

Simulation of Sub-molecular and Supra-molecular Fluids

D. Frenkel

F.O.M. Institute for Atomic and Molecular Physics, P.O. Box 41883,
1009 DB Amsterdam, The Netherlands

Abstract

In this lecture, I discuss two 'hard' problems in the numerical simulation of many-body systems. The first is the quantitative study of the slow (algebraic) decay of tagged-particle correlation functions in simple fluids. The second is the numerical study of phase equilibria in polymer systems.

Using conventional simulation techniques, many aspects of these problems cannot be studied with existing (super)computers. However, if we consider 'lattice-gas' versions of the same problems, then it turns out that a speed-up of 6-10 orders of magnitude can be achieved using a very simple algorithm. As a result, we can now test theoretical (mode-coupling) predictions for long-time tails with unprecedented accuracy. Similarly, certain phenomena in polymer physics, such as the polymer-induced clustering of colloids, that did thus far defy simulation, can now be observed and studied numerically.

1 Introduction

The algorithms that we use in Monte Carlo and Molecular Dynamics simulations have not changed fundamentally since they were first introduced in the fifties and early sixties [1]. This fact clearly illustrates something that hardly needs illustrating, namely that the 'founding fathers' of computer simulation were exceptional scientists. At the same time, this observation is a bit depressing. Even after 35 years of rapid growth in the number of applications of computer simulation to problems in physics and chemistry, the main increase in computing speed is still simply due to the increased

speed of computers. In other words: there are no short-cuts in the simulation of atomic and molecular fluids. The number of floating-point operations in a typical simulation may be somewhat larger than strictly necessary, but not by orders of magnitude.

This is indeed depressing news, because even with today's supercomputers, there are numerous properties of atomic or (macro)-molecular systems that defy numerical simulation. In this lecture I shall focus on two examples. The first example has to do with the numerical study of the velocity autocorrelation-function of a tagged particle in a fluid. The second concerns the properties of a mixture of colloidal particles and polymer molecules. At first sight, these two problems appear totally unrelated. However, I hope to show that there is an intimate connection between them. Before doing so, let us first consider the individual problems.

1.1 Long-time tails

In the history of the kinetic theory of fluids, 1969-1970 was a crucial year. In that year Alder and Wainwright [2] published a paper in which they demonstrated the breakdown of the 'Molecular Chaos' assumption. The Molecular Chaos assumption, originally introduced by Boltzmann as the 'Stoßzahlansatz', states that the collisions experienced by a molecule in a fluid are uncorrelated. One consequence of this assumption is that the velocity autocorrelation function (VACF) of a tagged particle in fluid should decay exponentially. What Alder and Wainwright found is that the VACF of a particle in a moderately dense fluid of hard spheres or hard disks does not decay exponentially but algebraically. These algebraic long-time tails are the consequence of coupling between particle diffusion and shear modes in the fluid.

The Alder-Wainwright simulations caused a complete overhaul of the kinetic theory of dense fluids. The subsequent theoretical analyses of algebraic long-time tails were either based on an extension of kinetic theory [3] or on mode-coupling theory [4]. For a review, see ref. [5]. In the mode-coupling theory by Ernst, Hauge and van Leeuwen [4], it is assumed that the long-time tail is the consequence of coupling between particle diffusion and shear modes in the fluid. To a first approximation the leading term in the long-time tail of the velocity ACF is given by:

$$\langle v_x(0)v_x(t) \rangle \approx \frac{D-1}{D} \frac{1}{\rho(4\pi(D_0 + \nu_0)t)^{D/2}} \equiv \frac{d_0}{t^{D/2}}, \quad (1)$$

where ρ is the number density, D_0 the ‘bare’ self-diffusion constant, ν_0 the kinematic viscosity and D the dimensionality. These ‘bare’ transport coefficients are obtained by computing the diffusion constant and the kinematic viscosity using Boltzmann’s molecular chaos assumption, i.e. ignoring any contribution of the long-time tails themselves. In a self-consistent mode-coupling theory, the transport coefficients that enter into the expression for the long-time tails are computed using information about the long-time tails themselves. I shall return to this point below.

