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Path Integration via Molecular Dynamics

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1   Introduction

The formulation by Feynman of quantum statistical mechanics in terms of path integrals[1] has had a considerable impact on our ability to analyze the properties of quantum many-body systems at finite temperature. Not only do path integrals possess mathematical elegance, but they can be rendered into a computationally tractable form with an inherent structure perfectly suited for implementation on modern day parallel computing architectures. Thus, it is possible to calculate numerous equilibrium observable properties, including both thermodynamic and structural quantities, in a computationally efficient manner compared to other quantum approaches. Moreover, path integrals can be formulated in a variety of statistical ensembles, including the canonical (NVT), isothermal-isobaric (NPT), grand-canonical (μVT), and others, allowing a variety of external conditions to be investigated.

In spite of the power of path integrals, several important outstanding issues remain unresolved. First is the difficulty associated with the calculation of dynamical properties, such as time correlation functions (from which transport properties and spectra are obtained) and rates. Second is the problem of treating many-fermion systems. Both of these involve what is referred to as the "sign problem" which arises from a need to compute averages of rapidly oscillating phase functions. Several of the lectures in this series will describe this problem and progress that has been made (see lectures by D. M. Ceperley, R. Ramirez, R. Egger, and S. Sorella). See also, for example, references 2-5 .

Path integration involves the calculation of many-dimensional integrals. Traditionally, path integration has been performed using Monte Carlo (MC) techniques[6–9]. In principle, it is also possible to use molecular dynamics (MD), i.e. the numerical solution of Newtonian type equations of motion, to compute a path integral. However, as was shown by Hall and Berne[10], the evaluation of path integrals by MD is beset with difficulties related to the nonergodic nature of the trajectories generated. (The source of the ergodicity problem will be made manifestly clear later when we explore the mathematical structure of the discretized path integral.) Only recently has an MD algorithm that explicitly treats the ergodicity problem become available[11, 12], making the evaluation of path integrals by MD methods almost as efficient as as an optimized MC approach. There are a number of reasons to prefer MD over MC in the evaluation of path integrals. First, MD moves are complete system moves, and, therefore, MD approaches are considerably easier to implement on parallel computing architectures. Second, as will be seen in the second lecture, the combination of path integration with the Car-Parrinello *ab initio* molecular dynamics[13], in which internuclear

forces are computed "on the fly" from electronic structure calculations, requires the use of an MD propagation algorithm. Third, MD allows the use of efficient adiabatic propagation schemes in the calculation of approximate quantum dynamical properties via the so called "centroid dynamics" approach[14–17], to be discussed in this lecture.

In this lecture, the path integral formulation of the canonical density matrix and quantum partition function will be introduced and a MD based algorithm for performing the path integral will be discussed in detail. In particular, it will be shown that the introduction of a variable transformation in the path integral in conjunction with an appropriate thermostatting scheme can yield a very efficient MD approach. Applications to a number of illustrative example problems will be presented.

2 The Density Matrix and Quantum Statistical Mechanics

In quantum statistical mechanics, one considers an ensemble of systems described by Hamiltonian H, with each member of the ensemble possessing a state vector $|\Psi^{(\kappa)}\rangle$, $\kappa = 1, ..., Z$ in the Hilbert space that evolves in time according to the Schrödinger equation. Z represents the number of members in the ensemble. Let $\{|\phi_i\rangle\}$ be a complete orthonormal set of vectors in the Hilbert space. Then each state vector can be expanded in this set according to

$$|\Psi^{(\kappa)}\rangle = \sum_i C_i^{(\kappa)}|\phi_i\rangle \tag{1}$$

In order to compute the expectation value of any observable represented by an operator A, one must compute the expectation value of A for each system in the ensemble $\langle\Psi^{(\kappa)}|A|\Psi^{(\kappa)}\rangle$ and average over the members of the ensemble. Thus,

$$\langle A \rangle = \frac{1}{Z}\sum_{\kappa=1}^{Z} \langle\Psi^{(\kappa)}|A|\Psi^{(\kappa)}\rangle \tag{2}$$

Substituting Eq.(1) into Eq. (2) gives

$$\langle A \rangle = \sum_{i,j} \left(\frac{1}{Z}\sum_{\kappa=1}^{Z} C_j^{(\kappa)*}C_i^{(\kappa)} \right) \langle\phi_j|A|\phi_i\rangle \tag{3}$$

where the term in parentheses represents the ensemble average of the product of expansion coefficients. Inspection of this formula reveals that the expectation value can be written as the trace of a matrix product:

$$\langle A \rangle = \sum_{i,j} \rho_{ij}A_{ji} = \mathrm{Tr}(\rho A) \tag{4}$$

where $A_{ji} = \langle\phi_j|A|\phi_i\rangle$, and the matrix ρ_{ij}, known as the *density matrix*, is given by

$$\rho_{ij} = \frac{1}{Z}\sum_{\kappa=1}^{Z} C_i^{(\kappa)}C_j^{(\kappa)*} \tag{5}$$

The corresponding operator ρ with matrix elements $\rho_{ij} = \langle \phi_i | \rho | \phi_j \rangle$ can be written in the form

$$\rho = \frac{1}{Z} \sum_{\kappa=1}^{Z} |\Psi^{(\kappa)}\rangle \langle \Psi^{(\kappa)}| \tag{6}$$

i.e., the ensemble average of the projection operator onto the state vector of each member of the ensemble. From Eq. (5), it is clear that ρ is hermitian, so that it can be diagonalized with a set of real eigenvalues w_i and a complete set of orthonormal vectors $|w_i\rangle$. Conditions on the eigenvalues w_i can be derived from Eq. (4) by setting $A = 1$. Then,

$$\text{Tr}(\rho) = \sum_i w_i = \frac{1}{Z} \sum_{\kappa=1}^{Z} \langle \Psi^{(\kappa)} | \Psi^{(\kappa)} \rangle = 1 \tag{7}$$

since $|\Psi^{(\kappa)}\rangle$ is normalized to 1 for each member of the ensemble. Also, by letting $A = |w_j\rangle \langle w_j|$, we find that

$$\text{Tr}(\rho|w_j\rangle \langle w_j|) = \sum_{i,k} w_i \langle w_k | w_i \rangle \langle w_i | w_j \rangle \langle w_j | w_k \rangle = w_j \tag{8}$$

and also that

$$\langle A \rangle = \frac{1}{Z} \sum_{\kappa=1}^{Z} \langle \Psi^{(\kappa)} | w_j \rangle \langle w_j | \Psi^{(\kappa)} \rangle = \frac{1}{Z} \sum_{\kappa=1}^{Z} |\langle w_j | \Psi^{(\kappa)} \rangle|^2 \geq 0 \tag{9}$$

Therefore, $w_j \geq 0, \forall j$. Combining these two results gives the following properties satisfied by the eigenvalues of ρ

$$0 \leq w_i \leq 1, \qquad \forall i$$
$$\sum_i w_i = 1 \tag{10}$$

i.e., the eigenvalues w_i of ρ have the properties of probabilities.

An equation of motion for the density matrix can be derived by introducing the quantum time evolution operator $e^{-iHt/\hbar}$ and using it to evolve the state vectors in time:

$$|\Psi^{(\kappa)}(t)\rangle = e^{-iHt/\hbar} |\Psi^{(\kappa)}(0)\rangle \tag{11}$$

Thus,

$$\rho(t) = \frac{1}{Z} \sum_{\kappa=1}^{Z} e^{-iHt/\hbar} |\Psi^{(\kappa)}(0)\rangle \langle \Psi^{(\kappa)}(0)| e^{iHt/\hbar}$$
$$= e^{-iHt/\hbar} \rho e^{iHt/\hbar} \tag{12}$$

Differentiating both sides with respect to time gives the equation of motion:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} (H\rho - \rho H) = -\frac{i}{\hbar} [H, \rho(t)] \tag{13}$$

Note the difference in sign from the usual Heisenberg equation $dA/dt = i[H, A]/\hbar$.

In equilibrium, the density matrix must have no explicit time dependence, i.e., $\partial\rho/\partial t = 0$. Eq. (13) implies that $[H, \rho] = 0$, so that ρ can be expressed as a pure function of H and can therefore be diagonalized simultaneously with H. Thus,

$$\rho = f(H) = \sum_i f(E_i)|E_i\rangle\langle E_i| \tag{14}$$

where E_i and $|E_i\rangle$ are the eigenvalues and eigenvectors of the Hamiltonian, respectively. Thus, the eigenvalues w_i of ρ are pure functions of the eigenvalues of H, however, they must still satisfy the properties Eq. (10). The particular form of the function $f(E_i)$ determines which particular ensemble ρ represents. For the canonical, or NVT, ensemble, one of the most commonly used ensembles, $f(E_i)$ takes the form

$$f(E_i) = \frac{e^{-\beta E_i}}{Z} \tag{15}$$

where $\beta = 1/k_\mathrm{B}T$. The normalization constant Z insures that Tr $\rho = 1$ and is given by

$$Z = \sum_i e^{-\beta E_i} = \mathrm{Tr}\left[e^{-\beta H}\right] \tag{16}$$

Z is the canonical partition function, which determines the thermodynamics of the ensemble. The canonical density matrix therefore takes the form

$$\rho = \frac{e^{-\beta H}}{Z} \tag{17}$$

and the expectation value of an operator A, according to Eq. (4), is computed from

$$\langle A\rangle = \frac{1}{Z}\mathrm{Tr}\left[A\,e^{-\beta H}\right] \tag{18}$$

We see, therefore, that in order to study the properties of systems in the canonical ensemble, we need to be able to evaluate traces such as occur in Eqs. (16) and (18). In the next section, we shall see how such traces can be expressed in terms of path integrals.

