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Monte Carlo Simulation Using the Fourier Transform of the Interatomic Potential

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When doing Monte Carlo simulations using continuous potentials, the evaluation of the configurational potential energy in *k*-space by Fourier transformation is shown to be a computationally attractive scheme for systems where the long-range interatomic interaction spans a dimension comparable to the size of the simulated system.

KEY WORDS: Monte Carlo.

We dedicate this paper to Howard Reiss in honor of his 65th birthday. In particular, FFA acknowledges with gratitude Howard's professional guidance and friendship over the last two decades.

The Monte Carlo technique has been developed and refined over the past three decades and is now one of the most powerful tools in statistical mechanics. While technical improvements, such as chain-link storage for continuous potentials and effective field boundary conditions for lattice systems, have speded up the sampling procedure, the basic technique remains that invented by Metropolis, Rosenbluth, Rosenbluth, Teller and Teller(1). In this article, we explore whether for certain systems a different implementation of calculating the configurational potential energy central to the Monte Carlo procedure might not be more effective. In particular, we have in mind systems in which the interatomic potential is long range; i.e., comparable or larger than the linear dimension of the simulated system.

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We write the total potential energy U for a given atomic configuration $(r_1, r_2,..., r_N)$ of N atoms interacting with a two-body interatomic potential V in the form

$$U = \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}'\, \rho(\mathbf{r})\, V(|\mathbf{r}-\mathbf{r}'|)\, \rho(\mathbf{r}') \tag{1}$$

where

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r}-\mathbf{r}_j) \tag{2}$$

is the one particle density of the system. We also adopt the basic idea, used in many other contexts, that the interatomic potential may be divided into a short-range, repulsive part V_0 and a long-range, usually attractive part V_1;

$$V(r) = V_0(r) + V_1(r) \tag{3}$$

with $V_0(r) = 0$ for $r > a$. An influential example is the extension by Howard Reiss of his Scaled-Particle theory of hard spheres to real fluids by treating the attractive energy as a uniform background, enabling him to make comparison with experiment$^{(2)}$. In the specific example described in our study, the interaction range cutoff a equals unity, and V_0 equals infinity for $r < 1$. The long-range potential V_1 is assumed to be nonsingular. We consider our finite system to be subject to periodic boundary conditions and express the one particle density in terms of its Fourier components

$$\rho(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{4}$$

$$\mathbf{k} = 2\pi \left(\frac{n_1}{L_1}, \frac{n_2}{L_2}, ..., \frac{n_\nu}{L_\nu} \right)$$

for a system confined to a ν-dimensional parallelpiped of volume $\Omega = L_1 L_2 \cdots L_\nu$. From Eqs. (1–4), we may write

$$U = U_0(\mathbf{r}_1,..., \mathbf{r}_N) + \frac{1}{2} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \hat{V}_1(\mathbf{k}) \hat{\rho}_{-\mathbf{k}} \tag{5}$$

where the short-range configurational energy U_0 is not transformed;

$$U_0(\mathbf{r}_1,..., \mathbf{r}_N) = \frac{1}{2} \sum_{i,j} V_0(|\mathbf{r}_i - \mathbf{r}_j|) \tag{6}$$

We note that the Fourier transform

$$\hat{V}_1(\mathbf{k}) = \int_\Omega d\mathbf{r}\, V_1(r)\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{7}$$

where the integration extends over the finite volume Ω, is equivalent to the solution of an eigenvalue problem

$$\int_\Omega d\mathbf{r}'\, V_1(|\mathbf{r}-\mathbf{r}'|)\, u_k(\mathbf{r}') = \hat{V}_1(\mathbf{k})\, u_k(\mathbf{r}) \tag{8}$$

where the periodic boundary conditions imply that the eigenfunctions are simply

$$u_k(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \tag{9}$$

The expression (4) is simply an expansion of the density operator in terms of this complete set. Siegert,(3) in his adaptation of the Stratonovich-Hubbard(4,5) transformation to classical statistical mechanics, has used the separation (3) and transformation (7–9) to express the configurational integral as an average over an ensemble of Gaussian random functions which play the role of an external single particle potential. Siegert's form of the configurational integral [e.g., see Eq. (3.4) of reference (6)], allows an exact integration over the volume of configuration space associated with the random variables. This integration produces a configurational potential energy in the Boltzmann factor of the form given by Eq. (5). The reader is referred to Wiegel(7) for a modern review of applications using Siegert's method.