Following this theoretical work, simulations were performed by Levesque and Ashurst [6] and, most extensively, by Erpenbeck and Wood [7, 8] with the aim to verify the validity of eqn. 1. For three-dimensional fluids these simulations are extremely expensive because very long simulations on very large systems must be performed. Even so, the system sizes studied in the simulations of Erpenbeck and Wood were such that it was essential to apply finite-size corrections to the corresponding mode-coupling theory before a meaningful comparison with the simulations could be made. Following such an approach, Erpenbeck and Wood found agreement between their simulation results for the VACF and a finite-size mode-coupling theory for a number of different densities. Nevertheless the statistical accuracy of their data was such that it was not meaningful to verify either the value of the exponent of the algebraic tail or the functional form of the density-dependent tail coefficient independently.

In the case of two-dimensional fluids there is another problem. Ever since the discovery of hydrodynamic tails, it has been realized that a consistent description of mode-coupling effects in a two-dimensional fluid would result in a long-time tail that decays faster than t^{-1} , because in $2D$ the self-diffusion constant D diverges. Moreover, the viscosity, which is proportional to the integral of the stress auto-correlation function, is also expected to diverge. Alder and collaborators resolved this difficulty by introducing time-dependent transport coefficients [9]. In this way, the hydrodynamic description could be made self-consistent. This self-consistent mode-coupling theory predicts that the decay of the VACF is slightly faster than t^{-1} , namely

$$\langle v_x(0)v_x(t) \rangle \sim \frac{1}{t\sqrt{\ln t}}. \quad (2)$$

Unfortunately, this correction to the t^{-1} -decay was too weak to be observed in Alder's simulations or, for that matter, in any subsequent simulation of hard disks.

Of course, one may argue that long-time tails themselves are almost impossible to detect experimentally and that this holds *a fortiori* for small corrections to these tails in two-dimensional fluids. However, the concepts that underly the self-consistent mode-coupling picture are used in many branches of physics. In that context, a direct test of this proto-typical self-consistent mode-coupling effect is of considerable importance.

In summary: the direct observation by 'conventional' computer simulation of corrections to the t^{-1} decay of the velocity ACF in a two-dimensional fluid is a problem that requires much more computing power than is presently available. Below, we shall see that with 'non-conventional' simulation techniques, the effect can, in fact, be observed.

1.2 Polymers

Let us next consider a second difficult problem in computer simulation, namely the direct simulation of phase equilibria involving polymers. Polymers are molecules with many internal degrees of freedom. The entropy associated with these degrees of freedom becomes increasingly important as the molecules grow more complex. In the limit of a long polymer chain one may even, to a first approximation, ignore the excluded volume effects, but never the conformational entropy.

This feature of complex molecules is, of course, well known and it poses a formidable challenge to computer simulators: it is essential that a numerical study of long chain molecules probes a representative sample of all accessible molecular conformations and positions. Much attention has therefore been paid to the development of efficient numerical schemes to sample polymer conformations. The recent review by Kremer and Binder [10] gives excellent account of Monte Carlo schemes to study lattice models of macromolecules. Most of the Monte Carlo techniques to sample chain con-

formations described in that review are based on some kind of *local* rule to rotate, change or break-and-remake bonds between polymer units. Although the existing techniques are quite sophisticated, the local nature of the algorithm results in slow *global* equilibration. Global equilibration may require large scale conformational changes of the molecules and, in the case of mixtures, appreciable changes in the local composition of the mixture. Such numerical problems are not limited to Monte Carlo simulations. In fact, although Molecular Dynamics simulations [11] have the advantage that they allow the molecules to perform collective motions in a natural fashion, the time scale for such diffusive motion is still very long.

Even more problematic than the simulation of equilibrium properties of polymer systems, is the computation of the chemical potential of chain molecules. The chemical potential is a quantity that is of central interest in the study of phase equilibria. In computer simulations of simple atomic or molecular systems, the chemical potential is often evaluated using the particle-insertion method first described by Widom [12]. This method exploits the relation between the excess chemical potential μ^{ex} (i.e. the chemical potential of a species minus the chemical potential of an ideal gas at the same density) and the change in the potential energy of the system ΔV_{test} , due to the insertion of a test particle at a random position in the fluid:

$$\mu^{ex} = -k_B T \ln \langle \exp(-\Delta V_{test}/k_B T) \rangle . \quad (3)$$

The angular brackets in eq. 3 denote an ensemble average over all possible configurations of the molecules already present in the system. In Monte Carlo simulations this average has a very simple interpretation: it can be thought of as the probability of acceptance of a (virtual) Monte Carlo move which consist of the random addition of a test particle to the system of interest.

