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Lifetime of Newton black films. A mean field analysis

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Résumé. — En utilisant l'approximation du champ moyen, nous avons calculé le temps de vie des bicouches qui sont thermodynamiquement instables pour une configuration initiale particulière dans le modèle de Widom pour les micro-émulsions. Pour des configurations initiales identiques de ce modèle de bicouches, nous étudions la dépendance du temps de vie en fonction de la magnétisation initiale de la couche centrale, de la température, et l'élasticité de la membrane amphiphilique.

Abstract. — Using a mean field approximation we calculate the lifetime of thermodynamically unstable bilayers of a specific initial conformation in the Widom model of microemulsions. For identical initial conformations of these model bilayers, we study the dependence of the lifetime on the initial magnetization of the central layer, the temperature, and the elastic curvature of the amphiphilic membrane.

1. Introduction.

Membrane, foam and emulsion bilayers are interesting examples of matter organized in two dimensions. These bilayers comprise two monolayers of amphiphile molecules (lipids or synthetic surface-active agents called surfactants, for example) which stick fast to each other. Amphiphile bilayers generally form at the boundary between two contacting phases which may be equivalent or different. In systems with highly developed interfaces, for instance foams, emulsions and suspensions, contact between the bubbles (in foams), the droplets (in emulsions) and the solid particles (in suspensions) is made through thin liquid films which are stabilized with surfactants. These films can gradually become thinner until they transform into very thin liquid films which are called « black » because they reflect virtually no light. The black films are thinner than about 20 nm, and in many cases they can consist of just monolayers of surfactant molecules. The stability of disperse systems depends on the stability of thin liquid films, and this may explain why these films have been an important object of study. The structures of amphiphilic membranes have been an active field of current research [1]. These membranes consist of either « monolayers » or « bilayers » [2] of

amphiphilic molecules. Monolayers of amphiphilic molecules appear, for example, in microemulsions [3], whereas bilayers of these molecules form most of the biological cells [4]. Significant progress has been made over the last few years in understanding the thermodynamic phases of complex fluids containing amphiphilic membranes [5]. Part of this work has been possible by using a class of models defined on a lattice [6]. The simplest lattice model of ternary microemulsions (oil plus water plus amphiphiles) is the Widom model [7]. The phase diagram of this model [8] and some generalized versions [9] of its are now well known. The structures of such systems confined in model pores by rigid walls have also been investigated [10]. There are several well-known regimes of parameters in the Widom model where the bilayers are thermodynamically unstable. Theoretical and experimental results on the stability and permeability of membrane, foam and emulsion bilayers are given by Exerowa *et al.* [11]. The lifetime of such unstable model bilayers has been studied using Monte Carlo simulations by Chowdhury and Stauffer [12]. The rupture mechanism of Newton black films (NBFs) is described by Chowdhury and Stauffer [13] using Monte Carlo simulations. The purpose of this paper is to study the dependence of the lifetime of such unstable model bilayers on the initial magnetization of the central layer, the temperature and the curvature elasticity of the amphiphilic membrane. The dynamical aspects of the Widom model of microemulsions is studied using the mean field approximation. The paper is organized as follows: in section 2 we describe the model and method, results and discussion are presented in section 3.

2. Model and method.

2.1 MODEL. — In Widom's model the molecules are identified with the bonds between two nearest neighbors on the lattice. Thus two neighboring up spins $\uparrow\uparrow$ correspond to a water molecule in the original interpretation, two neighboring down spins $\downarrow\downarrow$ 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 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 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, Widom's model has antiferromagnetic interactions $2M < 0$ to next-nearest neighbors, which thus tend to be antiparallel. Third, it has half as strong antiferromagnetic interactions $M < 0$ to the neighbors which are 2 lattice distances away. On the square lattice these neighbors are the third-nearest neighbors, have distance $\sqrt{3}$ and are not coupled directly. Since both in-plane and out-of-plane bonds correspond to molecules in Widom's model there are $2L$ layers of molecules corresponding to L lattice planes containing the spins. Widom's prescription for computing the curvature energy [14] of the amphiphilic membranes on discrete lattices gives rise to non-vanishing interaction between the second- and the fourth-neighbor spin pairs on a simple-cubic lattice in addition to those between the nearest-neighbor ones. The total interaction energy is given by

