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The Hybrid Monte Carlo Method for Polymer Chains

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Abstract:
The use of the Hybrid Monte Carlo method in simulating off-lattice polymer chains is discussed. I focus on the problem of finding efficient algorithms for long flexible chains. To speed up the simulation of such chains the Fourier acceleration technique is used. Numerical results are presented for four models with different repulsive interactions between the monomers.

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1 Introduction

The Hybrid Monte Carlo (HMC) method (Duane et al. 1987) was originally developed for Quantum Chromodynamics (QCD), and was specifically designed for simulations including the effects of dynamical quarks. It is based on a hybrid Langevin/molecular dynamics evolution in a fictitious time. In this way the whole system can be updated in parallel, which is important in QCD simulations since the effective action for QCD with dynamical quarks is highly nonlocal. By including a global accept/reject step, an "exact" Monte Carlo algorithm is obtained, free from finite-step-size errors.

The HMC method is very general and has later on been applied to various systems other than QCD. In this paper I discuss the use of HMC in simulating polymer chains (for a discussion of HMC for QCD, see e.g. Thomas Lippert's contribution to these proceedings). I focus on single linear chains with repulsive interactions between the monomers, such as screened or unscreened Coulomb interactions.

A HMC update of such a chain with N monomers requires a computer time of order N^2. This is fast for an update of the whole system, but plain HMC is still a bad choice of algorithm for these systems, compared to, for example, the pivot algorithm (Lal 1969; for a recent review on simulation methods for polymer systems, see Binder 1995). The reason is that short-wavelength modes tend to evolve much faster than long-wavelength modes. As a result, to have stability at short wavelengths, one must choose the step size so small that a very large number of steps are needed in order to generate significant changes in global quantities such as the end-to-end distance.

However, the HMC scheme leaves room for improvement. In particular, one has considerable freedom in defining the auxiliary Hamiltonian that governs the Langevin/molecular dynamics evolution. One method for speeding up the evolution is the Fourier acceleration method, in which the different Fourier modes are assigned different step sizes (or masses). This technique was introduced for Langevin simulations of field theories (Batrouni et al. 1985), and can be applied to HMC simulations too.

A Fourier accelerated algorithm is designed so that it speeds up the simulation of a given quadratic potential; the eigenmodes of this potential are updated with step sizes that are inversely proportional to their frequencies.

In this paper I present numerical results for two Fourier acceleration schemes, corresponding to different quadratic potentials. Most of the calculations were performed using a scheme corresponding to the potential with nearest-neighbor interactions only and uniform strength along the chain (Irbäck 1994). This algorithm is equivalent to performing plain HMC updates of the bond vectors connecting adjacent monomers along the chain. It turns out that this somewhat arbitrary choice of scheme gives a dramatic improvement of the efficiency for all the chains studied compared to plain HMC. An attractive feature of the algorithm is that short- and long-wavelength structure evolve at a similar speed. The efficiency is found to be somewhat higher

for the unscreened Coulomb potential than for the other potentials studied, which have shorter range.

Some of the systems were also simulated using a scheme that was obtained by an optimization procedure. Here the quadratic potential defining the scheme was determined variationally, for each system studied. Although the number of variational parameters is large, it turns out that this can be carried out relatively fast by using the method of Jönsson et al. (1995). This optimization procedure was tested for unscreened and screened Coulomb chains. The results were very similar to those obtained earlier, which shows that the first, simpler scheme might be close to optimal for these chains.

The plan of this paper is as follows. In Sect. 2 I define the models studied. The HMC method and the Fourier acceleration technique are described in Sects. 3 and 4, respectively. Numerical results are presented in Sect. 5.

2 The Models

Throughout this paper I consider a linear chain of N sites or monomers, with positions in three-dimensional space given by $\mathbf{x}_i$, $i = 1, \ldots, N$. Alternatively, the system can be described by the $N-1$ bond vectors $\mathbf{b}_i = \mathbf{x}_{i+1} - \mathbf{x}_i$, $i = 1, \ldots, N-1$, connecting adjacent monomers (see Fig. 1).

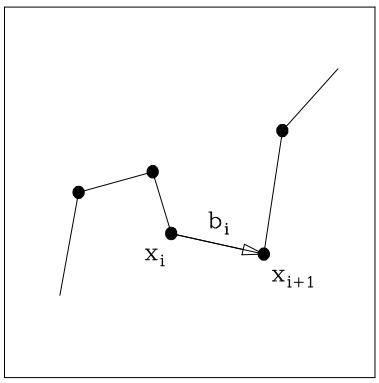

Fig. 1. Description of the chain.

