Nonergodicity in path integral molecular dynamics[a]

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Molecular dynamics can be used to evaluate the path integral representation of the density matrix. Implicit in this method is the assumption that the dynamical system is ergodic. It is shown here that this is not the case in many systems that are of interest. For example water or liquid neon can not be simulated by this method. Monte Carlo methods do not suffer from this weakness.

INTRODUCTION

Path integrals[1] offer a powerful method for simulating quantum systems. For example, the canonical partition Z function of a single quantum particle of mass m moving in a potential $V(r)$ can be approximated by the following path integral in the primitive algorithm.

$$Z_P = \left(\frac{2\Pi m P}{h^2 \beta}\right)^{3P/2} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_P \, e^{-\beta \Phi(\mathbf{r}_1,\ldots,\mathbf{r}_P)}, \qquad (1a)$$

$$\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_P) = \frac{mP}{2\beta^2 \hbar^2} \sum_{t=1}^{P} (r_t - r_{t+1})^2 + \frac{1}{P}\sum_{t=1}^{P} V(r_t), \qquad (1b)$$

where P is an integer, and where $\lim_{P\to\infty} Z_P = Z$. The function Φ can be regarded as a potential energy function and the integral then looks like a classical configurational partition function for a classical cyclic chain polymer with nearest neighbor harmonic forces, each segment of which moves in a potential $V(r)/P$. One method for evaluating this integral is to sample the configurations of the chain polymer using Monte Carlo techniques.[2,3] Alternatively the integral in Eq. (1) can be expressed differently by recognizing that the prefactor can be expressed in terms of an integral involving a set of P fictitious momenta,

$$Z_P = \left(\frac{m}{m'}\right)^{3P/2} \int d\mathbf{P}_1 \cdots d\mathbf{P}_P \int dr_1 \cdots dr_P \, e^{-\beta H'}, \qquad (2a)$$

$$H' = \sum_{t=1}^{P} \left\{ \frac{P_t^2}{2m'} + \frac{mP}{2\beta^2 \hbar^2} (\mathbf{r}_t - \mathbf{r}_{t+1})^2 + \frac{1}{P} V(\mathbf{r}_t) \right\}. \qquad (2b)$$

This looks like the canonical partition function for a classical chain polymer with Hamiltonian H' where the mass of each segment m' can be chosen for convenience. This suggests an attractive alternative to the Monte Carlo method.[4,5] Assuming that the classical system described by this Hamiltonian is ergodic one can solve the classical equations of motion corresponding to some initial state and then time average any dynamical variable over the trajectory to determine the statistical mechanical averages consistent with the partition function given by Eq. (2a). The initial state must be chosen so that the mean kinetic energy per particle is consistent with the desired temperature given by β^{-1} as is the standard practice in classical molecular dynamics. This method has been used with considerable success in two recent papers.[4,5]

It is the purpose of this note to show that this molecular dynamics approach to evaluating path integrals can be prob-

lematical. A trivial case is that of a free particle. Since then the effective Hamiltonian corresponds to a purely harmonic classical chain molecule, any sampling of the initial state assigns energy to the normal modes of this molecule and these energies are conserved. This system is not ergodic, and time averages will not agree with phase space averages. Of course in this case the system is unbounded in space so that the partition function does not exist. What happens when the quantum particle feels a potential function $V(r)$? In principle this will permit energies to be exchanged between the normal modes corresponding to the harmonic terms in Eq. (2b). If the temperature is very low then the dynamics may be in the KAM regime and the Hamiltonian flow will be confined to multidimensional Tori.[6] Again the system will be nonergodic and the molecular dynamics method will fail. Interestingly, the force constant in the harmonic part of the Hamiltonian grows larger with P while the potential experienced by any segment on the polymer chain decreases as $1/P$. Moreover the heavier the particle is, i.e., the more classical it is, the larger will be the harmonic force constant. In addition the higher the temperature the higher will be the force constant. From this it follows that the normal modes for systems of high mass and high temperature will be displaced to higher frequency whereas the frequencies characterizing the potential function $V(r)/P$ will get lower. The high frequency modes of the chain will therefore become far out of resonance with the external potential and again energy exchange between the high frequency modes of the polymer will be very slow or nonexistant. Ironically then, for systems that are almost classical the molecular dynamics method will be either very inefficient due to the long correlation times or nonergodic. Monte Carlo methods will, however, be valid because single particles are moved.

