COMPUTER SIMULATIONS OF WIDOM'S MICROEMULSION MODEL

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ABSTRACT - Microemulsions are mixtures of oil, water and ``soap" (amphiphilic molecules). The Widom model of 1986 describes them by a spin 1/2 Ising model with competing interactions to nearest and further neighbors. We review the Monte Carlo simulations of this Widom model, for static and dynamic properties.

1. INTRODUCTION

If poor people wash their dishes or rich people extract crude oil from the earth, in both cases "soap" may help. These soap molecules are called detergents for dish washing and are a part of the "brine" fluid pumped into the rocks for enhanced oil recovery. Thus not surprisingly, scientists at Shell Laboratories in Amsterdam made computer simulations for both problems. And I will report here on simpler simulations of a lattice model for microemulsions invented several years ago by Benjamin Widom[1] at Cornell University, for which together with Naeem Jan (Canada), Debashish Chowdhury (India), and others lots of simulations were made since 1987.

2. BASIC CONCEPTS

Microemulsions[2] consist of oil, water, and amphiphilic molecules. These amphiphilic molecules have hydrophilic head attracted by water, and a hydrophobic tail attracted by oil. For simplicity we denote the amphiphiles as ``soap" molecules. Since they can easily move between oil and water, the soap molecules can drastically reduce the interface tension between the oil phase and the water phase. As a result, one of the possible states of a microemulsion are small oil droplets in water, or small water droplets in oil, where the whole droplet surface is coated by soap to reduce the interface tension. The droplet radii are in the nanometer range; thus the microemulsion is transparent to light, differently from milk. A third possible phase for microemulsions is called bi-continuous, where water, oil, and soap are intermingled together in a non-periodic but also non-random way.
A simple computer simulation should use a lattice on which the molecules are moved by a Monte Carlo procedure.

Molecular dynamics simulations where molecules follow Newton's law of motion are usually much more demanding in computer time and programming effort. Each lattice site then carries a discrete variable, called a spin by physicists, which determines which type of molecule sits there. The obvious choice, taken by many authors[2], are three possible states for each spin, corresponding to oil, water, and soap. The elegance of the Widom model[1] and the reason that more Monte Carlo simulations were made for this than for other microemulsion models is that it uses only two states, spin up and spin down. The three types of molecules are then represented by the bonds between neighbor spins on the lattice: Two up spins correspond to water, two down spins to oil, one up and one down spin to soap. The spins are thus either hydrophilic or hydrophobic (molecules or parts of molecules). Also some of the molecular dynamics simulations[3] follow this simplification of only two types of elements; amphiphiles in these simulations are chains of hydrophilic and hydrophobic elements. Simplicity is a matter of taste but I find this Widom model simpler than the later lattice models[2] having at least three states for each spin. Also from the computational point of view the two states per site are easier to store and treat in single bits[4] than three or more states. A disadvantage is that we need now interactions to more than just nearest neighbors. On a square or simple cubic lattice the interaction energy (Hamiltonian) is

$$H = -J\sum S_iS_j - 2M\sum S_iS_k - M\sum S_iS_l, \quad S_i = \pm 1$$

with positive J and negative M, where all sums count each pair only once; the first sum goes over nearest neighbors, the second over next-nearest neighbors, and the third over neighbors two lattice constants away. No interaction with neighbors at distance $\sqrt{3}$ is used, and instead of the factor $2M$ one has also used a free interaction parameter here. This interaction energy is completely symmetric with respect to spin up or spin down; a difference between oil and water has been obtained by using a field term proportional to $\Sigma_i S_i$. When M is set to zero we recover the standard Ising model. This model now can be simulated with standard Monte Carlo techniques[5]: A spin is flipped with a probability proportional to $\exp(-\Delta E/k_BT)$ where ΔE is the energy change associated with such a flip. Ref.6 gives dirty tricks to facilitate vectorization. Many other lattice models have been studied but except for the three-phase coexistence to be discussed below few qualitative differences between their phase diagrams and those of the Widom model seem established. Thus we ignore them here and try to review only all simulations of the Widom model. Mean field theories[7] of the Widom model are useful qualitative guides but may give transition temperatures differing by a factor three from the simulation

value; they may also have difficulties in distinguishing between first and second order phase transitions. Since this conference is for physicists, we will use mainly a magnetic language to describe the Widom model results. Ferromagnetism with a positive (negative) spontaneous magnetization then corresponds to a water-rich phase (an oil-rich phase), paramagnetism to a more or less random mixture of water and oil. In both cases, soap separates the oil molecules from the water molecules. The Curie temperature corresponds to the demixing temperature; for lower temperatures oil and water no longer mix homogeneously.