Whether or not eqn. 3 can be used in practice depends on the value of this insertion probability. If the latter is very low, the statistical accuracy is low, and long runs are needed to obtain a reliable estimate of μ^{ex} . This limitation of the method is particularly relevant for polymer simulations where a naive application of the

particle-insertion method would result in extremely low insertion probabilities.

Clearly, the numerical study of the chemical potential of polymers is difficult. But even more difficult is the direct simulation of phase equilibria involving polymers. In this case, the number of chain molecules fluctuates, while the chemical potential (i.e. the osmotic pressure) is held constant. An example of considerable practical interest is a mixture of colloidal particles and (ideal) polymers. In this system, the polymers cause an 'entropic' attraction between the colloidal particles. Direct numerical simulation of this 'polymer-induced' clustering would be so time-consuming as to be almost prohibitive.

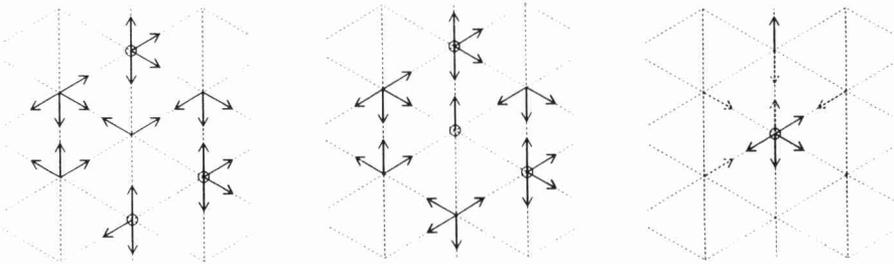
2 Towards the impossible

Having thus introduced two difficult, and apparently unrelated, problems in computational physics, I shall next show how progress can be made on both fronts using essentially the same technique. In order to do so, we first simplify both problems by discretizing space and, in the case of the long-time tails, time. For the polymer system this discretization is achieved by considering polymers as random walks on a lattice. This simplification is very popular in numerical work on polymers because it simplifies calculations appreciable while maintaining an essential feature of the problem, namely the very large number of possible conformations. Initially, we shall only consider non-self-avoiding polymers. However, I shall indicate to what extent the present approach can be (and has been) generalized to self-avoiding polymers. The problem of transport in an atomic fluid can also be cast in a space-time discretized form if we use Lattice Gas Cellular Automata (LGCA's) to model a simple fluid.

In LGCA's, the 'atoms' are constrained to move along the bonds joining the lattice sites. No two particles can move along the same bond in the same direction. The state of the lattice is completely specified by indicating which links are occupied and which are empty. This implies that lattice-gas particles are indistinguishable.

The time evolution of the system is governed by the following rules (see figure 1):

1. Propagation: all particles move in one time step (for convenience we choose $\Delta t = 1$) from their initial lattice position (say \mathbf{X}) to a new position ($\mathbf{X}' = \mathbf{X} + \mathbf{c}_\alpha$; where \mathbf{c}_α is the velocity of species α). The velocities \mathbf{c}_α are such that at the end of the propagation steps all particles are once more positioned at lattice sites.
2. Collision: the particles at all sites on the lattice undergo a collision that conserves the total number of particles and the total momentum at each site. These local collision rules may, or may not, be deterministic.



1. Illustration of the time-evolution of a two-dimensional lattice-gas cellular automaton on a triangular lattice. The model depicted here is known in the literature under the name FHP-III [13]. The arrows denote particles moving with speed 1 along the bonds linking neighboring lattice sites. The circles denote particles with speed 0. Left: typical initial configuration, just before a collision. Middle: at all lattice sites, particles collide in such a way that the number of particles and the momentum is conserved locally. Right: after the collision, the moving particles propagate to the neighboring lattice sites. This figure shows the new state of the central site. The dashed arrows show the previous positions of the particles that end up at this site.

Provided that the lattice has a sufficiently high symmetry (e.g. triangular in 2 dimensions) and the collision rules are sufficiently isotropic (for a discussion, see [14]), it can be shown that the equation that governs the time evolution of the ‘flow field’ of such a lattice gas becomes equivalent to the Navier-Stokes equation for an incompressible fluid in the limit that the flow velocity is much less than the particle velocity, and all spatial variations in the system occur on a scale that is large compared to the mean free path of the lattice gas particles. In this respect LGCA’s model atomic fluids. In particular, we should expect to observe long-time ‘hydrodynamic’ tails in the velocity ACF of a tagged particle in a lattice gas.