The energy function of the system has the form

$$E = \sum_{1 \le i < j \le N} \left(\frac{1}{2} \delta_{i,j-1} r_{ij}^2 + v(r_{ij}) \right) \quad , \tag{1}$$

where $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$ is the distance between monomers i and j. The first term in (1) is just a harmonic attraction that enforces the chain structure.

The behavior of the system at temperature T is defined by the partition function

$$Z = \int \mathrm{d}^N \mathbf{x}\, \delta(\mathbf{x}_{\mathrm{cm}}) \exp(-E/T) \ , \tag{2}$$

where the overall translational degree of freedom is eliminated by holding the center of mass, $\mathbf{x}_{\mathrm{cm}}$, fixed at the origin.

The system will be studied for four different choices of the potential $v(r)$ in (1). First I consider a simple model of a polyelectrolyte in a solution at finite salt concentration c_{s}. Here $v(r)$ is a screened Coulomb potential with inverse Debye screening radius $\kappa \propto \sqrt{c_{\mathrm{s}}}$,

$$v(r) = \frac{\exp(-\kappa r)}{r} \ . \tag{3}$$

This model is studied both with and without screening. Following Jönsson et al. (1995), I take $(T, \kappa) = (0.838, 0)$ (no screening) and $(T, \kappa) = (0.838, 1.992)$.

In addition to the unscreened and screened Coulomb potentials, I consider two potentials of intermediate range, given by

$$v(r) = \frac{1}{r^{\lambda}} \tag{4}$$

with $\lambda = 2$ and 2.5, respectively.

These choices of $v(r)$ lead to different values of the swelling exponent ν, which describes the scaling of the end-to-end distance r_{ee} with N; $r_{\mathrm{ee}} \sim N^{\nu}$, $N \to \infty$. The Flory result $\nu = 0.6$ is approximately correct for the short-range screened Coulomb potential, while $\nu = 1$ for the unscreened Coulomb potential. For the potential (4) with $2 \leq \lambda < 3$, Bouchaud et al. (1991) have predicted $\nu = 2/\lambda$ using a variational approach. For $\lambda = 2$ they also predicted a logarithmic correction to the power law behavior: $r_{\mathrm{ee}} \sim N(\ln N)^{-\alpha}$ with $\alpha = 1/2$.

3 HMC

In HMC the system evolves in a fictitious time t. The evolution is governed by a Hamiltonian which can be chosen as

$$H_{\mathrm{MC}} = \frac{1}{2} \sum_i \mathbf{p}_i^2 + \frac{E}{T} \ , \tag{5}$$

where the $\mathbf{p}_i$'s are auxiliary momentum variables.

The first step of the algorithm is to assign new, random values to the momenta, $\mathbf{p}_i(0)$, drawn from the distribution $P(\mathbf{p}_i(0)) \propto \exp(-\mathbf{p}_i^2(0)/2)$. The system is then evolved using a finite-step approximation of the equations of motion corresponding to H_{MC}. A popular choice is to use the leapfrog scheme

$$\mathbf{x}_i(t+\frac{\epsilon}{2}) = \mathbf{x}_i(t) + \frac{\epsilon}{2}\mathbf{p}_i(t) \tag{6}$$

$$\mathbf{p}_i(t+\epsilon) = \mathbf{p}_i(t) - \frac{\epsilon}{T}\nabla_i E(t+\frac{\epsilon}{2}) \tag{7}$$

$$\mathbf{x}_i(t+\epsilon) = \mathbf{x}_i(t+\frac{\epsilon}{2}) + \frac{\epsilon}{2}\mathbf{p}_i(t+\epsilon) \tag{8}$$

After n such leapfrog iterations, often referred to as one trajectory, the new configuration, $\{\mathbf{x}_i(n\epsilon)\}$, is subjected to a Metropolis accept/reject step, where the probability of acceptance is given by $\min(1, \exp(-\Delta H_{\rm MC}))$, $\Delta H_{\rm MC} = H_{\rm MC}(n\epsilon) - H_{\rm MC}(0)$.

Two important properties of the leapfrog scheme are that it is time-reversible and preserves phase space area. Given that the discretized equations of motion have these two properties, it can be shown that the scheme described above samples the desired distribution without finite-step-size corrections.

