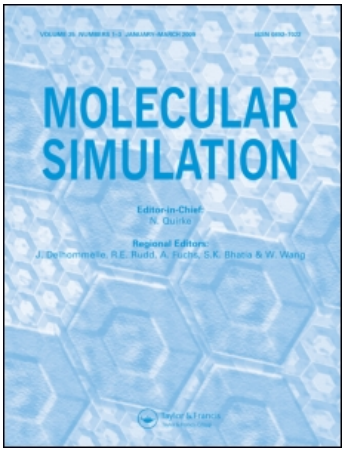

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CONVERGENCE PROPERTIES OF MONTE CARLO SIMULATIONS ON FLUIDS

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Convergence properties of standard Monte Carlo simulations for various fluid systems are studied both theoretically and experimentally. It turns out that pseudo-dynamic behaviour found for homogeneous fluids with periodic boundary conditions differs substantially from that for fluids at interfaces and for other inhomogeneous, anisotropic or less than three-dimensional systems. The results are applied to the problems of error estimation and the optimum frequency of measurement of the quantities.

KEY WORDS: fluid, dynamic Monte Carlo, correlation length, error estimation, measurement optimization

1. INTRODUCTION

Monte Carlo (MC) simulations (for a recent review see e.g. [1]) become a powerful tool for studying the equilibrium properties of matter only if the results include reliable information on errors. Unfortunately, raw data measured during the simulation are often strongly correlated and an estimation of errors need not be a trivial task. A simple method to estimate the error of the average based on dividing the series of data into subaverages underestimates systematically the errors. More sophisticated methods have been proposed [2–5], however, any method may fail if the amount of the data is insufficient. In addition, some methods are based on the assumption that the decay of autocorrelation coefficients is exponential (at least in long lags) and they again tend to underestimate the error. To know how the measured data are distributed and correlated, and thus how their averages converge to the ensemble expectation values, may help us to estimate the errors. In addition, *a priori* information on the error is important for estimating the amount of the computer time required to reach a given accuracy or even assessing the feasibility of a simulation project. Investigating the main sources of the errors might help us also to propose more efficient simulation algorithms.

The error depends on both the variance of a measured quantity and the correlation length of the series of data. The former is given entirely by the thermodynamics of the system in hand, the latter is determined also by the simulation procedure: acceptance ratios, frequency of measurements, etc. Determination of the correlation length is the main goal of the present work in which, after recalling some basic formulae in section 2, we investigate in section 3 the (pseudo) dynamic behaviour (convergence) of simulations considering simple model systems. The obtained theoretical results are compared with test simulations in section 4. Consequences to the problems of error

estimation and measurement optimization are discussed in sections 5 and 6, respectively.

2. BASIC FORMULAE

Let Q be a quantity which is to be studied by a MC simulation. The MC run produces a sequence of n measured values which we write as $\{Q_{mi}\}_{i=1}^{n}$ where m denotes the frequency of measurements and subscript mi means that the quantity was measured at time mi. We will use one sweep (one trial move is made with each particle) as the time unit throughout the paper.

The expectation value of Q is estimated by the average over the series of values computed during the simulation:

$$\langle Q \rangle_{\mathrm{MC}} = \frac{1}{n} \sum_{i=1}^{n} Q_{mi}. \tag{1}$$

The error ε of this estimate is given by the formula [3–5]:

$$\varepsilon = \left(\frac{\mathrm{Var}\, Q}{n} \left[1 + 2 \sum_{i=1}^{n} \left(1 - \frac{i}{n} \right) c_{mi} \right] \right)^{1/2}, \tag{2}$$

where c_t denotes the autocorrelation coefficient at lag t,

$$c_t = \frac{\mathrm{Cov}(Q_i, Q_{i+t})}{\mathrm{Var}\, Q} \equiv \frac{\langle (Q_i - \langle Q \rangle)(Q_{i+t} - \langle Q \rangle) \rangle}{\langle (Q_i - \langle Q \rangle)^2 \rangle}. \tag{3}$$

