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Monte Carlo simulations of spin-1/2 micelle and microemulsion models

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Résumé. — Le modèle de Widom de microémulsions est défini par un réseau cubique de spins d'Ising avec interactions ferromagnétiques de proche voisin, antiferromagnétiques de second voisin et antiferromagnétiques d'amplitude moitié à distance 2. Nous comparons les prédictions pour le diagramme de phase et les interfaces du groupe de Widom basées sur la théorie du champ moyen avec les résultats de nos simulations numériques. Nous trouvons qu'une des phases prédites est instable et, dans une autre, la température critique diffère d'un facteur 3. D'autres prédictions du champ moyen sont en bon accord avec nos simulations. Dans le cas de l'interface avec molécules amphiphiles entre *huile* et *eau*, nous observons de grandes largeurs à des températures plus élevées ; par ailleurs l'énergie d'interface s'annule à la limite de stabilité de la phase ferromagnétique à basse température, comme l'exige une description appropriée des microémulsions. Nous trouvons de grands amas dans le cas où le nombre de molécules, plutôt que leur potentiel chimique, est maintenu constant. Nous vérifions aussi les prédictions de Shnidman pour un modèle différent de solutions micellaires binaires et trouvons que ce modèle conduit également à des phases complexes.

Abstract. — The Widom model of microemulsions is defined by a spin-1/2 Ising simple cubic lattice with ferromagnetic nearest neighbor interactions, antiferromagnetic next-nearest neighbor interactions and half as strong antiferromagnetic interactions at distance = 2. We compare the mean-field predictions of the Widom group with our Monte Carlo simulations of the phase diagram and interfaces. One of the predicted phases is shown to be unstable, and in another the transition temperature differs by a factor 3. Other mean field predictions are in good agreement with our simulations. For the interface with amphiphilic molecules in between *oil* and *water* large widths are observed for higher temperatures, and the interface energy vanishes at the stability limit of the ferromagnetic phase at low temperatures, as is required for an appropriate description of microemulsions. Large clusters are found if the numbers of molecules, instead of their chemical potentials, are kept constant in the simulation. We also check Shnidman's predictions for a different model of binary micellar solutions and find that this model also leads to complex phases.

1. Introduction.

While water and oil are usually immiscible and have a large interface tension between them, *soap* (amphiphilic molecules) can drastically reduce this interface tension and facilitate the formation of invisibly small oil droplets immersed in water, or water droplets immersed in oil [1, 2]. Also more complex microemulsions can form. For computer simulations on a lattice, it is obviously possible to construct models [19, 24] where each lattice site can have three states, corresponding to water, oil or *soap*. Widom [1], on the other hand, used only two states,

spin up or *spin down* in magnetic language. Also Shnidman [2] suggested a different type of model based also on spin-1/2 lattice sites. In Widom's model, the molecules are identified with the bonds between two nearest neighbors on the lattice. Thus two neighboring up spins correspond to a water molecule in the original interpretation, two neighboring down spins to an oil molecule, and a pair of antiparallel neighbors to an amphiphilic molecule. In the latter case, the hydrophilic part of the amphiphile points in the direction of the up spin, and the hydrophobic part to the down spin. By construction, this model does not allow for oil molecules dissolved in water without amphiphiles surrounding them.

To allow for complex phases and low interface tensions, Widom's model consists of three types of

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interactions on the square or simple cubic lattice. Nearest neighbors are coupled *ferromagnetically* with an exchange energy $J > 0$, i.e. two neighboring spins prefer to be parallel. This facilitates the creation of like neighbors and hence the creation of water or oil molecules. In addition, the Widom model has antiferromagnetic interactions $2M < 0$ to next-nearest neighbors, which thus tend to be anti-parallel. Third, it has half as strong antiferromagnetic interactions $M < 0$ to the neighbors which are 2 lattice distances away. On the square lattice these latter neighbors are the third-nearest sites, whereas on the simple cubic lattice, the third-nearest neighbors have a distance $\sqrt{3}$ and are not coupled directly. The total interaction energy is therefore

$$E = -J \sum_{ij} S_i S_j - 2M \sum_{ij} S_i S_j - M \sum_{ij} S_i S_j \quad (1)$$

where $S = 1$ corresponds to up spins, $S = -1$ to down spins. The first sum goes over all pairs ($i < j$) of nearest neighbors, the second over all pairs ($i < j$) of next-nearest neighbors, and the third over all pairs ($i < j$) of neighbors which are two lattice constants apart. We neglect a *magnetic field* term which would correspond to a chemical potential difference between oil and water; in our simulations, up and down spins have equal rights. On the cubic lattice, each site has 6 nearest neighbors (J), 12 next-nearest neighbors ($2M$), and 6 distance = 2 neighbors (M). We refer the reader to reference [1] for a description and justification of this model.

If we neglect the antiferromagnetic interactions, i.e. for $M = 0$, we get the usual Ising model [3], with an oil-water miscibility gap vanishing on the simple cubic lattice at about $j = J/kT = 0.22$ ($j = 1/6$ in mean field theory). For temperatures below this critical *Curie* temperature, water and oil are not completely miscible and have a large interface tension. If instead we neglect the ferromagnetic interaction, $J = 0$, the lattice splits into decoupled sublattices with antiferromagnetic coupling between nearest and next-nearest neighbors on these sublattices. In three dimensions, these sublattices are face-centered cubic structures, and the fcc antiferromagnet with nearest and next-nearest neighbors has been studied extensively [4]. Its phase transition temperature seems to be near $m = M/kT = -0.6$, whereas mean field theory [5-7] predicts it to be at $m = -1/6$. This discrepancy by a factor 3 indicates, as was mentioned many years ago [4], that usual mean field theory does not seem capable of dealing with the complexity of the frustrated structure of the phases here.

The present paper thus aims to check by standard Monte Carlo simulations in three dimensions the predictions of mean field theory [5-7] for the Widom model [1]. In a preliminary note we pointed out that the nontrivial structure suggested in reference [1] for

most of the ordered microemulsion phase space was unstable on the square lattice [8]. The reply of the Widom group [9] suggests that the instability is mainly a two-dimensional problem due to rather strong fluctuations. Was this instability really a peculiarity of two dimensions? Is the phase diagram adequately described by mean field theory? How is the interface between the oil-rich and the water-rich phase structured? We first describe our simulation methods (section 2), then the stability problem (section 3), the phase diagram (section 4), the interface structure (section 5), and micelle formation (section 6). Section 7 looks at Shnidman's model, and section 8 summarizes our work. Parallel simulations of the Cornell group (K. A. Dawson, private communication) agree with some of our results.