The algorithm has two tunable parameters, the step size ϵ and the number of leapfrog steps in each trajectory, n. The trajectory length is $n\epsilon$. The choice $n = 1$ corresponds to a corrected Langevin algorithm.

4 Fourier Acceleration

In this section I give brief description of HMC for quadratic potentials. The performance of the algorithm can in this case be studied analytically (see e.g. Kennedy and Pendleton 1991). This analysis provides the background for the Fourier acceleration technique.

Suppose that the algorithm described in the previous section is applied to the chain given by (1) with $v(r) = 0$,

$$\frac{E}{T} = \frac{1}{2}\sum_i r_{i\,i+1}^2 \tag{9}$$

(for a quadratic potential the T dependence is trivial). The calculation of acceptance rate and autocorrelation times is most easily performed by transforming to the Fourier variables

$$\tilde{\mathbf{x}}_k = \sqrt{\frac{2}{N}}\sum_i \mathbf{x}_i \cos\frac{\pi k(i-1/2)}{N} \quad . \tag{10}$$

This orthogonal transformation diagonalizes the Hamiltonian,

$$H_{\rm MC} = \frac{1}{2}\sum_i \mathbf{p}_i^2 + \frac{E}{T} = \frac{1}{2}\sum_k \left(\tilde{\mathbf{p}}_k^2 + \omega_k^2\tilde{\mathbf{x}}_k^2\right) \quad , \tag{11}$$

where

$$\omega_k^2 = 4\sin^2\frac{\pi k}{2N} \quad . \tag{12}$$

The k-dependent autocorrelation function $C_k(t) = \langle \tilde{\mathbf{x}}_k(t) \cdot \tilde{\mathbf{x}}_k(0) \rangle$ is easy to calculate in the limit $\epsilon \to 0$, where the $\tilde{\mathbf{x}}_k$'s evolve as a set of uncoupled oscillators and the accept/reject step can be ignored since H_{MC} is conserved. For trajectory length $t_0 = n\epsilon$, one finds that $|C_k(t)| \propto \exp(-t/\tau_k)$ with autocorrelation time

$$\tau_k = \frac{t_0}{-\ln|\cos(\omega_k t_0)|} \quad . \tag{13}$$

In particular, this implies that the autocorrelation times for long-wavelength modes grow as N^2 for large N.

The average acceptance rate is found to be $P_{\mathrm{acc}} = \mathrm{erfc}(\frac{1}{2}\langle \Delta H_{\mathrm{MC}} \rangle^{1/2})$ (Gupta et al. 1990), where erfc is the complementary error function and

$$\langle \Delta H_{\mathrm{MC}} \rangle \sim \frac{\epsilon^4}{32} \sum_k \omega_k^4 \sin^2(\omega_k t_0) \qquad (\epsilon \to 0) \tag{14}$$

is the average energy change in one trajectory. This shows that it is primarily the short-wavelength modes that determine how small the step size must be taken in order to have a reasonable acceptance rate.

Since the step size must be small to maintain stability at short wavelengths, the evolution of long-wavelength modes becomes very slow; a large number of leapfrog steps is needed to produce significant changes in global observables. This problem can be overcome by introducing a k-dependent step size $\epsilon_k = \tilde{\epsilon}/\omega_k$. This technique is called Fourier acceleration. After modifying the algorithm in this way, one finds that $\tau_k = -\tilde{t}_0/\ln|\cos\tilde{t}_0|$, where $\tilde{t}_0 = n\tilde{\epsilon}$, independent of k. Here the autocorrelation times are expressed in units of simulation time rather than leapfrog steps. In estimating computational effort, one has to take into account that $\tilde{\epsilon}$ must be decreased with increasing N in order to keep a constant acceptance. However, this N dependence is weak, $\tilde{\epsilon} \sim N^{-1/4}$.

This Fourier accelerated algorithm can be formulated in a simple and useful alternative way by using the bond vectors $\mathbf{b}_i$. In fact, this algorithm is equivalent to a plain HMC in the $\mathbf{b}_i$'s with uniform step size. This is for linear chains. An advantage of the bond vector formulation is that it can be applied to branched structures too. The Fourier variable formulation, on the other hand, is, of course, well suited for cyclic chains.

The algorithm discussed so far speeds up simulations for the potential (9). For a general quadratic potential, one can proceed in the same way: diagonalize the potential and update the eigenmodes using step sizes that are inversely proportional to their frequencies.