If the simulation is correctly designed then $c_t \to 0$ for $t \to \infty$ and Equation (2) gives, for n large enough, the limit

$$\varepsilon = \left(\frac{\mathrm{Var}\, Q}{n} [1 + 2\tau] \right)^{1/2}, \tag{4}$$

where τ is the correlation length of quantity Q measured with frequency m,

$$\tau = \sum_{i=1}^{\infty} c_{mi}. \tag{5}$$

Let us suppose now that Q is an observable, i.e. a function which maps configurations into real numbers (e.g. virial pressure or one interval of the histogram to compute the radial distribution function). It may be viewed as a vector of a real Hilbert space with the scalar product defined by the Boltzmann expectation, $\langle Q_1 Q_2 \rangle$. Then the autocorrelation coefficients may be expressed as follows [6]:

$$c_t = \sum_{i=1}^{\infty} \lambda_i^t \langle Q E_i \rangle^2 / \mathrm{Var}\, Q \tag{6}$$

where real numbers λ_i, $1 > |\lambda_1| \geqslant |\lambda_2| \geqslant \ldots$, are eigenvalues of the stochastic operator (which is assumed to be compact) of one sweep and E_i are associated orthonormalized eigenvectors. Each eigenvalue defines a time scale of an "elementary process" in the sequence of configurations ($\tau_i = -1/\ln \lambda_i$ is sometimes called the correlation length of this process: if only one term is considered in sum (6) and the sum in (5) is replaced by an integral, τ_i is obtained). The expectation values $\langle Q E_i \rangle$

("coordinates" of "vector" Q in the basis formed by the eigenvectors) then define a "sensitivity" of a given measured quantity to the elementary processes.

It should be pointed out that not all quantities usually monitored in simulations are observables in the above sense. The chemical potential computed by the Widom's method [1] with the test particle put into a random place in a liquid may serve as an example. A different example of non-observable is shown in [7] along with an equivalent (i.e. having the same error) observable. Decomposition (6) need not hold in molecular dynamics simulations where oscillations with complex λ_i's may occur [8] and also if Q_{mi} are subaverages over measured data [9].

3. CONVERGENCE PROPERTIES OF THE SIMULATIONS

In this section we investigate the dynamic behaviour of MC simulations performed on fluid systems. According to microscopic mechanisms determining the simulation dynamics (which depend both on the system studied and the simulation procedure itself) we distinguish three typical cases which are dealt with in the respective subsections: (1) The dynamics is determined by properties of a single particle which moves independently in each step; a simple exponential decay of the autocorrelation coefficients (first order autoregressive process) is then obtained. (2) The dynamics is given by creation/annihilation of local density (concentration) fluctuations caused by a slow diffusion of molecules in the system; an algebraic decay may then occur. (3) The convergence is slowed down by the critical phenomena.

3.1 Simple Exponential Decay of Autocorrelations

As a first extremely simple model system, let us condiser a simple fluid (gas) which is dilute enough to allow a trial displacement of one MC step to be so long that a moving atom is placed effectively into a random place in the fluid. The move is accepted with the probability (acceptance ratio) a. Let us confine ourselves to pair-wise additive quantities (e.g. pressure, internal energy, radial distribution function) which we write in a form

$$Q = \sum_{1 \leqslant i < j \leqslant N} q(r_{ij}), \tag{7}$$

where r_{ij} denotes the distance (nearest-image distance, if necessary) between particles i and j and N is the total number of particles. In one move, $N - 1$ terms in sum (7) from the total number of $N(N-1)/2$ pairs change with probability a. We assume that all these changes are independent random variables and also that changes in consecutive steps are independent. Since the ratio of unchanged terms in one step is $1 - 2a/N$, it holds

$$c_t = (1 - 2a/N)^{Nt} \approx e^{-2at}, \tag{8}$$

i.e. only one exponentially decaying term remains in (6). A sequence of measured data with the autocorrelation coefficients possessing this property (namely $c_t = c_1^t$) is called the autoregressive process of the first order. For a more detailed definition see e.g. [2] and [10].

As a second model system, let us consider a (generally dense) fluid of molecules having attractive sites with deep and narrow potential wells. Many MC steps are then

required until a small attractive region is found where a bond may be created, but when the bond is established it is strong and it breaks in one MC step with a low probability. If this association/dissociation equilibrium determines the convergence, the sequence of energies corresponding to this bond forms the first order autoregressive process as above,

$$c_t = [1 - \exp(-\beta E)/(1 - p)]^t, \tag{9}$$

where p is the equilibrium saturation of the bond, E is its strength, and $\beta = 1/kT$. It may be easily shown that the total energy, i.e. the sum over all bonds, has the same autocorrelations provided that the bonds are independent. This behaviour was observed in the simulations on the primitive model of water with hydrogen bonds modelled by square wells [11, 12].