3 Path Integral Formulation of the Canonical Density Matrix and Partition Function

Consider a single quantum particle of mass m, with momentum, p and coordinate, x, in a one-dimensional potential $\phi(x)$ described by a Hamiltonian:

$$H = \frac{p^2}{2m} + \phi(x) \equiv K + \Phi \tag{19}$$

where K and Φ are the kinetic and potential operators, respectively. In statistical mechanics, one is interested in an ensemble of such systems, and, if the ensemble is characterized by a constant temperature, T, and volume (length in one dimension), then the ensemble is the canonical ensemble for which the density matrix is given by

$$\rho = e^{-\beta H} \tag{20}$$

where $\beta = 1/kT$. The partition function, $Z(\beta)$, is the trace of ρ. The starting point for the derivation of the path integral is the evaluation of this trace in the coordinate basis,

which is valid since the trace is independent of the basis in which it is evaluated. Since the coordinate basis is a continuous basis, the trace is calculated as an integral:

$$Z(\beta) = \text{Tr}\left(e^{-\beta H}\right) = \int dx \ \langle x|e^{-\beta H}|x\rangle$$

$$= \int dx \ \langle x|e^{-\beta(K+\Phi)}|x\rangle \tag{21}$$

In general, the operators, K and Φ do not commute, so that the exponential, $\exp[-\beta(K+\Phi)]$ cannot be evaluated directly. However, use can be made of the Trotter theorem, which states that for any two operators, A and B, which, in general do not commute,

$$e^{\lambda(A+B)} = \lim_{P\to\infty}\left[e^{\frac{\lambda}{2P}B}e^{\frac{\lambda}{P}A}e^{\frac{\lambda}{2P}B}\right]^P \tag{22}$$

The proof of the Trotter theorem is rather involved and will not be given here, however, the interested reader is referred, for example, to the book by L. Schulman[18], where a discussion of the proof is given. Substituting the Trotter theorem into Eq. (21) yields

$$Z(\beta) = \lim_{P\to\infty}\int dx \ \langle x|\left[e^{-\frac{\beta}{2P}\Phi}e^{-\frac{\beta}{P}K}e^{-\frac{\beta}{2P}\Phi}\right]^P|x\rangle \tag{23}$$

Define an operator, Ω

$$\Omega = e^{-\frac{\beta}{2P}\Phi}e^{-\frac{\beta}{P}K}e^{-\frac{\beta}{2P}\Phi} \tag{24}$$

so that the partition function can be written

$$Z(\beta) = \lim_{P\to\infty}\int dx \ \langle x|\Omega^P|x\rangle = \lim_{P\to\infty}\int dx \ \langle x|\Omega\cdot\Omega\cdots\Omega|x\rangle \tag{25}$$

Equation (25) involves a product of P factors of the operator, Ω. Since Ω involves a product of three separate exponentials, it is possible (as we shall see shortly) to evaluate the coordinate-space matrix elements $\langle x|\Omega|x'\rangle$ of this operator analytically. Therefore, in order to obtain an expression that involves these matrix elements, we introduce an identity operator between each pair of factors of Ω in Eq. (25) in the form of a closure or completeness relation of the coordinate-space eigenvectors, $|x\rangle$:

$$I = \int dx \ |x\rangle\langle x| \tag{26}$$

Since there P operators in the product in Eq. (25), $P-1$ such insertions are possible. Labeling the integrations as $x_2, ..., x_P$ and changing the integration variable "x" in Eq. (25) to "x_1" yields

$$Z(\beta) = \lim_{P\to\infty}\int dx_1\cdots dx_P \ \langle x_1|\Omega|x_2\rangle\langle x_2|\Omega|x_3\rangle\langle x_3|\cdots|x_P\rangle\langle x_P|\Omega|x_1\rangle$$

$$= \lim_{P\to\infty}\int dx_1\cdots dx_P \ \left[\prod_{i=1}^P\langle x_i|\Omega|x_{i+1}\rangle\right]_{x_{P+1}=x_1} \tag{27}$$

where the condition, $x_{P+1} = x_1$ is a result of the trace.

We now need to evaluate the coordinate space matrix elements of Ω:

$$\langle x_i|\Omega|x_{i+1}\rangle = \langle x_1|e^{-\frac{\beta}{2P}\Phi}e^{-\frac{\beta}{P}K}e^{-\frac{\beta}{2P}\Phi}|x_{i+1}\rangle \tag{28}$$

Note that the potential operators are functions of x alone, and they are acting directly on coordinate eigenstates. Thus, pulling out the corresponding eigenvalues, we have

$$\langle x_i|\Omega|x_{i+1}\rangle = e^{-\frac{\beta}{2P}\phi(x_i)}\langle x_i|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle e^{-\frac{\beta}{2P}\phi(x_{i+1})} \tag{29}$$

The coordinate space matrix elements of $\exp(-\beta K/P)$ can be evaluated by introducing another completeness relation for momentum eigenstates,

$$I = \int dp \, |p\rangle\langle p| \tag{30}$$

which allows the matrix elements to be written as

$$\langle x_i|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle = \int dp \, \langle x_i|p\rangle\langle p|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle \tag{31}$$

In the above expression, $K = p^2/2m$ now acts on one of its eigenstates from the left, yielding:

$$\langle x_i|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle = \int dp \, e^{-\beta p^2/2mP}\langle x_i|p\rangle\langle p|x_{i+1}\rangle \tag{32}$$

Using the following relation for the inner product of coordinate and momentum eigenstates:

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \tag{33}$$

we find

$$\langle x_i|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle = \frac{1}{2\pi\hbar}\int dp \, e^{-\beta p^2/2mP}e^{ip(x_i-x_{i+1})/\hbar} \tag{34}$$

Performing the momentum integral by completing the square, the above matrix element becomes

$$\langle x_i|e^{-\frac{\beta}{P}K}|x_{i+1}\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2\right] \tag{35}$$

Substituting Eq. (35) into Eq. (29) gives the following expression for the matrix elements of Ω:

$$\langle x_i|\Omega|x_{i+1}\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2 - \frac{\beta}{2P}\left(\phi(x_i)+\phi(x_{i+1})\right)\right] \tag{36}$$

Finally, substituting Eq. (36) into Eq. (27) yields, for the canonical partition function

$$Z(\beta) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots dx_P$$
$$\exp\left\{-\sum_{i=1}^{P}\left[\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2 + \frac{\beta}{P}\phi(x_i)\right]\right\}_{x_{P+1}=x_1} \tag{37}$$

where the fact that $(\beta/2P) \sum_{i=1}^{P}(\phi(x_i) + \phi(x_{i+1})) = (\beta/P) \sum_{i=1}^{P} \phi(x_i)$ since $x_{P+1} = x_1$. Eq. (37) involves the limit of a P-dimensional integral know as the *discretized path integral* for the partition function, oven denoted simply as $Z_P(\beta)$:

$$
Z_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P
$$

$$
\exp\left\{ -\sum_{i=1}^{P} \left[\frac{mP}{2\beta\hbar^2}(x_{i+1} - x_i)^2 + \frac{\beta}{P}\phi(x_i) \right] \right\}_{x_{P+1}=x_1} \tag{38}
$$

so that $Z(\beta) = \lim_{P \to \infty} Z_P(\beta)$. Before going on to describe how to evaluate Eq. (38) by MD methods, some discussion on the discretized path integral is in order.

4   The Continuous Limit

The analysis of the preceding section showed how to obtain the partition function as a discrete path integral. Here we shall show how to obtain the $P \to \infty$ limit and provide an interpretation of the result. Let us begin by extending the result of Eq. (38) to a general density matrix element. By a similar procedure, it can be shown that general matrix elements of the density matrix, $\langle x| \exp(-\beta H)|x' \rangle$ are given by

$$
\langle x|e^{-\beta H}|x' \rangle = \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} e^{-\frac{\beta}{2P}(\phi(x)+\phi(x'))}
$$

$$
\times \int dx_2 \cdots dx_P \, \exp\left\{ -\frac{mP}{2\beta\hbar^2} \sum_{i=1}^{P}(x_{i+1} - x_i)^2 - \frac{\beta}{P} \sum_{i=2}^{P} \phi(x_i) \right\}_{x_1=x, x_{P+1}=x'} \tag{39}
$$

Interestingly, an expression for the matrix elements of another similar exponential operator, the quantum time evolution operator $\exp(-iHt/\hbar)$ can be obtained from Eq. (39) by setting $\beta = it/\hbar$:

$$
\langle x|e^{-iHt/\hbar}|x' \rangle = \lim_{P \to \infty} \left(\frac{mP}{2\pi it\hbar} \right)^{P/2} e^{-\frac{it}{2P\hbar}(\phi(x)+\phi(x'))}
$$

$$
\times \int dx_2 \cdots dx_P \, \exp\left\{ \frac{imP}{2t\hbar} \sum_{i=1}^{P}(x_{i+1} - x_i)^2 - \frac{it}{P\hbar} \sum_{i=2}^{P} \phi(x_i) \right\}_{x_1=x, x_{P+1}=x'} \tag{40}
$$

Let us focus our attention on Eq. (40) for a short while. We shall return to the density matrix and partition function afterward. In order to obtain the continuous limit of Eq. (40), we introduce a parameter

$$
\epsilon = \frac{t}{P} \tag{41}
$$

so that the above path integral expression becomes

$$
\langle x|e^{-iHt/\hbar}|x' \rangle = \lim_{P \to \infty} \left(\frac{m}{2\pi i\epsilon\hbar} \right)^{P/2} e^{-\frac{i\epsilon}{2\hbar}(\phi(x)+\phi(x'))}
$$

$$
\times \int dx_2 \cdots dx_P \, \exp\left\{ \frac{im}{2\epsilon\hbar} \sum_{i=1}^{P}(x_{i+1} - x_i)^2 - \frac{i\epsilon}{\hbar} \sum_{i=2}^{P} \phi(x_i) \right\}_{x_1=x, x_{P+1}=x'} \tag{42}
$$

or, multiplying and dividing by ϵ in the first term in the exponential,

$$\langle x|e^{-iHt/\hbar}|x'\rangle = \lim_{P\to\infty} \left(\frac{m}{2\pi i\epsilon\hbar}\right)^{P/2} e^{-\frac{i\epsilon}{2\hbar}(\phi(x)+\phi(x'))}$$

$$\times \int dx_2 \cdots dx_P \, \exp\left\{\frac{i\epsilon}{\hbar}\sum_{i=1}^{P}\frac{m}{2}\left(\frac{x_{i+1}-x_i}{\epsilon}\right)^2 - \frac{i\epsilon}{\hbar}\sum_{i=2}^{P}\phi(x_i)\right\}_{x_1=x,x_{P+1}=x'} \quad (43)$$

