IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Boundary effects on a spin-model: microemulsions in a confined geometry

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys. A: Math. Gen. 24 L677

(http://iopscience.iop.org/0305-4470/24/12/004)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 01/06/2010 at 11:15

Please note that terms and conditions apply.

J Phys A. Math Gen. 24 (1991) L677–L683 Printed in the UK

LETTER TO THE EDITOR

Boundary effects on a spin model: microemulsions in a confined geometry

Debashish Chowdhury† and Dietrich Stauffer

Institut für Theoretische Physik, Universität zu Köln, Zülpicher Strasse 77, D-5000 Köln 41, Federal Republic of Germany

Received 17 April 1991

Abstract. Widom formulated a lattice model of microemulsions in terms of a spin-1/2 Ising system with nearest-neighbour ferromagnetic interaction and further-neighbour antiferromagnetic interactions. Through Monte Carlo simulation of the Widom model on a simple cubic lattice of size $L_x \times L_y \times L_z$ we have investigated the surface effects on the structure by imposing physically-motivated boundary conditions. In an interesting range of the interaction parameters we have observed novel structures in the 'narrow-gap geometry', i.e., $L_z \ll L_x = L_y$, when L_z is of the order of a few lattice constants.

Surface effects on the various phase transitions have been an active field of research in statistical mechanics [1]. Many 'universal' features of these effects have been discovered and most of the simple prototype systems have been thoroughly investigated. Moreover, several non-universal features of the effects of confining surfaces on simple fluids [2] as well as some complex fluids [3] have also received attention during the last few years. We are interested here in some general (non-universal) features of the surface effects on a spin model defined on a simple cubic lattice. This model, called the Widom model [4], was originally introduced as a model for ternary microemulsions [5]. Recently, Hansen *et al* [6] have proposed a generalization of the Widom model by adding a specific form of four-spin interaction so as to make the phase diagram of the model more realistic. We introduce the surfaces through appropriate choice of the boundary conditions in our Monte Carlo simulations of these models. We treat the walls in the same spirit as those in the earlier works on lattice gas models of confined simple fluids [2]. Our main interest here is in the 'narrow-gap' geometry where the thickness of the system is much smaller than both its length and breadth. Such narrow-gap 'slits' are regarded as model pores in porous media [2]. The novel structures that we observe in the narrow-gap geometry in our MC simulation are quite different from the corresponding structures in the wide-gap geometry for identical strengths of the interaction parameters. Our investigation not only contributes to the basic understanding of phase ordering in confined systems but our results may also find application in oil extraction technology [7] where oil, brine (a solution of inorganic salts in water) and surfactants form a complex fluid like the microemulsion [8].

† On leave from the School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India.

0305-4470/91/120677+07$03.50 © 1991 IOP Publishing Ltd

For the sake of completeness let us define the lattice models under investigation in this letter and summarize the main features of the phase diagrams of these models; these will be used subsequently to understand the effects of the confining walls on these phases. The Hamiltonian of the Widom model is given by

$$\mathcal{H} = -J\sum S_i S_j - 2M\sum S_i S_k - M\sum S_i S_l \qquad (1)$$

where the summations in the first, second and the third terms are to be carried out over, respectively, the nearest-neighbour, second-neighbour and fourth-neighbour spin pairs on a simple cubic lattice. The interaction $J > 0$ is ferromagnetic whereas $M < 0$ is antiferromagnetic; the limit $M = 0$ corresponds to the standard Ising model on a simple cubic lattice. It is often convenient to work with the parameters $j = J/k_B T$ and $m = M/k_B T$ where T is the temperature and k_B is the Bolzmann constant. The phase diagram of this model in the j, m plane has been studied extensively [9, 10]; the nature of the ordering depends on the ratio $r = m/j$, as expected. The high-temperature phase is paramagnetic for all values of j and m. The low-temperature equilibrium phase along all the lines for which $0 > r > -1/10$ is ferromagnetic whereas that along all lines with $-1/10 > r > -1/6$ is a layered structure. In the latter phase the successive spins are ordered like .... ↑↑↓↓↑↑↓↓ .. . in one direction but in the other two directions all spins are mutually parallel; hence the symbol $< 2 >$ is used to describe this phase. The transition from the paramagnetic phase to the ferromagnetic phase is second order whereas that between the other phases is first order.