For the sake of completeness we mention here a different mechanism leading also to the first order autoregressive process. If there exists an observable such that it is easy to sample the sub-space of the configuration space with this observable held fixed and difficult to generate a configuration with different value of this observable, the leading eigenvector E_1 will be close to this observable and sum (6) is again reduced to one term only. A grand-canonical ensemble serves as a typical example because creating and annihilating the particles is usually an extremely slow process (see section 3 of [7] for a detailed derivation). This need not hold true for the NPT simulation because volume fluctuations (if performed frequently enough) may efficiently push the volume to a value corresponding to a metastable equilibrium associated with a particular configuration.

3.2 Decay Caused by Density Fluctuations

The simple dynamic behaviour in the first two above cases was caused by a unique phenomenon related to one particle and its "local" properties. In dense liquids the displacements are short and a collective effect of all moving particles is essential. Macroscopically it may be viewed as creation and annihilation of local density fluctuations. Although the moves of two neighbouring particles are strongly correlated, these correlations rapidly decay with increasing distance. An extremely simple model of such a situation may be that of point-wise "molecules" (ideal gas) simulated by short displacements. All particles are independent in this model and the time development of the position of each particle is described by the Brownian dynamics. In [6] we studied a pressure-like quantity in periodic boundary conditions and determined the slowest mode of the decay of autocorrelations, i.e. the highest eigenvalue in (6). In this paper we generalize this result and estimate not only several highest eigenvalues λ_i, $i = 1, 2, \ldots$, but also the amplitudes $\langle QE_i\rangle^2/\mathrm{Var}\ Q$.

Let us consider first the cubic periodic simulation box with the edge of length b. The Green function of one Brownian particle with the initial position $\mathbf{r}$ and the final position $\mathbf{r}'$ at time t is conveniently expressed in the Fourier form as [6]:

$$G_t(\mathbf{r}', \mathbf{r}) = b^{-3} \sum_{\mathbf{k} \in \mathbb{Z}^3} \exp[2\pi i b^{-1} \mathbf{k}(\mathbf{r}' - \mathbf{r})] \exp[-(2\pi \mathbf{k}/b)^2 Dt], \tag{10}$$

where D is the autodiffusion coefficient. The autocorrelation coefficient of a pair-wise quantity Q (7) at lag t is then

$$c_t = \frac{\langle\langle \sum_{i<j} q(\mathbf{r}_i - \mathbf{r}_j) \sum_{i'<j'} q(\mathbf{r}'_{i'} - \mathbf{r}'_{j'}) \prod_{h=1}^{N} G_t(\mathbf{r}'_h, \mathbf{r}_h)\rangle'\rangle - \langle Q\rangle^2}{\langle Q^2\rangle - \langle Q\rangle^2}, \tag{11}$$

where $\langle\cdot\rangle$ denotes the configuration integral over all $d\mathbf{r}_h$ and $\langle\cdot\rangle'$ over $d\mathbf{r}'_h$. Inserting the Fourier transform,

$$q(\mathbf{r}) = \sum_{\mathbf{k}\in\mathbb{Z}^3} q_{\mathbf{k}} \exp[2\pi i b^{-1}\mathbf{k}\mathbf{r}], \tag{12}$$

into (11), we get

$$c_t = \sum_{\mathbf{k}\in\mathbb{Z}^3,\mathbf{k}\neq 0} q_{\mathbf{k}}^2 \exp[-8\pi^2 b^{-2} D\mathbf{k}^2 t] / \sum_{\mathbf{k}\in\mathbb{Z}^3,\mathbf{k}\neq 0} q_{\mathbf{k}}^2. \tag{13}$$

Typical functions $q(\mathbf{r})$ (the intermolecular potential to compute internal energy, the virial to compute pressure) attain high values for $\mathbf{r} \approx 0$ but approach zero for large $\mathbf{r}$. Consequently, they may be, within the scales larger than the dimension of the molecules (for low wave numbers $\mathbf{k}$), approximated by the δ-function and hence all the amplitudes $q_{\mathbf{k}}$ are approximately of the same magnitude, say unity. Both this approximation and the ideal gas approximation cease to hold for higher $\mathbf{k}$ (wave length less than the molecule diameter); note that otherwise the sum in the denominator of (13) would diverge. Hence,

$$\begin{aligned} q_{\mathbf{k}} &\approx 1, \quad |\mathbf{k}| < b/\sigma \\ &\quad\ 0, \quad |\mathbf{k}| > b/\sigma \end{aligned} \tag{14}$$

where σ denotes a typical dimension of a molecule. Since the number of vectors $\mathbf{k}$ with the lengths in the range $\langle k, k+1\rangle$ is in a three-dimensional (3D) space proportional to k^2, it holds

$$c_t \approx \sum_{k=1}^{b/\sigma} k^2 \exp[-8\pi^2 D b^{-2} k^2 t] / \sum_{k=1}^{b/\sigma} k^2. \tag{15}$$

