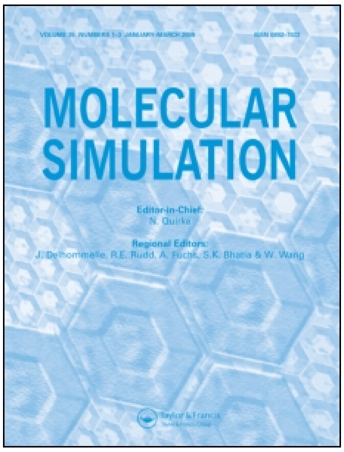

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DIRECT SAMPLING OF LOCAL DENSITY FLUCTUATIONS IN MONTE CARLO SIMULATIONS

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A novel method for accelerating Monte Carlo simulations of fluids based on a direct sampling of local density fluctuations by a multiparticle move is proposed. The method is expected to be particularly efficient for inhomogeneous pure fluids consisting of spherical or moderately nonspherical molecules which is confirmed by a sample simulation of a Lennard-Jones fluid in a slit pore. An analogous method for a mixture, a direct sampling of local concentration fluctuations by swapping particles of different species, is successfully tested on a liquid mixture of argon and nitrogen.

KEY WORDS: Fluid, Monte Carlo, density fluctuation, multiparticle move, particle swapping.

1 INTRODUCTION

During last two decades, the Monte Carlo simulation methods [1, 2] have been widely used in statistical mechanics to study both lattice and continuous systems. Due to usually considerable requirements on a computer time it is highly desirable to devise the pseudoexperiment as efficient as possible. The criterion of the efficiency may be generally formulated as follows [3]: *To minimize the error of a measured quantity of interest during the available computer time.*

To do this, one has three possibilities:

(1) To use programming tricks [1], better software (optimizing compilers) or hardware (faster computers).
(2) To optimize the values of free parameters of the simulation [3]: probability distribution of trial moves; frequencies with which displacements, rotations and other elementary moves are performed; frequency of measurements.
(3) To use more sophisticated methods.

As regards the last item, probably the most successful improvement over the original Metropolis algorithm was proposed by Pangali *et al.* [4]: The so called force-bias method uses a nonsymmetric distribution of a trial move (displacement or rotation) of one molecule biased in the direction of acting force (torque). Using the speed of equilibration and the autodiffusion as criteria, an increase in efficiency by the factor of 2 ~ 3 was found. The Brownian dynamics smart Monte Carlo due to Rossky *et al.* [5] makes use of a similar principle. Multiparticle moves in which all molecules are displaced independently in a random direction were considered by Chapman and Quirke [6].

The above methods try to improve each MC step without knowledge which process in the series of generated configurations is the slowest one and which thus determines the convergence rate and the errors of measured quantities. This "bottleneck process" should be the most important object of efforts to enhance the performance of MC simulations.

It has been shown in our previous papers [3, 7] that the long lag correlations in the series of configurations generated during a simulation of a pure fluid of spherical or moderately nonspherical molecules are caused by creation and annihilation of local density fluctuations, although the influence of these correlations depends on the system (e.g. boundary conditions) and on the quantity which is measured. To overcome this inefficiency a new method, a direct sampling of the density fluctuations by a multiparticle move, is proposed in section 2 and tested on a Lennard-Jones fluid in a slit pore.

Analogously, creation and annihilation of local concentration fluctuations (mixing of different species) is the slowest process in simulations on mixtures of moderately nonspherical molecules. The simulations may be thus enhanced by swapping unlike molecules provided that this change is accepted with a reasonable probability [8]. This method is tested in section 3 using an equimolar mixture of argon and nitrogen.

2 DIRECT SAMPLING OF LOCAL DENSITY FLUCTUATIONS

2.1 Principle of the Method

The multiparticle move proposed in this section displaces centres of all molecules in a fluid so that the fluid is compressed in one part of the simulation cell and proportionally expanded in another. Since the trajectories of neighbouring molecules during the move are almost parallel, the molecules may travel a longer distance than that achieved by single independent displacements. This additional move may increase the efficiency only if the following conditions are satisfied:

(i) The slowest process in the series of configurations generated in the course of the simulation is creation and annihilation of local density fluctuations, i.e. no slower process (as e.g. rotation of highly nonspherical molecules) is present. This condition is satisfied for fluids of spherical or moderately nonspherical molecules, especially for large systems. The influence of density fluctuations is less pronounced ($\frac{1}{4}$ of the correlation time) for systems with periodic boundary conditions than for systems bounded by hard walls with the same sizes of the simulation cell [3].