$$H = -J \sum_{NN} S_i S_j - 2M \sum_{2NN} S_i S_k - M \sum_{4NN} S_i S_\ell \quad (1)$$

where the summation in the first, second, and the third terms are to be carried out over, respectively, the nearest-neighbor (NN), second-neighbor (2 NN), and the fourth-neighbor (4 NN) spin pairs on a simple-cubic lattice. $S = 1$ corresponds to up spins, $S = -1$ to down spins. The interaction $J > 0$ is ferromagnetic whereas $M < 0$ is antiferromagnetic. We neglect

a magnetic field term which corresponds to a chemical potential difference between oil and water ; in our calculations, up and down spins have equal rights. The nonzero interaction M is essential to assign bending energy to the amphiphilic membranes in Widom's model (Gaussian curvature energy is not included [15] in (1)). 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 [7], for a description and justification of this model. We work with the parameters $j = J/K_B T$, $m = M/K_B T$, and $r = m/j = M/J$, where T is the temperature and K_B is the Boltzmann constant. The disordered fluid phase corresponds to the paramagnetic phase whereas the oil-rich and the water-rich phases correspond to the ferromagnetic phases of the spin system with positive and negative magnetization, respectively. It is now well established that in the parameter regime $-0.1 < r < 0$ the equilibrium structure of Widom's model is oil rich (water drops in oil) or water rich (oil drops in water) provided j is larger than a critical value j_c [12]. Therefore if a bilayer is created artificially in the system in this parameter regime, it would certainly be unstable. Using mean field theory we have studied the dependence of the lifetime of such unstable bilayers on the initial magnetization of the central layer $m_2(0)$ (i.e. the concentration of the amphiphilic molecules) as well as on T and m .

We now specify the initial structure and conformation of the model bilayers [12]. The system consists of Ising spins on a simple cubic lattice. A fraction C_0 of the spins in the central plane are initially in the down state (i.e. $-1 \leq m_2(0) \leq 0$), whereas all the other spins in the system are initially in the up state (see Fig. 1). The nearest neighbor bonds between the spins in the layer ($z = 3$) and the layer ($z = 2$) and those between the spins in the layer ($z = 2$) and the layer ($z = 1$) together represent a bilayer with an initial concentration C_0 of the amphiphilic molecules. There is a single layer containing water in between the two monolayers of amphiphiles constituting the bilayer. The spins in the two uppermost and the two lowermost lattice planes are kept « frozen » in the up state throughout the temporal evolution of the system in our mean field approximation. As a consequence of the Glauber dynamics the number of amphiphilic molecules in the model bilayer is not conserved during its temporal evolution. This case is examined by Chowdhry and Stauffer [13] using Monte Carlo simulations.

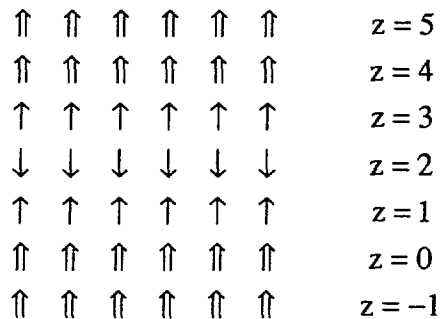


Fig. 1. — A schematic representation of the cross section of the initial configuration of the spin system in the XZ plane. This spin configuration corresponds to a bilayer with $C_0 = 1$ (i.e. $m_1(0) = m_3(0) = 1$, and $m_2(0) = -1$). The symbols \uparrow and \downarrow represent the spins which are up-dated, whereas the spins represented by $\uparrow\uparrow$ are kept frozen in their initial state.

