Novel Monte Carlo Approach to the Dynamics of Fluids: Single-Particle Diffusion, Correlation Functions, and Phase Ordering of Binary Fluids

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We propose a novel Monte Carlo scheme to study the late-time *dynamics* of a 2D hard sphere fluid, modeled by a tethered network of hard spheres. Fluidity is simulated by breaking and reattaching the flexible tethers. We study the diffusion of a tagged particle, and show that the velocity autocorrelation function has a long-time t^{-1} tail. We investigate the dynamics of phase separation of a binary fluid at late times, and show that the domain size $R(t)$ grows as $t^{1/2}$ for high-viscosity fluids with a crossover to $t^{2/3}$ for low-viscosity fluids. Our scheme can accommodate particles interacting with a softer pair potential $V(r)$. [S0031-9007(96)00823-X]

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With the advent of modern computers, there have been several large scale molecular dynamics (MD) [1], lattice-gas automata (LG) [2], and Langevin simulations (LS) [3] of the late-time dynamics of fluids. These simulations have been used to compute dynamical correlation functions and to study fluid flow in different geometries. MD and LS have also been used to study the dynamics of phase ordering of binary fluids, where the relative concentration of the fluids is coupled to the fluid velocity. In many such applications, one is interested in late-time hydrodynamical behavior. Since MD provides an accurate description of the microscopic physics, it may not probe dynamics at such late time, unless one makes a sizable computational investment. LS are a more coarse-grained description; however, the dynamical equations are too complicated to solve, and it is not clear that the various simplifying approximations made do not miss features which might affect the physics at large length and time scales.

There is a considerable advantage if Monte Carlo (MC) simulations could be used instead. MC simulations [4] have been remarkably successful in the study of the dynamics of alloys, magnets, and so on, *but have never been used to study the late-time dynamics of fluids*. This is because there is no natural way to incorporate the *momentum density* in a MC simulation. It seems eminently desirable to devise a MC scheme to handle the dynamics of fluids, since it is more coarse grained than MD and more microscopic than LS. This is what we attempt to do in this Letter. More recently, lattice Boltzmann (LB) [5] simulations have been employed with this specific goal in mind, but, since such simulations do not depend on the specific form of the Hamiltonian, one has to choose the equilibrium distribution functions consistent with interfacial profiles and equilibrium densities.

In this Letter, we present a novel MC technique which successfully simulates the fluidity of a fluid. Although the algorithm can be extended to dimensions $d \geq 2$, and to any pair potential, we demonstrate its efficacy for a hard sphere fluid in $d = 2$. We determine the single-particle diffusion coefficient and the long-time tail of the velocity autocorrelation function for dense fluids. We also study the kinetics of phase ordering of a binary fluid in 2D and compute the concentration correlation function to extract the growth laws described below.

A typical configuration of our model 2D fluid consists of hard spherical beads (vertices) (the number of beads N and the diameter of the beads a are fixed), restricted onto a finite planar region of area A. All the beads are linked together by straight flexible tethers (bonds) in such a way as to triangulate this region. The tethers do not intersect each other—each configuration is thus a *connected planar graph*. Since the particles are restricted to a 2D plane, the distribution of local coordination numbers is symmetric about 6. For numerical convenience we ensure that the local coordination number of every bead lies between 3 and 9. The hard spherical beads are, of course, infinitely repulsive at distances less than a. Moreover, the length of each flexible tether can vary between $l_{\min} = a$ and $l_{\max} = 5\sqrt{3}\,a$, the latter choice guaranteeing that half of the attempted MC moves are accepted. We distinguish between external (edge) vertices (V^E) and internal (bulk) vertices ($V^I k$). An external (edge) tether (T^E) connects two external vertices, while an internal (bulk) tether (T^I) connects at least one internal vertex.

Our Monte Carlo simulation should allow for configuration changes which sample *all permissible* regions in phase space. The configuration changes of our 2D fluid consist of the movement of beads with fixed connectivity (*bead moves*) and the movement of tethers with fixed vertex positions (*flip moves*). As we shall see below, the flip moves are crucial in maintaining fluidity. We shall use rigid boundary conditions (on a hexagonal frame), and so neither V^E nor T^E are moved.