In the next section two different Fourier acceleration schemes are tested. The first of these is that described above, corresponding to the potential (9). The other was obtained by an optimization procedure, starting from the general ansatz

$$\frac{E}{T} = \frac{1}{2} \sum_{ij} G_{ij}^{-1} \mathbf{b}_i \cdot \mathbf{b}_j \quad , \tag{15}$$

where the parameters G_{ij}^{-1} are elements of the inverse correlation matrix. For a given model and system size, these parameters were determined variationally by using the method of Jönsson et al. (1995). In implementing this algorithm, it is convenient to express the symmetric and positive definite matrix $\mathbf{G}^{-1}$ as the product of a matrix and its transpose, $\mathbf{G}^{-1} = \mathbf{W}\mathbf{W}^T$.

5 Numerical Tests

In this section I discuss numerical tests of the Fourier acceleration method. I begin with results obtained using the scheme corresponding to the potential (9), which was tested for all the four models defined in Sect. 2. I then discuss some results obtained using the "optimized" scheme corresponding to (15) with variationally determined parameters G_{ij}^{-1}.

Figure 2 shows the evolution of the end-to-end distance r_{ee} in two simulations of an unscreened Coulomb chain, one with and one without Fourier acceleration. Both runs were carried out using $N = 16$, $n = 1$, and a step size such that $P_{\mathrm{acc}} \approx 0.80$. From Fig. 2 it is evident that the evolution of r_{ee} is much faster in the simulation with Fourier acceleration. Due to the coordinate transformations (10), which were performed by using fast Fourier transform, the cost of each iteration is slightly higher for the Fourier accelerated algorithm, but this difference is negligible.

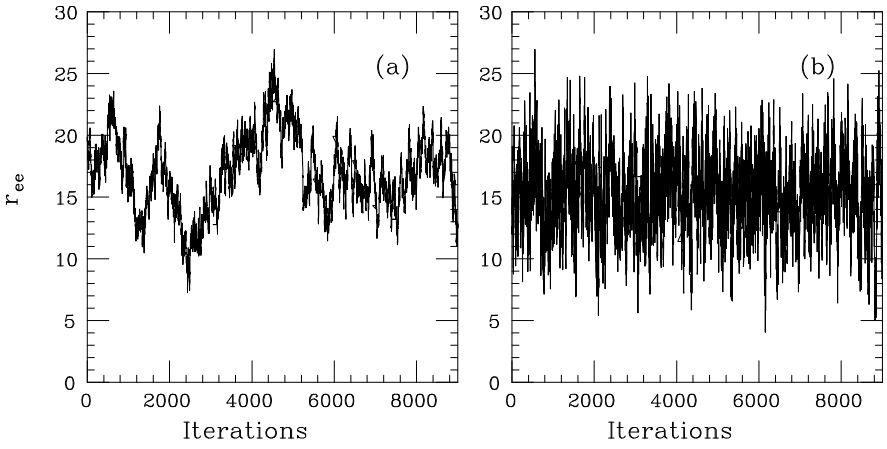

Fig. 2. The Monte Carlo evolution of the end-to-end distance in two HMC simulations of an unscreened Coulomb chain for $N = 16$: (a) without and (b) with Fourier acceleration.

To study how the efficiency of the Fourier accelerated algorithm depends on N, simulations were performed for N up to 512. The integrated autocorre-

lation time, which controls the statistical error, was calculated for a number of different observables. For details of these simulations, see Irbäck (1994).

An important issue is to what extent the efficiency depends on the length scale considered. To investigate this, the integrated autocorrelation time $\tau_{\mathrm{int},k}$ for $\tilde{\mathbf{x}}_k^2$ was measured for all possible k. As an example, Fig. 3 shows the results obtained for the chain with potential $v(r) = 1/r^2$ and $N = 512$. As can be seen from this figure, the k dependence of $\tau_{\mathrm{int},k}$ is weak. Similar results were obtained for other chains.

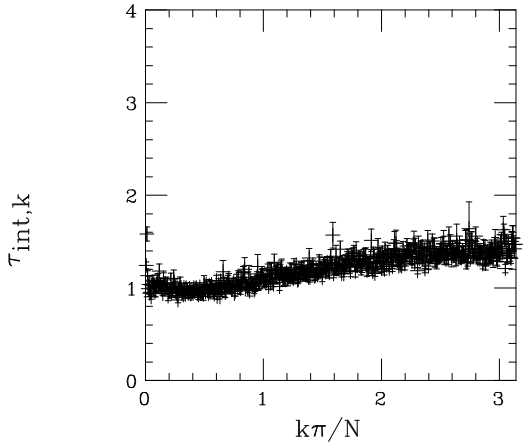

Fig. 3. The autocorrelation time $\tau_{\mathrm{int},k}$ in units of trajectories ($n = 104$) against k for a $N = 512$ chain with potential $v(r) = 1/r^2$.

