the many states thermally accessible to the particle. Therefore the probability density for the particle in the state ϕ_n is given by a Boltzman weighting of the state thus:

$$\phi_n^*(x)\phi_n(x) \exp(-\beta E_n)/Z \quad (10)$$

In which E_n represents the energy (eigenvalue) of the state ϕ_n and Z the normalising factor, which is given by

$$Z = \int \sum_n \phi_n^*(x)\phi_n(x) \exp(-\beta E_n) dx \quad (11)$$

This is of course the partition function for the states accessible to the particle. Therefore the average of a physical quantity can be obtained in a way that is analogous to the classical case i.e.

$$\langle A \rangle = \int \sum_n \phi_n^*(x) A \phi_n(x) \exp(-\beta E_n) dx / Z \quad (12)$$

In quantum mechanics, a more general way of expressing the partition function is by means of the density function $\rho(x, x'; \beta)$, which is defined as:

$$\rho(x, x'; \beta) = \sum_n \phi_n^*(x) \phi_n(x') \exp(-\beta E_n) \quad (13)$$

In terms of this function, the partition function may be expressed as:

$$Z = \int \rho(x, x; \beta) dx = Tr[\rho] \quad (14)$$

and the average of a physical quantity A as:

$$\langle A \rangle = \frac{1}{Z} Tr[A \rho(x, x'; \beta)] \quad (15)$$

In which the operation Tr (known as the *trace*) implies that the operator A acts first on functions of the coordinate x' and then x' is set equal to x for the integration. (In the case of the integral for Z the operator is unity.) These equations serve to show the central importance of the density function $\rho(x, x'; \beta)$ in the statistical mechanics of quantum systems.

We are now near to the heart of the PIMC method. We note that the form of the density function, expressed in terms of the wavefunctions ϕ_n , is analogous to the Green's function propagator. This suggests at once that any method that we can apply to solving the time dependent Schroedinger equation may also be applied to obtaining the partition function. All that is required is the formal substitution of the quantity $i\hbar^{-1}t$ by β . This is a powerful insight, since it means that we may use the short time approximation described above and other deductions based on the path integral concept to calculate the properties of a quantum mechanical ensemble. Thus the density function $\rho(x, x'; \beta)$ can be written directly as:

$$\begin{aligned} \rho(x, x'; \beta) &= (mP/2\pi\hbar^2\beta)^{P/2} \\ &\int \dots \int \exp(-\beta \sum_{j=1}^P \{mP/2(\hbar\beta)^2(x_j - x_{j-1})^2 + \\ &V(x_j)/P\}) dx_1 \dots dx_{P-1} \end{aligned} \quad (16)$$

Which is obtained directly from the expression for the Green's function $G(A,0;B,t)$ given earlier (Equation (9)), and we assume $x = x_0$ and $x' = x_P$.

The extension of this formula to three dimensional problems is trivial; we merely replace the coordinates x_j by the vectors \underline{r}_j and the pre-exponential factor becomes $(mP/2\pi\hbar^2\beta)^{3P/2}$. To evaluate the partition function Z it is necessary to integrate the trace of the density function, which means setting $\underline{r} = \underline{r}'$ (or equivalently, $\underline{r}_0 = \underline{r}_P$) and integrating over \underline{r} . We also note that we are still dealing with the partition function of a single particle. We now assume that the partition function for the ensemble of N particles is the product of N single-particle partition functions. These considerations lead to the following form for Z .

$$\begin{aligned}
Z &= \left\{ \frac{mP}{2\pi\hbar^2\beta} \right\}^{3PN/2} \\
&\int \dots \int \exp(-\beta \sum_{k=1}^N \sum_{j=1}^P \{ \frac{1}{2}\kappa(\underline{r}_{k,j} - \underline{r}_{k,j-1})^2 + \\
&V(\underline{r}_{k,j})/P \}) \prod_k^N \prod_j^P d\underline{r}_{k,j}
\end{aligned} \tag{17}$$

with

$$\kappa = \frac{mP}{\beta^2\hbar^2} \tag{18}$$

Where the index k refers to the k th particle (note that $\underline{r}_{k,0} = \underline{r}_{k,P}$). In this form the partition function reveals a surprising isomorphism: it is the same as the classical partition function for a system of ring polymers. To be more explicit: the quadratic term within the exponential corresponds to a ring of P “beads”, each of which is coupled to two neighbours via a harmonic spring with force constant κ . In addition each bead in the ring experiences the potential $V(\underline{r}_{k,j})/P$, which arises from the interactions between the different polymer rings. (It is worth pointing out that the reason a ring polymer results from this treatment, is that the application of the Tr or trace operation enforces the closure of the ring).

