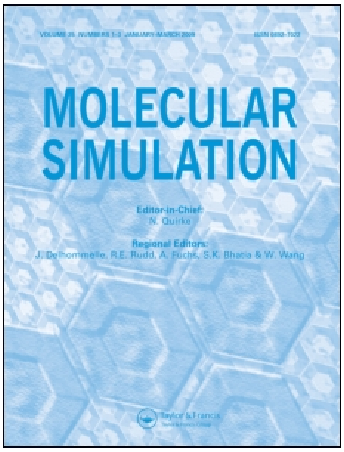

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MESOSCALE MODELING OF AMPHIPHILIC FLUID DYNAMICS

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So-called "vector models," in which surfactant molecules retain only translational and orientational degrees of freedom, have been used to study the equilibrium properties of amphiphilic fluids for nearly a decade now. We demonstrate that hydrodynamic lattice–gas automata provide an effective means of coupling the Hamiltonian of such vector models to hydrodynamic flow with conserved momentum, thereby providing a self-consistent treatment of the hydrodynamics of amphiphilic fluids. In this "talk", we describe these hydrodynamic lattice–gas models in two and three dimensions, and present their application to problems of amphiphilic–fluid hydrodynamics, including the dynamics of phase separation and the shear-induced sponge-to-lamellar phase transition.

Keywords: Vector models; Amphiphilic fluid dynamics; Mesoscale modelling

INTRODUCTION

Ternary Models of Amphiphilic Fluids

Ternary models of amphiphilic fluids include degrees of freedom and conserved order parameters for each of the three species present–namely oil, water and amphiphile. This is to be contrasted with binary (oil/water)

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models in which the presence of the surfactant is modelled by simply altering the properties of the oil/water interface (*e.g.*, by lowering the surface tension). The location of the amphiphile species is represented by a continuous density (for Eulerian models) or by discrete particle positions (for Lagrangian models).

Vector Models

Vector models are ternary models of amphiphilic fluid in which the amphiphile particles have orientational degrees of freedom, in addition to their spatial location. The most general models of this sort allow for a density of amphiphile in both (the Cartesian product of) physical and orientational space; that is

$$\mathcal{F}(x, \hat{n})$$

Lattice Vector Models

Vector models on a spatial lattice can either require the amphiphilic orientation to lie along the lattice vectors, or they can allow the orientation angle to vary continuously. An example of the former is a model introduced by Widom in the 1980's [1]. This lattice model of amphiphilic fluid is very similar to the Ising model, in that each site on a Cartesian grid can be in one of two states, which we label + and −. A very clever innovation of this model is that it situates the particles on the *links* between the lattice vertices, rather than on the vertices themselves. Links can be characterized by the states of the vertices they connect. Thus, each link can be in any one of four possible states: Links that connect two +vertices are said to contain water. Links that connect two-vertices are said to contain oil. Finally, links that begin at a−(−) vertex and end at a−(+) vertex are said to contain amphiphile whose hydrophilic end points toward the beginning (end) of the link. The great advantage of this model is that the representation itself literally forces the amphiphile to live on the interface between the oil and water, and orients it correctly.

The Hamiltonian for Widom's model includes two-spin interactions, which give the interface surface tension just as they do in the Ising model, but it also includes three-spin interactions, necessary to capture the rigidity or bending energy of the surface loaded with amphiphile. The model has been extensively simulated using grand canonical Monte Carlo. It has been able to reproduce much of the fascinating phenomenology associated with amphiphilic fluids. In particular, droplet, sponge and lyotropic phases are all seen, as are coexistence regions between these phases.

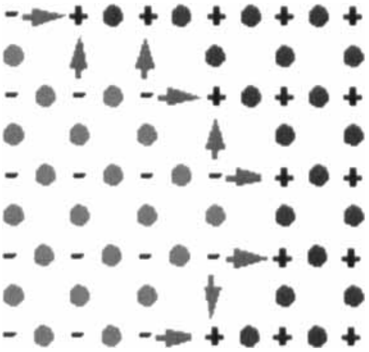


FIGURE 1 (See Color Plate XIX).

HYDRODYNAMIC LATTICE-GAS MODELS

Lattice-Gas Models for Viscous Fluid Flow

Though the above models have been successfully applied in equilibrium situations, we endeavor to study the *hydrodynamics* of amphiphilic fluids. Toward this end, we require a model that is capable of capturing the correct physics during the *approach* to equilibrium. A prerequisite for this is momentum conservation; that is, the total momentum of the water/oil/amphiphile system must be conserved. Such models are known as hydrodynamic lattice-gases, and they endeavor to take the same "minimalist" approach to fluids that the Ising model takes to ferromagnets. The object is not a precise model of the dynamics at the finest scales, but rather the invention a fictitious microdynamics whose *coarse-grained* behavior-in the thermodynamic limit-lies in the same universality class as the phenomenon under study. Along these lines, the most promising approaches model the fluid at the level of fictitious "molecules" that can move about and collide, as do molecules in a real fluid, conserving mass, momentum and (for compressible fluids) energy.