If $b \gg \sigma$ (the system is sufficiently large) and $8\pi^2 D b^{-2} t \ll 1$ (lag is not too long), sums in (15) may be replaced by integrals yielding

$$c_t \approx 3 \int_0^1 \exp[-8\pi^2 D\sigma^{-2} x^2 t] x^2 dx. \tag{16}$$

This expression gives a slow decay of autocorrelations

$$c_t \sim t^{-3/2} \tag{17}$$

for $t \to \infty$. There is, however, a confusion in this statement: For t long enough sums (15) cannot be replaced by integrals and the leading decay in c_t will still be exponential. Since $b \gg \sigma$, not only $c_t \ll 1$ for such long t, but also the sum of both the correct and the approximate c_t over all long t up to infinity (note that the sum of approximate c_t is convergent) is negligible and the value of the correlation length (5) will not be affected. Consequently, from the practical point of view the decay of autocorrelations for large 3D periodic systems is effectively algebraic with the exponent of $-3/2$.

Autocorrelation behaviour (16) is in a microscopic description obtained as a collective effect of diffusing particles. Macroscopically it may be interpreted as crea-

tion and annihilation of local density fluctuations. The autocorrelation behaviour of simulations on real fluids may differ from the above picture in several respects:

(a) It may be combined with another slow process (e.g. structural changes in dense liquids, especially of highly nonspherical particles).

(b) Particles in a dense liquid do not move independently. The effective (long lag) autodiffusion coefficient will be lower than that obtained in one Monte Carlo step (determined by the length and acceptance ratio of a move). On the other hand, information on local density (pressure) fluctuations propagate faster in the dense fluid which may diminish the correlation length.

(c) The cutoff approximation (14) is only qualitatively correct. Main differences are expected in the vicinity of the upper bound of integral (16).

The effective algebraic decay of autocorrelations (17) results from a superposition of exponential terms whose amplitiude rapidly decreases with increasing lag. This holds true for observables with comparable Fourier coefficients (to a certain wave number). If a particular quantity, as e.g. the Fourier component of the radial distribution function (the structure factor) of a low wave number, is measured then long lag autocorrelations will be more important and results will possess large errors.

It is worth noting that the error, determined by Equations (16), (5) and (4), does not depend on the box length. If the computer time to perform a single (one-particle) MC step does not depend on the number of particles N (in practice it is attainable e.g. for constant-cutoff or short-range potentials and algorithms using a neighbour list), the time of one sweep will be proportional to N. If Q is reduced by the number of particles (e.g. virial pressure or radial distribution function), variance Var Q is proportional to $1/N$ and an encouraging result is obtained, namely that the error does not depend on the number of particles.

On the contrary, the situation changes if one considers a fluid system in less than 3 dimensions, or an inhomogeneous system in which the boundary conditions or the quantity to measure break the 3D isotropy: for instance a periodic 2D system of planar molecules or a slit pore where the wall-wall density profile is a 1D quantity. Many important quantities are again close to a δ-function, e.g. density profiles or the pressure exerted on a wall of a slit pore (the wall-molecule forces are used to compute it). An approximation similar to (16) can be then analogously obtained with the long lag limit of $c_t \sim t^{-\dim/2}$. Sum (5) for this approximation, however, does not converge if dim ≤ 2 and thus the long lag autocorrelation behaviour will be described by the leading exponential term rather than the algebraic approximation. From the practical point of view it means that in these cases the errors grow with the volume (number of particles) of the system and the accuracy of the results for large systems deteriorates.

3.3 Critical Behaviour

The correlations of density and other local properties in growing scales of distances are typical for the critical point. If a MC method produces only a local change in one step (displacement of one molecule, one spin flip), the time autocorrelations will increase as well. It is convenient to describe this critical slowing-down by the so called dynamic critical exponent z which is defined via the asymptotic relation [13]

$$\tau_1(b)/\tau_1(b') = (b/b')^z \tag{18}$$

for large typical distances b and b' (e.g. box lengths of two systems with periodic boundary conditions). $\tau_1 = -1/\ln \lambda_1$ here denotes the largest correlation length of the stochastic operator.