The bead moves are effected by randomly choosing a bead i and then translating i to a random point (with a uniform distribution) within a square (of size $l = 2a$) centered on the old position of i. The movement is accepted if the new bond lengths lie between $l_{\min}$ and $l_{\max}$, and *the graph remains planar* (i.e., no bond intersections). With each particle i, we can identify a unique

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n-gon (concave or convex) whose vertices $\{v_1, v_2, \ldots, v_n\}$, arranged in cyclic order, are connected to i. Let us denote the areas of the triangles $\{iv_1v_2, \ldots, iv_{n-1}v_n\}$ as $\{A(iv_1v_2), \ldots, A(iv_{n-1}v_n)\}$. Planarity of the graph is retained if $A(iv_1v_2) + \cdots + A(iv_{n-1}v_n)$ remains unchanged after the move on i. Our unit of time is set by one Monte Carlo sweep (MCS), defined as N attempted bead moves.

Fluidity can be generated by a combination of bead and flip moves. The flip moves are a modification of the bond reconnection algorithm, developed to study the *equilibrium* behavior of fluid membranes [6]. A bond t_{ij} (connecting vertices i and j) is picked at random. With every internal bond t_{ij}, we can identify two triangles ijv_1 and ijv_2 on either side of t_{ij} which have the *smallest area*. This defines a quadrilateral, with i and j being a pair of opposite vertices. The bond t_{ij} is now flipped, only if v_1 and v_2 are not already connected by a bond, so that it now connects v_1 and v_2 (leaving the vertices i and j unconnected by a bond). This flip is accepted provided the length of $t_{v_1v_2}$ is less than the maximum allowed length $l_{\max}$, and if $t_{v_1v_2}$ *does not intersect any other tether* (planarity). Note that the total number of bonds is conserved during this operation. During one MCS, we make N_{flip} attempts at flipping bonds.

How well does this algorithm mimic the statics and dynamics of a simple fluid? The equilibrium properties of a simple fluid can be derived from the partition function $Z = \mathrm{Tr}_{\mathbf{g}}\mathrm{Tr}_{\rho} \exp(-\beta F[\mathbf{g}, \{\rho\}])$ **(**where $F = \int [\, g^2/2\rho_0 + V(\{\rho\})\,]$ is the free-energy functional of the local momentum density $\mathbf{g}(\mathbf{r}, t)$ and the mass density $\rho(\mathbf{r}, t)$ of the fluid**)**. In our simulation, we define the local velocity for the ith particle, $\mathbf{u}_i = \mathbf{g}_i/m$, as its vector displacement in a single MCS. Even though particle displacements are picked with a uniform distribution from a square of side l centered at the original position of the particle, large displacements, which have a high chance of violating the tethering and planarity constraints, are rejected. Clearly, the larger the coordination number of the ith particle, the higher is the chance that large displacements are rejected and so the smaller is $|\mathbf{u}_i|$. The displacements of particles i and j are clearly independent of each other and so, by the central limit theorem, the displacements (and hence the velocities) of particles tend to a normal (Maxwellian) distribution over several MC times. The time scale over which this happens is the velocity equilibration time τ_u. From equipartition, a computation of $\langle u_i^2 \rangle$ gives the kinetic temperature $2k_BT/m$, where m is the mass of the particle. On the other hand, the trace over ρ is identical to a sum over configurations with (dynamically) varying local coordination number. Since the tethering is dynamical, there is no restriction on the allowable configurations sampled by our fluid, and the system reaches equilibrium at late times.

Equilibrium is achieved through collisions between particles which result in velocity exchanges. In our simulations, "collisions" occur either through the rejection of certain MC moves due to the hard sphere constraint or through flip moves. Collisions resulting from flip moves transform particles with low coordination number to high, and vice versa. From our discussion above, this results in an exchange of velocities. It is clear that particle momenta (and angular momenta) are not conserved during an elementary "collision," and so our algorithm will not mimic fluid dynamics at short time scales. However, averaged over several collisions, both momenta and angular momenta can be seen to be conserved. Just as in a Langevin simulation, momentum is conserved only in a statistical sense. Our MC dynamics thus mimics the dynamics of a fluid over several collision time scales. Starting with a random triangulation (which we generate by repeated bead and flip moves on an initial triangular lattice), we allow the fluid to evolve via our MC algorithm. We measure various dynamical transport coefficients after discarding all configurations arising from, typically, the first ten Monte Carlo sweeps. The single-particle diffusion coefficient D_s can be extracted by measuring the mean-square displacement of a tagged particle (averaged over several initial conditions and particles) for different values of N_{flip} and density (Fig. 1). Not surprisingly, D_s (and hence the inverse viscosity η^{-1}) is an increasing function of N_{flip} (inset, Fig. 1) at constant density before it saturates.