Let us now briefly mention how a ternary microemulsion is modelled by this spin Hamiltonian [4]. Suppose, the system consists of oil, water and amphiphilic molecules, the latter being the surfactants. The nearest-neighbour ↑↑ pairs describe oil molecules and ↓↓ pairs describe water molecules whereas both ↑↓ and ↓↑ pairs correspond to amphiphilic molecules. It should also be noted that since both the in-plane bonds and the out-of-plane bonds correspond to molecules in the Widom model there are $2L$ layers of molecules corresponding to L lattice planes containing the spins. The disordered fluid phase corresponds to the paramagnetic phase whereas the oil-rich and water-rich phases correspond to the two ferromagnetic phases of the spin system with, respectively, positive and negative magnetizations. The layered phase $< 2 >$ corresponds to three layers of oil-rich fluid followed by an amphiphile-rich layer which, in turn, is followed by three layers of water-rich fluid followed by another amphiphile-rich layer, and so on.

We carry out MC simulation of the three-dimensional Widom model on a simple cubic lattice of size $L_x \times L_y \times L_z$ where the size of each of the molecules of oil, water and amphiphiles is identical to the lattice constant a. The confining walls are parallel to the XY plane so that L_z is the number of lattice planes, containing flippable spins, parallel to the walls. We are mainly interested in the 'narrow-gap' geometry where $L_z \ll L_x = L_y$. Our aim is to investigate if the structures observed in such a geometry are different from those in the 'wide-gap' geometry which corresponds to $L_x = L_y = L_z \gg 1$. In order to investigate the surface effects one must begin by defining the interactions of the spins with the surfaces of the confining walls. We can imagine three ideal situations:

(i) '*Oil-soaked*' walls; in this case the wall has an attractive interaction with oil and repulsive interaction with water. In the spin terminology, the wall prefers up-spin neighbours to down-spin ones. This type of wall–spin interactions can be modelled by assuming that the wall itself consists of 2 lattice planes of up spins at the top

and 2 planes of up spins at the bottom all of which are kept 'frozen' throughout the simulation (these four boundary planes are not counted for L_z).

(ii) '*Soap-soaked*' walls; in this case every spin in the 4 confining planes (2 at the top and 2 at the bottom) is surrounded by antiparallel in-plane neighbours as well as an antiparallel neighbour in the adjacent frozen plane. The soap-soaked walls represent those which attract only the amphiphilic molecules.

(iii) '*Dry walls*'; the wall neither attracts nor repels any of the three molecular species; it merely acts like an inert boundary. In this case the spins in the two successive lattice planes adjacent to the two walls have fewer neighbours than those deep inside the bulk. This situation can be effectively modelled by assigning $S = 0$ to each of the spins in the 4 lattice planes constituting the upper and the lower walls.

To summarize, we apply three types of rigid boundary conditions in the Z direction. However, periodic (actually, for efficient vectorization of the computer code on CRAY-YMP and NEC-SX3, helical) boundary conditions are applied in the X and Y directions.

We compute the equilibrium concentration profile of the three molecular species, namely, oil, water and amphiphiles, along the Z direction on the lattice. Let us denote the concentrations of oil, water and amphiphiles by the symbols $C_O(\ell), C_W(\ell)$ and $C_A(\ell)$, respectively, in the ℓth molecular layer, measured from the upper boundary. Suppose, $C_s(\ell)$ is the concentration of the molecular species s in the ℓth molecular layer and $C_s(\infty)$ is that in the bulk at very large (effectively infinite) distance from both the uppermost and the lowermost boundaries. Then, $C_s(\ell) - C_s(\infty)$ is a quantitative measure of the deviation from the bulk ordering caused by the walls.

In our MC runs often the initial spin configurations are chosen so as to minimize the time required for equilibration, always taking care that no spurious metastable configuration is introduced by the choice of the initial configuration. In fact, often we check that more than one initial configurations (in one of these all spins were up and in another randomly up and down with equal probability) lead to identical results within the statistical fluctuations of the data. We equilibrate the spin system by letting it evolve following Glauber single-spin-flip dynamics and then compute the concentrations of the molecules of the three species in every layer perpendicular to the Z direction. In our study of the Widom model we vary the temperature along fixed lines $r = m/j$ = constant.