(ii) The measured quantities are sensitive to creation/annihilation of density fluctuations. We have shown [7] that for fluids in periodic boundary conditions in three dimensions and for pair-wise additive quantities the large-scale density fluctuations have only moderate influence on the total error. This need not hold true for 2D or 1D systems or systems in which the measured quantities do not have 3D symmetry. The density profile in a pore (more exactly, some characteristics of it) may serve as the example.

(iii) An ensemble with a constant number of particles is used. Insertions of molecules into random places in the liquid and their deletions in the grand canonical Monte Carlo method sample the density fluctuations efficiently enough.

Trajectories of two neighbouring molecules simulated by the standard displacements are strongly correlated but these correlations rapidly decay if a distance between the molecules increases. That is why an ideal gas, i.e. a set of independent point-wise "molecules" travelling randomly according to the Brownian dynamics, is a good approximation if one is interested in large scale phenomena. The move of one molecule is in this approximation determined by the autodiffusion coefficient D and boundary conditions. The time development of probability density $\psi(t, \mathbf{r})$ of finding a molecule at position $\mathbf{r}$ at time t satisfies the equation of diffusion (or heat conduction)

$$D\Delta\psi(t, \mathbf{r}) = \partial\psi(t, \mathbf{r})/\partial t, \tag{1}$$

where Δ is the Laplace operator. As regards the boundary conditions, hard walls are imposed by the usual formula $\mathbf{n}\ \mathbf{grad}\ \psi = 0$, where $\mathbf{n}$ is the normal to the wall; soft walls may be approximated by hard ones. Solutions of (1) are linear combinations of functions

$$\psi_k(\mathbf{r})\lambda_k^t, \tag{2}$$

where subscript k labels eigenvalues, $1 > \lambda_1 \geqslant \lambda_2 \geqslant \ldots$; the trivial case $\lambda_0 = 1$ is omitted. The eigenvalues determine the speed of changes – decay of density fluctuations. The changes are described by the associated eigenfunctions $\psi_k(\mathbf{r})$ satisfying the equation:

$$D\Delta\psi_k(\mathbf{r}) = \ln\lambda_k\psi_k(\mathbf{r}). \tag{3}$$

The gradient $\mathbf{grad}\,\psi_k(\mathbf{r})$ has the meaning of the mass transfer associated with the diffusion and may thus serve to define the multiparticle move. We are interested only in the slow and large-scale changes which correspond to the several first eigenvalues. We propose the trial move via the implicit formula

$$\mathbf{r}_i' = \mathbf{r}_i + 2d\mathbf{f}\left(\frac{\mathbf{r}_i' + \mathbf{r}_i}{2}\right), \tag{4}$$

where $\mathbf{r}_i$ and $\mathbf{r}_i'$ denote old and new positions of a particle, respectively, i runs over all N molecules, d is a symmetric random variable (it holds $\mathrm{Prob}(d) = \mathrm{Prob}(-d)$ for its probability density), and the vector function $\mathbf{f}(\mathbf{r})$ is either the gradient $\mathbf{grad}\ \psi_k(\mathbf{r})$ or an approximation of it. If $\mathbf{f}(\mathbf{r})$ has bounded first derivatives and $|d|$ is small enough then (4) is a one-to-one mapping. In practice it is satisfied because d must be small to prevent overlaps of molecules. In addition, if $\{\mathbf{r}_i\} \to \{\mathbf{r}_i'\}$ and d satisfy (4) then the inverse move $\{\mathbf{r}_i'\} \to \{\mathbf{r}_i\}$ satisfies (4) with $-d$ instead of d. The implicit form of (4) then simplifies the accept/reject test.

The trial configuration $\{\mathbf{r}_i'\}$ is accepted with the probability (generalized Metropolis test [4, 5])

$$\min\left\{1, \frac{P(\mathbf{r}_i')}{P(\mathbf{r}_i)}\frac{T(\mathbf{r}_i' \to \mathbf{r}_i)}{T(\mathbf{r}_i \to \mathbf{r}_i')}\right\}, \tag{5}$$

where P is the Boltzmann probability of the configuration and T the transition probability of the move depicted in the parentheses. The ratio of the transition probabilities is given by the Jacobian of mapping (4),

$$\frac{T(\mathbf{r}_i' \to \mathbf{r}_i)}{T(\mathbf{r}_i \to \mathbf{r}_i')} = \prod_{i=1}^{N}\left|\det\left(\frac{\partial\mathbf{r}_i'}{\partial\mathbf{r}_i}\right)\right|, \tag{6}$$