A crucial test of whether our MC algorithm correctly describes the hydrodynamic behavior of fluids, is the occurrence of "long-time tails" in the measured velocity autocorrelation function $Z(t) \equiv \langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle$ of dense (or highly viscous) fluids [7]. We compute $Z(t)$ (averaged over several initial conditions and particles) for different values of N_{flip} and density. We find a convincing t^{-1} tail (Fig. 2) in the $Z(t)$ of high-density (large N) and high-viscosity (low $N_{\text{flip}} = 0.25N$) fluids. The inset of

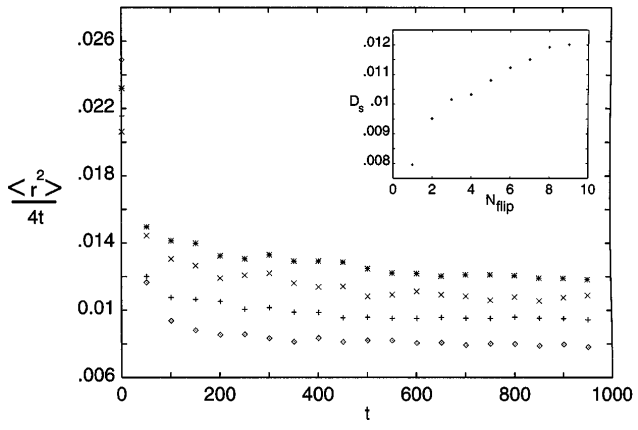

FIG. 1. The single-particle diffusion coefficient D_s at different N_{flip} for $N_{\text{flip}} = N$, $2N$, $5N$, and $9N$, going from bottom to top, is given by the value of $\langle r^2 \rangle/4t$ at the plateau. The inset shows D_s as a function of N_{flip} (in units of N). The area fraction $N\pi a^2/A = 0.14$ is kept fixed.

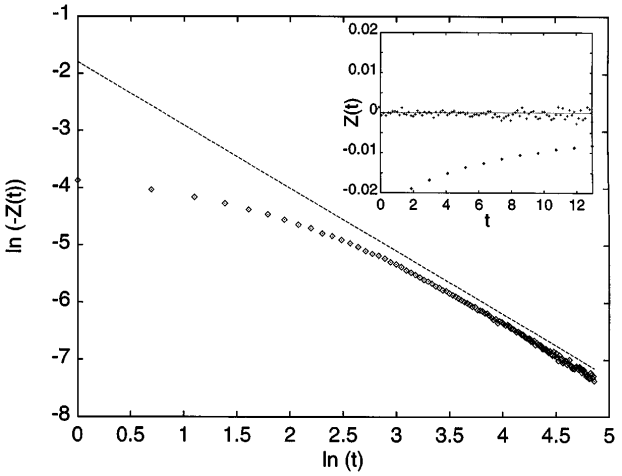

FIG. 2. The velocity autocorrelation function $Z(t)$ for high-density, high-viscosity fluids exhibits a clear t^{-1} long-time tail. Inset : $Z(t)$ decays to zero for low-viscosity fluids (the t^{-1} tail is displayed for comparison).

Fig. 2 shows the exponential decay (Enskog result) of $Z(t)$ for lower viscosity ($N_{\rm flip} = 10N$). Note that the early time fall from $Z(0) = 1$ does not show up since, for the densities under consideration, several collisions have taken place within one MC time step. The inset also displays the t^{-1} tail for comparison.

Encouraged by this success, we study the dynamics of phase separation of a binary fluid using our MC algorithm. Let us recount that, when two immiscible fluids, such as water + toluene, are cooled below their coexistence curve, they phase segregate into water-rich and toluene-rich regions, separated by sharp interfaces. At late times, the system enters a dynamical scaling regime [3], where the equal-time concentration correlation function behaves as $g(r,t) = g(r/t^z)$. The growth exponent z is independent of microscopic details and depends on the existence of conservation laws. The scaling form defines a characteristic length scale $R(t) \sim t^z$, which measures the typical distance between interfaces.