The limit $P \to \infty$ is equivalent to the limit $\epsilon \to 0$. Now, the points, $x_1, ..., x_P$ can be thought of as specific points of a continuous function $x(s)$, $s \in [0,t]$ such that $x_i = x((i-1)\epsilon)$ with $x(0) = x$ and $x(t) = x'$ as illustrated in the figure below: In
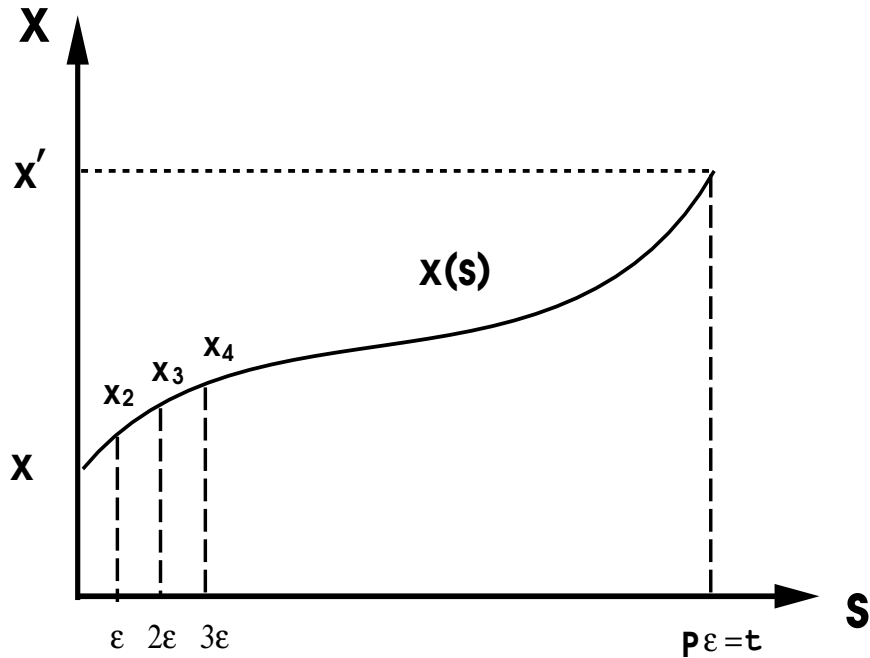

Figure 1. Illustration of the discretized path integral

this picture, several quantities appearing in Eq. (43) have limits that can be easily recognized. For example, the first term in the exponential will be recognized as the derivative with respect to s of $x(s)$:

$$\lim_{\epsilon\to0}\frac{x_{i+1}-x_i}{\epsilon} = \lim_{\epsilon\to0}\frac{x(i\epsilon)-x((i-1)\epsilon)}{\epsilon} = \frac{dx}{ds} \quad (44)$$

In addition, when the $\epsilon \to 0$ limit is taken of the sum appearing in the exponential, the result will be recognized as a Riemann sum or trapezoidal rule type of expression for a

continuous integral over s:

$$\lim_{\epsilon \to 0} \left[\frac{i\epsilon}{\hbar} \sum_{i=1}^{P} \frac{m}{2} \left(\frac{x_{i+1} - x_i}{\epsilon} \right)^2 - \frac{i\epsilon}{2\hbar} \left(\phi(x) + \phi(x') \right) - \frac{i\epsilon}{\hbar} \sum_{i=2}^{P} \phi(x_i) \right]$$

$$= \frac{i}{\hbar} \int_0^t ds \left[\frac{m}{2} \left(\frac{dx}{ds} \right)^2 - \phi(x(s)) \right]. \tag{45}$$

Finally, consider the integration measure

$$\left(\frac{m}{2\pi i \epsilon \hbar} \right)^{P/2} dx_1 \cdots dx_P.$$

As $P \to \infty$ and $\epsilon \to 0$, the number of points becomes infinte, and they become infinitely closely spaced. As Fig. 1 suggests, then integration becomes an integration over *all* continuous functions, $x(s)$ that begin at x and end at x'. A special notation is introduced to represent this "integration over all functions":

$$\lim_{P \to \infty, \epsilon \to 0} \left(\frac{m}{2\pi i \epsilon \hbar} \right)^{P/2} dx_1 \cdots dx_P \equiv \mathcal{D}x(s). \tag{46}$$

Combining Eq. (45) and Eq. (46) gives the following expression for the matrix element of the propagator:

$$\langle x | e^{-iHt/\hbar} | x' \rangle = \int_x^{x'} \mathcal{D}x(s) \exp \left\{ \frac{i}{\hbar} \int_0^t ds \left[\frac{m}{2} \left(\frac{dx}{ds} \right)^2 - \phi(x(s)) \right] \right\} \tag{47}$$

Eq. (47) is known as the *functional integral representation* of the path integral. In effect, it represents an integration over all functions, $x(s)$ with the boundary conditions $x(0) = x$ and $x(t) = x'$ and a weight given by the exponential appearing in Eq. (47). Such functions, $x(s)$, can also be regarded as "paths" between x and x', hence, Eq. (47) is also referred to as the continuous *path integral*, being an integration over all paths between x and x'.

The integrand appearing in the exponential in Eq. (47) has a special name in classical mechanics. It is known as the *Lagrangian*:

$$L(x, \dot{x}) = \frac{m}{2} \dot{x}^2 - \phi(x) \tag{48}$$

where $\dot{x} \equiv dx/ds$. The Lagrangian is simply the difference between the kinetic and potential energies, expressed as a function of the velocity, $\dot{x}$ and position, x. The reader may easily verify that the following *Euler-Lagrange* equation:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) - \frac{\partial L}{\partial x} = 0 \tag{49}$$

is equivalent to the Newton equation of motion $m\ddot{x} = -d\phi/dx$. Moreover, the integral of the Lagrangian over a specific path, $x(s)$, plays an important role in classical mechanics. It known as the *action* integral:

$$A[x(s)] = \int_0^t ds \ L(x(s), \dot{x}(s)) \tag{50}$$

Again, the reader may verify directly that the Euler-Lagrange equation, Eq. (49) results from extremization of the action

$$\delta A = 0 \tag{51}$$

with respect to the path. Paths that satisfy this extremization condition are known as *classical paths*. Thus, in terms of the action, the continuous path integral for the propagator can be written:

$$\langle x | e^{-iHt/\hbar} | x' \rangle = \int_x^{x'} \mathcal{D}x(s) \; e^{\frac{i}{\hbar} A[x(s)]} \tag{52}$$

The content of Eq. (52) is that the complete propagator is constructed by "summing" (integrating) over all paths between x and x' weighted by the complex exponential of the action for each path divided by $\hbar$. The sum over paths is illustrated in Fig. 2 below:

By virtue of Eq. (51), it is clear that classical paths will have the most significant contribution to the path integral, as a small change from a classical path will only cause small changes in the action, hence only small variations in the oscillating integrand of Eq. (52). For paths that differ substantially from classical paths, small changes will cause large changes in the action, and, hence, the oscillatory functions in Eq. (52) will fluctuate wildly, leading to positive and negative contributions that largely cancel out.
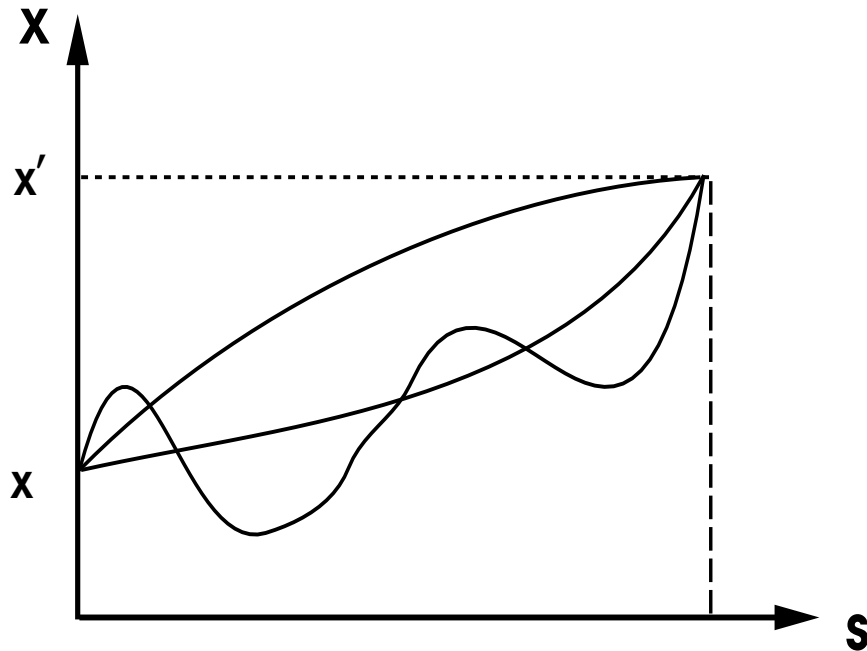

Figure 2. Illustration of the sum over paths

Turning, once again, to the density matrix, we noted above that an expression for the propagator could be obtained from the density matrix by letting $\beta = it/\hbar$. Conversely, the density matrix can be obtained from the propagator by letting $t = -i\beta\hbar$, i.e., by letting time be imaginary. For this reason, the canonical density matrix is often referred to as an *imaginary time* or *Euclidean* propagator. Taking the continuous limit of Eq. (39) leads to the following path integral expression for the density matrix:

$$\langle x|e^{-\beta H}|x'\rangle = \int_x^{x'} \mathcal{D}x(\tau) \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left[\frac{m}{2}\left(\frac{dx}{d\tau}\right)^2 + \phi(x(\tau))\right]\right\} \quad (53)$$

where τ is an imaginary time integration variable, $\tau \in [0, \beta\hbar]$, and the integration is now over all imaginary time paths, $x(\tau)$ beginning at x and ending at x'. Eq. (53) is known as a continuous *imaginary time path integral*. The quantity in the integrand of the exponential in Eq. (53) has the form of the kinetic plus potential energies expressed as a function of x and $\dot{x} = dx/d\tau$. This is know as the *Euclidean Lagrangian*

$$\mathcal{L}(x, \dot{x}) = \frac{m}{2}\dot{x}^2 + \phi(x) \quad (54)$$

and its integral over a continuous path $x(\tau)$ is called the *imaginary time* or *Euclidean* action:

$$S[x(\tau)] = \int_0^{\beta\hbar} d\tau\, \mathcal{L}(x(\tau), \dot{x}(\tau)) \quad (55)$$

Minimization of this action via $\delta S = 0$ leads to the same Euler-Lagrange equation of motion for the classical paths:

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) - \frac{\partial \mathcal{L}}{\partial x} = 0 \quad (56)$$

However, when the Euclidean Lagrangian is substituted into Eq. (56), the resulting equation of motion for the classical paths is

$$m\ddot{x} = \frac{d\phi}{dx} \quad (57)$$

which leads to motion on the inverted potential surface, $-\phi(x)$. Again, Eq. (57) must be subject to the condition, $x(0) = x$ and $x(\beta\hbar) = x'$ in order to obtain the appropriate classical paths. Thus, the density matrix can be expressed as an imaginary time path integral involving the Euclidean action:

$$\langle x|e^{-\beta H}|x'\rangle = \int_x^{x'} \mathcal{D}x(\tau)\, e^{-\frac{1}{\hbar}S[x(\tau)]} \quad (58)$$

Since $S[x(\tau)]$ is a minimum along the classical paths, paths satisfying Eq. (57) subject to the boundary conditions constitute the dominant contribution to the imaginary time path integral. Paths far from the classical paths will have large Euclidean actions and, therefore, will be severely damped out by the damped exponential appearing in Eq. (58).