2.1 Moment propagation

What is it that makes both the calculation of long-time tails and the simulation of polymer equilibria difficult? In the case of the long-time tails, we must sample a particular quantity (the product of the tagged-particle velocity at two different times) over many trajectories. In the polymer problem, we must count the number of allowed polymer conformations in the presence of other particles and, possibly, an external potential. However, in a conventional simulation we generate much more information than we need. For instance, in the polymer case, a Monte Carlo simulation will not only count the *number* of allowed conformations, but also their precise shape. Similarly, a Molecular Dynamics simulation will provide information about the complete history of all particles in the system, not just about one particular time-correlation function. Below, I shall indicate that it is possible to gain many orders of magnitude in computing speed, if we are willing the sacrifice such detailed, but usually irrelevant, information. This method was originally developed for the study of tagged-particle velocity-autocorrelation functions in lattice gases [15, 16, 17]. The ‘moment-propagation’ method allows us to compute certain averages of the n -body distribution function directly, without attempting to compute the function itself. This approach results in a very appreciable gain in computing speed: for instance, in the case of velocity autocorrelation functions in lattice gases, the method has resulted in a speed-up that varied between 10^6 and 10^{10} [15, 16]. Rather than explain how the moment propagation method works for lattice gases, I shall discuss its application

to polymers, as this is simpler. To this end, let us consider a specific example of some practical interest, namely a system of *ideal*, non-interacting polymers in the external potential provided by a dispersion of 'hard-sphere' colloidal particles.

As explained above, we assume that the ideal polymer conformations correspond to random walks on a lattice. Suppose that every lattice site has b neighbors, that the polymer consists of p segments and that there are N lattice sites. Clearly, for an ideal polymer in the absence of any obstacles, the total number of allowed conformations is $\Omega_{id} \equiv N \times b^p$. If obstacles are present, some random walks are blocked, and the total number of allowed conformations, Ω_T , is less than Ω_{id} . The 'brute-force' method to determine the ratio Ω_T/Ω_{id} would be to attempt a large number of insertions of chains with arbitrary conformation at random points on the lattice. The ratio of the number of 'accepted' trial moves to the total number of attempted insertions can be used to compute the excess chemical potential of an ideal polymer chain in this system:

$$\mu_{excess} = -k_B T \log \langle P_{acceptance} \rangle \quad (4)$$

This is the usual 'Widom' expression for the excess chemical potential [12]. However, unless the density of obstacles is quite low, the relative statistical error in the insertion probability will be quite large (see ref. [18]). Next, consider the 'moment-propagation' approach. To this end, let us first compute all N Boltzmann factors associated with the insertion of a point particle at any lattice site. Clearly, the sum of these Boltzmann factors is simply the partition function of a point-particle on a lattice, in an external potential. Let us denote the Boltzmann factor associated with site i as $f_i^{(0)} \equiv \exp(-u(\mathbf{r}_i)/k_B T)$. The partition function for a one-segment polymer (2 points) is computed as follows. Starting from site i , we have b ways to grow one segment. But all b directions will, in general, have different Boltzmann weights $f_j^{(0)}$, where j denotes one of the nearest neighbors of i . The total Boltzmann weight associated with the addition of a 1-segment polymer at site i is then:

$$f_i^{(1)} \equiv f_i^{(0)} \times \left(\sum_j^b f_j^{(0)} \right) \quad (5)$$

where the sum runs over the nearest neighbors of i . The partition function of a 1-segment polymer on a lattice is then simply:

$$Z_1 = \sum_{i=1}^N f_i^{(1)}, \quad (6)$$

(where, for convenience, I have assumed that the polymer 'head' and 'tail' are distinguishable). Repeating the same argument p times, it is clear that the Boltzmann factor associated with *all possible conformations* of a p -segment polymer starting at site i is given by:

$$f_i^{(p)} = f_i^{(0)} \times \left(\sum_j^b f_j^{(p-1)} \right). \quad (7)$$

And the total partition function is given by:

$$Z_p = \sum_{i=1}^N f_i^{(p)}. \quad (8)$$

The important fact to note is that the computation of Z_p , a quantity that depends on $N \times b^p$ conformations, requires only p iterations of $b \times N$ local 'propagations' of real numbers. For a fixed external potential, the partition function thus computed is *exact*. In a practical situation, as with the addition of polymer to a colloidal dispersion, the external potential is not fixed, but depends on the (continuous) coordinates of all M colloidal particles, $\{\mathbf{r}^M\}$. Hence, the total partition function of the polymer also depends on these coordinates: $Z_p = Z_p(\mathbf{r}^M)$.