Lattice models capable of doing this for the single-phase isotropic Navier-Stokes equations have been known only since 1986 [2, 3]. The simplest model of this sort employs a two-dimensional triangular grid, and associates particle velocities with the six lattice vectors. At each stage of the time evolution of the system, the particles *propagate* along their respective lattice vectors, and then collide in a manner that conserves mass and momentum. The simplest such collisions are illustrated below.

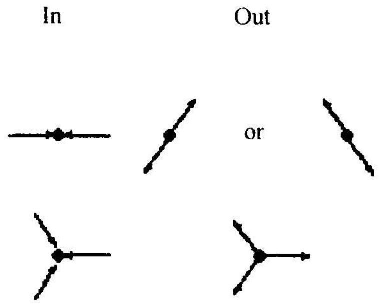


FIGURE 2

Subsequent to the above-mentioned 1986 work, hydrodynamic lattice gases were extended to three dimensions, and attempts were made to include soft potential interactions between the particles.

The Rothman–Keller Model for Immiscible Fluids

In 1988, Rothman and Keller [4] introduced a lattice–gas model for immiscible flow, such as that of oil and water. They accomplished this by tagging the lattice–gas particles with two "colors", to distinguish oil and water. Their collisions were required to conserve the total mass of each color separately, as well as the total momentum. They then skewed the collision outcomes to favor those that send particles towards sites dominated by other particles of the same color. This affinity of particles for other particles of the same color gives the two phases cohesion, and the interface surface tension.

To quantify the nature of this affinity, Rothman and Keller defined the *color field* to be the local gradient of the oil/water order parameter. For each outgoing state allowed by the conservation laws, they also defined a *color flux* to be the velocity–weighting of the oil/water order parameter. The negative of the dot product of these is the *color work* and is lowest when outgoing particles propagate up the gradient of their own color. By weighting the outgoing states according to the Boltzmann factor of the corresponding color work, Rothman and Keller were able to achieve immiscibility of the two phases below/above critical values of the temperature/density, interfacial surface tension, phase separation with hydrodynamics, *etc.*

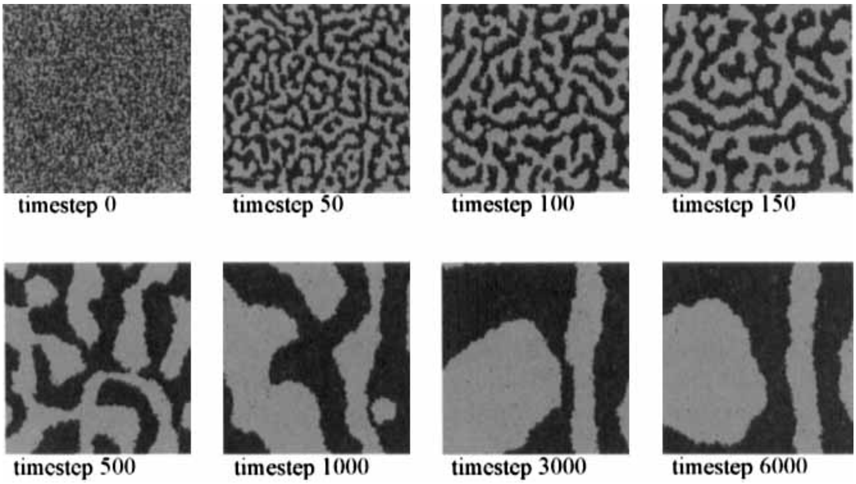


FIGURE 3 (See Color Plate XX).

Because of the hydrodynamic nature of the model (sufficiently far from interfaces, the Rothman – Keller model reduces to that of Frisch, Hasslacher and Pomeau, and hence correctly models Navier – Stokes flow) one can test dynamic as well as equilibrium properties. Hence, the surface tension can be measured numerically either using Laplace's law for stationary bubbles of one fluid surrounded by the other (an equilibrium situation), or by measuring the dispersion relation for capillary waves at the interface (a dynamic situation). Remarkably, agreement is found between these different methods of measuring the surface tension, indicating a certain thermodynamic consistency of the model.

Lattice – Gas Model for Amphiphilic Fluids

In 1995, Boghosian, Coveney and Emerton [5] extended Rothman and Keller's lattice – gas model to include an amphiphile species. The resulting model is effectively a combination of a lattice vector model and a hydrodynamic lattice gas. It conserves the masses of oil, water and amphiphile separately, as well as the total momentum. Unlike Widom's model, the amphiphile orientation is not tied to the lattice vectors, but rather allowed to rotate with continuous angular orientation. (This is not thought to be a terribly important feature of the model, however, and we note that an even more discretized version of the model could be worked out if the orientations were required to be discrete.)

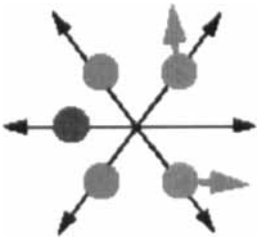


FIGURE 4 (See Color Plate XXI).