Concerning the practical implementation of the Monte Carlo method, the question of whether Eq. (5) is more useful than the conventional direct summation over particle pairs is, of course, answered by whether it is computationally faster! For ease of addressing this issue, we assume that the long-range interaction V_1 scales with a distance parameter R_c $(2R_c < L)$ and is negligible beyond R_c, L being the linear size of the simulated system. The number of k-vectors N_k needed for an accurate representation of the interatomic potential is the same for systems with the same R_c/L. In a later demonstration, we take V_1 to be represented by a Gaussian function and find that as $R_c \to L/2$ (i.e., as the range of interaction approaches the size of the simulated system) the number N_k of k-vectors needed for comparable accuracy decreases as $1/R_c$. This decrease is expected to be a general feature. For the standard Monte Carlo particle displacement, the calculation of the potential energy change is proportional to N_k operations for the long-range contribution and is a fixed number of operations N_0 (independent of volume) for the short-range contribution (i.e., a direct sum over a finite and small number of pairs for $r < a$ using neighbor tables or chain-link). Hence, for an N-particle system, the Monte Carlo computational burden goes as $N(N_k + N_0)$. In this case, as R_c increases for fixed N and L, the computational burden decreases since N_k decreases. For fixed R_c/L, the burden scales as N. This is to be compared with the calculation of the long-range potential energy change using the direct summation over pairs which is proportional to the number of particles N_1 within the "sphere of influence" of the long-range interaction, hence proportional to R_c^ν in ν-dimensions. Here, the Monte Carlo computational burden goes as $N(N_1 + N_0) \to N^2$ as $R_c \to L/2$; i.e., it increases as R_c increases for fixed N and L. For fixed R_c/L, the burden scales as N^2. For a long-range interatomic interaction, the Fourier method looks favorable.

As a demonstration of the two methods, we have carried out Monte Carlo simulations for a two-dimensional system of 195 atoms interacting with the Gaussian pair potential,

$$\begin{aligned} V_0(r) &= \infty, \qquad r < 1 \\ V_1(r) &= -\omega e^{-r^2/\sigma^2}, \qquad 0 \leqslant r \leqslant \infty \end{aligned} \tag{10}$$

For $\sigma \ll L$, the eigenvalues can be evaluated analytically;

$$\hat{V}_1(k) = -\pi\sigma^2\omega e^{-\sigma^2 k^2/4} \tag{11}$$

In numerical comparisons of Eq. (10) with the back transform of Eq. (7), we learned that Eq. (11) is an excellent approximation for $\sigma < L/4$.

In Fig. (1), we compare the hard-core/Gaussian potential with the familiar Lennard-Jones 12:6 potential. The atoms were initialized in a triangular lattice of 13 by 15. The reduced density $d^* = da^2$ and reduced temperature $T^* = T/\omega$ were taken as 0.8 and 1.0, respectively. The computational box was approximately square with length of $15.6a$. Simulations were done for σ equal to 1, 2 and 3 using explicit pairwise summation (with neighbor tables and $R_c = 2.5\sigma$) and using the Fourier transform energy evaluation technique. Fig. (2) shows the radial distribution function for $\sigma = 1$. Most relevant to this study is Fig. (3), where a comparison is made of the computational burders τ using the two different energy evaluation techniques as a function of σ for fixed N and L. Consistent with our earlier observations, τ scales quadratically with σ when the real-space evaluation of U is used and inversely with σ when the k-space evaluation is used. The cross-over is at approximately $\sigma = 1.5$. Of course, these dependences are not exact because of the evaluation of the short-range contribution, updating