2. Computational methods.

We used standard Monte Carlo [3] methods (one computer word per site) for our simulations on a SUN 3/50 work station, which made about 12 thousand spin flip attempts per second. Lattices up to $100 * 100 * 100$ (and $200 * 200 * 48$ for interfaces) were employed, with up to 10 000 sweeps through the lattice. We used helical boundary conditions and avoided any test for neighbors outside the lattice by storing the two uppermost and the two lowermost planes of the lattice in extra buffers. Lower-quality runs were also performed on smaller systems with periodic boundary conditions to confirm that the main results were not due to the spiral boundary condition. For our studies of the bulk phases, these buffers were updated after every sweep; for our interface studies they were kept in their original state (all spins up or all spins down) for the whole simulation, thus ensuring a certain stability for the interface. Initially, the spins were put into the suspected ground state configuration. Then we investigated each spin consecutively, flipping it with probability $1/(1 + \exp(\Delta E/kT))$ where ΔE is the energy change connected with that spin flip. The order parameter $\Psi(t)$ is then determined as a function of time t (in Monte Carlo steps per site) through the overlap with the initial configuration of the $N = L * L * L$ spins [10]:

$$\Psi(t) = \sum_i (S_i(t) S_i(0))/N. \quad (2)$$

In an investigation of ferromagnetism, where initially all spins are up, this order parameter is the magnetization. In some runs we also started with randomly oriented spins; then we checked visually for ordered structures or looked for instabilities in the energy (hysteresis).

We also employed a combination of Monte Carlo and mean field theory. The modified mean-field

theory adopted here allows for spatial fluctuations in the following manner : consider a lattice of sites and allow each spin to flip by standard Glauber dynamics. But now the energy change of the central spin is determined by

$$E_i = -JS_i \left(\sum S_j \right) * \mu$$

where μ is the average magnetization of the lattice (or more generally the order parameter Ψ). The method is identical to the standard Metropolis algorithm when the system is completely ordered, $\mu = 1$. This approach allows an efficient check of the complicated phase diagram and the relative stability of the ground states of the Widom model.

The Shnidman model was investigated on a VAX 11/780 using periodic boundary conditions.

In total, the present work without the runs used for reference [8] took about a thousand hours of CPU time.

3. Stability against interface formation.

In the standard Ising ferromagnet ($M = 0$) the order parameter relaxes first rapidly and then slowly towards its equilibrium state. In the Widom model, on the other hand, we found the order parameter Ψ often to be nearly stable and close to unity for a long time, until it decayed first slowly and then rapidly towards zero. Inspection of the resulting configurations on the square lattice [8] showed the reason : Due to zero interface energy, some supposed ground states can be unstable at any finite temperature. Specifically, we looked at quite strong antiferromagnetic coupling, $M/J = -2$, and with the initial state on the square lattice consisting of horizontal parallel lines of up spins alternating with parallel lines of down spins. Each line with up spins has upper and lower neighbor lines consisting of down spins only, and each down line is bordered by up lines. Thus on any vertical line, the spins alternate up and down. Widom [1] had originally suggested this layered structure for strong enough antiferromagnetic coupling.

After many Monte Carlo sweeps through the lattice, we still observed such horizontal layered domains. But they coexisted with domains layered vertically. Of course, the thermal energy of such layered structures is independent of their orientation, just as the thermal (free) energy of up and down domains in a ferromagnet is the same. Such ferromagnetic domains are stable because a large interface tension between up and down domains makes it energetically impossible to create huge domain walls by thermal fluctuations. In the Widom model, on the other hand, an elementary through tedious calculation at zero temperature showed [8] that the interface energy between vertical and hori-

zontal layers is exactly zero, independent of the ratio M/J . Thus at all finite temperatures, entropy effects will destroy the original single-domain ground state and will lead to the coexistence of many medium-sized domains of different orientations for the same layered structure : Long range order is destroyed, and the ground state is unstable at any finite temperature.

In three dimensions, we also found the structure of planes of up spins, adjacent to parallel planes of down spins, to be unstable : the interface energy between domains of horizontal planes and domains or vertical planes of parallel spins is exactly zero at zero temperature, independent of the ratio M/J . Thus again this structure is unstable at any finite temperature. This interface energy is zero not just at special values for the M/J , [6, 7, 11] but in the whole region of the phase diagram where the layers of horizontal planes of up spins adjacent to horizontal planes of down spins were thought to be stable. And this effect applies to both two and three dimensions.

We also looked at the other ground states suggested in reference [7], e.g. two parallel planes of up spins neighboring two parallel planes of down spins. Here we found a nonzero interface energy when horizontal layers meet vertical layers. This result does not prove that these configurations are stable at low temperatures. For there could be other ways in which different domains meet each other with zero interface energy. For example, on the square lattice, in addition to the 90 degree intersections of horizontal and vertical lines, also 45 degree intersections of horizontal and diagonal lines were also observed with zero interface energy, figure 1 of reference [8]. Similar but more complicated interfaces with zero energy might be possible for the other groundstates in three dimensions. We have not looked for them, but that does not prove that they do not exist.

All these stability problems seem to be related to the special choice of taking the next-nearest-neighbor antiferromagnetic coupling $2M$ ($\gamma = 2$) to be exactly twice as strong as the distance = 2 interaction M . With a ratio $\gamma = 3$ instead of 2, on the square lattice the formerly unstable lines were found numerically to be stable, and the exact evaluation of the zero-temperature interface energy gives a finite difference when comparing a single-domain ground state with the interface-states mentioned above. This effect was also found in 3 dimensions, for γ different from 2. The special property of the choice $\gamma = 2$ in the Widom model [1, 5, 7] was also noted in reference [11]; the special case $J = 0$, $\gamma = 2$, was pointed out many years ago [4]. Thus we will study below also the formerly unstable layers for $\gamma = 2.1$, when the *accidental* degeneracy at $\gamma = 2$ is removed and the layers have become stable.