The phase separation dynamics of a 2D binary fluid is described by a (conserved) concentration density $\phi(\mathbf{r},t)$ coupled to a (conserved) momentum density $\boldsymbol{\pi}(\mathbf{r},t)$. A variety of theoretical (based on dimensional analysis [3,8]) and numerical (MD [9] and LS [10]) techniques have been used to understand the late stage dynamics of a 2D binary fluid, but have, unfortunately, given rise to conflicting results. The theoretical analysis and LS contend that, as in 3D, the growth crosses over from a viscosity dominated $R \sim t$ to an inertia dominated $R \sim t^{2/3}$. On the other hand, extensive MD simulations [9] report a late-time $R \sim t^{1/2}$ growth.

Our model 2D binary fluid consists of two types of hard spheres, A and B [the total number of A (N_A) and B (N_B) beads are fixed, $N = N_A + N_B$]. The local concentration ϕ_i, defined as the difference in the densities of A and B, takes values $+1$ (for A) and -1 (for B). The dynamics of ϕ is described by the usual Kawasaki exchange, which conserves $\sum_i \phi_i$. Thus, locally, ϕ_i evolves by exchanging particles at vertices i and j, where j is connected to i by a tether, with a transition probability which obeys detailed balance [4] $W(i \leftrightarrow j) = [1 - \tanh(\Delta E/2k_BT)]/2$, where ΔE is the energy difference between the final and the initial configuration. The energy is calculated using the Ising Hamiltonian

$$H_{\rm ex} = -J \sum_{\langle ij \rangle} \phi_i \phi_j \,, \tag{1}$$

where the sum over $\langle ij \rangle$ is over vertex pairs connected by a tether.

In addition to the two MC moves described above, each Monte Carlo sweep now includes $N_{\rm ex}$ attempts at performing Kawasaki exchanges. Note that the Boltzmann weights associated with particle movements and the bond flips do not involve $H_{\rm ex}$. It is clear that fluctuations in the local exchange energy are related to fluctuations in the local coordination number, which, in turn, are related to fluctuations in the local velocity. In this way, the concentration variable ϕ gets coupled to the velocity u.

At time $t = 0$, our 2D binary fluid is a homogeneous (50-50) mixture of A and B in equilibrium at a high temperature T. We quench to below the critical temperature, $T < T_c \approx 2.25J$ (for a triangular lattice). The homogeneous state is unstable at this temperature, and evolves into a final phase-separated state by the slow annealing of interfaces, conserving the order parameter ϕ during the process. A time sequence of typical configurations of ϕ (resembling those in Ref. [3]) clearly exhibits statistical self-similarity at late times. As a quantitative measure, we compute the circularly averaged pair correlation function $g(r,t) \equiv N^{-1} \sum_{\mathbf{x}} \langle \phi(\mathbf{x}+\mathbf{r},t)\phi(\mathbf{x},t) \rangle$, averaged over several realizations of the initial configurations of ϕ (it was sufficient to average over ten realizations for good statistics). The domain size $R(t)$ is extracted from the first zero of the correlation function $g(R(t),t) = 0$. The

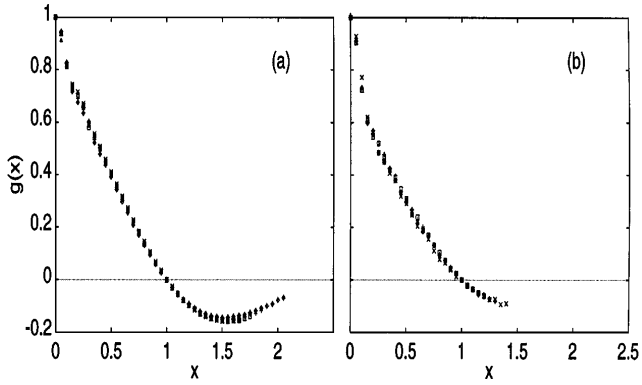

FIG. 3. Scaling functions for the correlation function $g(r,t)$ at (a) high viscosity ($N_{\rm flip} = 30N$) and (b) low viscosity ($N_{\rm flip} = 100N$). Here $x = r/R(t)$ is the scaling variable.

correlation function $g(r,t)$ exhibits dynamical scaling, $g(r,t) = g(r/R(t))$, at late times (Fig. 3), both for high-viscosity $N_{\rm flip} = 30N$ [Fig. 3(a)] and for low-viscosity $N_{\rm flip} = 100N$ [Fig. 3(b)] fluids. Our study seems to indicate that the scaling function depends on the viscosity of the fluid.

