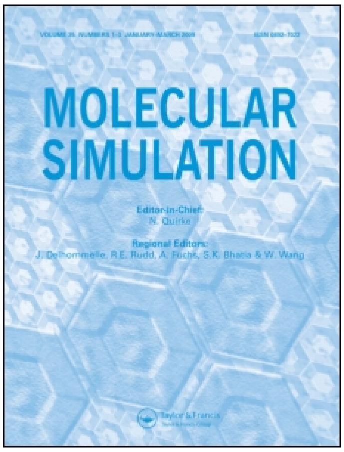

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Self Assembly of Bilayers in a Lattice Model of Amphiphile and Solvent Systems

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Preliminary Communication

SELF ASSEMBLY OF BILAYERS IN A LATTICE MODEL OF AMPHIPHILE AND SOLVENT SYSTEMS

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The results of a Metropolis Monte Carlo simulation of a three dimensional lattice model of an amphiphile and solvent mixture are presented. In the model each amphiphile molecule is represented as a connected chain of lattice sites with one site representing the head and the remaining chain sites representing the tail of the molecule. The remaining sites on the lattice represent solvent molecules. The amphiphiles interact through a nearest neighbour potential which includes head-solvent and tail-solvent interactions. No prior assumption is made about the structures which may be observed.

The cluster size distribution and cluster structure is studied as a function of temperature and head-solvent interaction. If the tail-solvent interaction is solvophobic and the head-solvent interaction is solvophilic, a micellar region is observed in the phase diagram. For sufficiently solvophilic head-solvent interactions the low temperature phase exhibits self assembly into castellated bilayer structures.

KEY WORDS: Amphiphile, lattice model, self assembly, bilayer, micelle.

1. INTRODUCTION

Amphiphilic materials display a rich variety of phases when dissolved in a suitable solvent and are of great importance in chemical and biological systems, with lipid bilayers being of fundamental importance in forming biological interfaces. There is much experimental evidence for the properties of amphiphilic materials [e.g. 11], but the theory of micellar association and the self assembly of bilayers is much less advanced.

There is an extensive literature on the use of lattice models to describe three phase microemulsions [e.g. 5]. In these models the surfactant is usually represented as a single bond or site in an Ising type model. This approach is satisfactory in regions of the phase diagram where the correlation length is much greater than the size of an amphiphile and hence the structure of the amphiphile can be ignored. However, the formation of micelles and the detailed structure of bilayers depends closely upon the packing of the amphiphile chains. This can be studied by considering chains constrained on a lattice and such systems have been considered in a mean field approximation [e.g. 1, 9]. These authors derive results for the amphiphile packing and bond order parameters. Haan and Pratt [7] have carried out Metropolis Monte Carlo simulations on a set of chains on a diamond lattice constrained to form a connected micellar structure. We report here preliminary results from a Metropolis Monte Carlo simulation of a three dimensional lattice model in which the amphiphiles are represented by chains and allowed to assemble freely into the preferred microstructure. The system shows self assembly into bilayer and micellar structures.

2. METHOD

We consider a lattice model [3, 4] of an amphiphile and solvent mixture which represents an incompressible solution of N_A amphiphile molecules and N_S solvent molecules. The molecules occupy the sites of a regular lattice with coordination number c. Each amphiphilic molecule is represented by a flexible chain of s adjacent sites with one site on the end of the chain representing the solvophilic head and the remaining $(s - 1)$ representing the flexible solvophobic tail. Each chain segment is considered to represent several repeat units in a real amphiphilic molecule. The remaining sites in the lattice represent solvent molecules. There are no unoccupied sites. The total number of sites on the lattice is $M = sN_A + N_S$. If only nearest neighbour interactions are assumed and the chains are assumed fully flexible, the potential energy of the system may be written:-

$$\frac{U}{kT} = \beta\,(n_{TS} + \gamma n_{HS} + \eta n_{HH})$$

where n_{TS}, n_{HS} and n_{HH} are the total number of tail-solvent, head-solvent and head-head bonds. The parameter β is the ratio of the tail-solvent energy to kT, γ is the ratio of the head-solvent bond energy to the tail-solvent bond energy and η is the ratio of the head-head bond energy to the tail-solvent bond energy. It can be shown [2], that the lattice imposes constraints on the number of each type of possible bond and that for nearest neighbour interactions there are only three independent bond parameters. In order to represent normal amphiphilic behaviour, the tail-solvent interaction is chosen to be solvophobic ($\beta > 0$) and the head-solvent interaction is chosen to be solvophilic ($\gamma < 0$).