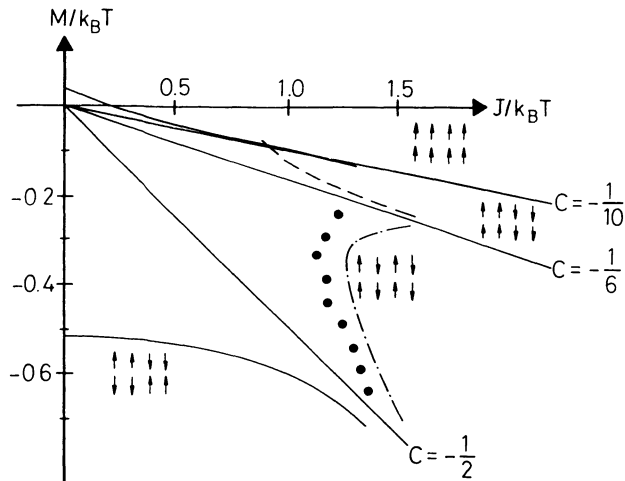


Fig. 1. — Phase diagram. The solid curve near the J axis gives the apparent stability limit for ferromagnetism, the dashed line that for the structure $\langle 2 \rangle$, the dashed-dotted line for $\langle 1 \rangle$, and the solid line in the lower part that for the structure $\langle 2:1 \rangle$. These structures are also symbolized by the unit cells of arrows; perpendicular to the paper plane, all spin orientations are the same. The dotted line shows how the dashed-dotted line is shifted if the parameter γ increases from 2 to 2.1. We also mark the lines of constant ratio $c = M/J = m/j$.

4. Phase diagram.

From now on we use the notation of reference 7 : $j = J/kT > 0$, $m = M/kT < 0$, $c = m/j$. A ground state denoted by $\langle i : m : n \rangle$ means periodicities $2i$, $2m$ and $2n$ in the three lattice directions. Thus in the first direction we have i up spins followed by i down spins, followed again by i up and i down spins, etc. If all spins in one direction are parallel, the corresponding infinite period is omitted in the $\langle imn \rangle$ symbol; thus $\langle 1 \rangle$ describes the unstable layered phase discussed in the previous section : in one direction we have up-down-up-down-up-down... ordering, in the other direction(s) all spins are parallel, for both the square and the simple cubic lattice.

Reference [7] gives for very low temperatures the following ground states :

all spins parallel $c > -1/10$ (3a)

$\langle 2 \rangle$ $\begin{matrix} + + - - + + - - + + \\ + + - - + + - - + + \\ + + - - + + - - + + \end{matrix}$ $-1/10 > c > -1/6$ (3b)

$\langle 1 \rangle$ $\begin{matrix} + - + - + - + - + - \\ + - + - + - + - + - \\ + - + - + - + - + - \end{matrix}$ $-1/6 > c > -1/2$ (3c)

$\langle 2:1 \rangle$ $\begin{matrix} - - + + - - + + - - \\ + + - - + + - - + + \\ - - + + - - + + - - \end{matrix}$ $-1/2 > c$. (3d)

In these four cases, all planes before and behind the plane of our schematic representation are ident-

ical to the plane shown. In addition, reference [7] has the structure $\langle 2:2 \rangle$ coexisting with $\langle 1 \rangle$, equation (3c), and the nonplanar structure $\langle 2:2:2 \rangle$ coexisting with $\langle 2:1 \rangle$, equation (3d). For the border cases like $c = -1/10$, one has additional possibilities : then ferromagnetism can coexist not only with $\langle 2 \rangle$ but also with $\langle 3 \rangle$, $\langle 4 \rangle$, ..., (but not $\langle 1 \rangle$), all having exactly the same ground state energy. Reference [7] predicts some of these phases like $\langle 3 \rangle$ to dominate at intermediate temperatures.

We started from one of the configurations shown in equation (3) in the appropriate parameter range for $c = m/j$ and then diminished m or j (i.e. heated up the lattice) until within the observation time the order parameter, equation (2), decayed towards zero. Infinite temperature corresponds to $m = j = 0$, and zero temperature to infinite m and j in this notation. Thus if hysteresis exists, our method finds the stability limit for superheating, not the one for undercooling. Our phase transition temperatures determined in this way mean that for higher temperatures the configurations are very different from the initial ground state ; they do not exclude that a different type of long-range ordering occurs for temperatures higher than this transition temperature, as predicted in reference [7] for some cases.

Figure 1 shows our effective transition temperatures, mostly based on 200 time steps in $20 * 20 * 20$ or $18 * 18 * 18$ systems, with an accuracy of about 0.02 for the transition value of m or j . 35 sequences of runs with increasing temperature were used for this diagram. In a few selected cases, we confirmed for $50 * 50 * 50$ or $48 * 48 * 48$ lattices and up to 1 000 time units the position of the phase transition. The border of the ferromagnetic region was already determined in reference [8] using $30 * 30 * 30$ systems and 10 000 time steps.

Near the lines $c = m/j = -1/2$ and $c = m/j = -1/6$ our results are qualitatively compatible with the mean field prediction [5] : the transition lines seem to go to infinity (zero temperature) there since other, more complicated, structures occur. No such effect, however, was observed near the crucial line $c = m/j = -1/10$, where ferromagnetism (oil-water) coexists with other ground states. The two transition lines for ferromagnetism and for the structure $\langle 2 \rangle$ cross each other near $j = 0.9$, $m = 0.087$, that is at temperatures about three times lower than mean field theory predicts. Actually, at $j = 1$, $m = -1/10$, we found within our numerical accuracy both the ferromagnetic state and the $\langle 2 \rangle$ configuration to be equally stable (see Fig. 4).

The structure $\langle 2:2:2 \rangle$ seems to be as stable as $\langle 2:1 \rangle$, whereas the stability region for $\langle 2:2 \rangle$ (tubes [25]) was smaller than for $\langle 1 \rangle$, and $\langle 3 \rangle$ seemed less stable than $\langle 2 \rangle$. We also looked at a modified Widom model where the ratio γ of next-nearest-neighbor interaction to distance = 2 interac-

tion was not 2 but 2.1. The resulting stability line for structure $\langle 1 \rangle$ is also shown in our figure 1. In this modified model the surface energy of horizontal planes meeting vertical planes no longer vanishes. Finally, the $\langle 2:2 \rangle$ structure with two parallel diagonals [8] of up spins neighboring two parallel down diagonals has at $\gamma = 2$, stability limits between that for $\langle 1 \rangle$ at $\gamma = 2$ and that for $\langle 1 \rangle$ at $\gamma = 2.1$.