3. EQUILIBRIUM

To describe the results at finite temperatures we use Widom's notation $j = J/k_BT$ and $m = M/k_BT$ to describe the phase diagram. In three dimensions for $m = 0$ we get the second-order Ising transition at $j = 0.221656$ between a ferromagnet and a paramagnet. For negative m ferromagnetism is becoming more difficult, and the phase transition temperature is diminished (j increases). At about $j = 0.9$, $m = -0.09$ a higher order critical point is reached, and from then on the phase diagram becomes more complicated[8]. Near that higher-order point the interface tension gets very small[8], as required for microemulsions. We increase the positive ratio $r = -m/j$ and then for a fixed r decrease the temperature (increase j). Then for small r up to 0.1 we find the above-mentioned second order phase transition from paramagnetism to ferromagnetism. For large r we find first-order phase transitions to various periodic phases, like one plane of spins up, the next plane down, and so on in an up-down period of length two. These periodic phases are expected to depend on the lattice structure and are thus hardly realistic; we might identify them with liquid crystals. The transition between ferromagnets and paramagnets, on the other hand, is known to occur also without a lattice in a similar way[9] and thus is much less determined by the lattice approximation of the Widom model. Therefore for a discussion of microemulsions we restrict ourselves to ratios r between zero and about 0.1. (In two dimensions the phase diagram is similar but somewhat simpler[10,11].)

Most of the phase diagram of ref. 8 was confirmed by the simulations of ref. 12. Near $j = 1.1$, $m = -0.12$ some discrepancy appeared (ferromagnetism or layered phase ?), with ref.5 later reconfirming ref.8. With a low-temperature perturbation expansion, ref.12 found a phase with period six: Three planes of up spins followed by three planes of down spins, and so on. This phase was not found in the Monte Carlo simulations[8,5] perhaps because their temperature was not low enough. (Ref.11

gives the oil, water and soap concentrations as a function of j, m, and "magnetic field".)

Lots of recent Ising research concerns the behavior near solid walls, and also for the Widom model such simulations were made. In particular, is the correlation function (concentration profile) near the wall monotonic or oscillating? The simulations[13] indicate that the concentrations decay monotonically (oscillatory) in the paramagnetic phase if for the same interaction ratio r at lower temperatures the ordered phase is ferromagnetic (periodic). Perhaps only paramagnetic phases with oscillating correlations should be identified with the bicontinuous phase of microemulsions.

If the free space between the walls gets smaller and smaller, and the walls are replaced by a more disordered geometry, we have microemulsions in porous media: Oil and brine in rocks. The extreme limit is the randomly diluted Widom model, where single sites randomly either carry a spin ($S_i = \pm$) or are inert ($S_i = 0$). In this extremely fine "sand" the critical temperature was found to decrease roughly linearly with increasing sand concentration, until at some threshold is seems to vanish, in both two [19] and three[6] dimensions. Monte Carlo simulations are not very suited for the very low temperatures near that threshold; series expansions could be helpful here.

Microemulsions may produce micelles of a fixed size, that means small oil droplets surrounded by soap molecules and swimming freely in the water (or alternatively water drops in oil). Does the ferromagnetic phase of the Widom model show such micelles? Yes and no! The answer is yes if we regard a single spin as a nanodroplet of oil (or water). Then at low temperatures in the ferromagnetic region nearly all spins show in one direction, with very few *isolated* spins pointing oppositely. These isolated overturned spins then correspond to micelles. Of course, such "micelles" occur also in the simple Ising model. If, on the other hand, we identify the single spins with single molecules, then a micelle is a cluster of many parallel spins. And of course, again as in normal Ising models[14], such clusters do exist[8]. But the cluster size distribution decays monotonically whereas experimentally micelles seem to have a preferred size. Note that in molecular dynamics simulations[3] a peak in the cluster size distribution was observed only when the soap molecules were rather long, and not when they were short as in the Widom model.

Another disadvantage of the Widom model is the lack of the experimentally observed three-phase coexistence of oil-rich, water-rich, and bicontinuous phases. So far we may either have coexistence of water-rich and oil-rich phases

(magnetization up and magnetization down), or the bicontinuous phase (paramagnet) alone, since the phase transition is second order. (Ferromagnetic and layered phases may coexist but this is not what we are looking for.) If as a function of temperature one may get a first-order transition, then near that transition ferro- and paramagnet may coexist, leading to the desired three-phase coexistence in the microemulsion model. This property can be achieved by adding a four-spin interaction[15] to the energy.

4. DYNAMICS

This section discusses the bursting of soap bubbles, the mixing process, and electrical transport.