The interaction Hamiltonian of the model is substantially more complicated than Rothman and Keller's "color work". To understand the Hamiltonian, let us continue to adopt Rothman and Keller's nomenclature whereby the oil/water order parameter is thought of as a color potential, so that its gradient is the color field and its current is the color flux. Further abusing this electrostatic analogy, we suppose that the surfactant particles are *color dipoles*; this is reasonable, since a surfactant particle has hydrophilic and hydrophobic ends just as a dipole can be thought of as attached positive and negative charges. Thus, several new terms are included in the Hamiltonian to model the potential due to these color dipoles and their interaction with color charges. In particular, there is an interaction between color dipoles and color charges that causes the surfactant to align along the oil/water interface, and another interaction between dipoles and dipoles that gives the interface bending energy.

The model has been generalized to three dimensions, using the projected face-centered hypercubic lattice. Reduced collision sets are used to make the model computationally tractable in that case. The code is called ME3D, and various results obtained with this code are given below.

RESULTS AND PHENOMENOLOGY

Equilibrium Phases in Two and Three Dimensions

The two dimensional model has been studied in some detail, and preliminary three dimensional results have been obtained as of this writing. The model is able to track the formation and saturation of droplet phases in two and three dimensions (two dimensional evolution shown here):

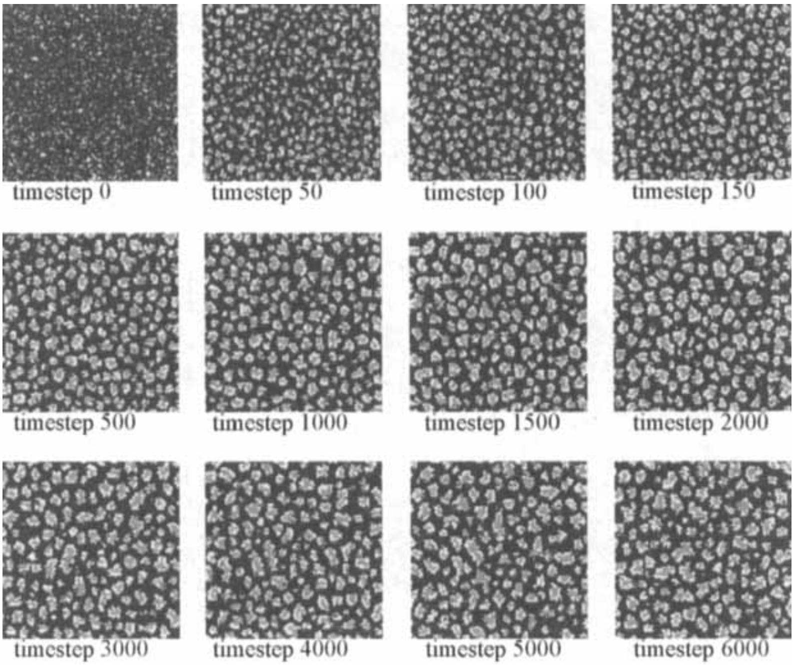


FIGURE 5 (See Color Plate XXII).

It can track micelle (binary water/surfactant) formation in two and three dimensions (three dimensions shown here; arrows denote surfactant orientation): (See Fig. 6)

Higher surfactant concentrations give rise to sponge phases in two dimensions: (See Fig. 7)

and in three dimensions: (See Fig. 8)

Still higher surfactant concentrations in three dimensions give rise to the subtle wormlike-micelle phase: (See Fig. 9)

and to lamellar phases: (See Fig. 10)

More interesting than the equilibrium phenomenology described above are the *dynamic* phenomena that this model makes it possible to study. These are described in the following slides.

Dynamics of Phase Separation

In the time evolution of the two-dimensional droplet and sponge phases shown above, it is evident that the phase separation saturates after a time. This is in marked contrast to the case of two immiscible fluids, for which

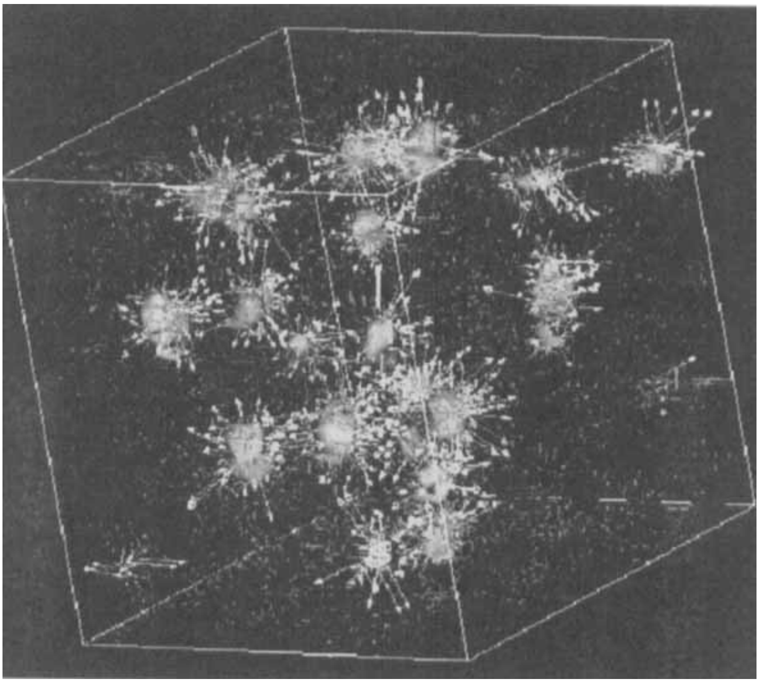


FIGURE 6 (See Color Plate XXIII).