The most appealing aspect of this isomorphism is the fact that we can use conventional Monte Carlo methods to calculate the properties of the classical polymer system and translate them into the properties of the quantum mechanical system. There is no special difficulty in doing this, though it is important to be aware of the physical interpretation, in the quantum mechanical sense, to avoid some potential pitfalls. Before discussing these aspects we should point out that the Monte Carlo method is not the only option available to us. What is required is some means of sampling the configuration space available to the ring polymers and to that end both molecular dynamics and stochastic dynamics may also be used. However it must not be thought that these methods can be used to give the time dependent properties of the system; the formulation of the method does not support it.

3 The Properties of the Isomorphic Ring Polymer

The system of isomorphic polymers is one in which the potential energy may be written as:

$$U_{eff} = \sum_{k=1}^N \sum_{j=1}^P \left\{ \frac{1}{2} \kappa (\mathbf{r}_{k,j} - \mathbf{r}_{k,j-1})^2 + V(\mathbf{r}_{k,j})/P \right\} \quad (19)$$

We have already remarked on the nature of the quadratic term; classically it is equivalent to the intramolecular interactions of a harmonic ring polymer. What is its physical significance in the quantum mechanical case? Since we have replaced a classical “point” particle by a more delocalised polymer, we may guess that it reflects the “Heisenberg uncertainty” in the position of the particle. This intuitively appealing idea is supported by the properties of the spring constant κ . If the mass of the particle is large, or if the temperature is high (i.e. β is small), κ is large and the ring polymer will tend to be tightly bound into a small volume. These conditions correspond to the classical limit. Conversely, a small mass or a low temperature will weaken the spring constant and the polymer will delocalise to a much greater extent.

A feature of the ring polymers we should discuss is the number of beads P . In practice this has to be determined by experience. There are however some facts which we need to bear in mind. Firstly, the short time (or high temperature) approximation inherent in the derivation of the partition function requires that the number of beads be sufficiently large to justify the approximation. Thus a rapidly varying potential function implies a need for a large number of beads. Secondly, the presence of the number P in the spring constant κ implies that the appropriate choice of P will be influenced by the mass of the particle and the temperature of the system. Thus we find that simulations of argon below the triple point require about 5 beads [6] and liquid neon requires 20-40 beads [7]. Simulations of the electron in molten potassium chloride have required about 200 beads [8] and the electron in liquid ammonia several thousand beads [9].

The second term of the effective potential U_{eff} is the $V(\mathbf{r}_{k,j})/P$ term, which corresponds to the interaction between different polymer rings. We notice the presence of the bead number P in the denominator. The significance of this is that it effectively reduces the interaction between beads on different rings by a factor P . As a result of this, we find that beads on different polymers are allowed to approach each other more closely than the original classical particles. In other words, the beads have a greater ability to “tunnel” into classically forbidden regions. This is exactly the kind of behaviour we expect for quantum systems and it is gratifying to see that the formulae permit it.

As for the potential $V(\mathbf{r}_{k,j})$, there are one or two subtleties that must be considered. In principle, it may be treated as the sum of pair interactions between sites (beads) on different polymers, as is normally done in classical simulations. However we should point out an important difference. Namely; each bead on a given polymer ring can only interact with *one* bead on the different polymer ring. It does *not* interact with them all. The reason for this lies in the correspondence

between the time dependent Green's function and the temperature dependent density function. The former is constructed from a partition of a time interval into P sub-intervals. The potential energy function is evaluated once for each sub-interval and the contributions all derive from that time interval (i.e. all contributions are evaluated at the same instant in time). Translation of this feature into the calculation of the density function shows that, since each bead corresponds to a time sub-interval in the original Green's function, a bead on a given polymer can only interact with the corresponding bead on another. Another way of saying this is that corresponding beads on different polymers exist at the same moment in imaginary time and can only interact with beads existing at the same moment. Thus we write the potential term as:

$$V(\mathbf{r}_{k,j}) = \sum_{j=1}^P \sum_{k=2}^N \sum_{k'} U(|\mathbf{r}_{k,j} - \mathbf{r}_{k',j}|) \quad (20)$$

Where $U(|\mathbf{r}_{k,j} - \mathbf{r}_{k',j}|)$ is a suitable pair potential, such as the Lennard-Jones potential.

This feature of the inter-polymer potential has two useful consequences. Firstly, the number of bead-bead interactions that must be calculated is considerably less than in a real simulation of a classical polymer. This represents a great reduction in computational cost. Secondly, the straightforward empirical (e.g. Lennard-Jones) potential can be used in the simulation without modification. This aspect only becomes apparent when one tries to simulate quantum systems with wavepackets, since there the basic potential must be modified to take into account the delocalisation of the particle over the wavepacket [5]. In the PIMC case, we are restricted to dealing with corresponding beads on each ring and the delocalisation of the rest of the ring does not enter into consideration.