We also looked for interesting structures at temperatures above our phase transitions, by starting with a random orientation of spins. For $j = 0.01$ and $m = -0.4$ as well as $j = 1$, $m = -0.55$, a $36 * 36 * 36$ lattice showed no indication of any long-range order by inspection ; however, parallel spins showed a certain tendency to align along straight lines. Figure 2 gives an impression of the sharpness of the transition involved : at $j = 0$ and $m \cong -0.51$ the order parameter decays first slowly, then rapidly towards zero whereas for $j = 0$, $m = -0.52$ it fluctuated about 0.977 for all 5 000 time steps. This transition thus seems to be first order, within the accuracy of this simulation ($50 * 50 * 50$ lattice). (Of course, nucleation thresholds at first order phase transitions always do slightly depend on the observation time). The resulting stability limit of about $m = -0.515$ for $j = 0$ agrees excellently with the simulations of figure 10 in reference [4] but disagrees by a factor 3 from the prediction $m = -1/6$ in the mean field theory of reference [7]. These results were also confirmed by the mean field Monte Carlo method described above.

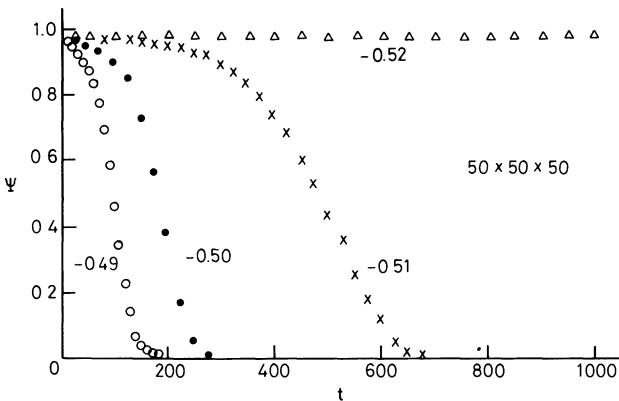


Fig. 2. — Decay of order parameter with time at $j = 0$, m near $-1/2$ as indicated by the numbers on the curves. The deviation from the pseudo-equilibrium value observed for short times seems to increase exponentially with time until the order parameter is appreciably reduced. We start with configuration $\langle 2:1 \rangle$ as marked in figure 1 for this region of the phase diagram.

Figure 3 shows hysteresis loops, or their absence, for selected values of the ratio $c = m/j$. The energy $-E$ per site, in units of J , is shown as a function of j for heating as well as for cooling curves (i.e. we

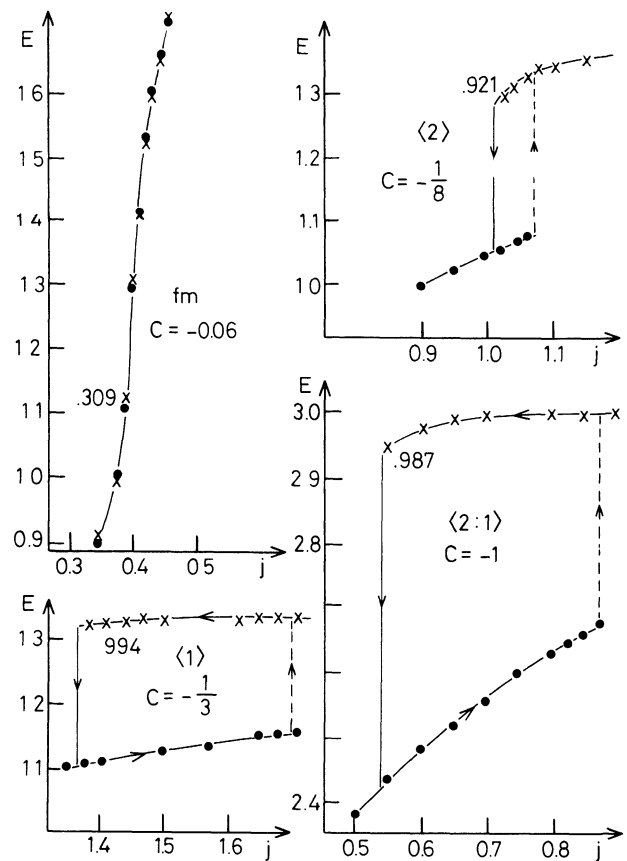


Fig. 3. — Hysteresis loops for various ratios $c = m/j$, as shown. We started either from a random configuration (dots) or from the ordered groundstate (\times), corresponding to that ratio c , as indicated by $fm =$ ferromagnetism, $\langle 2 \rangle$, $\langle 1 \rangle$, and $\langle 2:1 \rangle$. E is the negative energy per site and is 2.1, 1.375, 1.333, and 3, respectively, at zero temperature. Note that the temperature increases from the right to the left and that we use the same scaling of E and j for all four cases. The number in the upper left corners of the loops indicate the smallest observed nonzero order parameter.

started from either a completely ordered or a completely random configuration). At $c = -1/3$ and $c = -1$ we see strong hysteresis, for $c = -0.06$ we do not see it, and $c = -1/8$ shows weak hysteresis. Thus the transition from ferromagnetism to paramagnetism is second order, as expected, whereas the complex phases are bounded by first order transitions. (While the decay of the ordered phase was easy to observe, a complete built-up of order from a random initial state was observed only for simple ferromagnetism. The stability limit for the disordered phase was found by checking whether the negative energy E was stable or increased slowly with time). Typically we looked at 500 time steps for lattice sizes from $18 * 18 * 18$ to $100 * 100 * 100$. As a test, for $m = 0$ we got the usual second-order phase transition of the Ising model.

To find the equilibrium phase transition, where

the two states become stable, we created an interface in our system (Ref.[3], page 39) : half of the lattice started with the ordered phase, and in the other half the spins were initially random. Usually either the ordered or the disordered phase grew at the expense of the other in the later time development, as monitored by changes in the average order parameter Ψ . The equilibrium transition is defined as that point where both phases remained about equally strong in the subsequent time development. In the three first-order phase transition of figure 3, we found these transitions near $j = 1.04, 1.59$ and 0.69 for $c = -1/8, -1/3,$ and $-1,$ respectively ; for $j = 0$ it was near $m = -0.59$. For low temperatures near the line $c = -1/10$, the two ferromagnetic phases and the eight phases $\langle 2 \rangle$ seem to coexist in equilibrium. Phase $\langle 2 \rangle$, on the other hand, seems to win there over phase $\langle 3 \rangle$, which thus is missing in our phase diagram of figure 4. For example, along the line $c = -1/10$, we started with three phases (two interfaces) : ferromagnetism, $\langle 2 \rangle$ and $\langle 3 \rangle$, in a $96 * 96 * 96$ lattice : we found phase $\langle 3 \rangle$ always to shrink, for $1.1 \leq j \leq 1.6$ (see also Fig. 1).