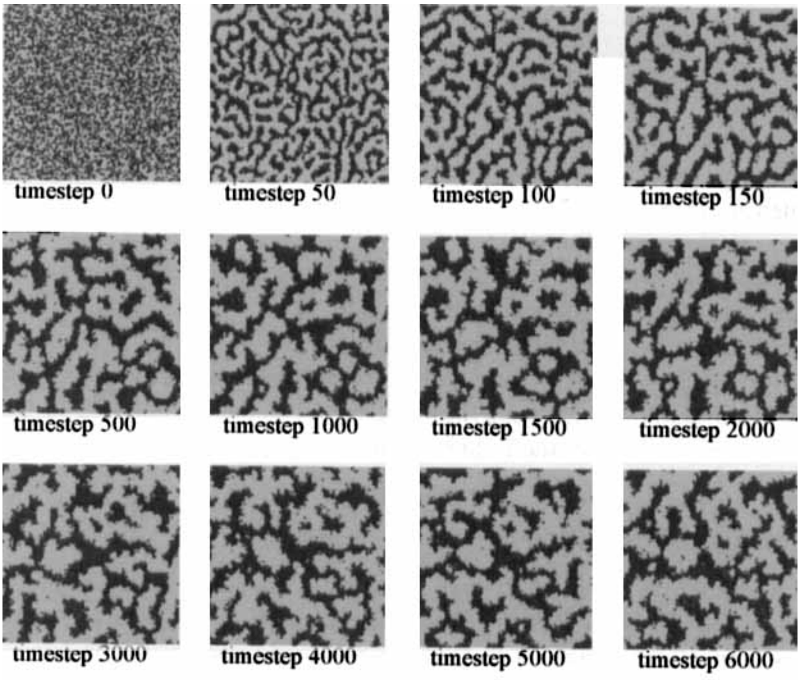


FIGURE 7 (See Color Plate XXIV)

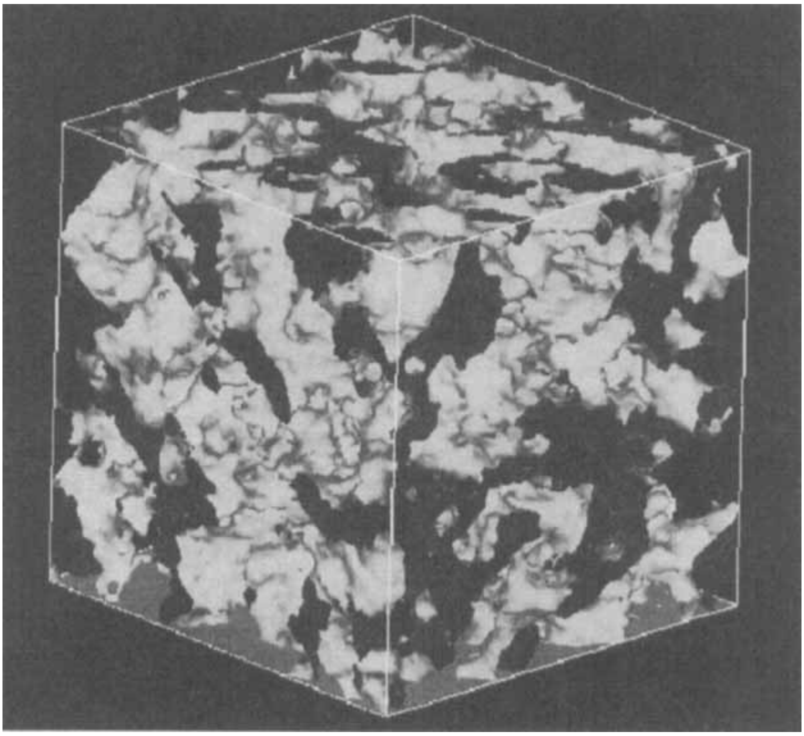


FIGURE 8 (See Color Plate XXV)

power-law growth is expected and observed. The physical reason for this saturation is that if the growth continued there would be insufficient interfacial area to accomodate the surfactant. Since the surfactant pays a heavy free-energy penalty for living off the interface, it becomes energetically favorable for the growth to halt. This can be seen more clearly by comparing the time dependence of the structure function for oil/water separation (no amphiphile): (See Fig. 11)

with that for an emulsion droplet phase: (See Fig. 12)

Note that the latter saturates at late times. The time dependence of the characteristic size has been fit to a stretched exponential function, since that form has been proposed by experimental studies of Wilcoxon, Martin and Odinek [6]. (See Fig. 13)

More results along these lines are described in [7].