There is a common consensus that the static critical behaviour of fluids is well described by the lattice gas (at most one particle may occupy a vertex of a lattice and the particles occupying the neighbouring vertices attract each other) which is equivalent to the Ising ferromagnet [14]. A common simulation procedure of the lattice system is then equivalent to the grand-canonical ensemble simulation of the fluid. Note that the critical fluid is dilute enough so that the common grand-canonical simulation may work efficiently, i.e. with a reasonable probability of insertions and deletions of molecules; in addition, displacements and rotations are not necessary although they may improve the efficiency. The dynamic critical exponent for the Ising system on a simple cubic lattice was determined to be $z = 1.99 \pm 0.03$ [13]. As regards an NVT ensemble simulation, we analogously assume that the trial displacement places a molecule into a random position in the system and one MC step is thus equivalent to two opposite attempted spin-flips for the Ising system.

In assessing the influence of the critical slowing-down for fluids on the expected errors one should take into account that:

(1) The number of particles to be moved in one sweep grows as $\sim b^3$ and the computer time increases at least at the same rate (in other words, $z \geq 5$ if the time is measured in single MC steps).
(2) The error depends on the variance of the quantity of interest and its critical behaviour.
(3) The correlation length, Equation (5), and thus the error depend also on fast correlations while the exponent z is defined by the slowest one. As follows from (6), the crucial question is what are the coordinates of the quantity in the basis defined by the critical stochastic operator. In investigating the Ising ferromagnet the magnetization is used as a natural quantity distinguishing the phases; since its global inversion is the slowest process in the one-flip MC, the magnetization is close to eigenvector E_1 (*cf.* the end of sub-section 3.1). The analogous quantity for the grand-canonical (μVT) and probably also for isobaric (NPT) ensembles is density.

Density is constant in the NVT ensemble so that the slowest mode of the μVT ensemble is not present here. Further, there is a close analogy with the Brownian dynamics studied in sub-section 3.2: In both cases the correlation length grows with the square of a typical distance, although the mechanisms are totally different. From the Brownian dynamics we obtained that the errors of pair-wise quantities did not depend on the system size. That is why it may be expected that the decay of autocorrelations of pair-wise quantities for fluids in the periodic boundary conditions in the critical region will be again far from the exponential decay and also that the effective dynamic critical exponent for the NVT simulation will decrease.

Both the critical phenomena and short displacements (see sub-section 3.2) slow down the convergence because in both cases it is necessary to sample the density fluctuations on various scales of distances. We are afraid that the combination of both, a critical fluid simulated by short displacement, might be especially inefficient. We thus strongly recommend that long displacements (into a random place in the fluid) be used, or even omitted in the case of a grand-canonical ensemble.

4. SIMULATION RESULTS

Several fluid systems were simulated to test the above theoretical conclusions. A simple (although biased [5]) estimator

$$\mathrm{Cov}(Q_i,Q_{i-t}) = \mathscr{E}(Q_iQ_{i-t}) - \mathscr{E}(Q_i)\mathscr{E}(Q_{i-t}), \tag{19}$$

where $\mathscr{E} \equiv (n-t)^{-1}\sum_{i=t+1}^{n}$, was used to compute covariances, and $c_t = \mathrm{Cov}(Q_i,Q_{i-t})/\mathrm{Cov}(Q_i,Q_i)$. Typical number of independent measurements, $n/(1+2\tau)$, was around several hundred which means that the expected error of the first several autocorrelation coefficients is several per cent; the results for longer lags are thus unreliable. Certain information about the errors of the autocorrelation coefficients may be obtained by their fluctuations and by violation of a monotonous decrease predicted by (6).

The first system studied was the homogeneous Lennard-Jones fluid contained in a periodic cubic simulation cell. Reduced units were used to measure both the energy and distance. The intermolecular pair potential then reads as

$$u(r) = 4(r^{-12} - r^{-6}). \tag{20}$$

The potential was cut off at $r = 4$ and shifted to be continuous for all atom–atom separations r. The probability distribution of trial moves was uniform in a sphere of radius r_d with excluded concentric sphere of radius $r_d/2$, *cf.* [6]. The value of r_d was set so that the acceptance ratio was about $0.2 \div 0.25$. The presented results are a fraction of a more extensive project aiming at an accurate equation of state of Lennard–Jonesium which will be published elsewhere [15].