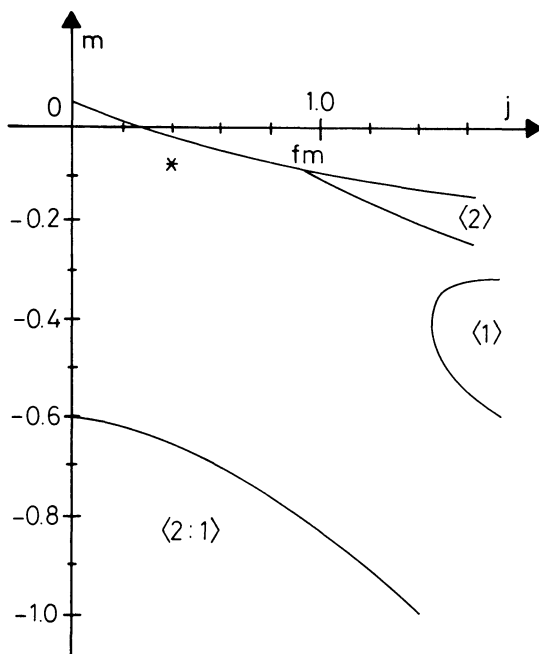


Fig. 4. — Equilibrium phase transitions (two-phase coexistence) between paramagnetic phase and the complex phases $\langle 2:1 \rangle$, $\langle 1 \rangle$ and $\langle 2 \rangle$. For the ferromagnetic (fm) phase, this transition line agrees with that of figure 3 (second-order transition). The star indicates the limit of phase $\langle 1 \rangle$ within the mean field approximation [7].

For applications to microemulsions, the crucial behavior seems to be ferromagnetism near $c = m/j = -1/10$ at low temperatures, where the domain wall energy between up and down ferromag-

netic domains vanishes [5, 6] at zero temperature proportional to $j + 10m$. For microemulsions, the ferromagnetic regime near that particular ratio of m/j corresponds to oil separated from water at zero temperature by a single layer of amphiphiles, with these soap molecules strongly diminishing the interface tension. At somewhat higher temperatures, there are a few amphiphiles and even fewer water molecules in the oil phase, and a few amphiphiles and fewer oil molecules in the water ; the interface separating them now becomes thicker (see next section). The ferromagnetic phases then correspond to water-in-oil or oil-in-water, whereas the « paramagnetic » or the $\langle 2 \rangle$ phase might be identified with the microemulsion phase.

5. Interfaces.

We have used lattices of size $L * L * H$ to study interfaces perpendicular to the z axis, where z varies from 1 to H . (Actually our z varies from -1 to $H + 2$ because of the four buffer planes). This work concentrated on the ferromagnetic phase but could be extended to the more complicated structures of equation (3) and the previous section. We determined the density profile where the density (z) is the fraction of up spins in a particular lattice plane. Initially all spins in the lower half were up and all spins in the upper half ($z > H/2$) were down :

$$+++++-----$$

Buffer spins with $z < 1$ always remain up, and buffer spins with $z > H$ always point down. The width W of the interface was determined through [12]

$$W^2 = \int z^2 w(z) dz - \left(\int z w(z) dz \right)^2 \quad (4a)$$

with the statistical weight given by the density gradient :

$$w(z) = - (d\rho/dz)/(\rho_1 - \rho_2) . \quad (4b)$$

Here ρ_1 and ρ_2 are the densities in the up and the down phase far away from the interface and the buffer planes at the ends of the sample. An alternative definition of the width W uses the maximum gradient :

$$W = (\rho_1 - \rho_2)/[-(d\rho/dz)]_{\max} . \quad (5)$$

In addition, we calculated the interface energy (not the interface tension which is a free energy) by comparing the system containing an interface with an otherwise identical system (even using the same random numbers) without an interface. For the latter system we took initially all spins up. The difference in the total average energies is then the interface energy.

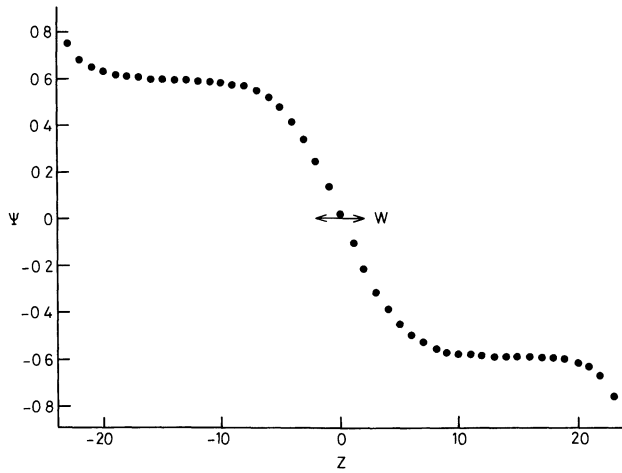


Fig. 5. — Interface profile $\rho = \psi$ near the ferromagnetic stability limit $j = 0.3$ $m = 0.01$. The computer needed two days to make 500 steps on the $200 * 200 * 48$ system. We show the probability of a spin to be oriented up, as a function of the position perpendicular to the interface. The interface width W from equation (4) is also shown. For each unit area of the lattice, the interface carries in the average 1.6 excess amphiphiles. The bulk phases consist of 67 % water (or oil), 24 % amphiphile, and 9 % oil (or water); for low temperatures at $j = 0.1$, $m = -0.01$, these percentages are 95, 3 and 2.