Shear-induced Sponge-to-Lamellar Phase Transition

Lamellar phases in two dimensions are forbidden by the Peierls instability for any temperature greater than zero. The presence of a velocity shear can

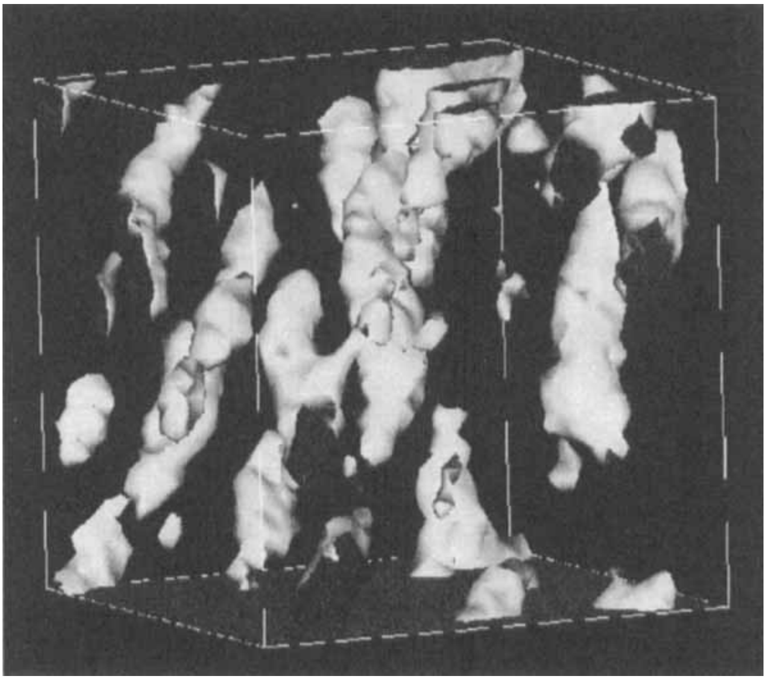


FIGURE 9 (See Color Plate XXVI)

raise this critical temperature to a value greater than zero, giving rise to an effective *shear-induced sponge-to-lamellar phase transition*. Again, this is a peculiarly hydrodynamic phenomenon. It has been observed experimentally, but has heretofore been very difficult to simulate. Our model exhibits this transition, as was described in [8].

The presence of the transition can be inferred by comparing the evolution of the system to a sponge phase without shear: (See Fig. 14)

to the formation of a lamellar phase in the presence of shear: (See Fig. 15)

Note that all other parameters of the model, including the concentrations of the various species and the various coupling coefficients in the Hamiltonian, were fixed from the one simulation to the other.

Amphiphilic Flow in Porous Media

Numerous industrial applications involve amphiphilic fluid flow in porous media. Examples include enhanced petroleum recovery, *in situ* remediation of hydrophobic pollutants, and the use of detergent to launder cloth. In all three of these cases, advantage is made of the ability of amphiphile to break up a hydrophobic phase into droplets that are smaller than the characteristic

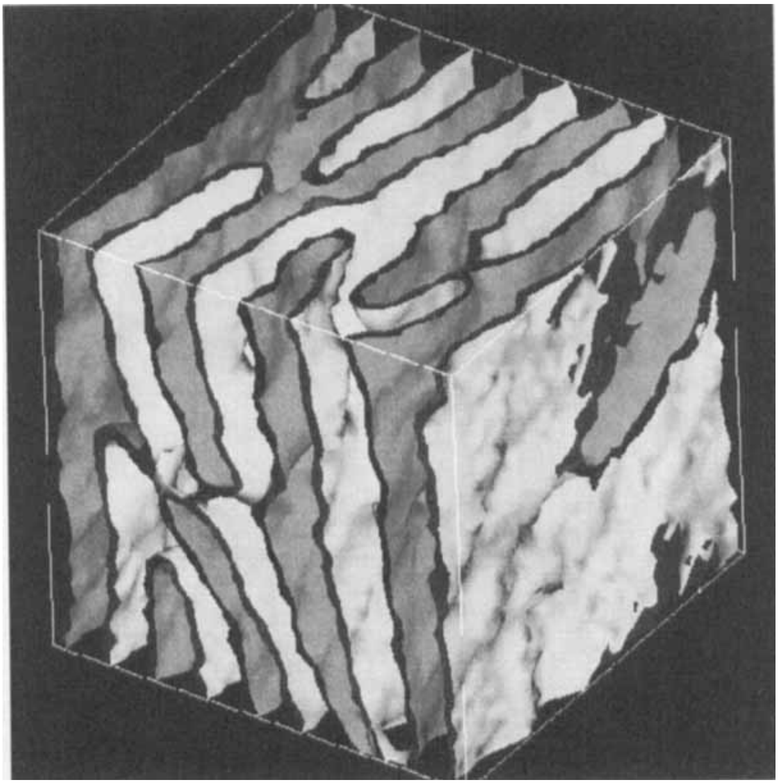


FIGURE 10 (See Color Plate XXVII)