Most of our calculations are carried out for systems with $L_x = L_y = 22$. We find that, within the statistical fluctuations of our data, identical results are obtained by using systems with larger length and breadth. All the results in the narrow-gap geometry are obtained by averaging the data over 5 MC runs for each set of values of the parameters. Our preliminary computations on the Widom model have been carried out on the SUN workstations with a maximum speed of 0.04 million updates per second (MUPS). Most of the production runs have been made using the CRAY-YMP at the supercomputer center HLRZ at Julich; the maximum speed of computation [11] achieved with only one processor is approximately 3.6 MUPS, nearly three times slower than the Köln University NEC-SX3 for this model.

We observe that in the wide-gap geometry even in the paramagnetic phase, not too far from its limit of stability, the oil-soaked walls enforce short-ranged order, characteristic of the corresponding low-temperature phase, close to the walls. All the features of the concentration profiles we observe in the wide-gap geometry are consistent with the corresponding results obtained earlier by MC simulation [10] with

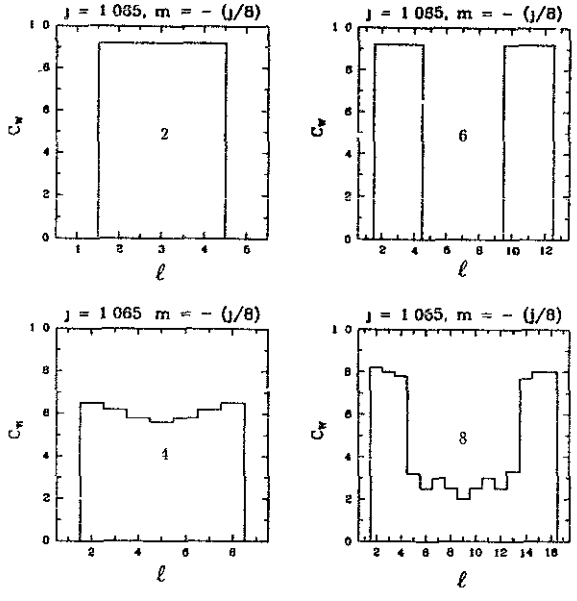

Figure 1. Concentration profile of water in the presence of *oil-soaked* walls in the narrow-gap geometry The labels 2, 4, 6 and 8 are the thicknesses L_z of the spin system measured in the units of the lattice constant. The strengths of the interaction parameters are $j = 1\,065$ and $m = -(j/8)$. Note that for $L_z = 2$ and $L_z = 6$ the periodicity of the oscillation is consistent with the periodicity of the structured phase $< 2 >$ exhibited by the spin system in the wide-gap geometry for the same values of the interaction parameters, whereas the concave-shaped middle portions of the profiles observed for $L_z = 4$ and $L_z = 8$ do not exhibit this periodicity. Note the change of scale for ℓ along the X axis

periodic boundary conditions in all the three directions. In contrast to the constructive influence of the oil-soaked walls, the soap-soaked walls have a destructive influence on the ordering in the confined system. This effect is, of course, expected on simple physical grounds.

In the parameter regime $-1/10 > r > -1/6$, where the structure $< 2 >$ is observed in the wide-gap geometry, we observe quite different novel structures in the narrow-gap geometry for intermediate values of j. As an example, we have shown in figure 1 the concentration profiles for $j = 1.065$ ($m = -(j/8)$) for several different values of L_z ($L_z = 2n$, with $n = 1, 2, 3, 4$). Since the molecules sit on the bonds between the nearest-neighbour spins, $L_z = 2n$ means that the layer index ℓ runs from 1 to $4n + 1$ for the molecules between the walls. Interestingly, although the structures observed are also consistent with that of the $< 2 >$ phase for odd n the structures observed for even n are quite different (figure 1). When L_z is an even multiple of 2 the system prefers, for energetic reasons, to have majority of the spins in the two layers adjacent to both the oil-soaked walls in the down state. Consequently, the system is filled with a water-rich fluid if $L_z = 4$. For the same reason, the central portion of the $L_z = 8$ system is oil-rich.