Finally, returning to the partition function, recall that $Z(\beta)$ is the trace of the density matrix, which can now be expressed in terms of an imaginary time path integral:

$$Z(\beta) = \int dx \ \langle x | e^{-\beta H} | x \rangle$$

$$= \int dx \int_x^x \mathcal{D}x(\tau) \ e^{-\frac{1}{\hbar} S[x(\tau)]} \tag{59}$$

The imaginary time path integral expression for $Z(\beta)$ states that one must first calculate the diagonal density matrix elements by performing a sum over all imaginary time paths, $x(\tau)$ that begin and end at the same point, x, via the boundary condition, $x(0) = x(\beta\hbar) = x$, and then integrate over all values of x. This sum is illustrated in Fig. 3 below: Since these
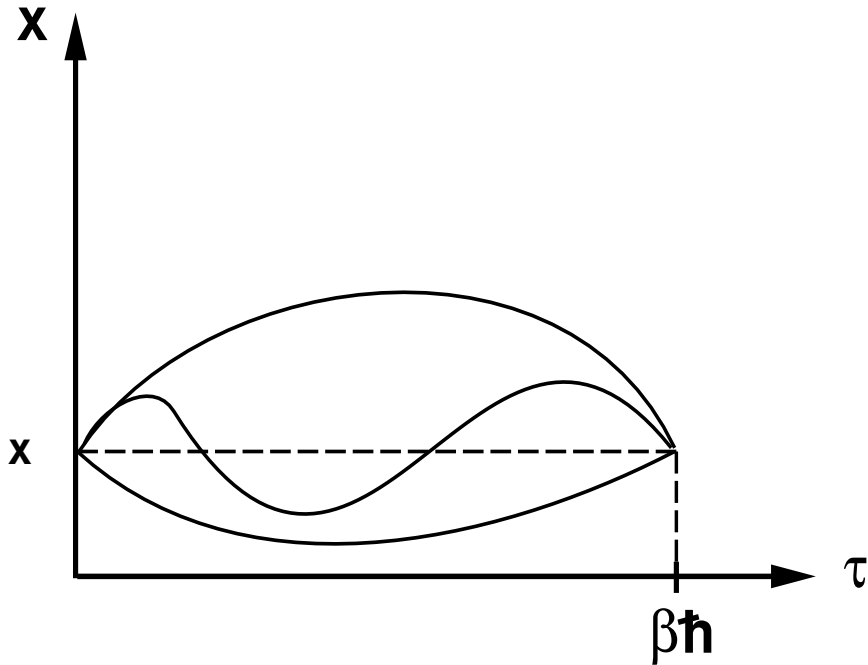

Figure 3. Illustration of the sum over cyclic imaginary time paths

imaginary time paths are cyclic, in that they return to their starting values in imaginary time $\tau = \beta\hbar$, Eq. (59) is often written in the shorthand form:

$$Z(\beta) = \oint \mathcal{D}x(\tau) \ e^{-\frac{1}{\hbar} S[x(\tau)]} \tag{60}$$

where $\oint$ indicates and integration over all cyclic paths that satisfy the condition $x(0) = x(\beta\hbar)$.

5 Thermodynamics and Expectation Values in Terms of Path Integrals

Suppose we wish to compute the expectation value of an operator, $\hat{O}$ that is purely a function of the operator, x, $\hat{O} = \hat{O}(x)$. By definition, the expectation value of $\hat{O}$ is

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}\left[\hat{O}e^{-\beta H}\right]}{\mathrm{Tr}\left[e^{-\beta H}\right]} = \frac{1}{Z(\beta)}\mathrm{Tr}\left[\hat{O}e^{-\beta H}\right] \tag{61}$$

Once again, carrying out the trace in the coordinate basis gives

$$\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \int dx \, \langle x|\hat{O}e^{-\beta H}|x\rangle$$

$$= \frac{1}{Z(\beta)} \int dx \, o(x)\langle x|e^{-\beta H}|x\rangle \tag{62}$$

where $o(x)$ is the corresponding eigenvalue of $\hat{O}$ obtained by acting on a coordinate eigenstate. Substituting in the continuous imaginary time path integral expression for the diagonal density matrix element, the expectation value of $\hat{O}$ can be written as a continuous path integral of the form:

$$\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \oint \mathcal{D}x(s) \, o(x(s))e^{-\frac{1}{\hbar}S[x(s)]} \tag{63}$$

It can also be written as the limit of a discrete path integral:

$$\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \lim_{P\to\infty} \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}$$

$$\times \int dx_1 \cdots dx_P \, o(x_1) \exp\left\{-\sum_{i=1}^{P}\left[\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2 + \frac{\beta}{P}\phi(x_i)\right]\right\}_{x_{P+1}=x_1} \tag{64}$$

Recognizing, however, that the integral in Eq. (64) is invariant under a cyclic relabeling of all of the path integration variables, $x_1 \to x_2$, $x_2 \to x_3$, etc., such a cyclic relabeling can be performed P times, the resulting expressions added together and then divided by P to yield:

$$\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \lim_{P\to\infty} \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}$$

$$\times \int dx_1 \cdots dx_P \frac{1}{P}\sum_{i=1}^{P} o(x_i) \exp\left\{-\sum_{i=1}^{P}\left[\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2 + \frac{\beta}{P}\phi(x_i)\right]\right\}_{x_{P+1}=x_1} \tag{65}$$

A finite P expression for $\langle \hat{O} \rangle$ can be obtained by substituting $Z_P(\beta)$ for $Z(\beta)$ and writing

$$\langle \hat{O} \rangle_P = \frac{1}{Z_P(\beta)} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2}$$

$$\times \int dx_1 \cdots dx_P \frac{1}{P} \sum_{i=1}^{P} o(x_i) \exp \left\{ -\sum_{i=1}^{P} \left[\frac{mP}{2\beta\hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \phi(x_i) \right] \right\}_{x_{P+1}=x_1}$$

$$(66)$$

so that the true expectation value is obtained in the limit $P \to \infty$:

$$\langle \hat{O} \rangle = \lim_{P \to \infty} \langle \hat{O} \rangle_P \tag{67}$$

Note that the quantity

$$f(x_1, ..., x_P) = \frac{1}{Z_P(\beta)} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2}$$

$$\exp \left\{ -\sum_{i=1}^{P} \left[\frac{mP}{2\beta\hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \phi(x_i) \right] \right\}_{x_{P+1}=x_1} \tag{68}$$

satisfies the properties of a P-dimensional probability distribution function, i.e. it is positive definite and integrates to unity. Defining the quantity

$$o_P(x_1, ..., x_P) = \frac{1}{P} \sum_{i=1}^{P} o(x_i) \tag{69}$$

the expectation value can be written as an average with respect to the probability distribution function $f(x_1, ..., x_P)$:

$$\langle \hat{O} \rangle_P = \langle o_P(x_1, ..., x_P) \rangle_f \equiv \int dx_1 \cdots dx_P \, o_P(x_1, ..., x_P) f(x_1, ..., x_P) \tag{70}$$

The quantity $o_P(x_1, ..., x_P)$ is called an *estimator* for the operator $\hat{O}$. In the limit $P \to \infty$, the average of $o_P(x_1, ..., x_P)$ with respect to the probability distribution $f(x_1, ..., x_P)$ will yield the true expectation value of $\hat{O}$:

$$\langle \hat{O} \rangle = \lim_{P \to \infty} \langle o_P(x_1, ..., x_P) \rangle_f \tag{71}$$

Estimators play an important role in path integral calculations. Any observable quantity will have a corresponding estimator, i.e. a function of $x_1, ..., x_P$ whose average gives, in the limit $P \to \infty$, the true expectation value of that observable.

Estimators for thermodynamic quantities can be derived as well. These are often obtained as derivatives of the partition function. Consider the total internal energy, E, given by

$$E = -\frac{\partial}{\partial \beta} \ln Z(\beta) = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta)}{\partial \beta} \tag{72}$$

The estimator is obtained by substituting $Z_P(\beta)$ for the true $Z(\beta)$ and computing the required derivative. The reader may easily verify that the resulting expression is

$$E_P = \langle \varepsilon_P(x_1, ..., x_P) \rangle_f \tag{73}$$

where the estimator, $\varepsilon_P(x_1, ..., x_P)$ is given by

$$\varepsilon_P(x_1, ..., x_P) = \frac{P}{2\beta} - \sum_{i=1}^{P} \left[\frac{mP}{2\beta^2 \hbar^2} (x_{i+1} - x_i)^2 - \frac{1}{P}\phi(x_i) \right] \tag{74}$$

Equation (74) is known as the *primitive energy estimator*. The true total thermodynamic internal energy will be given as the $P \to \infty$ limit of the average of this estimator with respect to the distribution function $f(x_1, .., x_P)$. However, owing to the quadratic term in Eq. (74) and its linearly P-dependent prefactor, this estimator is somewhat difficult to work with numerically, especially as P becomes large, as was originally shown by Hermann Bruiskin and Berne[19]. These authors showed that the convergence error in this estimator grows with P. In order to rectify this, they derived an equivalent form of the estimator using the virial theorem that involves only the potential and its first derivative. The alternative estimator, known as the *virial estimator* is given by

$$\varepsilon_P^{(\mathrm{vir})}(x_1, ..., x_P) = \frac{1}{2\beta} + \frac{1}{P} \sum_{i=1}^{P} \left[\frac{1}{2}(x_i - x_c)\frac{\partial \phi}{\partial x_i} + \phi(x_i) \right] \tag{75}$$

where x_c is a quantity known as the *path centroid* and is simply the geometric center of the path given by

$$x_c = \frac{1}{P} \sum_{i=1}^{P} x_i \tag{76}$$

or, in the continuous limit,

$$x_c = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau \; x(\tau) \tag{77}$$

This quantity is of central importance in the development of semi-classical effective potentials via the approach of Feynman and Kleinert[20] and can also be used to obtain approximate quantum dynamics via the so called centroid dynamics method[14–17].