In the work presented here the above model has been simulated using the Metropolis [10] Monte Carlo technique on a simple cubic ($c = 6$) lattice with $32 \times 32 \times 32$ lattice sites. The simulations have been carried out for 512 amphiphiles and hence an effective volume concentration of 4.7%. Each amphiphile has one head segment and two tail segments ($s = 3$) and periodic boundary conditions are assumed. We also set $\eta = 0$ and hence ignore head-head interactions.

The system is cooled in temperature steps of $\beta^{-1} = 0.01$ from a high temperature configuration in which the amphiphiles are placed randomly on the lattice. The last configuration at each temperature forms the starting configuration at the next temperature. The simulation follows earlier work in two dimensions [3] in making no prior assumptions about the form of the structures which may be observed. A similar assumption is made by Larson [8] in a lattice model of a three phase system. At each temperature approximately 3×10^8 attempted moves were performed with one tenth of the moves being discarded for thermalisation. The cluster size distribution was determined every 512×10^3 attempted moves and hence a thermal average for this quantity determined. The simulation was repeated for several values of γ, the head-solvent interaction. The amphiphiles were moved using reptation moves and the cluster counting was carried out using an 'ant' technique [e.g. 6]. The simulation was performed on an array of 12 transputers.

3. RESULTS

The results for the three dimensional lattice are found in general to be consistent with the two dimensional results although higher transition temperatures are observed and the amphiphiles have greater freedom of movement so that equilibrium appears to be reached more easily.

For all values of γ it is found that at high temperatures the amphiphiles remain principally monomeric. When the head-solvent interaction $\gamma = 1$, which corresponds to solvophobic interaction, the system shows normal phase separation at some critical temperature and the amphiphiles form a single large, compact cluster. When $\gamma = -1.0$ the system exhibits a temperature region where micelle like clusters exist. A typical cluster size distribution is shown in Figure 1 and it can be seen that it shows a weak minimum similar to that observed in two dimensions.

At low temperatures for $\gamma = -1.0$ and $\gamma = -1.6$ it is interesting to note that a castellated bilayer structure self assembles. This is shown in Figures 2 and 3. Analogous structures were observed in the two dimensional simulation [3].

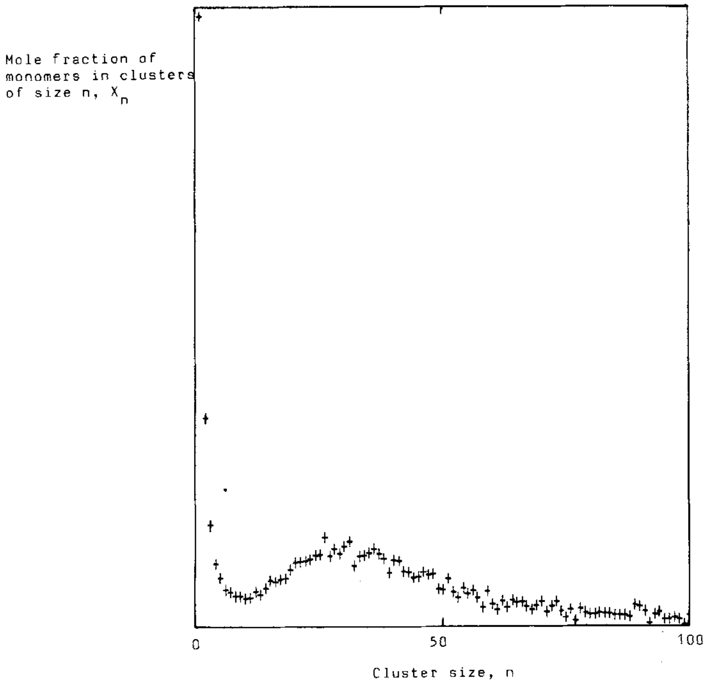

Figure 1 Cluster size distribution at reduced temperature $\beta^{-1} = 0.93$ for head solvent interaction $\gamma = -1.0$.