where $\partial\mathbf{r}_i'/\partial\mathbf{r}_i$ denotes the matrix of the partial derivatives. Using Cartesian coordinates (labelled by Greek letters) we obtain from (4) and (6)

$$\frac{T(\mathbf{r}_i' \to \mathbf{r}_i)}{T(\mathbf{r}_i \to \mathbf{r}_i')} = \prod_{i=1}^{N} \frac{\det\left[\delta_{\alpha\gamma} + d\mathbf{f}_{\gamma,\alpha}\left(\frac{\mathbf{r}_i' + \mathbf{r}_i}{2}\right)\right]}{\det\left[\delta_{\alpha\gamma} - d\mathbf{f}_{\gamma,\alpha}\left(\frac{\mathbf{r}_i' + \mathbf{r}_i}{2}\right)\right]}, \tag{7}$$

where ",α" in the subscripts denotes the derivative and $\delta_{\alpha\gamma}$ is the Kronecker delta. Since (4) is a one-to-one mapping, the denominator of (7) is neither zero nor negative.

2.2 Slit Pore

The above method was tested on a slit pore, i.e. a fluid contained between two parallel walls. Since the usual periodic boundary conditions were imposed along x- and y-axes parallel to the walls, the slowest process is the move of the molecules along the z-axis across the pore. It is described by the eigenfunctions

$$\psi_k(z) = \cos(k\pi z/b), \tag{8}$$

where $k = 1, 2, \ldots, z = 0$ at wall 1, and $z = b$ at wall 2. The move then changes only z-coordinates of all particles (see Figure 1ab),

$$z_i' = z_i + 2d\sin\left(\frac{k\pi}{b}\frac{z_i' + z_i}{2}\right). \tag{9}$$

This equation for z_i' does not have an analytic solution. Since d is small, direct iterations starting from $z_i' = z_i$ and using equation (9) as an assignment statement rapidly converge to the root. The ratio of transition probabilities (7) reads as

$$\frac{T(\mathbf{r}_i' \to \mathbf{r}_i)}{T(\mathbf{r}_i \to \mathbf{r}_i')} = \prod_{i=1}^{N} \frac{1 + \frac{dk\pi}{b}\cos\left(\frac{k\pi}{b}\frac{z_i' + z_i}{2}\right)}{1 - \frac{dk\pi}{b}\cos\left(\frac{k\pi}{b}\frac{z_i' + z_i}{2}\right)}, \tag{10}$$

which with the accept/reject test (5) completes the implementation of the method the the slit pore.

The test calculations were carried out for 256 Lennard-Jones atoms which, in reduced units, interact via the potential

$$u(r) = 4(r^{-12} - r^{-6}). \tag{11}$$

The boundary conditions along x- and y-axes had period 6 and thus the potential was

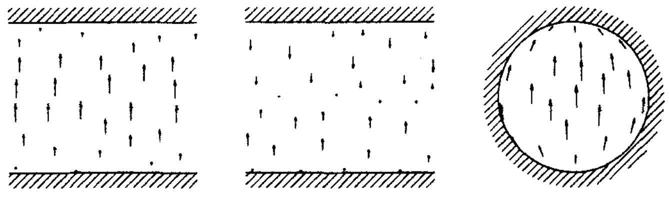

Figure 1 Multiparticle moves to sample the local density fluctuations. (a): slit pore, the slowest transversal mode; (b) slit pore, the second slowest transversal mode; (c) cylindric pore, the slowest transversal mode.

cut off at the atom-atom separation $r = 3$. The wall-wall separation was $b = 10$ (system A of [7]). The wall-atom potential was a $10 - 4$ potential obtained by averaging the interactions of the identical Lennard-Jones atoms distributed on the walls and it was not cut off. The surface densities of the atoms were $\frac{1}{4}$ and $\frac{3}{4}$ per square unit on the respective walls. The reduced temperature was 2 and the effective bulk number density, computed from the z-density profile in the central region of the pore, was approximately 0.804.