The approach sketched above is not limited to completely random polymer conformations. In fact, it is simple to exclude 180° reversals or to account for the different weight of gauche and trans conformations [19]. In the latter case, instead of adding the random walks coming from all different directions to a given lattice site, we can separately store for every nearest-neighbour bond $i \rightarrow j$, the total number of walks that arrived at site i along bonds other than $j \rightarrow i$. With this bookkeeping device, it is easy to count all non-reversing random walks.

2.2 Self-avoiding polymers

In many applications, we do not only wish our polymer conformations to be non-reversing, but also self-avoiding. This latter condition cannot be implemented in a 'local' iterative algorithm based on eq. 7. Rather, the test for self-overlap has to be made after a particular non-self-avoiding polymer conformation has been selected. In practice, a large number of non-reversing random walks are sampled and the fraction of self avoiding walks (SAW's) is computed. Multiplying this fraction with the total number of non-reversing random walks, yields an estimate of the total number of SAW's.

In order to arrive at a correct sampling of the fraction of SAW's, we must generate a number of no-self-avoiding polymer conformations with the appropriate Boltzmann weight. This is easily achieved because we already know the total number of random walks of length $p, p-1, p-2, \dots, 1$ starting from any lattice site i , ($Z_p(i), Z_{p-1}(i), \dots, Z_1(i)$). We now use this information as follows. First we select the starting position i of a non-self-avoiding random walk of length p with a probability proportional to $Z_p(i)$. Next we consider all neighbours j of site i . The total number of NSAW's of length $p-1$ starting from site j is equal to $Z_{p-1}(j)$. We now continue our random walk from i to j with a probability proportional to $Z_{p-1}(j)$. Next we consider all NSAW's of length $p-2$ starting from any of the sites neighboring j , and so on.

It should be stressed that we can enumerate the total number of NSAW's exactly (and cheaply), but that sampling of SAW's is a 'biased' Monte Carlo process that can be more time-consuming.

2.3 Grand-canonical simulations

An interesting application of the moment-propagation scheme is that it allows us to perform simulations of a polymer system *at constant osmotic pressure*, Π . This corresponds to a very common experimental condition. To see how this can be achieved, let us consider the partition function of n ideal polymers of length p in an external field. Clearly,

$$Z_p^{(n)}(\mathbf{r}^M) = [Z_p^{(1)}(\mathbf{r}^M)]^n / n! , \quad (9)$$

where $Z^{(1)}$ ($z^{(n)}$) denotes the partition function for one (n) polymer(s). Now let us transform to an ensemble where the polymer chemical potential, μ , is held constant. To be specific, let us again consider the polymer colloid mixture. For convenience, we assume that the total number of colloid particles is held constant. The potential energy function that describes the direct interaction between the colloid particles is denoted by $U(\mathbf{r}^M)$. The partition function for this constant M, V, T, Π -ensemble is:

$$\Xi = \int d\mathbf{r}^M \exp(-U(\mathbf{r}^M)/k_B T) \sum_{n=0}^{\infty} \exp(n\mu/k_B T) [Z_p^{(1)}(\mathbf{r}^M)]^n / n! , \quad (10)$$

where we have omitted the constant prefactor. Clearly, the summation in equation 10 yields an exponential,

$$\exp(z Z_p^{(1)}(\mathbf{r}^M)) ,$$

where we have used the shorthand notation $\exp(\mu/k_B T) \equiv z$. Equation 10 is the starting point for Monte Carlo simulations at constant Π [20]. In such simulations, the relative probability of different colloid configurations is proportional to:

$$P(\mathbf{r}^M) = \exp[-U(\mathbf{r}^M)/k_B T + z Z_p^{(1)}(\mathbf{r}^M)] . \quad (11)$$

Note that $Z_p^{(1)}$, which describes the polymer-induced interaction between colloidal particles, can be calculated exactly for every colloid configuration. Of course, such constant- Π simulations are not limited to polymer colloid mixtures. Another interesting application is the simulation of polymer-induced forces between two surfaces. It is worth pointing out that in constant- Π simulations we have no direct knowledge of the actual polymer positions and conformations (although some averages can be computed easily). This demonstrates clearly that great gains in computational efficiency can be made by throwing away ‘irrelevant’ information.