2.2 MEAN FIELD APPROXIMATION. — We consider the spins of the system described by the Hamiltonian (1) which is represented by the spin variable (S_i). They also interact with a large heat bath, at a constant temperature which will not be treated explicitly. The heat bath

functions only in giving rise to spontaneous flips of spins by exchanging the energy. Using the mean field method, the equations of motion are given by :

$$\gamma \frac{dm_z}{dt} = -m_z + \tanh \left\{ \beta J [r(m_{z-2} + m_{z+2}) + (1+8r)(m_{z-1} + m_{z+1}) + (4+12r)m_z] \right\} \quad (2)$$

with $z = 1, 2, 3$ and the initial conditions $m_z(t=0) = m_z(0)$, and the boundary conditions $m_{-1}(t) = m_0(t) = m_4(t) = m_5(t) = 1$.

The functional free energy of the system is given by :

$$F[m_z] = \sum_{z=1}^3 \left\{ \frac{T}{2J} [(1+m_z) \text{Ln}(1+m_z) + (1-m_z) \text{Ln}(1-m_z) - 2 \text{Ln}(2)] - \frac{m_z}{2} (r(m_{z-2} + m_{z+2}) + (1+8r)(m_{z-1} + m_{z+1}) + (4+12r)m_z) \right\}. \quad (3)$$

At the global minimum of (3), the magnetization per site in the layer z is $\langle S_z \rangle = m_z^{\text{min}}$ and the free energy of the system is $F = F[m_z^{\text{min}}]$. If we define the function $f(m_z)$ as follows,

$$f(m_z) = \tanh \left\{ \beta J [r(m_{z-2} + m_{z+2}) + (1+8r)(m_{z-1} + m_{z+1}) + (4+12r)m_z] \right\} \quad (4)$$

equations (2) become :

$$\int_{m_z(0)}^{m_z(t)} \frac{dm_z}{m_z - f(m_z)} = -\frac{t}{\gamma} \quad (5)$$

Using the general trapezes formula [17], the magnetizations are given by :

$$m_z(t) = m_z(0) - \frac{\frac{Nt}{\gamma}}{\frac{m_z(0) + m_z(t)}{2} + \sum_{i=1}^{N-1} \frac{1}{x_{i,z} - f(x_{i,z})}} \quad z = 1, 2, 3 \quad (6)$$

where $x_{i,z} = m_z(0) + i \frac{m_z(t) - m_z(0)}{N}$ and N is the subdivision number of the interval $[m_z(0), m_z(t)]$. Equations (6) are solved by iteration. Different initial guesses can lead to two solutions, namely

$$m_1(t) > 0, \quad m_2(t) > 0, \quad m_3(t) > 0 \quad \text{or} \quad m_1(t) > 0, \quad m_2(t) < 0, \quad m_3(t) > 0.$$

the one which makes the variational functional (3) smallest is selected as the global minimum.

3. Results and discussion.

The equilibrium configuration of the model (1) under the boundary conditions mentioned in figure 1 [12] is an oil rich fluid (ferromagnetic in the spin terminology) for j higher than a critical value j_c in the range $0 < r < -0.1$. Therefore, the bilayer created in the system by the choice of the initial spin configuration is unstable. We are interested in the lifetime of such unstable bilayers. We implement the time evolution of the system by updating the magnetizations of the three central layers according to equations (6). As a consequence of the Glauber dynamics the number of amphiphilic molecules in the model bilayer is not conserved

during its temporal evolution. However the rupture of the bilayer is defined in our mean field approximation by the transition of the magnetization of the central lattice plane from a negative to a positive value. Hence we define the lifetime (τ) of the bilayers by the following properties,