4 Thermodynamic and Structural Calculations

In classical Monte Carlo simulations one of the simplest quantities to calculate is the energy of the system. The expression for this is obtained from the partition function in the form of a derivative:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z. \quad (21)$$

Application of this rule to the partition function for the system of isomorphic polymers gives

$$\langle E \rangle = \left\langle \frac{3PN}{2\beta} - \sum_{k=1}^N \sum_{j=1}^P \left\{ \frac{1}{2} \kappa (\mathbf{r}_{k,j} - \mathbf{r}_{k,j-1})^2 + V(\mathbf{r}_{k,j})/P \right\} \right\rangle \quad (22)$$

The first two terms on the right represent the kinetic energy of the system. The last term represents the potential energy. This expression for the energy of the quantum system (which should **not** be confused with the potential energy U_{eff} of the isomorphic polymers that drives the Monte Carlo

simulation) has been the subject of much discussion in the literature. Herman *et al* [10] have shown that this form for the energy is subject to fluctuations that grow linearly with the number of beads in the polymer rings and consequently leads to poor estimates of the energy. For this reason they have proposed a new form of the energy estimator based on the virial. In the many-particle systems we are concerned with here, the estimator takes the form [13]

$$\langle E \rangle = \left\langle \frac{3PN}{2\beta} + \sum_{k=1}^N \sum_{j=1}^P \left\{ \frac{1}{2}(\mathbf{r}_{k,j} - \mathbf{r}_{k,1}) \cdot \frac{\partial}{\partial \mathbf{r}_{k,j}} V(\mathbf{r}_{k,j})/P \right\} \right\rangle. \quad (23)$$

(Where $\mathbf{r}_{k,1}$ refers to the first bead on the k th ring.) This estimator is considered to be more accurate than that given in Equation 22. However we have found that, for the systems we have studied, this is not the case. This may be due to the relatively small numbers of beads in the rings we have used (since our particles; neon and argon atoms, are almost classical), which do not adequately reflect the differences between the two estimators, or to the steepness of the Lennard-Jones potential, which generates large fluctuations in the virial term.

The virial of the quantum system is obtained from the derivative of the inter-polymer potential energy:

$$\langle \Phi \rangle = \left\langle \frac{1}{P} \sum_{j=1}^P \sum_{k=2}^N \sum_{k'=1}^k \left\{ (\mathbf{r}_{k,j} - \mathbf{r}_{k,j-1}) \cdot \frac{\partial}{\partial \mathbf{r}_{k,j}} U(|\mathbf{r}_{k,j} - \mathbf{r}_{k',j}|) \right\} \right\rangle \quad (24)$$

which may be used to calculate the pressure \mathcal{P} :

$$\mathcal{P} = (2\langle KE \rangle - \langle \Phi \rangle)/3V \quad (25)$$

where KE is the quantum mechanical kinetic energy:

$$KE = \frac{3PN}{2\beta} - \sum_{k=1}^N \sum_{j=1}^P \left\{ \frac{1}{2} \kappa (\mathbf{r}_{k,j} - \mathbf{r}_{k,j-1})^2 \right\}. \quad (26)$$

A useful quantity to calculate in these quantum systems is the mean-square radius (\mathcal{X}^2) of the polymer rings. This is given quite simply by the formula:

$$\mathcal{X}^2 = \left\langle (NP)^{-1} \sum_{k=1}^N \sum_{j=1}^P |\mathbf{r}_{k,j} - \mathbf{R}_k|^2 \right\rangle \quad (27)$$

where \mathbf{R}_k is the position of the centre of mass of the polymer ring;

$$\mathbf{R}_k = \frac{1}{P} \sum_{j=1}^P \mathbf{r}_{k,j}. \quad (28)$$

The usefulness of this quantity is that it provides a ready measure of the delocalisation of the quantum particle. In this respect it rather resembles the mean-square width parameter ξ_j^2 , encountered in semiclassical simulations of gaussian wavepackets and which roughly corresponds to the mean-squared-width of the wavepackets [5]. It is of the same order of magnitude as the square of the thermal deBroglie wavelength ($\lambda = (\hbar/\sigma)^2/m\varepsilon$) for the Lennard-Jones system.