NONERGODICITY IN NEON

In this note we demonstrate these problems on a system containing two neon atoms interacting with a Lennard-Jones potential at a temperature of 40 K. To avoid dissociation an additional harmonic potential is imposed between the neon atoms. At this temperature NMM shows that that $P = 40$ gives excellent agreement with exact quantum mechanics.[7] For $P = 40$ Monte Carlo also gives agreement with exact quantum mechanics. Molecular dynamics gives very poor agreement. The details follow.

Two neon atoms are assumed to interact through a LJ 12-6 potential plus a harmonic potential

$$V(\mathbf{r}) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \tfrac{1}{2}k(r - r_0)^2, \qquad (3)$$
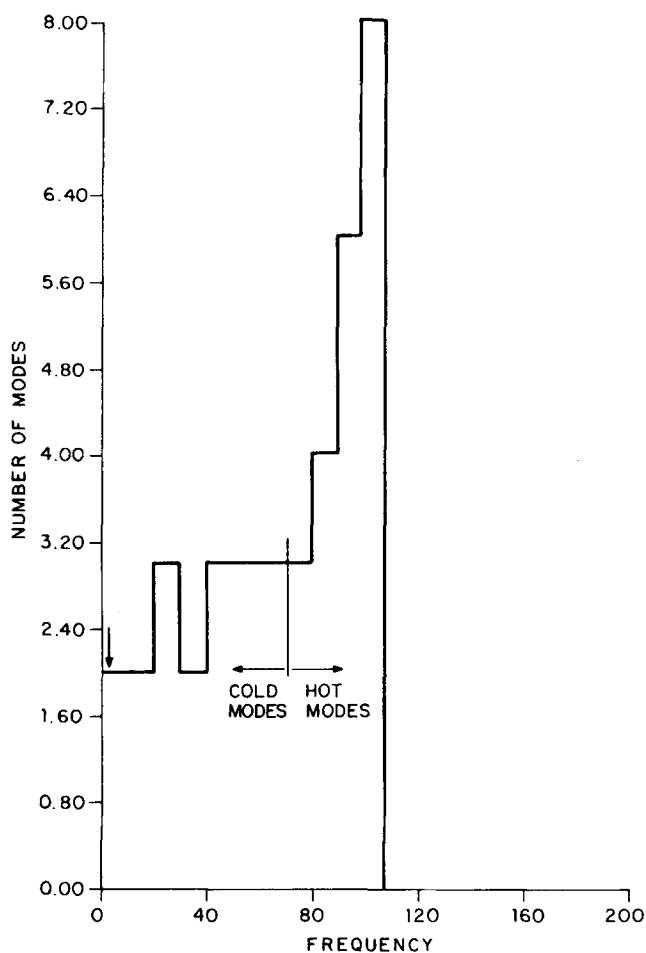
FIG. 1. The frequency distribution of the 117 vibrational normal modes for the relative coordinate to two neon atoms in an isomorphic cyclic chain polymer containing 40 beads. (120 degrees of freedom): These modes are divided into 57 low frequency modes and 60 high frequency modes. The verticle arrow indicates the harmonic frequency of the neon–neon pair potential.
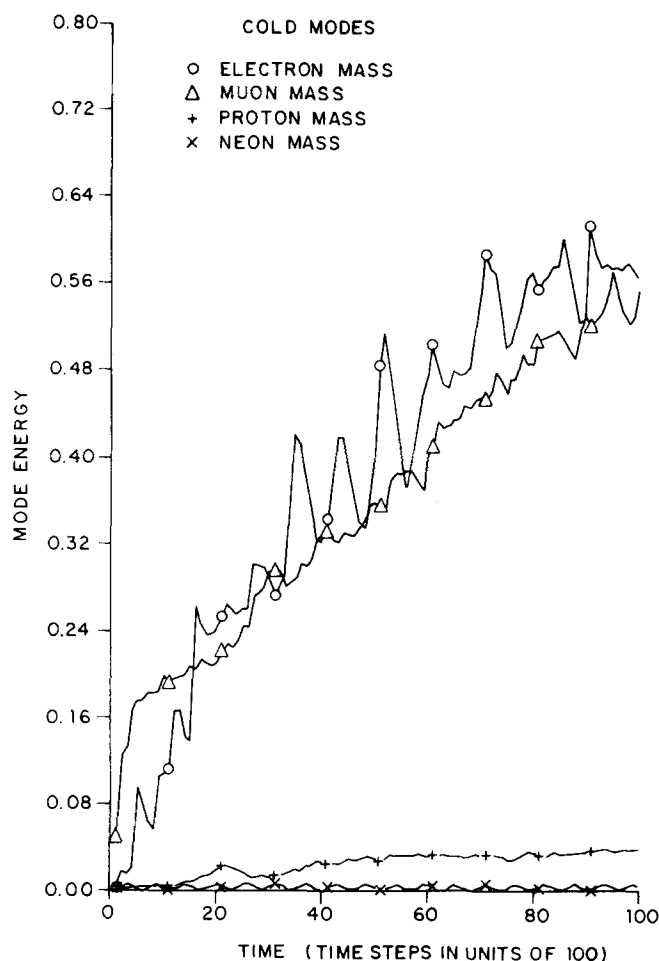
FIG. 2. The total energy (in units of the expected energy at equipartition) of the 57 low frequency modes as a function of number of time steps. The initial state was chosen such that the total energy was in the 60 high frequency modes. As indicated these curves correspond to different masses.