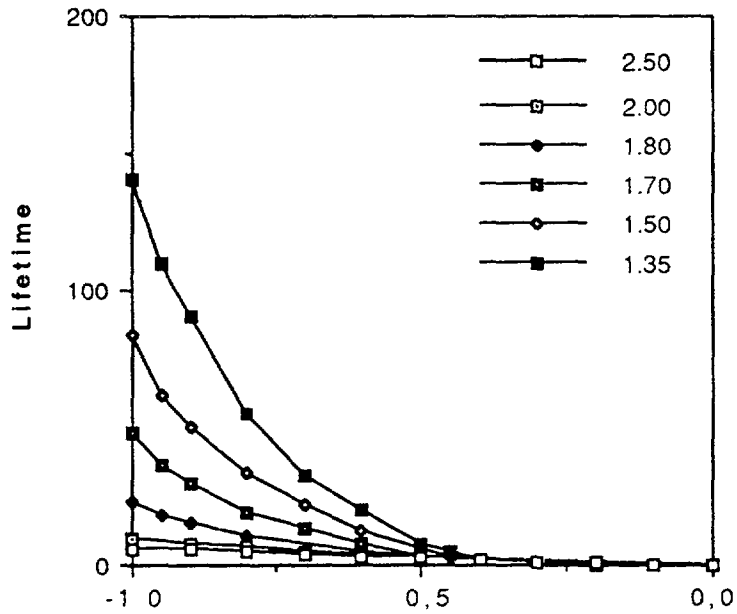
$$\begin{cases} m_1(t) = m_3(t) > 0 & \text{and } m_2(t) < 0 & \text{for } t < \tau \\ m_1(t) = m_3(t) > 0 & \text{and } m_2(t) > 0 & \text{for } t > \tau . \end{cases} \quad (7)$$

In order to study the lifetime of the model bilayers as a function of $m_2(0)$ at several temperatures we have computed τ for $m_2(0) = -0.1$ to $m_2(0) = -1.0$ by varying j and m along the line $r = \text{const}$, where the numerical value of the constant was chosen arbitrarily. We compare our results to those of the Monte Carlo simulations of reference [13]. For this, r is chosen to be $-\frac{1}{15}$. In figure 2a the lifetime τ is shown as a function of $m_2(0)$ for several values of j . Higher j (and m) corresponds to a lower temperature. At any given finite temperature, τ is small for small and intermediate values of $m_2(0)$ but increases sharply near $m_2(0) = -1.0$. The lifetime of the model bilayer is maximum at $m_2(0) = -1.0$. Moreover, for a given initial magnetization $m_2(0)$, $\tau(T)$ decreases when increasing temperature in agreement with Monte Carlo simulations results [12]. The lifetime calculated with mean field approximation is greater than that of Monte Carlo simulations for a fixed temperature T .