One MC step was defined so that with the probability $p[k]$, $k = 1, 2$, multiparticle move (9) was performed while with the probability $1 - p[1] - p[2]$ the usual displacement was made. About $5 \div 6$ million steps were performed for each simulation. The uniform distribution on $\langle -\delta, -\delta/2\rangle \cup \langle \delta/2, \delta\rangle$ was used for d in equation (9) with the values of δ set so that the acceptance ratios were about 0.37. The distribution of the trial displacements was uniform in the sphere of radius 0.3 with the removed concentric sphere of radius 0.15. The obtained acceptance ratio of displacements was 0.20; no detailed study was made whether this value is optimum or not. It was, however, suggested [3] that lower acceptance ratios are better if the long-range density fluctuations are to be sampled while higher ratios are better if a close neighbourhood of a molecule is to be sampled. It follows from this consideration that higher acceptance ratios of the displacements are preferred if multiparticle moves (9) are used.

Five observables were recorded: the virial pressure, two forces (pressures) exerted on the respective walls, and the first two central moments of the density profile. The latter two observables are defined by

$$\mu_k = \sum_{i=1}^{N} \left(z_i - \frac{b}{2}\right)^k, \tag{12}$$

$k = 1, 2$. (More exactly, z_i should be measured from the centre of mass which is not, for our asymmetric pore, exactly in the geometrical centre $z = b/2$). The low order moments are the worst observables to measure; they are close to the eigenvectors of the stochastic operator corresponding to the highest eigenvalues. Although the moments themselves are not of a great importance (especially the first one is useless for a symmetric pore), they are present in other quantities as e.g. the force acting on a wall (all moments) or the density at the central region of the pore (even moments).

The quantities were measured with the frequency of 512 MC steps. Their errors are given, for a sufficiently large number of measurements n, by the formula [3, 9]

$$\left(\frac{1 + 2\tau}{n} \operatorname{Var} Q\right)^{1/2}, \tag{13}$$

where $\operatorname{Var} Q$ is the variance and τ the correlation length (time) of the quantity measured with the frequency given above,

$$\tau = \sum_{t=1}^{\infty} c_t, \tag{14}$$

where c_t is the autocorrelation coefficient at lag t.

Since $\operatorname{Var} Q$ is a thermodynamic quantity which does not depend on the simulation method we use the value $1 + 2\tau$ (which is proportional to the square of the error) as the test to compare the methods. Estimating τ by means of formula (14) is not, however, simple because the infinite series (14) converges badly, especially if the slow processes (which we would like to sample more efficiently) are present. The coefficients

Table 1 Correlation length τ for five observables and four simulations on the Lennard-Jones fluid in a slit pore. $p[k]$, $k = 1, 2$, are probabilities of multiparticle moves (9), P denote pressure, μ central moment of the density profile across the pore, and "CPU time" the relative computer time of one MC step. The values of $1 + 2\tau_{16}$ are proportional to the approximate errors of the respective quantities measured over a fixed number of MC steps.

$p[1]$	$p[2]$	CPU time			$2\tau_{16} + 1$		
			P_{vir}	$P_{wall\,1}$	$P_{wall\,2}$	μ_1	μ_2
0	0	1	11.5	11.0	10.4	393	89
2^{-8}	0	1.34	9.9	8.2	8.2	36	92
2^{-8}	2^{-8}	1.69	10.0	4.5	4.7	30	34
2^{-9}	2^{-9}	1.36	9.3	5.7	5.0	31	30

with long lags are known only with a low accuracy which makes their extrapolation up to infinity difficult. From theoretical reasons the decay of c_t is exponential at sufficiently long lags which leads us to use the following approximation

$$\tau_T = \sum_{t=1}^{T-1} c_t + \frac{c_T}{1 - (c_T/c_{T/2})^{2/T}}. \tag{15}$$

The lower cut-off lag T is used, the greater systematic error of τ_T is expected because c_t differ from the simple exponential decay; it can be shown (using [3], Equation (12)) that τ_T underestimates the correct τ. On the other hand, for longer T the statistical inaccuracy of c_T and $c_{T/2}$ may give very inaccurate or even nonsense values of τ_T. The series of τ_T with increasing cut-off lag T might be investigated to obtain the optimum T; this procedure, however, would introduce a subjective factor into interpretation of the data. That is why we used the relatively low fixed value $T = 16$ in all cases; the correct τ is thus underestimated especially when the slow processes are present, i.e. if the classical simulation methods are used. The statistical error of τ_{16} (estimated by comparing the results for $P_{\text{wall}\,1}$ and $P_{\text{wall}\,2}$ and for other quantities whose errors should be almost the same) are at most ten per cent.

The results are summarized in Table 1 along with the additional computer time required to perform the multiparticle moves. The increase of efficiency for the moments of the wall-wall density profiles caused by the corresponding modes of the multiparticle move is evident. It can be even estimated that probabilities of these moves smaller than 2^{-9} would be sufficient to achieve a substantial improvement and the computer time would be saved.