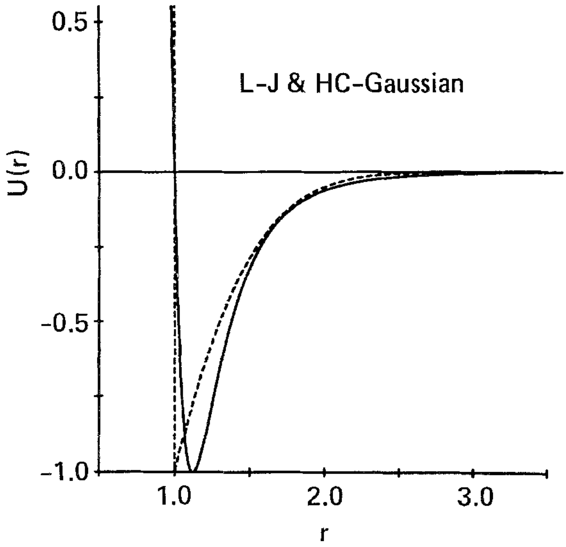

Fig. 1. Comparison of the hard-core/Gaussian potential (dashed) with the familiar Lennard-Jones 12:6 potential (solid).

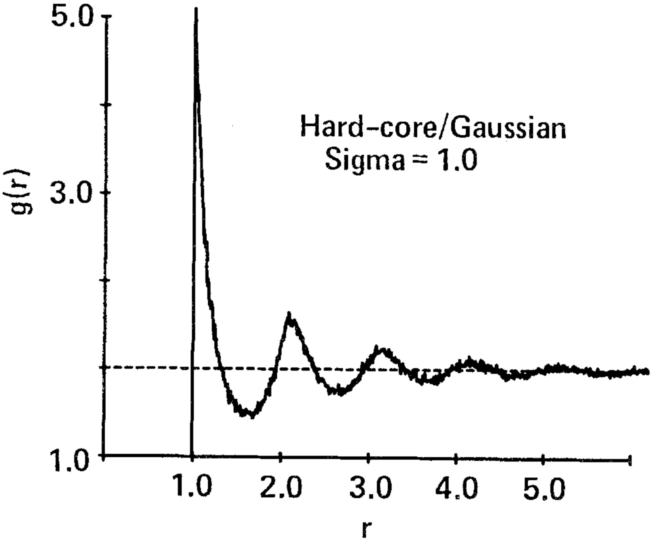

Fig. 2. Radial distribution function for the hard-core/Gaussian 2D liquid at $d^* = 0.8$ and $T^* = 1.0$.

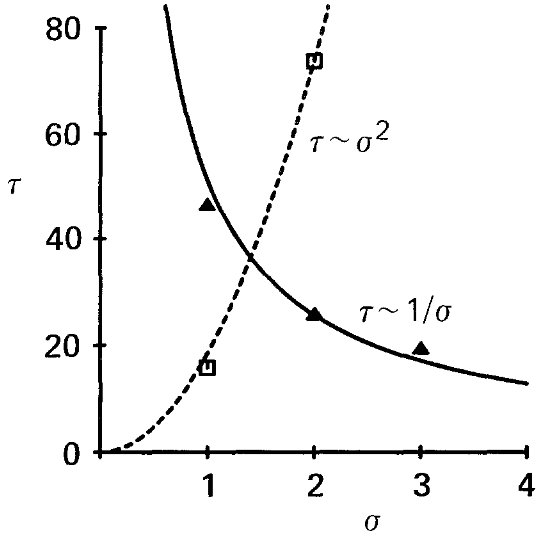

Fig. 3. A comparison of the Monte Carlo computational burdens τ as a function of σ where the potential energy is evaluated using (□) the direct-space pairwise summation technique and (▲) the k-space Fourier transform technique. The number of particles N and the computational box length L are constant.

the neighbor tables and total energy after a fixed number of Monte Carlo moves, and other overhead operations. In any event, evaluation of the configurational potential energy in k-space looks very attractive for systems where the long-range interatomic interaction spans a dimension comparable to the size of the simulated system. The three-dimensional Coulomb system might be the most favorable system for the Fourier method.

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