Other thermodynamic estimators can be derived, for example, for the pressure[21] or heat capacity[22], however, details of the derivations will not be given here. Rather, we will next turn our attention to the problem of computing path integrals and quantum observable properties via molecular dynamics.

6 Path Integral Molecular Dynamics

The continuous functional integral representation of the path integral is mathematically elegant and can be used for formal manipulations, however, it is not suitable for direct numerical evaluation. The latter requires the discrete, finite P form of the partition function given by

$$Z_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P$$
$$\exp\left\{ -\sum_{i=1}^{P} \left[\frac{mP}{2\beta\hbar^2}(x_{i+1} - x_i)^2 + \frac{\beta}{P}\phi(x_i) \right] \right\}_{x_{P+1}=x_1} \tag{78}$$

Introducing a "chain frequency"

$$\omega_P = \frac{\sqrt{P}}{\beta\hbar} \tag{79}$$

and an effective potential

$$U_{\text{eff}}(x_1, ..., x_P) = \sum_{i=1}^{P} \left[\frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P}\phi(x_i) \right]_{x_{P+1}=x_1} \tag{80}$$

Eq. (78) can be written as

$$Z_P(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P \; e^{-\beta U_{\text{eff}}(x_1,...,x_P)} \tag{81}$$

When written in this manner, the quantum partition function looks like a classical configurational partition function for a P-particle systems, where the P particles are discrete points along a cyclic path. This is illustrated in Fig. 4 below: Since the discrete cyclic
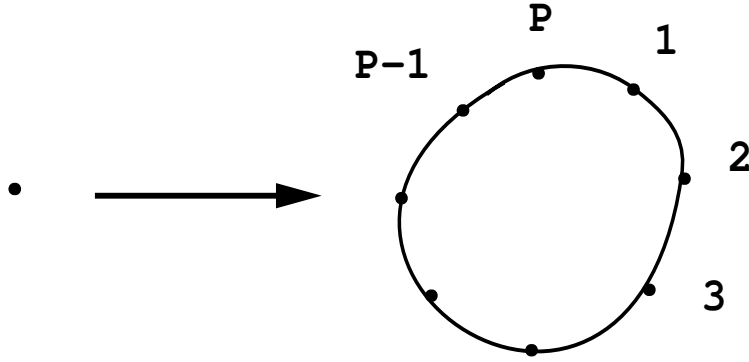

Figure 4. Illustration of the connection between a single quantum particle and the discretized P-point ("bead") path

path resembles a beaded necklace, the P particles are often referred to as "beads." Owing to the quadratic term in Eq. (80), the beads are coupled to each other by nearest neighbor harmonic springs with frequency ω_P, as the figure illustrates. Moreover, each bead is separately subject to the external potential, $\phi(x)$, i.e. $\phi(x)$ acts on only one bead at a time and gives rise to *no additional* coupling between the beads.

In order to make the connection between the quantum partition function and the fictitious P-particle classical system more manifest, consider supplementing Eq. (81) by a set of P Gaussian integrals and writing

$$Z_P(\beta) = \mathcal{N} \int dp_1 \cdots dp_P \int dx_1 \cdots dx_P \; \exp\left\{ -\beta \left[\sum_{i=1}^{P} \frac{p_i^2}{2\tilde{m}_i} + U_{\text{eff}}(x_1, ..., x_P) \right] \right\} \tag{82}$$

The new Gaussian variables are regarded as fictitious classical "momenta" so that the constants, $\tilde{m}_i$ have units of mass. Note that these Gaussian integrals are uncoupled and can be performed analytically to yield, $\prod_{i=1}^{P}(2\pi\tilde{m}_i/\beta)^{P/2}$, and the overall constant $\mathcal{N}$ can be chosen so as to reproduce the correct prefactor in Eq. (81). Thus, we have complete freedom to choose the $\tilde{m}_i$ as we like. Writing the partition function in this manner, however, gives it the form of a P-dimensional classical phase space integral for the fictitious classical system consisting of P beads. This connection between the quantum system and the P-particle fictitious classical system is known as the *classical isomorphism*[23]. The true quantum system is recovered as the number of fictitious classical beads, P, becomes infinite.

Having connected the quantum partition function to a fictitious classical partition function, Eq. (82) can be evaluated, at least in principle, using classical molecular dynamics (MD) based on equations of motion derived from a fictitious classical Hamiltonian of the form

$$H(p,x) = \sum_{i=1}^{P} \frac{p_i^2}{2\tilde{m}_i} + U_{\text{eff}}(x_1, ..., x_P)$$

$$= \sum_{i=1}^{P} \left[\frac{p_i^2}{2\tilde{m}_i} + \frac{1}{2}m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P}\phi(x_i) \right]_{x_{P+1}=x_1} \tag{83}$$

where $p \equiv \{p_1, ..., p_P\}$ and $x \equiv \{x_1, ..., x_P\}$. Such an approach is doomed to failure, however, as was established in 1984 by Hall and Berne[10]. The reason for this is due to the quadratic term in Eq. (83). First, as P becomes large, the effective force constant between the beads, $m\omega_P^2$ grows linearly with P. At the same time, the contribution from the external potential is attenuated by a factor of $1/P$ so that the harmonic forces dominate. This causes MD trajectories to remain very close to the invariant tori described by the $\phi = 0$ system and not explore the full available phase space. Second, since the quadratic term couples all of the beads, there are many time scales buried in this term, and the highest frequency of these will limit the time step that can be used. This means that lower frequency modes will be inadequately sampled, leading to very slow convergence of observable quantities. Third, ordinary MD will generate a microcanonical distribution of H, i.e. a distribution function of the form $\delta(H(p,x) - E)$, where E is the conserved energy. Clearly, this is not the form appearing in Eq. (82), which requires a canonical distribution of the form $\exp(-\beta H)$.

In order to solve these problems, we introduce a new MD based approach which includes the following features:

i. a change of integration variables in Eq. (82), which serves to uncouple the harmonic term, and a corresponding reformulation of the fictitious classical Hamiltonian;

ii. a multiple time scale numerical integration algorithm that treats the inherent time scales of the harmonic and external potential terms with appropriate time steps;

iii. a highly efficient canonical MD method that rigorously generates a canonical phase space distribution.

First, since the integration variables in Eq. (82) are completely arbitrary, we are free to change them with the aim of uncoupling the quadratic term. To this end, there are several

possibilities. Consider, first, a simple change of variables of the form:

$$u_1 = x_1$$
$$u_i = x_i - x_i^*$$
(84)

where

$$x_i^* = \frac{(i-1)x_{i+1} + x_1}{i}$$
(85)

This transformation is known as a *staging transformation* as it is based on the *staging Monte Carlo* approach of Ceperley and Pollock[6]. Note that the inverse of this transformation can be expressed in a convenient recursive fashion:

$$x_1 = u_1$$
$$x_i = u_i + \frac{i-1}{i}x_{i+1} + \frac{1}{i}u_1 \qquad i = 2, ..., P$$
(86)

where the $i = P$ term is used to start the recursion. It can also be expressed directly by

$$x_1 = u_1$$
$$x_i = \sum_{j=i}^{P} \frac{i-1}{j-1}u_j \qquad i = 2, ..., P$$
(87)

If Eq. (86) is substituted into Eq. (82), the resulting expression for the partition function is

$$Z_P(\beta) = \mathcal{N} \int dp_1 \cdots dp_P \int du_1 \cdots du_P \exp\left\{-\beta\left[\sum_{i=1}^{P} \frac{p_i^2}{2\tilde{m}_i} + U_{\text{eff}}^{(\text{stage})}(u_1, ..., u_P)\right]\right\}$$
(88)

where the transformed effective potential is

$$U_{\text{eff}}^{(\text{stage})}(u_1, ..., u_P) = \sum_{i=1}^{P}\left[\frac{1}{2}m_i\omega_P^2 u_i^2 + \frac{1}{P}\phi(x_i(u_1, ..., u_P))\right]$$
(89)

and $x_i(u_1, ..., u_P)$ are the linear transformation functions defined by Eq. (86) or Eq. (87). In Eq. (89), the masses, m_i are given by

$$m_1 = 0$$
$$m_i = \frac{i}{i-1}m$$
(90)

and are known as the *staging masses*. The important feature of Eq. (89) is the fact that the quadratic term is completely uncoupled in terms of the u variables. Note, also, that the variable u_1 does not appear in the transformed harmonic term, since $m_1 = 0$. This uncoupled mode represents collective motion of the entire cyclic chain. This suggests that an effective MD scheme can be obtained based on the equations of motion derived from the effective fictitious classical Hamiltonian

$$H^{(\text{stage})}(p, u) = \sum_{i=1}^{P} \frac{p_i^2}{2\tilde{m}_i} + U_{\text{eff}}^{(\text{stage})}(u_1, ..., u_P)$$

$$= \sum_{i=1}^{P}\left[\frac{p_i^2}{2\tilde{m}_i} + \frac{1}{2}m_i\omega_P^2 u_i^2 + \frac{1}{P}\phi(x_i(u_1, ..., u_P))\right]$$
(91)

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Note that this Hamiltonian is not equivalent to the Hamiltonian in Eq. (83), nor should it be. The Hamiltonian in Eq. (91) generates a different dynamics that will sample the full configuration space more effectively. The Hamiltonian in Eq. (91) suggests that the optimal choice of the masses, $\tilde{m}_i$ is

$$\tilde{m}_1 = m$$
$$\tilde{m}_i = m_i \tag{92}$$

since, with this choice, all of the staging modes, $u_2, ..., u_P$ will move on the *same time scale*, thereby leading to efficient sampling of all modes in an MD scheme. The equations of motion derived from Eq. (91) are

$$\dot{u}_i = \frac{p_i}{\tilde{m}_i}$$
$$\dot{p}_i = -\frac{\partial U_{\text{eff}}^{(\text{stage})}}{\partial u_i} = -m_i \omega_P^2 u_i - \frac{\partial \phi}{\partial u_i} \tag{93}$$

The forces, $\partial \phi / \partial u_i$, are obtained via the chain rule using Eq. (86) which gives a convenient recursive form for the partial derivatives:

$$\frac{\partial \phi}{\partial u_1} = \frac{1}{P} \sum_{i=1}^{P} \frac{\partial \phi}{\partial x_i}$$
$$\frac{\partial \phi}{\partial u_i} = \frac{\partial \phi}{\partial x_i} + \frac{i-2}{i-1} \frac{\partial \phi}{\partial x_{i-1}} \tag{94}$$

This form is especially convenient since the bead forces, $\partial \phi / \partial x_i$ can be computed directly given the form of the potential.