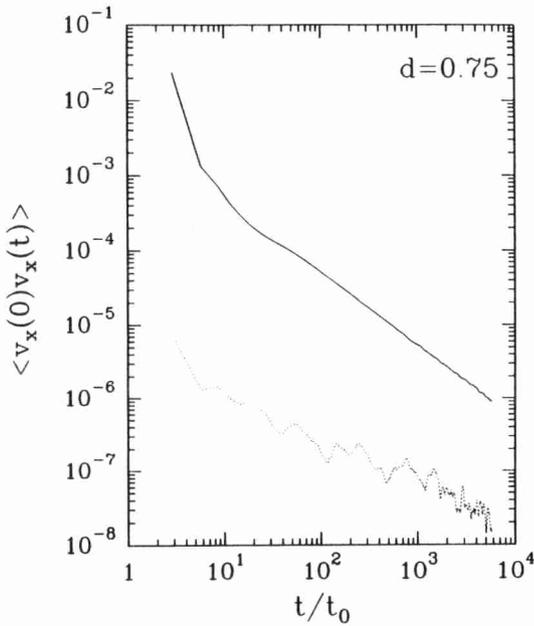
3 Results

In this section I show two examples that illustrate the power of the moment-propagation method. The first example concerns the ob-

ervation of self-consistent mode-coupling effects in hydrodynamic long-time tails. The second example shows results of a grand-canonical polymer+colloid simulation. In both cases, the examples are not meant to be anything more than an illustration. For a detailed discussion, the reader is referred to the relevant publications [21, 20].

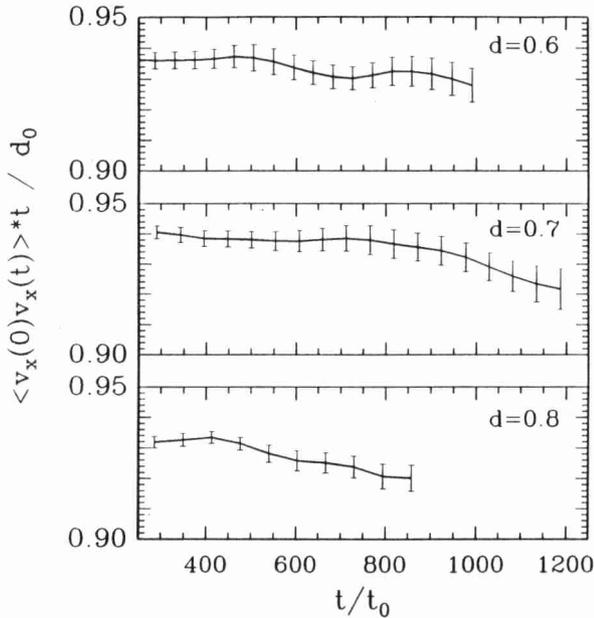
3.1 Long-time tails

Lattice-gas cellular automata were first introduced as a model for hydrodynamic fluids [22] as a computationally 'cheap' model for a simple fluid. The number of collisions per CPU-second in a lattice gas is at least 4 order-of-magnitude larger than in a hard-sphere fluid. It was therefore hoped that the direct simulation of the tagged-particle motion in a LGCA would yield very accurate data on the algebraic decay of the VACF. In fact, very extensive simulations on two-dimensional LGCA's were performed by several groups [23, 24] with precisely this aim. But the results were disappointing. In fact, the statistics on the long-time tails were poor (typically, an accuracy of 0.3% was the best that could be achieved) and the tails were almost completely swamped in noise. We have applied the moment-propagation method to a model for a lattice-gas on a triangular lattice (to be precise, the 'FHP-III'-model described in ref [13]). Use of the moment-propagation method results in a very drastic reduction of the statistical noise by a factor that can be as much as 10^5 for long times (see figure 2). This noise reduction would correspond to a gain of 10^{10} in computing speed. Admittedly, we have not compared the two techniques on the same computer, but this is not expected to change the picture by more than a factor 10^3 (and probably less). Note that figure 2 shows a very clear non-exponential decay at long times. We can now compare the results of such a simulation with the predictions of lowest order mode-coupling theory (see ref. [25]). Such a comparison is shown in figure 3. The figure clearly shows that the observed tail falls below the predictions of lowest-order mode coupling theory at all densities studied. It should be noted however that the truly asymptotic regime described by eqn. 2 only dominates at times of the order of 10^{20} time-steps. This is inaccessible at present, and



2. Velocity ACF of a tagged particle in a two-dimensional lattice-gas cellular automaton (FHP-III model, see fig. 1). The density d denotes the fractional filling of the lattice. Time is expressed in units of the 'mean-free time' t_0 . t_0 is the time that characterizes the initial ('Boltzmann') decay of the VACF. At this density, t_0 equals 0.346 time steps of the lattice gas. The best simulations of the velocity ACF of hard disks extend to some 10^2 mean-free times.