If we look at time-dependent effects we have to distinguish between models with fixed particle numbers (canonical ensemble) and those with fixed interaction constants J, M, magnetic field (grand canonical ensemble). The first method is computationally easier, the second more realistic. But also the first method is adequate if we study nucleation events proportional to exp(-energy/k_BT).

As we all know, soap bubbles burst after some time. Very thin soap films, called Newton black films, are thought to have a monolayer of water separated from the air (or a solid) by two layers of amphiphiles. We model this Newton black film by the Widom model (replacing oil by air in our interpretation). Thus we take one layer of down spins on top, one layer of up spins in the middle, and one layer of down spins at the bottom as our initial configuration of the film. In the simulations all these spins can flip up and down with the usual probabilities. The neighbor planes above the upper layer and below the lower layer are kept spin down. Thus initially we have a plane of water molecules separated from the surrounding air by soap.

This configuration was found in our simulations[13,16] to be metastable. Somewhere a hole (small cluster of down spins) is formed in the water layer which then grows and lets the soap bubble burst. However, the lower the temperature was, the longer was the lifetime of this configuration as is shown in Fig.1. For long lifetimes we see a nice Arrhenius law as in standard nucleation theories: lifetime proportional to exp(-E_0/k_BT) with some energy barrier E_0 which a hole has to overcome before it can grow and destroy the bubble. The lifetime is much shorter if initially we have already some down

spins also in the (predominantly up) center plane; with 20 percent such down spins the lifetime is very short. This behavior agrees qualitatively with that found experimentally by Exerowa and Kashchiev[17]; no such behavior was found for the simple Ising model, $M = 1$.

One difference between laboratory and computer experiment is that in the Widom model we did not find completely stable films whereas in experiments their lifetime was found to diverge at some critical water concentration in the central layer. While we had found (see previous sections) periodic layered phases in fully three-dimensional phases, the present set-up with only one water layer is different and apparently not stable. Indeed, when we increase the thickness of the simulated water layer [13] its lifetime increased drastically.

An entirely different question for microemulsions is: Given a vessel with oil on top, soap in the middle, and water at the bottom, how long does it take before we get a homogeneous (bicontinuous) phase ? Clearly, we now must use a canonical ensemble where molecules diffuse through the system. Since in the Widom model the molecules sit on the bonds between the spins, it is no longer sufficient (as it is in usual Ising models with fixed magnetization) to flip nearest neighbor antiparallel spin pairs. We must check that the number of up neighbors of the two spins to be flipped are equal (not counting the two spins to be flipped); and only if that is the case may we consider flipping both spins with the appropriate thermal probability.

As a result, the calculation is quite time consuming. Moreover, the relaxation to equilibrium is quite slow, roughly logarithmically in time[11], as also found in another model [18]. It would be interesting to make experiments to check this pseudo-logarithmic dependence which may arise from the superposition of many exponentially decaying Fourier components due to the normal diffusion law [11].

A third type of dynamics concerns electrical transport: When does an electric current flow through the microemulsion? A simple model assumes that only water carries the current. Then in the Widom model a continuous path of up spins is required to give a finite conductivity. Such percolation transitions are known[14] already in Ising models to be different from the demixing transitions. For the Widom model[20], electrical conduction sets in if the water concentration exceeds about 0.1. Gelatine dissolved in the nanodroplets may couple them to a rigid gel, which is then a third type of transition[20].

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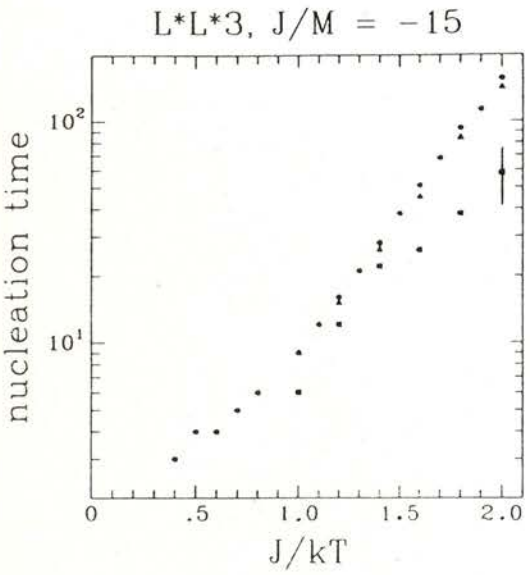

Fig.1: Nucleation time versus inverse temperature for large Widom films. A straight line corresponds to an Arrhenius law. The soap bubble is defined as bursting if the largest hole covers at least five percent of the total area[16].

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