Equations (93) alone are not sufficient to give a satisfactory path integral MD scheme, however, since they still only generate a microcanonical distribution, $\delta \left(H^{(\text{stage})}(p, u) - E \right)$. In order to ensure that a proper canonical distribution is generated, Eqs. (93) must be coupled to a thermostatting method. Although many such approaches exist, our experience has been that the extended system methods such as the Nosé-Hoover chain[24] or generalized Gaussian moment[25] are the most effective. Both of these schemes can be rigorously shown to generate a canonical distribution in the physical phase space variables, (p, u). It is also possible to write the partition function in the form

$$Z_P(\beta) = \mathcal{N} \int dp_1 \cdots dp_P \int du_1 \cdots du_P \, \delta \left(\sum_{i=1}^{P} \frac{p_i^2}{2\tilde{m}_i} - K_0 \right)$$
$$\times \exp \left\{ -\beta U_{\text{eff}}^{(\text{stage})}(u_1, ..., u_P) \right\} \tag{95}$$

and employ an isokinetic method following the approach recently introduced by Minary and Tuckerman[26], which has also been shown to be highly effective and offers the advantage of simplicity. Here, we shall show how to employ the Nosé-Hoover chain (NHC) approach. In the NHC approach, a set of M additional "heat bath" variables, $\eta_1, ..., \eta_M$ is introduced along with a set of corresponding momenta, $p_{\eta_1}, ..., p_{\eta_M}$, such that the kth variables control the kinetic energy fluctuations in the $(k-1)$st variables, where $k = 0$ corresponds to the physical momenta. For example, for a particle moving in a one-dimensional

potential described by equations of motion of them form $\dot{x} = p/m$, $\dot{p} = -d\phi/dx$, the thermostatted equations take the form

$$\dot{x} = \frac{p}{m}$$

$$\dot{p} = -\frac{d\phi}{dx} - \frac{p_{\eta_1}}{Q_1}p$$

$$\dot{\eta}_k = \frac{p_{\eta_k}}{Q_k}$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - kT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1}$$

$$\dot{p}_{\eta_k} = \frac{p_{\eta_{k-1}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1}}}{Q_{k+1}}p_{\eta_k}$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT \tag{96}$$

where $Q_1, ..., Q_M$ is a set of thermostat mass parameters (having units of energy×time^2) that control the time scale on which these variables evolve. Equations (96) conserve the following energy:

$$H' = \frac{p^2}{2m} + \phi(x) + \sum_{k=1}^{M}\left[\frac{p_{\eta_k}^2}{2Q_k} + kT\eta_k\right] \tag{97}$$

Note that H' is *not* a Hamiltonian for Eqs. (96). The proof that Eqs. (96) generates a
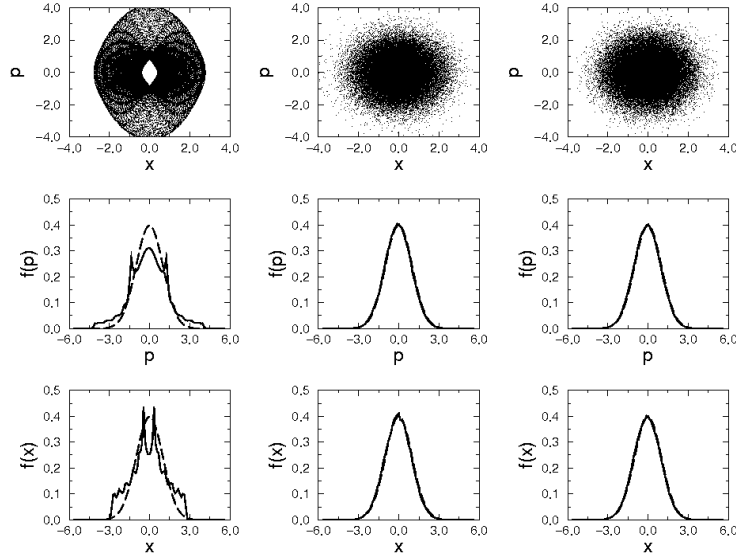

Figure 5. Poincaré sections, probability distributions, $f(x)$ and $f(p)$ of position and momentum for a harmonic oscillator with potential $\phi(x) = m\omega^2 x^2/2$ with $m = 1$, $\omega = 1$. Left column shows results for $M = 1$ (Nosé-Hoover thermostat), middle column shows, $M = 4$, and right column shows, $M = 6$.

correct canonical distribution can be found in the recent work of Tuckerman, *et al*[27]. Figure 5 shows that these equations are capable of generating a correct canonical distribution for a simple harmonic oscillator described by $\phi(x) = m\omega^2 x^2/2$ for $M > 1$ (note that $M = 1$ corresponds to the more familiar Nosé-Hoover thermostat, which fails for a harmonic oscillator).

Path integral MD is dominated by harmonic motion. Therefore, it is *absolutely crucial* to couple a thermostat to *each degree of freedom* in the system. This means *each* Cartesian direction of *each* mode variable. Failure to do so will result in a scheme that does not converge. Therefore, the complete path integral MD equations take the form:

$$\dot{u}_i = \frac{p_i}{\tilde{m}_i}$$

$$\dot{p}_i = -m_i\omega_P^2 u_i - \frac{\partial\phi}{\partial u_i} - \frac{p_{\eta_{1,i}}}{Q_i}p_i$$

$$\dot{\eta}_{k,i} = \frac{p_{\eta_{k,i}}}{Q_k}$$

$$\dot{p}_{\eta_{1,i}} = \frac{p_i^2}{\tilde{m}_i} - kT - \frac{p_{\eta_{2,i}}}{Q_2}p_{\eta_{1,i}}$$

$$\dot{p}_{\eta_{k,i}} = \frac{p_{\eta_{k-1,i}}^2}{Q_{k-1}} - kT - \frac{p_{\eta_{k+1,i}}}{Q_{k+1}}p_{\eta_{k,i}}$$

$$\dot{p}_{\eta_{M,i}} = \frac{p_{\eta_{M-1,i}}^2}{Q_{M-1}} - kT \tag{98}$$

The conserved energy of these equations is

$$H' = \sum_{i=1}^{P}\left\{\frac{p_i^2}{2\tilde{m}_i} + \frac{1}{P}\phi(x_i) + \sum_{k=1}^{M}\left[\frac{p_{\eta_{k,i}}^2}{2Q_k} + kT\eta_{k,i}\right]\right\} \tag{99}$$

The thermostat mass parameters are chosen to evolve on the time scale of the harmonic forces, and, therefore are assigned values according to:

$$Q_k = \frac{1}{\beta\omega_P^2} \qquad \forall\ k \tag{100}$$

Figure 6 illustrates the performance of the path integral MD scheme for a harmonic oscillator, $\phi(x) = m\omega^2 x^2/2$ with

$$\frac{m\omega}{\hbar} = 0.03 \qquad \beta\hbar\omega = 15.8$$

and $P = 400$. The figure shows how the virial energy estimator converges if straightforward microcanonical MD is used compared to the algorithm in Eqs. (98) and compared to staging Monte Carlo. It can be seen that the simple microcanonical MD performs extremely poorly, however, when Eqs. (98) are used, the algorithm is almost as efficient as the staging Monte Carlo, as measured by the error bar as a function of block size[28]. Figure 7 also shows what happens if a single global thermostat is used instead of a thermostat on each degree of freedom. This comparison serves to underscore the warning given above that each degree of freedom requires its own thermostat.
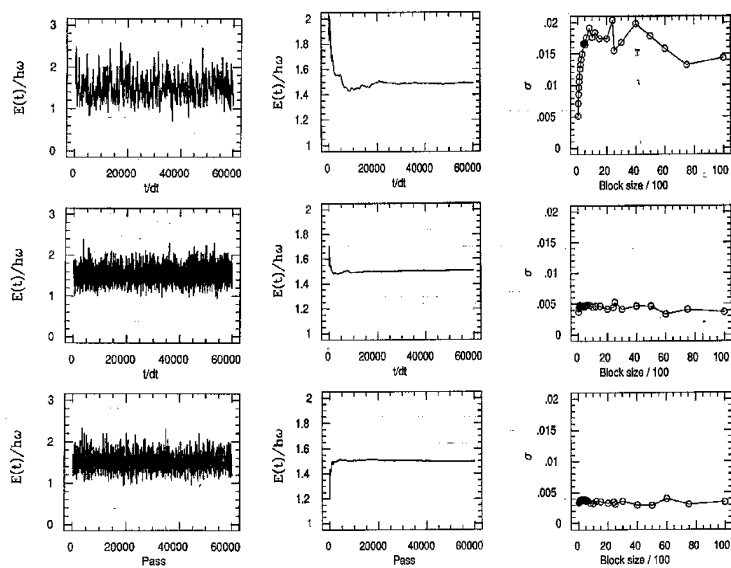
Figure 6. Instantaneous and cumulative value of the virial energy estimator and the associated error bar as a function of block size for standard microcanonical MD (top row), the staging MD algorithm presented (middle row), and staging Monte Carlo using the Ceperley and Pollock algorithm for the harmonic oscillator example .
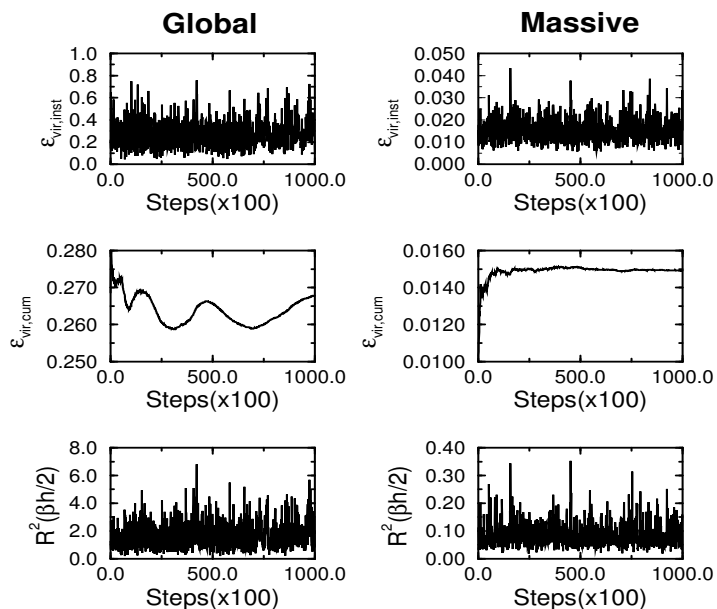

Figure 7. Illustration of the problem inherent with the use of a global thermostat in path integral MD by examination of the instantaneous and cumulative values of the virial energy estimator and the spread of the path, defined as the distance between furthest points on the path integral chain.