Novel structures are also observed in case of soap-soaked walls for intermediate values of j. As an example, we show the concentration profiles of water and oil with

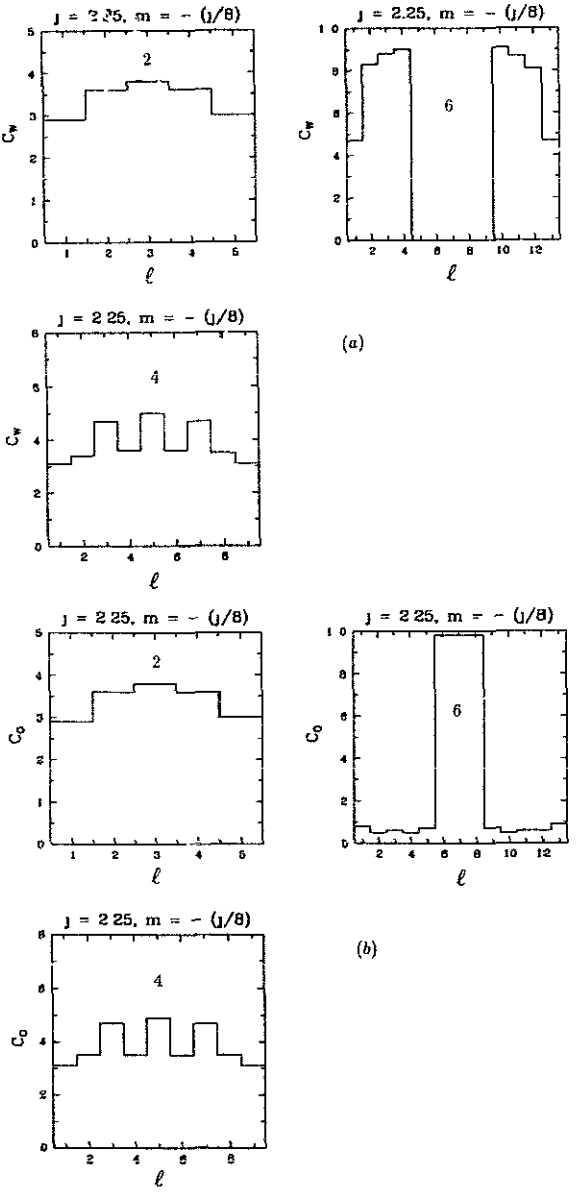

Figure 2. Concentration profiles of (*a*) water and (*b*) oil in the presence of it soap-soaked walls in the narrow-gap geometry. The labels 2, 4 and 6 are the thicknesses L_z of the spin system measured in the units of the lattice constant. The strengths of the interaction parameters are $j = 2.25$ and $m = -(j/8)$. Note that for $L_z = 2$ and $L_z = 6$ the periodicity of the oscillation are consistent with the periodicity of the structured phase $< 2 >$ exhibited by the spin system in the wide-gap geometry; however, the structure observed for $L_z = 4$ is quite novel. Note the scale change along both the axes.

soap-soaked walls for $j = 2.25$ in figures 2(*a*) and (*b*). Note that the structure for $L_z = 4$ is specially interesting as it does not exhibit the periodicity of the structure $< 2 >$.

In cases of oil-soaked walls as well as soap-soaked walls we also observe that with the gradual increase of j (keeping r fixed) the system gradually adjusts the relative concentrations of oil and water in the various layers so as to deform the structure smoothly over to the structure $< 2 >$ in the limit $j \to \infty$ (i.e., $T \to 0$). For example, for both types of walls the structures observed in our simulation for $m = -(j/8)$ with $j = 4.0$ is almost indistinguishable from that observed in the wide-gap geometry.

The dry walls have a trivial effect on the nature of the ordering; the ordering gets weakened near the walls because of lower interaction energy. For example, for $j = 1.065$ and $m = -(j/8)$ the concentration of water in the water-rich layers adjacent to the walls are lower than that in the water-rich layers closer to the middle of the pore. Similarly, the concentration of oil in the oil-rich layers also decreases as we move from the centre of the pore towards the walls. Consequently, for the same values of the interaction parameters the order characteristic of the $< 2 >$ phase is observed in a $22 \times 22 \times L_z$ system only if L_z is at least 14.