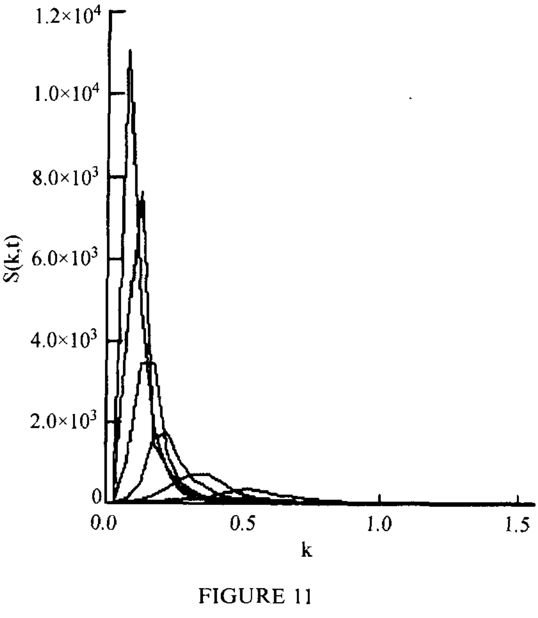


FIGURE 11

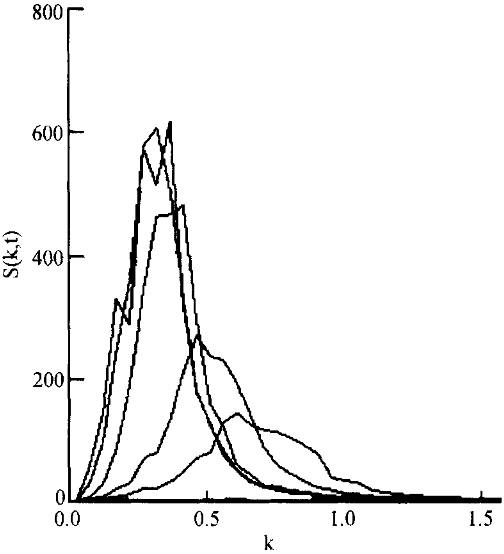


FIGURE 12

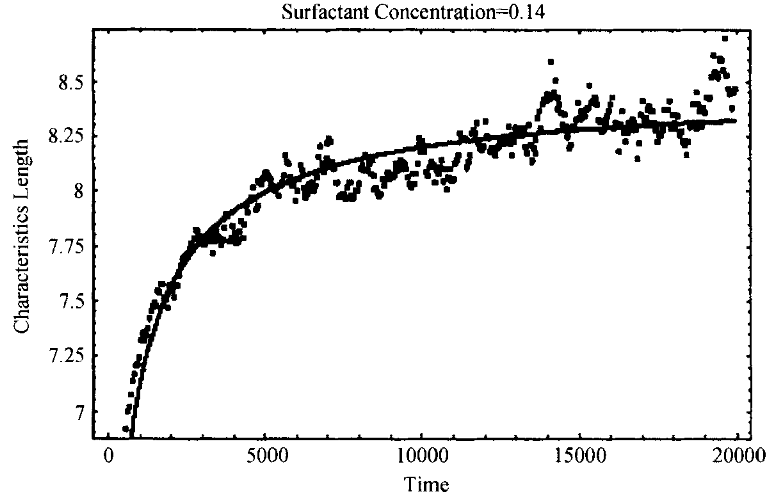
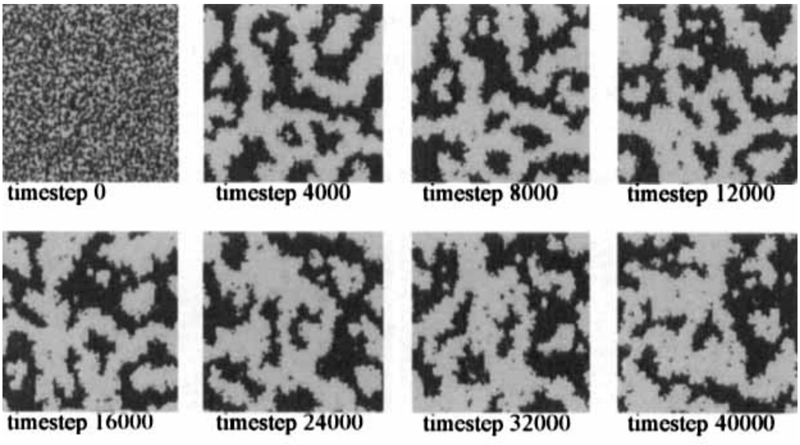