For completeness, we mention another possible transformation that can be used to uncouple the harmonic potential term. This is the so called *normal mode* transformation obtained by performing a Fourier expansion of the discrete cyclic path:

$$x_j = \sum_{l=1}^{P} c_l e^{2\pi i (j-1)(l-1)/P} \tag{101}$$

The coefficients, c_l are complex, so that the normal mode variables, u_l are given by

$$u_1 = c_1$$
$$u_P = c_{(P+2)/2}$$
$$u_{2l-2} = \text{Re}(c_l)$$
$$u_{2l-1} = \text{Im}(c_l) \tag{102}$$

Associated with the normal mode transformation is a set of normal mode frequencies:

$$\lambda_{2l-1} = \lambda_{2l-2} = 2P \left[1 - \cos \left(\frac{2\pi(l-1)}{P} \right) \right] \tag{103}$$

from which a set of normal mode masses can be obtained by

$$m_l = m\lambda_l \tag{104}$$

The path integral MD equations, Eqs. (98) are equally valid for the normal mode transformation, and simply require using Eqs. (102) to determine the forces and Eq. (104) in place of the staging masses. The normal mode method has the advantage that the mode, u_1 is given, in terms of the bead variables, by

$$u_1 = \frac{1}{P} \sum_{i=1}^{P} x_i \tag{105}$$

i.e. the path centroid. Therefore, the normal mode method should be used when one wishes to compute quantum free energy profiles or perform approximate quantum dynamics via the centroid dynamics approach.

In order to complete the path integral MD scheme, a reversible multiple time scale integration method is needed. In order to illustrate how such a scheme is constructed, consider, first a simple one-particle, one-dimensional classical system described by a Hamiltonian $H = p^2/2m + \phi(x)$. The equations of motion

$$\dot{x} = \frac{p}{m} \qquad \dot{p} = F(x) \tag{106}$$

where $F(x) = -\phi'(x)$, can be cast in an operator form:

$$\dot{x} = iLx \qquad \dot{p} = iLp \tag{107}$$

where iL is the *Liouville operator* given by

$$iL = \frac{p}{m}\frac{\partial}{\partial x} + F(x)\frac{\partial}{\partial p} \tag{108}$$

The equations of motion can now be solved formally by

$$x(t) = e^{iLt}x(0) \qquad p(t) = e^{iLt}p(0) \tag{109}$$

where the operator $\exp(iLt)$ is called the *classical propagator*. Although we cannot evaluate its action directly on an initial condition, $\{x(0), p(0)\}$, we can approximate it for a small time interval, Δt, using the Trotter theorem. Note that iL is composed of two terms, iL_1 and iL_2 given by

$$iL_1 = \frac{p}{m}\frac{\partial}{\partial x} \qquad iL_2 = F(x)\frac{\partial}{\partial p} \tag{110}$$

If Δt is small, then we may approximate

$$e^{iL\Delta t} = e^{iL_2\Delta t/2}e^{iL_1\Delta t}e^{iL_2\Delta t/2} + \mathcal{O}(\Delta t^3) \tag{111}$$

Note that, although the error in one step is of order Δt^3, the error accumulated by applying the operator in Eq. (111) N times to generate a trajectory of real time length t will be of order $N\Delta t^3 = t\Delta t^2 = t^3/N^2$. Now, each operator appearing in Eq. (111) can be shown to generate a simple translation of the variable on which it acts:

$$e^{iL_2/\Delta t/2}p = p + \frac{\Delta t}{2}F(x)$$

$$e^{iL_2/\Delta t/2}x = x \tag{112}$$

as can be easily shown by Taylor expanding the exponentials. Similarly,

$$e^{iL_1/\Delta t}p = p$$

$$e^{iL_1/\Delta t}x = x + \Delta t\frac{p}{m} \tag{113}$$

Therefore, the action of the operator in Eq. (111) on an initial condition, $\{p(0), x(0)\}$, generates three sequential updates:

$$p' = p(0) + \frac{\Delta t}{2}F(x(0))$$

$$x(\Delta t) = x + \Delta t\frac{p'}{m}$$

$$\text{Compute new force}$$

$$p(\Delta t) = p' + \frac{\Delta t}{2}F(x(\Delta t)) \tag{114}$$

or as a pseudocode, beginning with values $x = x(0)$ and $p = p(0)$:

$$p \longleftarrow p + \frac{\Delta t}{2}F(x)$$

$$x \longleftarrow x + \Delta t\frac{p}{m}$$

$$\text{Compute new force}$$

$$p \longleftarrow p + \frac{\Delta t}{2}F(x) \tag{115}$$

At the output, x and p hold the values of $x(\Delta t)$ and $p(\Delta t)$, respectively. The schemes, (114) and (115) can easily be shown to be equivalent to the familiar velocity verlet algorithm

$$x(\Delta t) = x(0) + \Delta t\frac{p(0)}{m} + \frac{\Delta t^2}{2m}F(x(0))$$

$$p(\Delta t) = p(0) + \frac{\Delta t}{2}\left[F(x(0)) + F(x(\Delta t))\right] \tag{116}$$

but derived in a powerful way using operator calculus. The technique of writing down a factorization of the classical propagator based on terms in the Liouville operator and then translating each operator into an update step in a pseudocode is a useful technique in developing numerical integrators in that it avoids the need to write down explicit finite difference equations such as Eqs. (116), which can be very cumbersome for complex sets of equations such as the path integral MD equations, Eqs. (98).

In order to illustrate the power of the operator approach, we will develop a simple multiple time scale integrator, which will form the basis of the algorithm to be used for the path integral MD equations. Suppose the potential, $\phi(x)$, contains a dominant fast term, $\phi_{\text{fast}}(x)$ and a slower term, $\phi_{\text{slow}}(x)$,

$$\phi(x) = \phi_{\text{fast}}(x) + \phi_{\text{slow}}(x) \tag{117}$$

These will give rise to fast and slow forces, $F_{\text{fast}}(x) = -\phi'_{\text{fast}}(x)$ and $F_{\text{slow}}(x) = -\phi'_{\text{slow}}(x)$, respectively. Let us construct a reference system from the fast part of the potential with a Liouville operator

$$iL^{(\text{ref})} = \frac{p}{m}\frac{\partial}{\partial x} + F_{\text{fast}}(x)\frac{\partial}{\partial p} = iL_1^{(\text{ref})} + iL_2^{(\text{ref})} \tag{118}$$

and a correction

$$iL' = F_{\text{slow}}(x)\frac{\partial}{\partial p} \tag{119}$$

Using the Trotter theorem, we break up the classical propagator as follows:

$$e^{iL\Delta t} = e^{iL'\Delta t/2} e^{iL^{(\text{ref})}\Delta t} e^{iL'\Delta t/2} \tag{120}$$

where Δt is chosen to be appropriate to the slow motion. However, in order to integrate the fast reference system accurately, we need a smaller time step. Let $\delta t = \Delta t/n$. The idea of multiple time scale integration is to integrate the reference system for n steps using the time step, δt according to the propagator:

$$\begin{aligned}
e^{iL\Delta t} = \; & e^{iL'\Delta t/2} \\
& \times \left[e^{iL_2^{(\text{ref})}\delta t/2} e^{iL_1^{(\text{ref})}\delta t} e^{iL_2^{(\text{ref})}\delta t/2} \right]^n \\
& \times e^{iL'\Delta t/2}
\end{aligned} \tag{121}$$

The action of this operator on an initial condition, $x = x(0)$, $p = p(0)$ can be written as a

pseudocode:

$$p \longleftarrow p + \frac{\Delta t}{2} F_{\text{slow}}(x)$$

for istep $= 1$ to n

$$p \longleftarrow p + \frac{\delta t}{2} F_{\text{fast}}(x)$$

$$x \longleftarrow x + \delta t \frac{p}{m}$$

Compute new fast force

$$p \longleftarrow p + \frac{\delta t}{2} F_{\text{fast}}(x)$$

endfor

Compute new slow force

$$p \longleftarrow p + \frac{\Delta t}{2} F_{\text{slow}}(x) \tag{122}$$

The advantage of such a scheme in path integral MD is that the fast forces are very simple harmonic oscillator forces while the slow forces will usually be very expensive interparticle forces. Hence, the costly evaluation of the slow forces need only be done every n steps, thereby saving considerable CPU time. This scheme, known as the *reversible reference system propagator algorithm* (r-RESPA) was first introduced by Tuckerman, Martyna and Berne in 1992[29] and proves to be very effective in path integral MD calculations. Incorporation of the NHC thermostat couping into the scheme is somewhat more involved and will not be discussed in detail here. Suffice it to say that an additional operator iL_{NHC} is introduced which governs the evolution of the heat bath variables, and this operator is incorporated into the fast reference system. Details of how to factorize this operator and incorporate it into the r-RESPA algorithm are given in Ref.[30].

7 Many-Body Path Integrals

In this final section, we discuss the formulation of many-body quantum systems in terms of path integrals. Here, we shall focus on the case in which spin statistics can be neglected. This is generally an acceptable approximation at most temperatures of interest. However, a discussion of spin statistics in path integrals will be provided by other lectures in this series.