The series of the autocorrelation coefficients of the virial pressure for the first five systems defined in Table 1 are drawn in Figure 1 along with the theoretical curves. It is seen that the simple exponential decay computed from the acceptance ratio, Equation (8), gives a good description of the autocorrelations only for the dilute and high temperature system *a*. It is, however, quite inadequate for denser systems: the autocorrelation coefficients are many times greater than those given by (8) telling us that more complex processes take place. An alternative description, Equation (16), seems to be more successful in the case of dense liquids (far from the critical point) although it requires an *a posteriori* determination of one vaguely defined parameter, namely a typical size of a molecule σ. Its value obtained by examining Figure 1 lies around 0.5; it is greater for more dilute fluid and smaller for denser fluid in accord with intuitive expectations.

Table 1 Parameters of simulations on the Lennard-Jones fluid. The number of particles is 512 and the cutoff of the potential is 4; reduced units are used. T denotes temperature, ρ density, r_d maximum displacement length, a acceptance ratio, D autodiffusion coefficient, and n number of sweeps

System	T	ρ	r_d	a	$D \times 10^3$	$n/1000$
a	4.85	0.4	1.303	0.204	31.8	1.4
b	4.85	0.6	0.569	0.233	5.36	4.1
c	4.85	1.0	0.240	0.232	0.660	4.9
d	0.81	0.95	0.146	0.243	0.209	14.6
e	0.81	0.801	0.198	0.252	0.472	10.9
f	0.81	0.8645	0.168	0.262	0.328	9.6
g	0.81	0.8645	0.168	0.262	0.328	44.0 (a)

[a] $N = 118$, cutoff = 2.55.

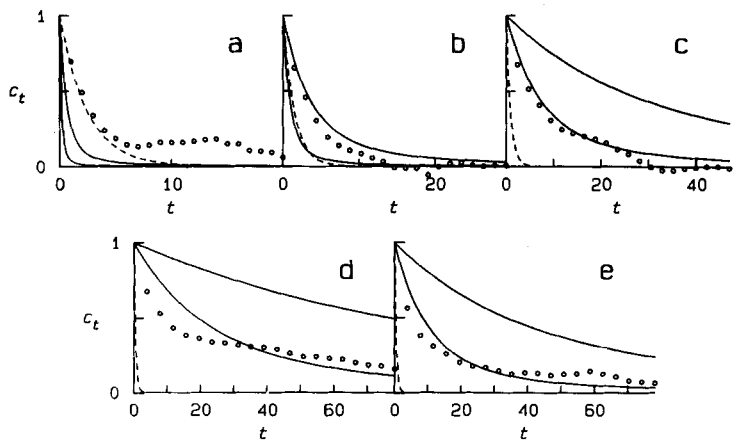

Figure 1 The time correlation functions of the virial pressure for MC simulations on the Lennard-Jones fluid in periodic boundary conditions at different state points and the same numbers of particles. o: MC; – – –: Equation (8); ——: Equation (16) with $\sigma = 1$ (upper curve) and $\sigma = 0.5$ (lower curve). See Table 1 for the definition of the systems.

The series of autocorrelation coefficients of the virial presure for two equivalent systems which differ in the number of particles and the potential cut-off only are compared in Figure 2. The curves are, within statistical errors, similar which is in agreement with the theoretical prediction that the error does not depend on the size of the system. In the molecular dynamics (MD) calculation which is included for a comparison we have used 256 atoms in a periodic box. Instead of cutting off, the potential was modified in the region $r \in (3, 3.332)$ so that the force was continuous. A fifth-order predictor-corrector method was used to integrate the Newton equations. All forces were computed twice (once for a predictor and once for a corrector) within one step of length 0.006 in reduced time units (defined so that a mass of the atom is unity). The t-axis of the graph was scaled so that the same number of pair interactions was computed in all cases though it is slightly more expensive to compute forces in

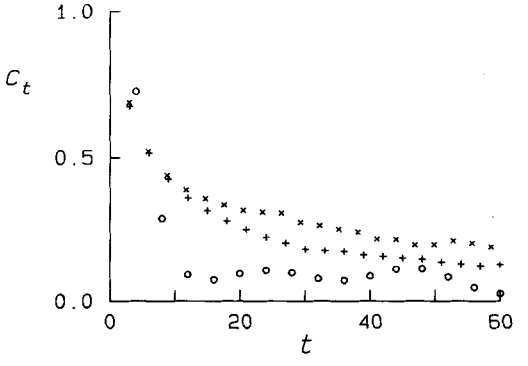

Figure 2 The time correlation functions of the virial pressure for MC and MD simulations on the Lennard-Jones fluid in periodic boundary conditions for $\rho = 0.8645$ and $T = 0.81$. x: MC, 512 atoms (system f); +: MC, 118 atoms (system g); o: MD, 256 atoms.