FIGURE 13

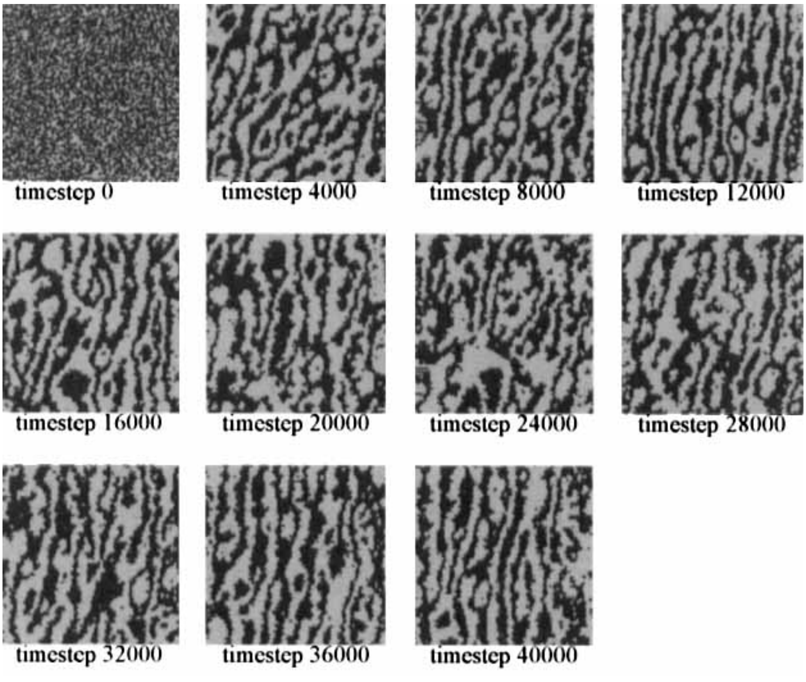
pore size. The hydrodynamic lattice-gas model of amphiphilic fluids makes it possible to study this effect in some detail. Complicated boundary conditions are simple to treat, using bounce-back boundary conditions [2, 3] that ensure that the hydrodynamic velocity goes to zero at the pore walls. It



timestep 0 timestep 4000 timestep 8000 timestep 12000

timestep 16000 timestep 24000 timestep 32000 timestep 40000

FIGURE 14 (See Color Plate XXVIII)



timestep 0 timestep 4000 timestep 8000 timestep 12000

timestep 16000 timestep 20000 timestep 24000 timestep 28000

timestep 32000 timestep 36000 timestep 40000

FIGURE 15 (See Color Plate XXIX)

is also possible to give the boundaries a color charge and even a color dipolar charge to control their wetting properties. The first frame of the following figure shows the porous medium itself. The resident hydrophobic fluid is not rendered in order to simplify the visualization. The next four frames show the temporal evolution of a hydrophilic invading species (suppressing the porous medium, and resident fluid for clarity). The last frame shows the porous medium and the invading fluid. (See Fig. 16)

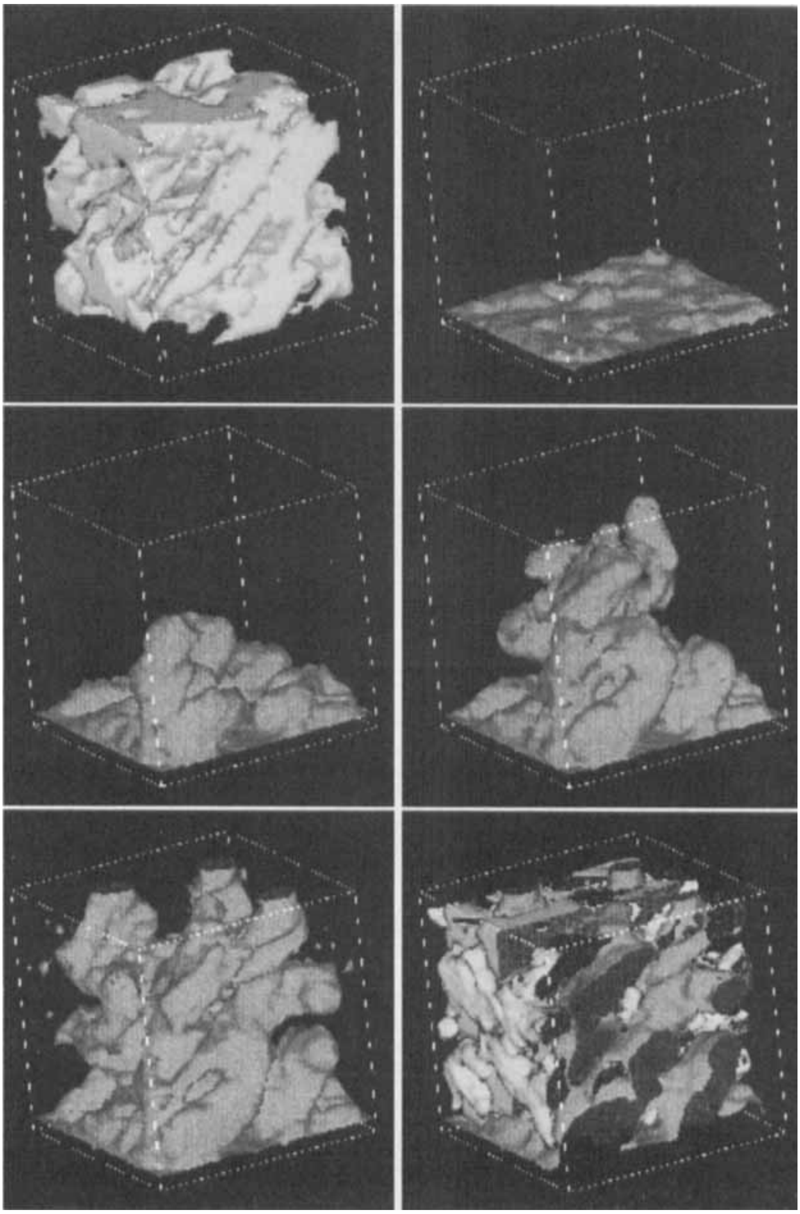


FIGURE 16 (See Color Plate XXX)