The velocity ACF is indicated by a drawn curve, while the estimated statistical error is shown as a dotted curve. Note that the signal-to-noise ratio hardly deteriorates with increasing time. Note also that the statistical noise at long times is of the order of $2 \cdot 10^{-8}$ which is 5 orders of magnitude better than the best 'conventional' result for the same model system.



3. This figure shows the long-time tail of a tagged particle in a two-dimensional lattice-gas cellular automaton, divided by the tail predicted by lowest order mode coupling theory. In this theory, the expression for the hydrodynamic tail is of the form d_0/t (see eqn. 1). The explicit expression for d_0 is given in ref. [25]. The density (i.e. the fractional filling of the lattice) is denoted by d . The time is expressed in units t_0 (see fig. 1). For $d = 0.6, 0.7$ and 0.8 , t_0 equals 0.454, 0.379 and 0.315, respectively.

If the simulation results were adequately described by lowest-order mode-coupling theory, all curves would be constant at a value of 1.0. However, the figure shows that the velocity ACF is in all cases *lower* than the value predicted by the first-order mode-coupling theory. Moreover, all curves show, on average, a weak, negative slope. Both effects are in agreement with the predictions of self-consistent mode-coupling theory.

almost certainly, also in the future. For more details, the reader is referred to [21].

3.2 Simulations at constant osmotic pressure

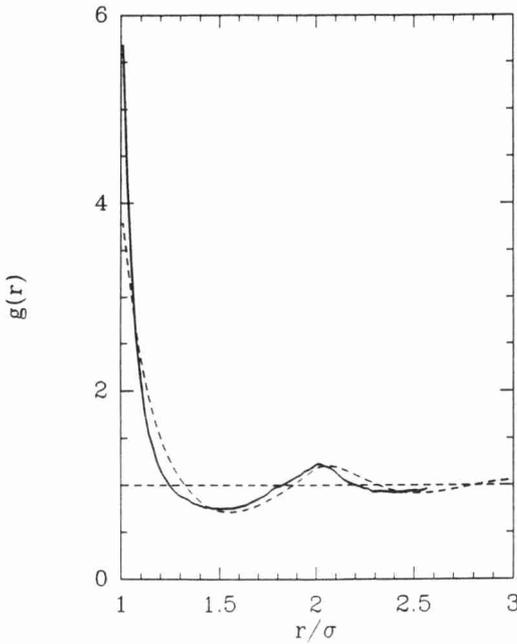
The second example is concerned with a well known phenomenon in colloid chemistry, namely that the addition of polymer to a colloidal suspension causes an effective attraction between the colloidal particles. This attraction is purely entropic in origin. It stems from the fact that the total number of allowed polymer conformations is larger when two colloidal particles are close together than when they are far apart. Using the techniques described in section 2.3, it proved possible to observe this effect directly in a computer simulation. Figure 4 shows the radial distribution function, $g(r)$, of a system of three-dimensional hard spheres ('colloidal particles') in contact with a polymer reservoir, such that the polymer 'osmotic pressure' is held constant. For the sake of comparison, the same figure also shows $g(r)$ for the same system in the absence of polymers. Clearly, the addition of polymer to the hard-sphere suspension has resulted in a strong tendency of the spheres to cluster. A more quantitative discussion of this phenomenon can be found in ref. [20]

4 Conclusion

In this paper I have shown how, sometimes, a change of algorithm can make a difference. I have indicated how a numerical technique that was originally devised to study time-correlations in 'sub-molecular' fluids, has been extended to study the structure and phase-behavior of 'supra-molecular' fluids. This opens the way to the numerical study of a class of problems that did, thus far, defy simulation.

Acknowledgements

This work was carried out in collaboration with Martin van der Hoef, Evert Jan Meijer and Germonda Mooij. In addition, I grate-



4. Radial distribution function of a system of hard spheres ('colloidal particles') at a reduced density of $\rho^* = 0.56$. The dashed curve shows the result for the pure hard-sphere system. The drawn curve shows the effect on $g(r)$ of addition of polymer.