MD than energies in MC. (Direct comparison of computer times was impossible because we used different computers and programming languages). The MD seems to be more efficient than MC, and further efficiency might be gained by a more sophisticated integration method. Nonetheless, an accurate comparison should contain a detailed study of long-lag correlations caused probably also by the density fluctuations and oscillations (the sound).

The autodiffusion coefficient entering formula (16) was measured over 23.4 sweeps. Since this value is comparable with the correlation lengths in the system, lower long-lag autodiffusion coefficients are expected. On the other hand, we detected considerable higher values for shorter lags which causes the short-lag terms in (15) more pronounced. Faster decrease of c_t for smaller t than predicted by (16) is then observed.

The second system studied was a slit-pore with the wall-wall separation $b = 10$ (system A) and $b = 7$ (system B) along z-axis and periodic boundary conditions along x- and y-axes with period 6, and containing 256 (A) and 169 (B) Lennard–Jones atoms, respectively. The potential was cut off at the atom–atom serparation $r = 3$. 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 1/4 and 3/4 per square unit on the respective walls. The reduced temperature was 2 and the effective bulk densities, computed from the z-density profile in the central region of the pore, were approximately 0.804 (A) and 0.811 (B).

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

$$\mu_k = \sum_{i=1}^{N} z_i^k, \tag{21}$$

$k = 1, 2$, where z_i is the z-coordinate of particle number i measured from the centre of the pore. (More exactly, z_i should be measured from the centre of mass which is not, for our asymmetric pore, in its geometrical centre.) 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 practical 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 theory (see sub-section 3.2) gives for the autocorrelations of mode k the following formula

$$c_t = \exp[-2\pi^2 b^{-2} D k^2 t], \tag{22}$$

where b is the thickness of the pore. The autodiffusion needed in (22) was measured along the x- and y-axes over 32 sweeps. Two pairs of values were used for the thickness; either the defined values 10 and 7 which, however, ignore the fact that no particle can approach the wall due to the repulsive forces, or the effective values $b = 8.84$ (A) and $b = 5.79$ (B) corresponding to the effective bulk densities.

Both the experimental and the theoretical results are collected in Figure 3. It is seen that the autocorrelation behaviour for the moments of the density profile is in a good agreement with the theoretical predictions, especially when the effective pore widths are used. The dynamic behaviour of pressure which contains both the short- and

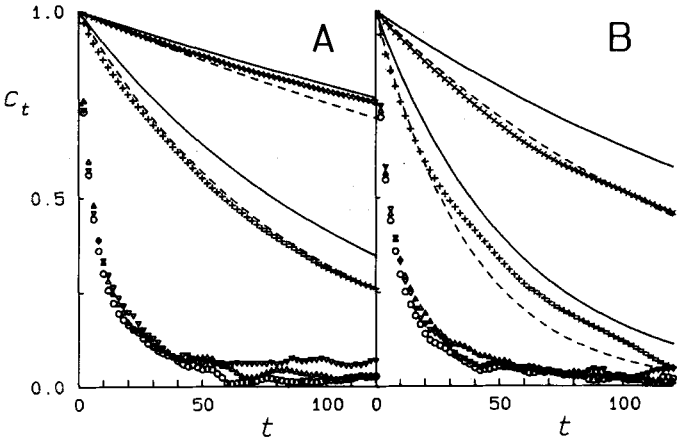

Figure 3 The time correlation functions of different quantities for MC simulations on the Lennard-Jones fluid in an asymmetric slit-pore. △: pressure on wall 1; ▽: pressure on wall 2; ○: virial pressure; ×: first central moment (centre of mass) of the wall-wall density profile; +: second moment; ——: Equation (22) for $k = 1$ (upper curve) and 2 (lower curve); – – –: Equation (22) with the effective pore width.

long-lag contributions well exemplifies a general problem of estimating errors: The long-lag correlations are still present in the system but they are hidden in a short-lag noise and thus may be easily overlooked and errors will be underestimated.