Having seen that the k dependence is weak, let us now focus on one observable, the end-to-end distance. To get a measure of computational effort, I consider the integrated autocorrelation time for this quantity, E, in units of leapfrog steps. The results for E were found to be well described by a power law, $E \propto N^{z'}$, for all the four models studied. This means that the computer time required to generate a given number of independent measurements grows as $N^{2+z'}$, since the cost of each leapfrog step scales quadratically with N. The fitted values of the exponent z' are given in Table 1 and lie between 0.6 and 0.9. Although the differences are not large, the efficiency of the algorithm shows a clear tendency to improve with increasing range of the potential.

A popular method for simulations of long flexible chains is the pivot algorithm (Lal 1969). The elementary pivot move is as follows: choose a random site i along the chain, and apply a randomly chosen rotation/reflection to the part of the chain consisting of sites $i + 1$ to N. This method was thoroughly tested for self-avoiding walks on a lattice by Madras and Sokal (1988), and was found to be very powerful for global quantities. In the pure pivot algo-

Table 1. Fitted values of the exponent z'.

$v(r)$	z'
$1/r$	0.66(2)
$\exp(-\kappa r)/r$	0.82(2)
$1/r^2$	0.76(3)
$1/r^{2.5}$	0.79(3)

rithm, short-wavelength structure evolves much slower than long-wavelength structure. This contrasts sharply with the weak k dependence that was seen above for Fourier accelerated HMC.

Figure 4 shows results for the scaling of r_{ee} with N in the two models with $v(r) = 1/r^{\lambda}$ and $\lambda = 2$ and 2.5, respectively. The effective exponent $\nu_N = (2\ln 2)^{-1} \ln[r^2_{\mathrm{ee}}(2N)/r^2_{\mathrm{ee}}(N)]$ is plotted against $1/\ln N$. An asymptotic behavior of the type $r_{\mathrm{ee}} \sim N^{\nu}(\ln N)^{-\alpha}$ corresponds to $\nu_N \approx \nu - \alpha/\ln N$. The results are in good agreement with the predictions of Bouchaud et al. (1991). The line shows the prediction for $\lambda = 2$ ($\nu = 1$ and $\alpha = 1/2$).

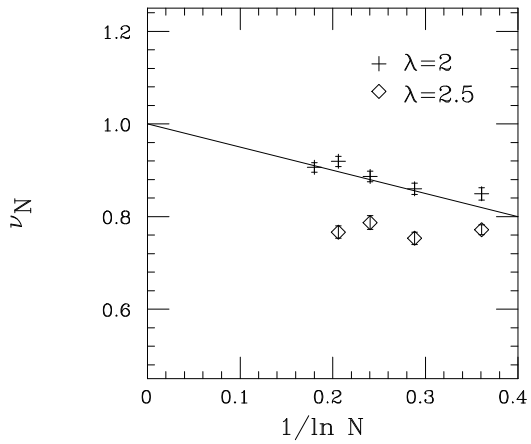

Fig. 4. The effective exponent ν_N against $1/\ln N$ for the two models with $v(r) = 1/r^{\lambda}$ and $\lambda = 2$ and 2.5, respectively.

The results presented so far were obtained using the Fourier acceleration scheme corresponding to (9). As mentioned above, this scheme is equivalent to a plain HMC in the bond vectors $\mathbf{b}_i$, which corresponds to the choice $G^{-1}_{ij} = \delta_{ij}$ in (15). I now turn to the optimization procedure, where the

parameters G_{ij}^{-1} are determined variationally. The algorithm obtained in this way was tested for unscreened and screened Coulomb chains. The efficiency was found to be very similar to that of the previous algorithm. At least partly, this can be explained by the that fact the variations in frequency among the eigenmodes of the optimized $\mathbf{G}^{-1}$ turn out to be fairly small. For example, for the screened Coulomb chain the inverse frequencies vary between 0.96 and 1.21 for $N = 16$, and between 0.96 and 1.49 for $N = 64$.

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