Figure 5 shows the density profile for high temperatures near the stability limit of ferromagnetism. At low temperatures ($j = 1$, $m = -0.1$) the profile is nearly sharp, with the density jumping from nearly $\rho = 1$ to nearly $\rho = -1$ if we go from one plane to the next. For microemulsions this situation corresponds to one monolayer of amphiphiles separating nearly pure water and oil. If we put in three amphiphiles between water and oil, that means a spin profile $+++--$, at the beginning of the simulation, this configuration quickly reverts to the sharp interface mentioned before. More complicated initial configurations, like

$+++++--+-$,

remain for a long time. (Note that

$++++-+-$

actually corresponds to bulk water in the bottom part, covered by a layer of amphiphiles, a layer of oil, an amphiphile layer, a water layer, another soap layer and then only oil on top; the distance between these layers is half a lattice constant. These molecules sit on the bonds of the lattice, not on the sites).

At higher temperatures, the density profile is more smooth and extends over several lattice constants. Additional interface planes inserted at the beginning, as described for lower temperatures, are quickly destroyed by the thermal fluctuations.

This difference between high and low temperatures is easily understood if we simply set $m = 0$. Then we have the usual three-dimensional Ising model, which has a finite small interface width for temperatures below the roughening temperature [12, 13] at about $j = 0.4$. For higher temperatures, the interface width increases logarithmically with the linear dimension L of the system. In addition, and presumably more important even at fixed lattice size the interface width increases with increasing temperatures because of the divergence of the intrinsic thickness (the correlation length) at the critical temperature of demixing. Apparently this behavior of the interface width is not restricted to $m = 0$ but also found in the microemulsion model with negative m : higher temperatures lead to a thicker interface. Also, if at $j = 0.3$, m decreases from zero to the phase transition at $m = -0.01$, the width

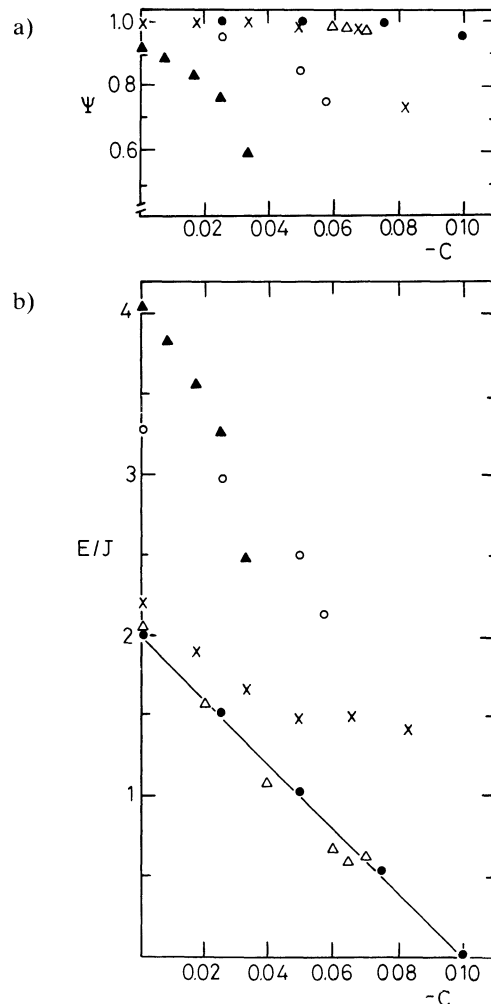


Fig. 6. — Order parameter Ψ (Fig. 6a) and surface energy E_s (Fig. 6b) (per unit area) for $j = 0.3$ (+), 0.4 (o), 0.6 (x), 0.8 (triangles), and 1.0 (dots), as a function of $c = m/j$ in the ferromagnetic region of the phase diagram between the J axis and the stability limit. The solid line for the surface energy is the exact ground-state result.

increases drastically. However, we found no clear evidence of an increase of the width with increasing lattice size for $j = 0.3$, $0 \geq m \geq -0.01$ near the stability limit.

The surface energy goes to zero, if at constant j , the parameter m approaches the stability limit for ferromagnetism at very low temperatures, as shown in figure 6. However, at higher temperatures it seems to increase near the stability limit since there the surface thickness is larger (second order transition to paramagnetism?). At low temperatures the variation of the interface energy with m is much smoother than that of the order parameter (density difference). By choosing parameters at low temperatures close to the stability limit one thus has a microemulsion model with an interface tension between oil and water which can be taken as low as one wishes, and still mostly pure water and pure oil in the adjacent phases as predicted by Widom [1] and Dawson [6]. Nevertheless we could not see drastic shape differences between the usual Ising clusters of overturned spins and the corresponding clusters in the present model; the latter ones might be somewhat more rectangular.

6. Micelle formation.

Real microemulsions may exhibit a phase of isolated micelles. These micelles may be oil droplets in water, coated by amphiphiles, or water droplets in oil, also coated by amphiphilic molecules. 50 to 100 Angstrom [23] is a typical size for these micelles. In the original formation of the Widom model, the bonds between sites represent single molecules and thus may be identified with a molecular diameter. Thus a micelle should be a geometrical structure of more than several lattice constants in diameter. In the simulations described above we rarely saw large droplets. However, this lack of large micelles may be just an artifact of the simulation method employed, not of the Widom model itself. For we worked in a grand canonical ensemble of constant chemical potentials, whereas real soap solutions have a fixed number of oil, water and surfactant molecules. Similarly, in the usual Ising model, simple computer simulations work with a fixed magnetic field (Glauber kinetics; fixed chemical potential in a lattice gas), whereas in a real fluid the number of molecules is fixed (Kawasaki kinetics). Starting with all spins up in a large Glauber model, we will not see any phase separation of liquid and gas. If we start with a random distribution of spins, we see such phase separation at low enough temperatures, but the size of the droplets grows in time until the whole system is one domain. With Kawasaki dynamics, where we shift a molecule (up spins) from one site to an empty neighbor site (down spin), we may end up with two large domains (of up and down magneti-

zations) which no longer grow in time. None of these methods gives numerous droplets with size independent of time.

For microemulsions the situation is different. If most of the material is water, but we have oil and more surfactant in the system than can be dissolved in the water, then oil and surfactant molecules must somehow cluster together. If the water-oil interface tension is very low due to surfactant molecules at the interface, then it is energetically more favorable to have many large oil droplets (coated with a monolayer of surfactant) than one huge oil phase. The number of droplets and their size must be such that all soap molecules which cannot be dissolved in the water are used up in coating the oil droplets. In this way, the micellar phase should be seen if we work with fixed numbers of soap, oil and water molecules and select the concentrations suitably.