The domain size $R(t)$, determined from both the correlation function and the interfacial energy density, is found to scale as $R(t) \sim t^z$. As a preliminary check, we perform the usual Kawasaki dynamics in the absence of any bond flip and obtain a clean $t^{1/3}$ Lifshitz-Slyozov growth. On introducing the flip moves that mimic fluidity, we see a dramatic crossover to a growth influenced by hydrodynamics. For high-viscosity fluids, $N_{\rm flip} = 30N$, Fig. 4 shows a growth consistent with $R \sim t^{1/2}$ at late times, before finite size effects become apparent. A log-log plot for $N = 7500$ shows a $z = 0.48 \pm 0.03$. Simulations for larger system sizes and longer times give the same value of z, indicating that this value of the exponent is robust up to the late times we have investigated. This growth law is in agreement with MD simulations [9]. On the other hand, for low-viscosity fluids $N_{\rm flip} = 100N$, Fig. 4 shows a late time exponent $z = 0.6 \pm 0.05$, indicating a crossover from the viscosity dominated $t^{1/2}$ growth to the inertia dominated $t^{2/3}$ growth. Thus we expect $R \sim t^{1/2}$ when $t \ll t_\times$, and $R \sim t^{2/3}$ when $t \gg t_\times$, where the crossover time $t_\times \sim \eta^\alpha$. Indeed, recent LB simulations [11] have seen the $t^{2/3}$ growth for low-viscosity fluids. At higher viscosities they see an early time $t^{1/3}$ growth, and claim a crossover to a later time $t^{2/3}$. *However, their published data* [11] *clearly indicate a crossover to* $t^{1/2}$. We claim that the LB results are consistent with our MC simulations. As is clear from the above discussion, our computational costs are low. This crossover from $z = 1/2$ for high viscosities to $z = 2/3$ for low viscosities can be understood theoretically, and we defer a discussion to another paper [12].

In this Letter, we have presented the first Monte Carlo algorithm to describe the *late-time dynamics of fluids* in two dimensions. A novel feature of this algorithm is the incorporation of the momentum density of fluids using a dynamical triangulation scheme. We have tested this code on a hard sphere fluid and have computed the long-time tail of the velocity autocorrelation function. We have studied the phase separation dynamics of a binary fluid and find that the domain size $R(t) \sim t^{1/2}$ for high viscosity and crosses over to $R(t) \sim t^{2/3}$ for low-viscosity fluids, with a crossover time depending on the viscosity. This algorithm can be easily extended to arbitrary pair potentials $V(r)$ by weighting the bead moves by $\exp[-V(r)/k_BT]$. In a subsequent publication we hope to develop an analogous MC algorithm to study the late-time hydrodynamics of fluids in three dimensions.

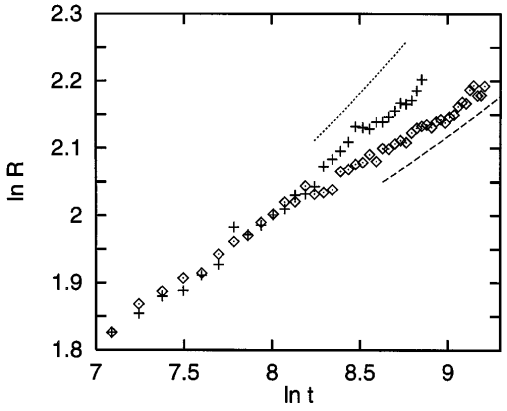

FIG. 4. Domain size (log-log plot) $R(t)$ scales as ($\diamond$) $t^{1/2}$ for high viscosity ($N_{\rm flip} = 30N$) and ($+$) $t^{2/3}$ for low viscosity ($N_{\rm flip} = 100N$). The lines with slopes $1/2$ and $2/3$ are aids to the eye.

We have enjoyed discussions with Surajit Sengupta, Sriram Ramaswamy, and Rahul Pandit.

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