5. ERROR ESTIMATION FOR PERIODIC BOUNDARY CONDITIONS

The key problem when estimating the error of the measured quantity (4) is summing up the infinite series for the correlation length (5). Only several first autocorrelation coefficients are measurable during the simulation with reasonable accuracy. The extrapolation of the series of the autocorrelation coefficients based on the assumption that the decay is exponential for long lags [2, 3] leads to an underestimation of the errors, see Equation (6). It is especially serious for quantities such as pressure or energy for 3D systems with periodic boundary conditions where the long-lag decay is far from the exponential one. More reliable estimate can be obtained by considering the correct long-lag behaviour, Equations (16) or (17).

If mT is chosen so that c_{mT} is accurate enough, if approximation (17) is valid, and if the sum of the autocorrelation coefficient from mT by m to infinity may be replaced by an integral, it holds

$$1 + 2\tau = 1 + 2\sum_{t=1}^{T-1} c_{mt} + (4T + 1)c_{mT} \tag{23}$$

The error is then given by (4).

6. MEASUREMENT OPTIMIZATION

The choice of the frequency of measurements m (number of MC steps between two

measurements) influences the efficiency of the simulation: If m is too low, many data are obtained but these data are so correlated that no new information is obtained and the computer time is wasted. If, on the other hand, m is too long, data are independent but their number is insufficient for obtaining a good statistics. Hence there should be an optimum frequency of measurements m_{opt}.

In [6] m_{opt} was found under the assumption that the measured series of data forms the first order autoregressive process, i.e. that it holds $c_t = c_1^t$. In sub-section 3.2 we showed that the dynamic behaviour for the 3D periodic boundary conditions differs significantly from the first order autoregressive process. Here we generalize the theory to the case when the autocorrelation coefficients may be written in a form

$$c_t = \varphi(At), \tag{24}$$

where an unkown parameter A defines time scaling and φ is a known function ($\varphi(t) = \exp(-t)$ for the first order autoregressive process, $\varphi(t) \approx 3\int_0^1 \exp(-tx^2)x^2dx$ for 3D periodic boundary conditions (16)). The value of A can be computed from one known autocorrelation coefficient, $A = \varphi^{-1}(c_t)/t$.

Let T_s and T_m be computer times required to perform one sweep and one measurement, respectively. Then the error to be minimized is

$$\varepsilon = \left(\text{Var } Q(1 + 2\tau)\frac{mT_s + T_m}{\text{total time}}\right)^{1/2} \tag{25}$$

and $m_{opt} = x_{opt}/A$; x_{opt} solves the equation

$$\tau(x) + [x + r]\tau'(x) + \frac{1}{2} = 0, \tag{26}$$

where

$$\tau(x) = \sum_{t=1}^{\infty} \varphi(xt), \tag{27}$$

$\tau'(x)$ is the derivative, and $r = AT_m/T_s$.

Particularly, for 3D periodic boundary conditions and approximation (16) it holds with the accuracy better than 1 per cent:

$$\varphi^{-1}(x) = \left(\frac{1.32934 + 7.6193x - 6x^2}{x + 2.71x^2 + 1.25x^3}\right)^{2/3} - 0.707 \tag{28}$$

and

$$x_{opt} = \left[\left(\frac{261.9}{13.375 + r} + 10.418\right)r\right]^{0.4-1/(15+1.07r)} \tag{29}$$

7. CONCLUSIONS

The dynamic (convergence) behaviour of observables measured in the course of MC simulations contains generally both the slow (long-lag) correlations and the fast (short-lag) ones. Although for some systems the sequence of measured data forms the first order autoregressive process which simplifies an interpretation of the data and estimation of errors, the situation for many important systems is not so simple. The

slow correlations correspond (for not extremely structured liquids) to a development of density or concentration fluctuations in the bulk fluid while the fast ones to local changes in liquid structure. This phenomenon causes problems in a reliable estimation of the statistical errors because the slow correlations are hardly detectable in the noise of the fast ones, especially if the latter occur with large amplitudes; the slow correlations may, however, significantly contribute to the total error. Any information on the behaviour of the slow correlations may thus help us to obtain more reliable error estimates. For example, we have shown that the time decay of autocorrelation coefficients for common simulations in three dimensions with periodic boundary conditions satisfies the power-law with exponent $-3/2$.

The obeservation that the main source of the errors is often caused by inefficient sampling of the local density fluctuations (concentration fluctuations in the case of mixture), i.e. slow autodiffusion, has led us to recommend long trial displacements (low acceptance ratios) [6]. A MC step which would sample directly the slow processes – a collective move in the case of a pure fluid or swapping the molecules of different species for a mixture – might thus increase the efficiency of fluid simulations. This problem will be dealt with in a subsequent paper.

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