This type of canonical ensemble is not easily realized in the Widom model, since there the molecules are represented by bonds between the spins, not by the spins themselves. Keeping the number of up spins fixed, as in a Kawasaki model, would not keep any of the number of molecules fixed. We thus try a simpler version where only the amphiphile concentration is fixed, whereas oil and water molecules can be *created* or *annihilated* as before. (One could imagine a microemulsion in contact with is water vapor.) Since each soap molecule corresponds to a pair of up-down neighbor spins, a simulation with constant numbers of amphiphiles is thus a simulation at constant nearest-neighbor interaction energy. We thus consider a spin for flipping if and only if it has as many up as down spins as nearest neighbors. Only if up and down neighbors cancel each other, do we calculate the interaction energy with the next-nearest and distance = 2 neighbors and flip the spin according to the appropriate Boltzmann probabilities, as before. Because of these interactions with more distant neighbors and because of sequential instead of simultaneous updating, our simulation differs from the $Q2R$ cellular automat [18].

To get a clear picture of possible micelles, we simulated this Widom model with constant amphiphile concentration on the square instead of the simple cubic lattice. Since most spins cannot be flipped, the simulation of each spin flip attempt is about ten times faster now than the above simulation on the cubic lattice. To combine a low amphiphile concentration with a high initial oil concentration, we started with double rows of up spins (oil) separated by ten rows of down spins (water), and then flipped 3 percent of all spins randomly. Figure 7 shows our results, corresponding to an amphiphile concentration of about 13%. We see that the initial linear structure is quickly dissolved into a few large and quite random looking domains, which do not

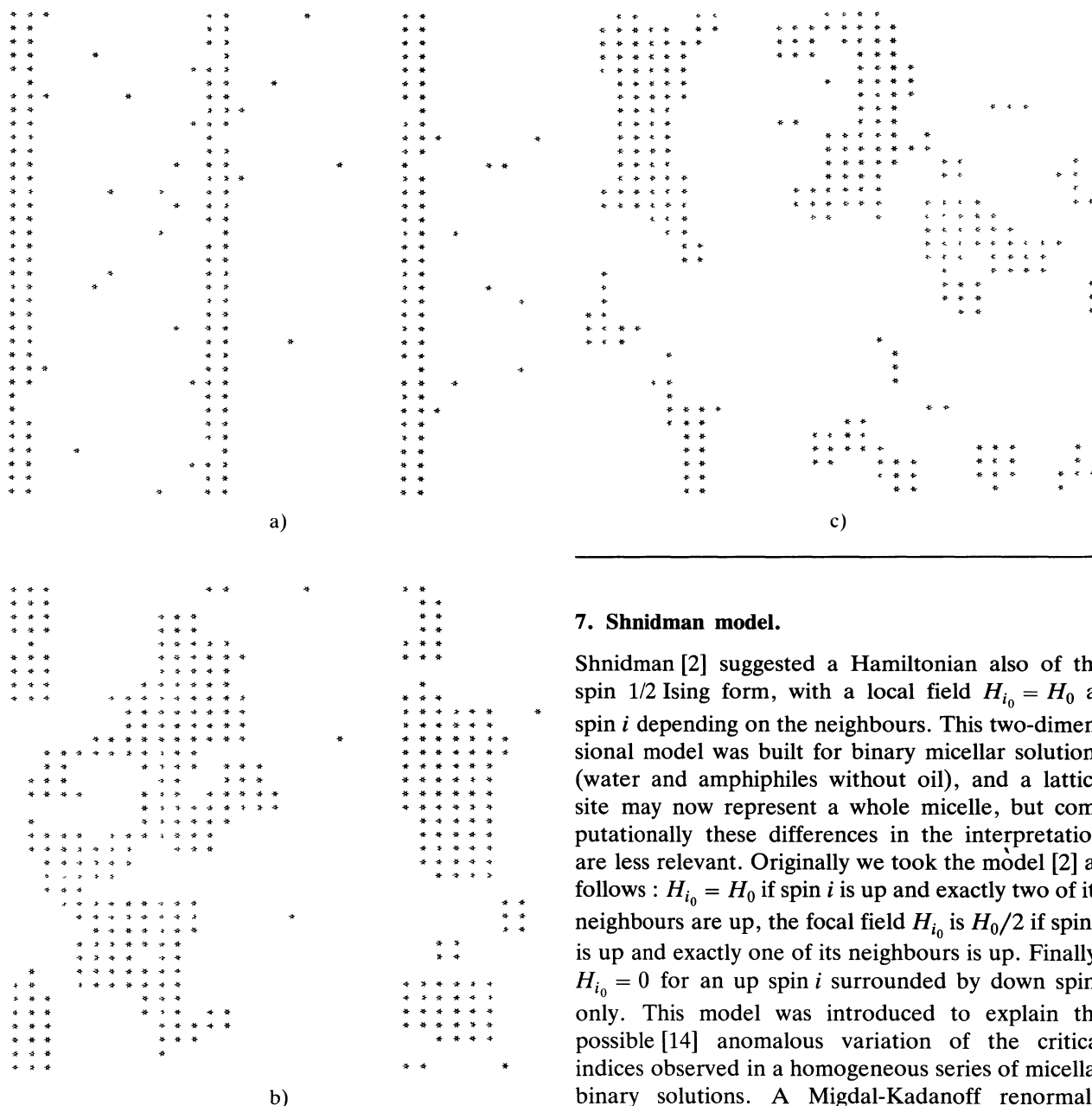


Fig. 7. — Formation of micelles in a simulation at fixed number of amphiphiles. Starting from an artificial initial configuration (Fig. 7a), rather large domains of up spins (stars) have developed after 1 000 time steps (Fig. 7b) which no longer increase even after 1 000 000 time steps (Fig. 7c). This simulation was made for a 36×36 square lattice.

grow with time even when one million Monte Carlo steps per spin are made. This model thus displays at least some aspects of micelle formation: large domains are formed, the size of which does not grow in time.

In this sense we may identify the ferromagnetic phase with solutions of separated micelles, and the various layered or more complicated phases with bicontinuous microemulsions.