Consider an N-particle quantum system in a volume, V at temperature, T, described by a Hamiltonian of the form

$$H = \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2M_I} + \phi(\mathbf{R}_1, ..., \mathbf{R}_N) \tag{123}$$

If the derivation of Sec. 3 is followed for the N-particle Hamiltonian, the resulting discrete

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path integral expression for the partition function is

$$Z(N, V, T) = \lim_{P \to \infty} \left[\prod_{I=1}^{N} \left(\frac{M_I P}{2\pi\beta\hbar^2} \right)^{3P/2} \int_{D(V)} d\mathbf{R}_I^{(1)} \cdots d\mathbf{R}_I^{(P)} \right]$$

$$\times \exp\left\{ -\beta \left[\sum_{i=1}^{P} \left(\sum_{I=1}^{N} \frac{1}{2} M_I \omega_P^2 \left(\mathbf{R}_I^{(i+1)} - \mathbf{R}_I^{(i)} \right)^2 + \frac{1}{P}\phi(\mathbf{R}_1^{(i)}, ..., \mathbf{R}_N^{(i)}) \right) \right] \right\} \quad (124)$$

where the integral is defined over the domain, $D(V)$ defined by the containing volume. The partition function now describes a fictitious classical system consisting of N cyclic chains, each containing, P beads. Again, we note that the interaction potential, $\phi(\mathbf{R}_1, ..., \mathbf{R}_N)$, only acts betweeen beads with the same bead index, i. This is illustrated in Fig. 8 below.
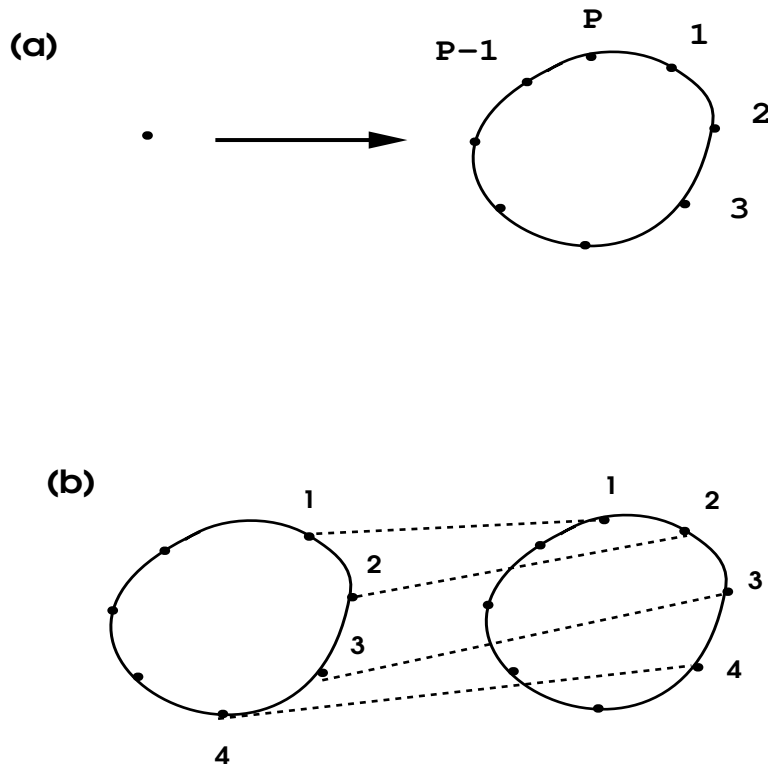

Figure 8. Illustration of the interaction between two discrete paths in a many-body path integral.

The path integral MD scheme of the previous section is easily extended to the N-particle system. For each cyclic chain, a staging or normal mode transformation is made and the complete set of mode equations of motion is written down by extending Eqs. (98). Note that a separate thermostat is still coupled to *each* degree of freedom, for a total of $3NP$

thermostat chains!! Although this may seem like a large number of extra variables, since each chain contains $2M$ variables, the CPU time required to integrate these variables is still negligible compared to the time required to evaluate the potential and forces. Fig. 9 below shows the performance of the method on a simple system, a single water molecule in a box of volume, $150\,\text{Å}^3$. The potential comes from "on the fly" electronic structure calculations
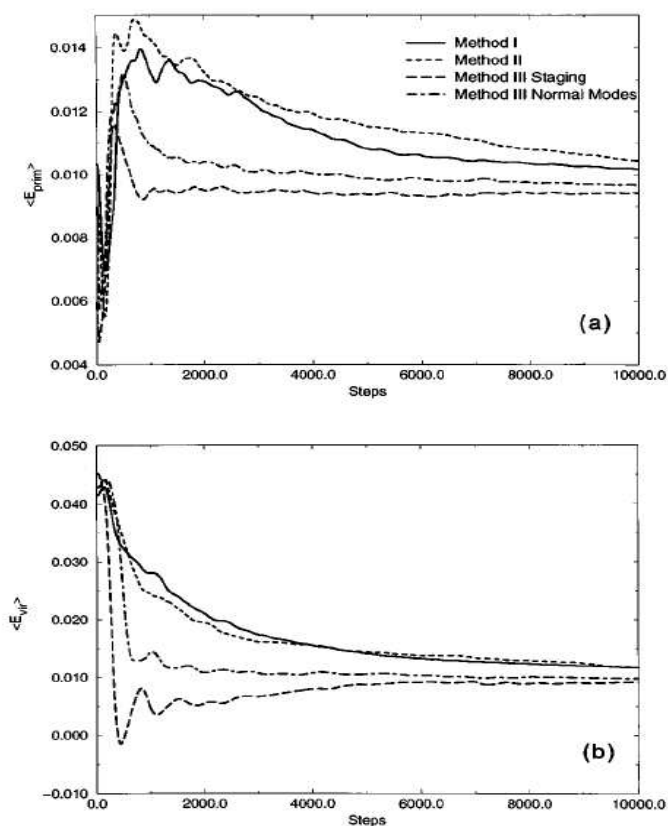

Figure 9. Performance of the staging (Method III – staging), normal mode (Method III – normal modes) compared to a path integral MD simulation with no variable transformations and no thermostats (Method I) and to a path integral MD simulation with a thermostat on each time slice (Method II). The figure compares the convergence of the virial and primitive energy estimators including equilibration segments.

coupled to the path integral (to be discussed in the lecture on *ab initio* path integrals) and shows, again, the convergence of the primitive and virials energy estimators for standard microcanonical MD, path integral MD with a single thermostat on each time slice, and the recommended thermostat on each degree of freedom. Clearly, the recommended scheme outperforms the other methods rather dramatically.

8 Summary

In summary, we have introduced the path integral formulation of quantum statistical mechanics in both the discrete and continuous formulations and shown how to compute path integrals using molecular dynamics. In particular, we have shown that a variable transformation that uncouples the harmonic bead-bead interaction term is necessary together with the coupling of the system to a thermostat on each degree of freedom in order to have an efficient scheme. We have introduced an efficient multiple time scale integrator for the path integral MD equations and, finally, we have extended the scheme to many-body systems in which the spin statistics can be neglected.

References

1. R. P. Feyman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York (1965).
2. D. F. B. Tenhaaf, H. J. M. Vanbemmel, J. M. J. Vanleeuwen, M. Vanssarloos and D. M. Ceperley, *Phys. Rev. B* **51**, 13039 (1995).
3. M. Boninsegni, C. Pierleoni and D. M. Ceperley, *Phys. Rev. Lett.* **72**, 1854 (1994).
4. G. Krilov, E. Sim and B. J. Berne, *Chem. Phys.* **268**, 21 (2001).
5. G. Krilov, E. Sim and B. J. Berne, *J. Chem. Phys.* **114**, 1075 (2001).
6. E. L. Pollock and D. M. Ceperley, *Phys. Rev. B* **30**, 2555 (1984).
7. M. Sprik, M. L. Klein and D. Chandler, *J. Chem. Phys.* **83**, 3942 (1985).
8. D. F. Coker, D. Thirumalai, and B. J. Berne, *J. Chem. Phys.* **86**, 5689 (1987).
9. D. M. Ceperley, *Rev. Mod. Phys.* **67**, 279 (1995).
10. R. W. Hall and B. J. Berne, *J. Chem. Phys.* **81**, 3641 (1984).
11. M. E. Tuckerman, B. J. Berne, G. J. Martyna, and M. L. Klein, *J. Chem. Phys.* **99**, 2796 (1993).
12. M. E. Tuckerman, D. Marx, M. L. Klein and M. Parrinello, *J. Chem. Phys.* **104**, 5579 (1996).
13. R. Car and M. Parrinello, *Phys. Rev.Lett.* **55**, 2471 (1985).
14. J. Cao and G. A. Voth, *J. Chem. Phys.* **99**, 10070 (1993).
15. J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5106 (1994).
16. J. Cao and G. J. Martyna, *J. Chem. Phys.* **104**, 2028 (1994).
17. D. Marx, M. E. Tuckerman and G. J. Martyna, *Comp. Phys. Comm.* **118**, 166 (1999).
18. L. Schulman, *Techniques and Applications of Path Integration* John Wiley & Sons, New York (1981).
19. M. Herman, E. F. Bruskin, and B. J. Berne, *J. Chem. Phys.* **76**, 1347 (1982).
20. R. P. Feymman and H. Kleinert, *Phys. Rev. A* **34**, 5080 (1986).
21. G. J. Martyna, A. Hughes, and M. E. Tuckerman, *J. Chem. Phys.* **110**, 3275 (1999).
22. J. P. Neirotti, D. L. Freeman and J. D. Doll, *J. Chem. Phys.* **112**, 3990 (2000).
23. D. Chandler and P. G. Wolynes, *J. Chem. Phys.* **74**, 4078 (1981).
24. G. J. Martyna, M. E. Tuckerman and M. L. Klein, *J. Chem. Phys.* **97**, 2635 (1992).
25. Y. Liu and M. E. Tuckerman, *J. Chem. Phys.* **112**, 1685 (2000).
26. P. Minary and M. E. Tuckerman (to be submitted).
27. M. E. Tuckerman, Y. Liu, G. Ciccotti and G. J. Martyna, *J. Chem. Phys.* **115**, 1678 (2001).

28. J. Cao and B. J. Berne, *J. Chem. Phys.* **91**, 6359 (1989).
29. M. E. Tuckerman, G. J. Martyna and B. J. Berne, *J. Chem. Phys.* **97**, 1990 (1992).
30. G. J. Martyna, M. E. Tuckerman, D. J. Tobias and M. L. Klein, *Mol. Phys.* **87**, 1117 (1996).