where $\epsilon/k_B = 35.8$ K, $\sigma = 2.74$ Å, $k = 4\epsilon/\sigma^2$, and $r_0 = 2^{1/6}\sigma$.

The effective Hamiltonian for the relative motion is given by

$$H' = \sum_{t=1}^{P} \left\{ \frac{P_t^2}{2\mu'} + \frac{\mu P}{2\beta^2 \hbar^2}(r_t - r_{t+1})^2 + \frac{1}{P} V(r_t) \right\}, \quad (4)$$

where μ' is an arbitrary reduced mass and μ is the real reduced mass of two neon atoms.

Newton's equations of motion for the relative motion

$$\frac{d^2 r_t}{d\tau^2} = -\left(\frac{\mu P}{2\beta^2 \hbar^2} \right) [2r_t - r_{t-1} - r_{t+1}] - \frac{1}{P} \frac{\partial V(r_t)}{\partial r_t} \quad (5)$$

[where τ is the time variable divided by $(\mu')^{1/2}$] were integrated for several sets of initial conditions. Since the Hamiltonian corresponds to a cyclic harmonic chain polymer, each bead of which experiences a LJ plus Harmonic potential [diluted by a factor of $1/P$, cf. Eq. (4)], it is useful to study how energy is transfered between the normal modes of the cyclic harmonic chain. Since the chain has 40 beads there are 120 degrees of freedom, three of which are attributable to the com of the chain. The frequency distribution of these 117 modes is shown in Fig. 1. The "harmonic frequency" of the

LJ plus Harmonic potential is indicated by a verticle arrow in this figure. The low frequency modes correspond to the long wavelength "breathing modes" of the chain. We sample the initial momenta and normal mode positions of the 60 highest normal modes from a Maxwell–Boltzmann distribution at 40 K. The remaining 57 normal modes are given zero momenta and normal mode displacements. The center of mass of the chain is given zero momentum and given one of three possible initial positions: (a) $R = 2^{1/6} \sigma$, (b) $R = 1.5\sigma$, and (c) $R = \sigma$. The question to be answered is: How long does it take the energy to flow from the high frequency modes to the low frequency modes in molecular dynamics? Figure 2 shows among other things how the normal mode energy of the set of low frequency modes changes in time for the initial state $R = \sigma$. Similar results were found for the other two metial states which we regard as extremes to be found in a liquid state simulation. It should be clear from this figure that the energy transfer for Neon is extremely slow and that to reach equipartition an impractically long run is required. Although it is impossible to tell from this curve whether or not the system is ergodic, we suspect that it is not. This question can be answered by determining the maximal Lyapunov exponent, but since the poor convergence implies that MD should not be used for the simulation we do not bother to

make these more exhaustive studies. Figure 2 also shows how the energy of the low frequency modes change in time if the mass is changed to that of an electron, a muon, or a proton, i.e., $m = m_e$, $m = 206.8 \, m_e$, and $m = m_H$. Clearly energy exchange is rapid for the electron and muon but not for a proton or neon. Nevertheless it should be noted that simulation of systems of such small mass requires P to be large. Because for increased P the force constants are large MD simulations of electrons and protons at low temperatures should lead to similar problems.

It is important to note that for Ne because energy transfer between the low and high frequency modes is inefficient any initial internal configuration will not relax quickly. To do so would require large amplitude changes in the low frequency modes which is precluded by the slow exchange. It was seen that the center of mass is equilibrated efficiently. Thus if one picks an initial configuration in which the chain is extended the chain will remain extended; that is more de-localized in space than would be consistent with quantum statistics. This would overpredict the amount of tunneling into classically forbidden regions. Likewise if the chain is initially too contracted it will also remain this way, and the simulation will predict classical behavior.

In closing it is worth noting that Metropolis Monte Carlo works for all masses and molecular dynamics gives poor results for large masses. In a forthcoming paper on quantum effects in water, we show that molecular dynamics with periodic resampling of the momenta circumvents the problem outlined here.[8]

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