7. Shnidman model.

Shnidman [2] suggested a Hamiltonian also of the spin 1/2 Ising form, with a local field $H_{i_0} = H_0$ at spin i depending on the neighbours. This two-dimensional model was built for binary micellar solutions (water and amphiphiles without oil), and a lattice site may now represent a whole micelle, but computationally these differences in the interpretation are less relevant. Originally we took the model [2] as follows: $H_{i_0} = H_0$ if spin i is up and exactly two of its neighbours are up, the focal field H_{i_0} is $H_0/2$ if spin i is up and exactly one of its neighbours is up. Finally, $H_{i_0} = 0$ for an up spin i surrounded by down spins only. This model was introduced to explain the possible [14] anomalous variation of the critical indices observed in a homogeneous series of micellar binary solutions. A Migdal-Kadanoff renormalization group transformation in which H_0 played the role of a marginal operator was utilized by Shnidman to determine the varying critical exponents as a function of H_0 .

This result was questioned by Caflisch *et al.* [15] who concluded that the only critical fixed point in this model is the Ising critical point, without genuine non-universality. Reatto [16] pointed out that in the renormalization analysis the field H_0 should also be renormalized, and then the only-nontrivial fixed point obtained within the Migdal-Kadanoff *RG* is the Ising critical point. He also suggested a transformation (slightly different from Shnidman's) such that H_{i_0} becomes a multispin interaction. The corresponding *RG* analysis was not actually performed in reference [16], and since these arguments are not rigorous, the question remained unresolved. Similarly, also Crisanti and Peliti [17] questioned the

reliability of Shnidman's renormalization transformations. Our Monte Carlo simulation intends to clarify these controversies.

In this model we found on the square lattice for $H_0 = 0.01$ (in units of kT) a behavior similar to the Ising model without a field, and for larger $H_0 = 0.1$ and 0.2 a non-zero magnetization, as for Ising ferromagnets in a field. We visually examined the configurations, starting from random spin orientations, for the presence of other ground states and found no features distinguishable from that of a normal Ising model in a weak magnetic field; no onset of periodicity was found. Thus we confirm the conclusions of references [15-17]: the only critical point in this model seems to be $H_0 = 0$, the normal Ising transition. This result did not change if we require for $H_{i_0} = H_0$ the two up neighbors to be on opposite sides of the central up spin and $H_{i_0} = 0$ if they formed a corner [16].

Shnidman and Zia [21] have suggested further refinements to the Hamiltonian descriptions of the micellar binary systems. They suggest now a ferromagnetic interaction between distance = 2 pairs. Then e.g. the square lattice may be considered as four interpenetrating sublattices. For zero coupling

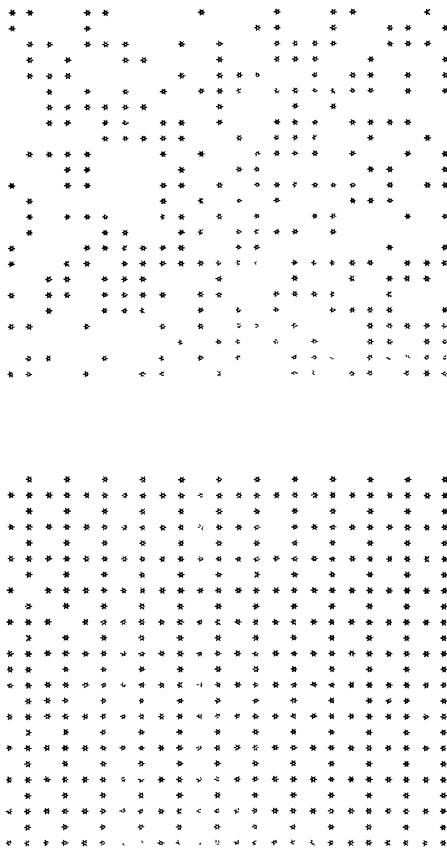


Fig. 8. — Non-trivial phase observed in the refined Shnidman model, where we started from a random configuration (top) and end up with an ordering structure after 100 times steps.

between these sublattices there are 16 possible groundstates. In some sense this model is reminiscent of the 8-vertex model, where there are two interpenetrating sublattices with only ferromagnetic interaction and a 4-spin interaction coupling the two sublattices [22]. The strength of the 4-spin interaction determines the continuously varying critical exponents, and in the language of renormalization group we have a line of fixed points. It remains open, however, whether this refined Hamiltonian shares this property with the 8-vertex model. Our Monte Carlo simulations now show phases clearly distinct from the ferromagnetic ones. For example, figure 8 shows the state observed for $K_0 = K_1 = 1.15$ and $J = 0.47$ in units of kT , using the notation of reference [21] without the factor \tilde{t} in equation (4) there. Similar pictures were obtained, at different parameters, with \tilde{t} included. This full model [21] orders chess board like for $K_0 = K_1 = 0$ and $J > 1.05$; for $K_0 = 0$ and $0 < K_1/kT < 1$, the transition point for J shifts only slightly to higher values. The full phase diagram and the critical properties of this model requires further study.

8. Summary.

The Widom model has a lot of complicated properties, which presumably are not all related to microemulsions. Crucial is the fact, that near $c = m/j = -1/10$ at low temperature, and for larger m/j ratios at higher temperatures, the stability of the ferromagnetic phase (separation of oil and water) ends. For more negative c , the preferred phase is the structure $\langle 2 \rangle$, which corresponds to consecutive planes of three monolayers of oil, one of amphiphiles, three monolayers of water *bonds*, one of amphiphiles, again oil, amphiphile, ... When heated, the ferromagnetic phase ends in a second-order phase transition, whereas the various *microemulsion phases* (complex structures) end with first order transitions including hysteresis and a jump in the energy. The oil-water interface energy goes to (nearly) zero if c decreases towards that stability limit, at low temperatures.

We have also shown that at least one of the phases predicted by mean field theory is unstable and that the position of the transition sometimes differs quite strongly from the result of our computer experiment. Many qualitative aspects of mean field theory, and in particular the importance of the value $c = m/j = -0.1$, have been confirmed. The ferromagnetic transition line was quite accurately predicted by mean field theory [1, 5, 7] whereas for the complex phases the errors are larger.

Of course, the Widom and Shnidman models are not the only theories for microemulsions. There are spin-1 descriptions, where each site can be in one of three states [19, 24] and also more phenomenological

models, as reviewed in reference [20]. Actually, the model of reference [19] reduces to the Widom model with general γ and nonzero *magnetic field*, if one assumes the parameters H and Δ of reference [19] to be positive, equal and very large. The Widom model thus seems to us the most simple description,

whereas more complicated models might be more realistic. It remains to be seen which model is best for membranes and soap bubbles [26].

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