In summary, we have studied the effects of the confining walls on the equilibrium structure of a specific spin system which was introduced originally by Widom to represent ternary microemulsions in bulk. In two earlier studies [11, 12] of the Widom model on randomly diluted lattices a finite fraction of all the lattice sites were 'dry' ($S = 0$); in this scenario 'pores' could be as small as the molecular size. Thus, the effects of the pores on microemulsions have been incorporated more realistically in our model ($L_x = L_y \gg L_z > 1$) than those in [11, 12]. However, we must point out that we have considered only single 'pores' in the form of 'slits' [2]; the real porous materials, of course, consist of an interconnected network of pores of various shapes and sizes. Moreover, quantitative comparison with future experiments may also require re-investigation of the surface effects using more realistic models of microemulsions, e.g., the spin-1 model [5]. In this letter we have focused attention on the narrow-gap geometry. In fact, the pores in our study were so narrow that it is more appropriate to designate these as micropores [13]. Only the main results for the Widom model have been summarized in this letter. For the generalized Widom model [6] we have observed similar effects of the walls when the structure corresponding to the wide-gap geometry was layered. The details of our results will be reported elsewhere [14].

We thank Amnon Aharony and David Andelman for suggesting this work, Alex Hansen and Michael Schick for valuable discussions, the referee for useful comments, Alexander von Humboldt Stiftung (for a fellowship to DC) and the joint German-Norwegian Research Cooperation (through the grant BMFT-0326657D) for financial support and Supercomputer Center HLRZ, Jülich, for Cray time.

References

[1] Binder K 1983 *Phase Transition and Critical Phenomena* vol 8, ed C Domb and J L Lebowitz (New York: Academic) p 1
Diehl H W 1986 *Phase Transition and Critical Phenomena* vol 10, ed C Domb and J L Lebowitz (New York: Academic) p 75

[2] For reviews see
Evans R 1990 *J. Phys.: Condens. Matter* **2** 8989
Sarman S 1990 *Liquids at Interfaces (Les Houches XLVIII)* ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: North-Holland)
[3] Wertheim M S, Blum L and Bratko D 1990 *Micellar Solutions and Microemulsions* ed S H Chen and R Rajagopalan (Berlin: Springer)
[4] Widom B 1986 *J. Chem. Phys.* **84** 6943
[5] For a recent review of the lattice models of microemulsions, see
Gompper G and Schick M 1991 *Modern Ideas and Problems in Amphiphilic Science* ed W M Gelbart, D Roux and A Ben-Shaul, in press
see also Schick M 1991 *Physica* **172A** 200
[6] Hansen A, Schick M and Stauffer D 1991 *Preprint*
[7] Healy R N and Reed R L 1974 *Soc. Pet. Engng J.* **14** 491; 1977 *Soc. Pet. Engng J.* **17** 129
[8] Neumann H J and Paczynska-Lahme B 1988 *Prog. Colloid Polymer Sci.* **77** 123
[9] Dawson K A 1987 *Phys. Rev.* A **35** 1766
Dawson K A, Lipkin M D and Widom B 1988 *J. Chem. Phys.* **88** 5149
Widom B 1989 *J. Chem. Phys.* **90** 2437
Dawson K A, Walker B L and Berera A 1990 *Physica* **165A** 320
Levin Y and Dawson K A 1990 *Phys. Rev.* A **42** 1976
Berera A and Dawson K A 1990 *Phys. Rev.* A **42** 3618
[10] Jan N and Stauffer D 1988 *J. Physique* **49** 623
[11] Stauffer D, Ho J S and Sahimi M 1991 *J. Chem. Phys.* **94** 1385
[12] Velgakis M J 1989 *Physica* **159A** 167
[13] Powles J G, Dornford-Smith A and Evans W A B 1991 *Phys. Rev. Lett.* **66** 1177
[14] Chowdhury D and Stauffer D 1991 to be published