The present results were obtained for a system of 108 hard spheres in osmotic equilibrium with a bath of chain-molecules with 10 segments. The length of the fully stretched chain-molecule is 5% less than the diameter of the spheres. Hence, these 'polymers' can only cause short-ranged attractions. The osmotic pressure has been chosen such that the average number of polymer molecules in the system is $1.4 \cdot 10^3$.

fully acknowledge the many contributions and suggestions of Matthieu Ernst, Henk Lekkerkerker and Ilja Siepmann. The work of the FOM Institute is part of the scientific program of FOM and is supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek' (NWO)

References

- [1] Many early papers on computer simulation can be found in the following reprint collection: G. Ciccotti, D. Frenkel and I. R. McDonald, **Simulation of Liquids and Solids**, North-Holland, Amsterdam, 1987.
- [2] B. J. Alder and T. E. Wainwright, *Phys. Rev.* **A1**:18(1970).
- [3] J.R. Dorfman and E.G.D. Cohen, *Phys. Rev. Lett.* **25**:1257(1970), *Phys. Rev.* **A6**:776(1972), **A12**:292(1975).
- [4] M.H. Ernst, E.H. Hauge and J.M.J. van Leeuwen, *Phys. Rev.* **A4**:2055(1971).
- [5] Y. Pomeau and P. Résibois, *Physics Reports* **19**:63(1975).
- [6] D. Levesque and W.T. Ashurst, *Phys. Rev. Lett.* **33**:277(1974).
- [7] J.J. Erpenbeck and W.W. Wood, *Phys. Rev.* **A26**:1648(1982).
- [8] J.J. Erpenbeck and W.W. Wood, *Phys. Rev.* **A32**:412(1985).
- [9] B.J. Alder and T.E. Wainwright and D. Gass, *Phys. Rev.* **A4**, 233(1971).
- [10] K. Kremer and K. Binder, *Computer Physics Reports*, **7**:259(1988).
- [11] K. Kremer, G. S. Grest and I. Carmesin, *Phys. Rev. Lett.* **61**:566 (1988)
- [12] B. Widom, *J. Chem. Phys.* **39**:2808 (1963).
- [13] D. d'Humières and P. Lallemand, *Complex Systems* **1**, 599(1987).
- [14] U. Frisch, D. d'Humières, B. Hasslacher, P. Lallemand, Y. Pomeau and J.-P. Rivet, *Complex Systems* **1**, 649(1987).
- [15] D. Frenkel in: **Cellular Automata and Modeling of Complex Physical Systems**, P. Manneville, N. Boccara,

- G. Y. Vichniac and R. Bidaux (editors), Springer, Berlin, 1989, p.144.
- [16] D.Frenkel and M.H.Ernst, *Phys. Rev. Lett.* **63**:2165(1989).
- [17] M.A. van der Hoef and D.Frenkel, *Phys. Rev. A* **41** :4277 (1990).
- [18] J.I.Siepmann, *Mol.Phys.* **70**:1145(1990). J.I.Siepmann and D.Frenkel, *Mol. Phys.* (in press)
- [19] G. C. A. M. Mooij and D. Frenkel, *Mol. Phys.* **74**:41(1991)
- [20] E. J. Meijer and D. Frenkel, *Phys. Rev. Lett.* **67**:1110(1991).
- [21] M.A. van der Hoef and D. Frenkel, *Phys. Rev. Lett.* **66**:1591(1991).
- [22] U. Frisch, B. Hasslacher and Y. Pomeau, *Phys. Rev. Lett.* **56**:1505(1986).
- [23] J.-P. Boon and A. Noullez in: **Proceedings of workshop on Discrete kinetic theory, lattice gas dynamics and foundations of hydrodynamics**, World Scientific, Singapore, 1989.
- [24] P.M.Binder and D.d'Humières, Los Alamos preprint LA-UR-1341(1988) and P.M. Binder in **Cellular Automata and the modeling of complex physical systems**, P.Manneville, N.Boccaro, G.Y.Vichniac and R.Bidaux, editors. Springer, Berlin, 1989, p.155.
- [25] M.H.Ernst in: **Proceedings of the Les Houches Summer-school on Liquids, Freezing and the Glass Transition**, J.P.Hansen and D.Levesque, editors, North-Holland, Amsterdam, 1990.