To simulate the effect of surfactant in this context, we conducted another similar run, but this time with the addition of surfactant to the invading hydrophilic fluid. The following simulation of the ME3D code shows the effect of this surfactant in breaking up the interface. (See Fig. 17)

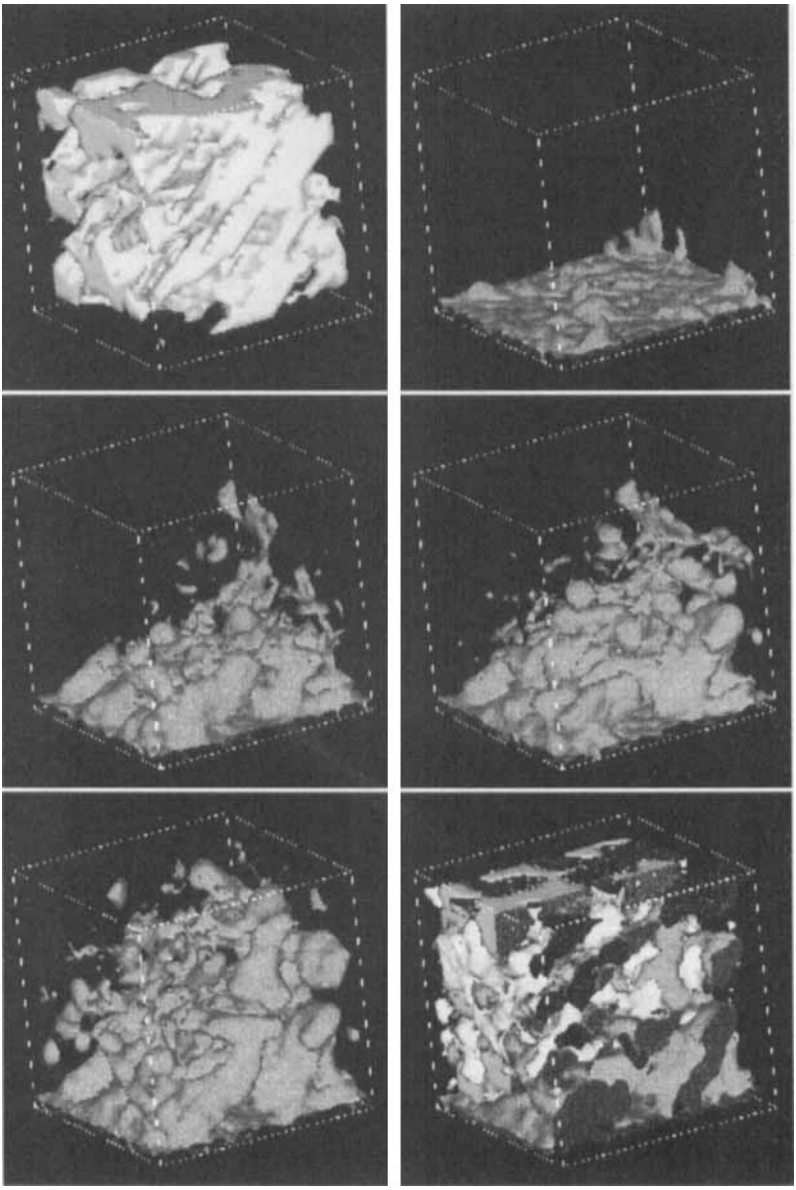


FIGURE 17 (See Color Plate XXXI)

Comparing this graphic with the previous one, we can see that the surfactant gives rise to fine, filiamentary structures in the interface between oil and water. These structures are reflective of a reduced surface tension which "loosens" small droplets of the resident hydrophobic species so that the invading fluid can pump them out. More extensive and quantitative simulations of amphiphilic flow in porous media using the ME3D code can be found in reference [9].

CONCLUSIONS

We have shown that the hydrodynamic lattice–gas methodology makes it possible to add momentum conservation and real viscous hydrodynamics to vector models of amphiphilic fluids. We have used this to study nonequilibrium or dynamical processes that have previously been difficult to address. The most computationally heroic MD simulations to date are barely able to see the self-assembly of a single emulsion droplet. The lattice–gas method, by contrast, is able to study the growth and saturation of many such droplets and larger structures, as can be seen in the above figures. The price paid is the inability of the method to correctly treat microscopic chemistry-dependent details. Nevertheless, for *universal* properties of amphiphilic–fluid hydrodynamics, we expect that the method–along with closely related lattice Boltzmann treatments–will be a method of choice for some time to come.

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