Unlike the moments, the pressures on the walls are sensitive to all modes (8) which is confirmed by a moderate decrease of the errors whenever the multiparticle moves are used. Compared with the classical simulation ($p[1] = p[2] = 0$), the errors per a unit of computer time are significantly smaller for the last simulation ($p[1] = p[2] = 2^{-9}$). We expect that using more modes but with lower probabilities would yield a further improvement of the efficiency.

On the contrary, the error of the virial pressure is not significantly affected by the direct sampling of the density fluctuations. It is in accordance with the theoretical expectations because the virial is a pair-wise quantity which is only marginally sensitive to long-scale fluctuations. In addition, the fluctuations along the x- and y-axes are present, too.

2.3 Cylindric Pore

As a second example let us consider a cylindric pore in an external field perpendicular to the axis of the pore. The axial symmetry of the pore is broken and the same will hold for typical observables relevant to this system. These are expected to be sensitive to moves of molecules across the pore in the direction of the field.

We introduce the Cartesian coordinates with the origin in the centre of the pore and the y-axis parallel to the external field. Both the y- and x-axes are perpendicular to the axis of the pore. The radius of the pore is set to unity.

The solution of (1) is expressed in the factorized form using the polar coordinates (r, ϕ)

$$\psi(r, \phi) \;=\; b_{k,l}(r) r^k \exp(ik\phi), \tag{16}$$

where functions $b_{k,l}(r)$ (which can be expressed through the Bessel functions) are continuous at $r = 0, k \geq 0$, and integer $l, l \geq \delta_{k,0}$, denotes the number of zero points of $b_{k,l}(r)$ for $0 \leq r < 1$. The case $k = 0$ corresponds to axially symmetric solutions. From many solutions we confine ourselves to the slowest mode $b_{1,0}(r)$, see Figure 1c.

It is not necessary for our purposes to know the exact $b_{1,0}(r)$ (which cannot be expressed by elementary functions) but it is reasonable to satisfy exactly the boundary conditions, $\partial\psi/\partial r = 0$ for $r = 1$. The simplest approximation of $b_{1,0}(r)$ (with the correct values of the zeroth and first derivatives, $b_{1,0}(0) \neq 0$ and $b'_{1,0}(0) = 0$) satisfying the boundary conditions is $1\text{-r}^2/3$ which gives

$$\psi(x,y) \;=\; (1 - \frac{x^2 + y^2}{3})y \tag{17}$$

in Cartesian coordinates. The move is then defined by equations (4) and (7) with $\mathbf{f} = \mathbf{grad}\,\psi$. Faster modes (with higher k or l) may be obtained in the same way. Their efficient use is determined by similar circumstances as in the case of the slit pore.

3 DIRECT SAMPLING OF LOCAL CONCENTRATION FLUCTUATIONS BY SWAPPING UNLIKE MOLECULES

The slowest process in simulations of mixtures of moderately nonspherical molecules in large systems with a constant number of particles is creation and annihilation of local concentration fluctuations. In other words, many one-step displacements are required to intermix the unlike species in a dense liquid. This process is even slower than creation and annihilation of local density fluctuations in a pure fluid because the particles are indistinguishable.

To sample this slow process more efficiently a swapping of molecules of different species was recommended [8]. This additional MC step in its typical implementation will consist of a random choice of both particles and the standard Metropolis acceptance test according to a change of energy caused by the swapping. The new step may be efficient only if the unlike molecules are similar enough to ensure a sufficiently high acceptance ratio, otherwise problems analogous to those in the grand canonical ensemble will arise. (In the latter case it may be more efficient to use directly the grand canonical simulation with tricks for easier inserting the particles [10]).

To test the method an equimolar mixture of Lennard-Jones (LJ) atoms and LJ diatomics was used with the parameters corresponding to argon and nitrogen [11]:

Table 2 Correlation length τ for species-species energies and three simulations on the equimolar mixture of Ar and N_2. p denotes probability of the MC move marked in brackets and "CPU time" the relative computer time of one MC step. The values of $1 + 2\tau_8$ are proportional to the approximate errors of the respective quantities measured over a fixed number of MC steps.

p[Ar]	*p[N_2]*	*p[Ar-N_2]*	*CPU time*	$2\tau_8 + 1$ *Ar-Ar*	*Ar-N_2*	*N_2-N_2*	*Total*
0.4	0.6	0	1	41	54	25	9.5
0.4	0.58	0.02	1.01	12.2	14.2	8.8	7.8
0.3	0.5	0.2	1.18	4.5	3.7	2.9	8.9