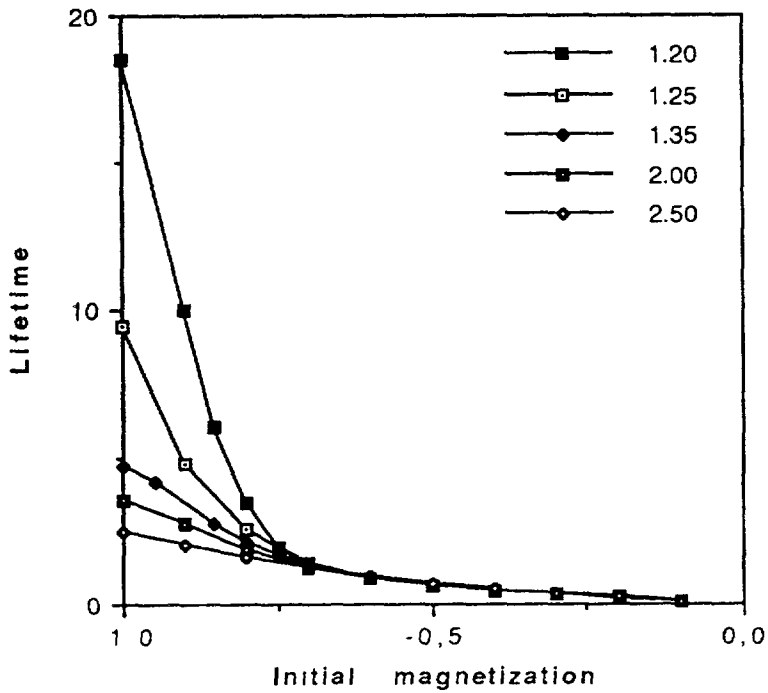
As explained in reference [12], nonzero M distinguishes an amphiphilic membrane from an interface in the Ising model. In order to show that we are observing dynamical properties of membranes and not those of interfaces in the Ising model we have represented τ as a function of $m_2(0)$ for the same numerical values of j as those of figure 2 a but always keeping $m=0$ (Ising model). We find that both the qualitative as well as quantitative features of $\tau(m_2(0))$ data for the model (1) are quite different from those for a simple Ising model but in agreement with Monte Carlo simulations. When $m = 0$, $\tau(m_2(0))$ is much smaller than check for $m \neq 0$, and for a given $m_2(0)$, τ is almost independent of T for all $m_2(0)$ smaller than a certain initial magnetization of the central lattice plane (see Fig. 2b). In fact, we observed that even for $m_2(0) = -0.5$, τ is almost independent of temperature when j is varied over an order of magnitude. Thus $\tau(m_2(0) = -0.5) = 0.44$ for $j = 4$ whereas $\tau(m_2(0) = -0.5) = 0.74$ for $j = 0.5$. This must be contrasted with $\tau(m_2(0) = -1) = 9.45$ for $j = 0.8$ and $\tau(m_2(0) = -1) \approx 2.475$ for $j = 0.5$. In order to compare quantitatively our results, obtained by the mean field approximation, with those of the Monte Carlo simulations we give the lifetime of some initial concentration for $j = 0.4$ and $m = 0$. $\tau(m_2(0) = -0.95) \approx 2.085$ for mean field approximation, whereas $\tau(m_2(0) = -0.95) \approx 1.86$ for Monte Carlo simulations [12]. In order to study the dependence of τ on m within the mean field approximation, we have kept j fixed at an arbitrarily chosen value $j = 1/1.5$ and computed τ for several values of m (see fig. 3). The dependence of the lifetime τ on the temperature, for several values of the initial central magnetization $m_2(0)$, and fixed value of $r = -\frac{1}{15}$ is represented in figure 4, from which it is clear that the lifetime τ increases with increasing temperature. In agreement with the results of Monte Carlo simulations, we find that τ increases when increasing $|m|$. Thus, $|m|$, tends to stabilize the model bilayer (1).

4. Conclusion.

Using a simple mean field theory that is a good approximation to Monte Carlo results we have studied the dependence of the lifetime on the initial magnetization of the central lattice plane of thermodynamically unstable bilayers of a specific initial conformation in Widom's model of microemulsions. The lifetime of this bilayer is an increasing function of the initial



a)



b)

Fig. 2. — The lifetime τ of the bilayer dependence on the initial magnetization $m_i(0)$ for different temperatures, and (a) $r = -\frac{1}{15}$, (b) $r = 0$. The number accompanying each curve denotes the value of the temperature.