The calculation of the radial distribution function for a many-particle system presents no special difficulty in PIMC if we remember to consider only pairs of corresponding beads on different ring polymers. Thus we may write:

$$g(r) = \frac{1}{PN\rho} \left\langle \sum_{k=2}^N \sum_{k'=1}^k \sum_{j=1}^P \delta(|\underline{r} + \underline{r}_{k,j} - \underline{r}_{k',j}|) \right\rangle \quad (29)$$

Thus we see that the PIMC method has all the tools required to calculate the standard structural and thermodynamic properties of a many-particle quantum mechanical system. We now conclude with a short account of our work on neon and argon.

5 The Simulation of Neon and Argon.

We have carried out PIMC simulations with the “primitive” high temperature algorithm described above for Lennard-Jones argon (solid) [6] and neon (liquid and solid) [14].

In the case of argon ($T^* = 0.5$ and 0.33) 4 and 5 beads are sufficient. The main objective was the calculation of the quantum correction to the free energy [6]. The corrections to the Helmholtz free energy and the internal energy are - as expected - small (2-3%). The effect on the pressure and hence the chemical potential however, is large: 0.35 and 0.5 (=15 and 21 mpa). We also find that at these state points the (quasi) harmonic approximation is unsatisfactory. Our results indicate that in the study of low temperature phase equilibria in solids the results obtained by classical MC and MD simulations should be treated with caution and that for molecular solids the harmonic approximation is not reliable.

In the PIMC simulations of neon 20-30 beads were required. At the experimental triple point ($\rho^* = 0.808$, $T^* = 0.666$) the quantum correction to the internal energy is 10% and that to the pressure is ~ 20 mpa. At $\rho^* = 0.725$, $T^* = 0.95$, where experimental data for $g(r)$ are available, these agree very well with the PIMC results but differ at small r from the classical MC result (as has also been found by Berne et al. for a slightly different state point [7]).

It is pleasing to note that for systems where quantum effects are fairly important but do not predominate (e.g. neon as against helium) many particle PIMC simulations can be carried out by the simple “primitive” algorithm and that recourse to the much more sophisticated sampling schemes of Pollock and Ceperley [11]. or that of Sprik *et al.* [12] - while possibly more economical in computing time - is not necessary.

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Appendix

The Green's Function Propagator

The Green's function propagator represents a formal solution of the time dependent Schroedinger equation;

$$\mathbf{H}\psi = i\hbar \frac{\partial}{\partial t} \psi \quad (30)$$

in which we assume that the Hamiltonian operator \mathbf{H} is *not* an explicit function of time and that the solution is known at time zero i.e. $\psi = \psi(x, 0)$ at $t = 0$. (We also assume here that the problem

is one-dimensional). Since \mathbf{H} does not contain the time explicitly equation (30) has a solution of the form

$$\phi_n(x, t) = \phi_n(x) \exp(-i\hbar^{-1} E_n t) \quad (31)$$

where $\phi_n(x)$ is an eigenfunction of the operator \mathbf{H} and E_n is the corresponding eigenvalue i.e.

$$\mathbf{H}\phi_n(x) = E_n\phi_n(x) \quad (32)$$

Since the set of functions $\phi_n(x)$ are orthogonal, the initial wavefunction $\psi(x, 0)$ may be expanded as a linear combination of eigenfunctions;

$$\psi(x, 0) = \sum_n a_n \phi_n(x) \quad (33)$$

in which the coefficients a_n are evaluated from the integrals:

$$a_n = \int \psi(x, 0) \phi_n^*(x) dx \quad (34)$$

(which is proved by multiplying both sides of (33) by $\phi_n^*(x) dx$ and integrating over x .) Exploiting the relations (31) to (34), it is apparent that a general solution of equation (30) would have the form:

$$\psi(x, t) = \sum_n a_n \phi_n(x) \exp(-i\hbar^{-1} E_n t). \quad (35)$$

Which is easily seen to satisfy both equation (30) and the initial condition $\psi = \psi(x, 0)$ at $t = 0$. Substituting (34) into (35) gives the expression:

$$\psi(x, t) = \int \sum_n \phi_n^*(\xi) \phi_n(x) \exp(-i\hbar^{-1} E_n t) \psi(\xi, 0) d\xi \quad (36)$$

Which may be more succinctly written as

$$\psi(x, t) = \int G(\xi, x; t) \psi(\xi, 0) d\xi \quad (37)$$

with

$$G(\xi, x; t) = \sum_n \phi_n^*(\xi) \phi_n(x) \exp(-i\hbar^{-1} E_n t) \quad (38)$$

which is recognisable as the Green's function described in the text of the article. It is apparent from its role in the equation (37) that the Green's function represents a formal solution to equation (30) since the wavefunction $\psi(x, t)$ is readily obtained once it has been derived. Extensions to problems of higher dimensionality may also be derived in this way.