$\sigma_{Ar} = 3.4039$ Å, $\varepsilon_{Ar}/k = 117.7$ K, $\sigma_N = 3.3078$ Å, $\varepsilon_N/k = 36.673$ K, $l/\sigma_N = 0.3292$, where σ and ε are the LJ parameters and l is the intramolecular N-N distance. The simplest Lorentz-Berthelot mixing rule $\sigma_{Ar\text{-}N} = (\sigma_{Ar} + \sigma_N)/2$, $\varepsilon_{Ar\text{-}N} = (\varepsilon_{Ar}\varepsilon_N)^{1/2}$ was applied. The typical liquid state point with density 1070 kg/m^3 and temperature $T = 100$ K was chosen. The number of molecules was 64 (32Ar + 32N_2) and the site-site potentials were cut off at the half of the box size. The common periodic boundary conditions were imposed.

Four observables were recorded: the Ar-Ar energy (the sum of all argon-argon pair interactions), the Ar-N_2 and N_2-N_2 energies, and the total internal energy. In the course of the simulation, a randomly chosen Ar atom was attempted to displace with probability p[Ar] (see Table 2), a combined move (displacement and rotation) of a randomly chosen N_2 molecule was attempted with probability p[N_2], and the swapping of a randomly chosen Ar-N_2 pair was tried with probability p[Ar-N_2]. The acceptance ratios of the first two moves were set to 0.30 and 0.37, respectively. The acceptance ratio of swapping was 0.29. The measurements were taken with the frequency of 128 steps. the total number of steps was 1.4×10^6 for each simulation. The errors were again expressed in terms of $1 + 2\tau$, see Section 2.2. The same procedure was applied to estimate τ although in this case the convergency of τ_T with increasing T was very slow and especially the results for p[Ar-N_2] = 0 are seriously underestimated.

The results are shown in Table 2. It is seen that the efficiency of MC computations of the partial energies rises once the probability of swapping increases. The total energy is not apparently affected by the new move because the Ar and N_2 molecules resemble each other (if they did not, the method would be inefficient). Similar behaviour is expected for the site-site correlation functions (which are of greater practical importance) in comparison with the averaged ones which does not distinguish the kind of the molecules.

It should be noted that, like for a pure fluid, the influence of the concentration fluctuations on the speed of the MC simulations will be even more pronounced for mixtures at interfaces, in pores, etc. Fast sampling of the concentration fluctuations is also naturally achieved in the grand canonical ensemble simulation because the molecules are added into a random place in the liquid.

4 CONCLUDING REMARKS

In molecular dynamics (MD) simulations a statistical system develops in the deterministic way so that the convergence is determined by the thermodynamic properties.

The efficiency can be affected only by technical details of a simulation procedure. This does not hold true for the Monte Carlo methods: Any algorithm is good which yields the Boltzmann (or other suitable) probability distribution of configurations and the only criterion of the efficiency is the error of the measured quantity.

The common MC algorithms move only one particle in one step which (for usual intermolecular potentials) saves the computer time. However, this method may cause that some processes in the Markov chain of the configurations are sampled ineffectively (i.e. the correlation length in the series of observables sensitive to these changes is long and the error is large). For instance, in simulations of liquid water the slowest process may be a restructuralization of a network of hydrogen bonds. One can hardly imagine a method to sample this complex process more efficiently. The situation is more clear for less structured liquids (made up of moderately nonspherical molecules) where the slowest process is creation and annihilation of local density (for a pure fluid) or concentration (for a mixture) fluctuations, although not all important quantities are sensitive to this process. We have shown that these processes may be efficiently sampled by additional MC moves: multiparticle moves compressing a pure fluid in one part of the simulation cell and diluting it in another, and two-particle moves swapping the unlike molecules in a mixture.

We conclude the discussion with a remark on the relationship between the MC and MD methods. The correlations in the series of configurations in MC, and thus in the series of measured quantities, are sums of exponentially decaying terms. An overdamped oscillator may serve as a mechanical analogy. For a pure fluid we removed the slowest terms by special multiparticle moves. These moves correspond to sound waves in real systems which are sampled by the MD method without any additional effort and which may lead to faster "damped oscillations" in the series of configurations. This phenomenon lends support to the MD. However, no analogy exists for mixtures and other systems where particular tricks may enhance the performance of MC.

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