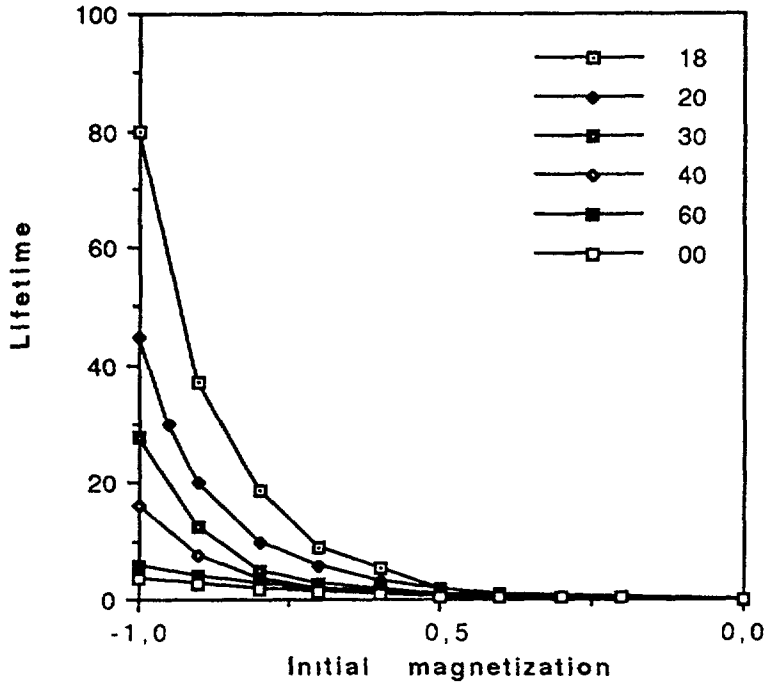


Fig. 3. — The lifetime τ of the bilayer dependence on the initial magnetization $m_2(0)$ at a fixed value of temperature ($T/J = 1.5$). The number accompanying each curve is the value of $(-1/r)$.

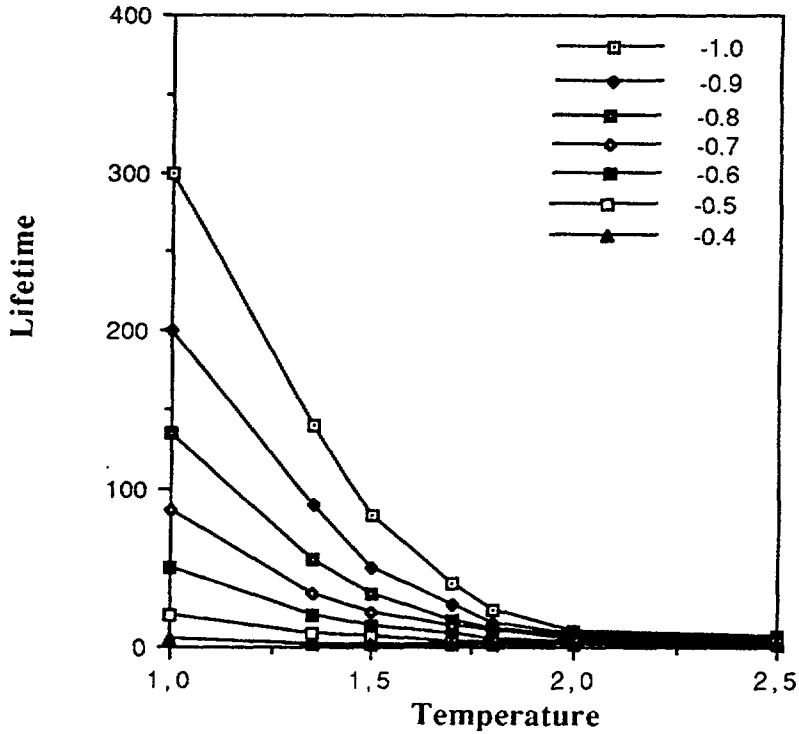


Fig. 4. — The lifetime τ of the bilayer dependence on the temperature for a fixed value of the ratio $r = -1/15$. The number accompanying each curve denotes the value of the initial magnetization $m_2(0)$.

concentration, and decreases with increasing temperature. Our results are in agreement with experiments of Exerowa *et al.* [11] and Monte Carlo simulations [12].

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