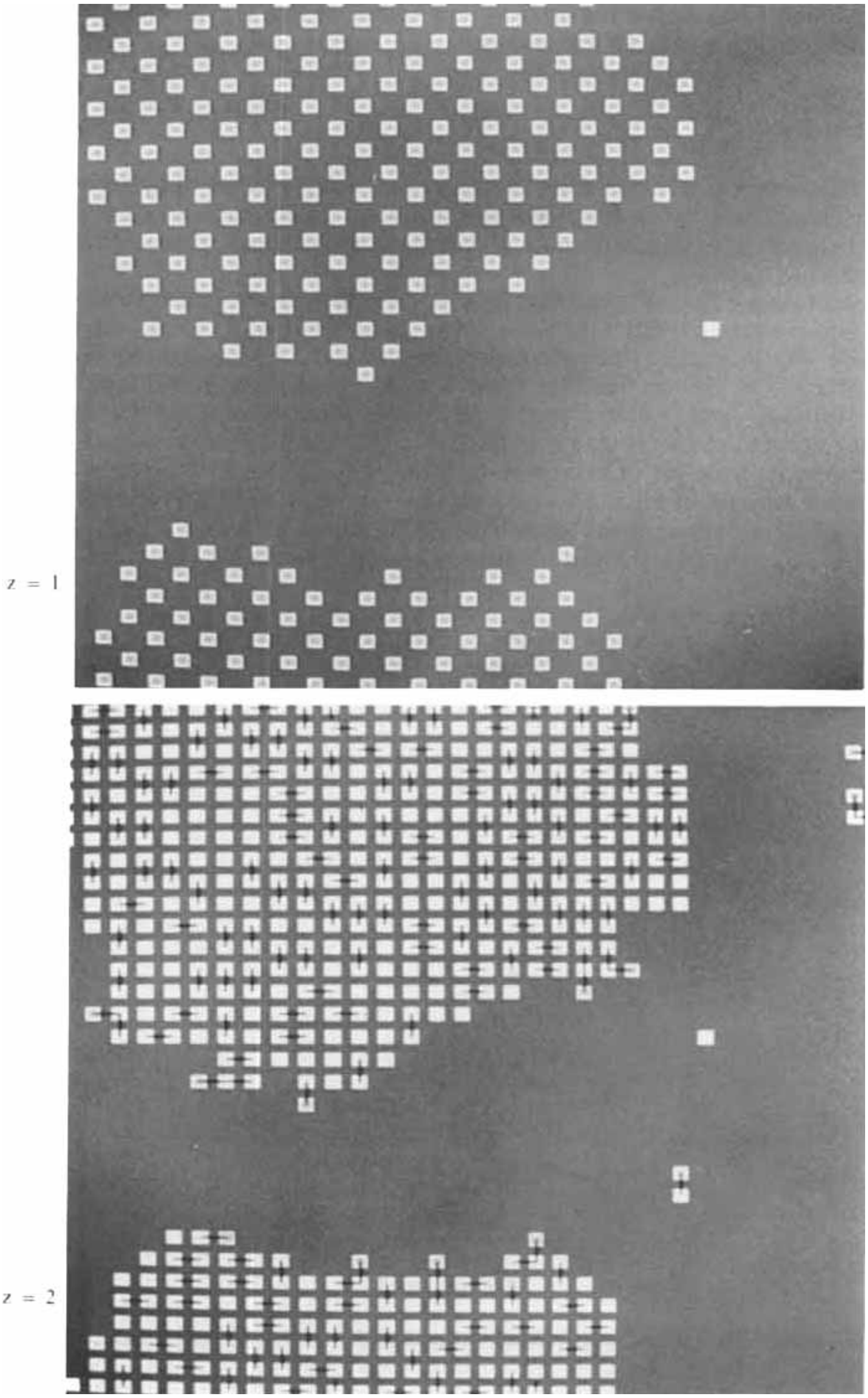

Figure 2 (*See* colour plate X). Castellated bilayer formed at low temperatures for head solvent interaction $\gamma = -1.6$. Pictures show successive planes in z direction of lattice. Head segments are coloured red, tail segments yellow, and solvent sites blue.

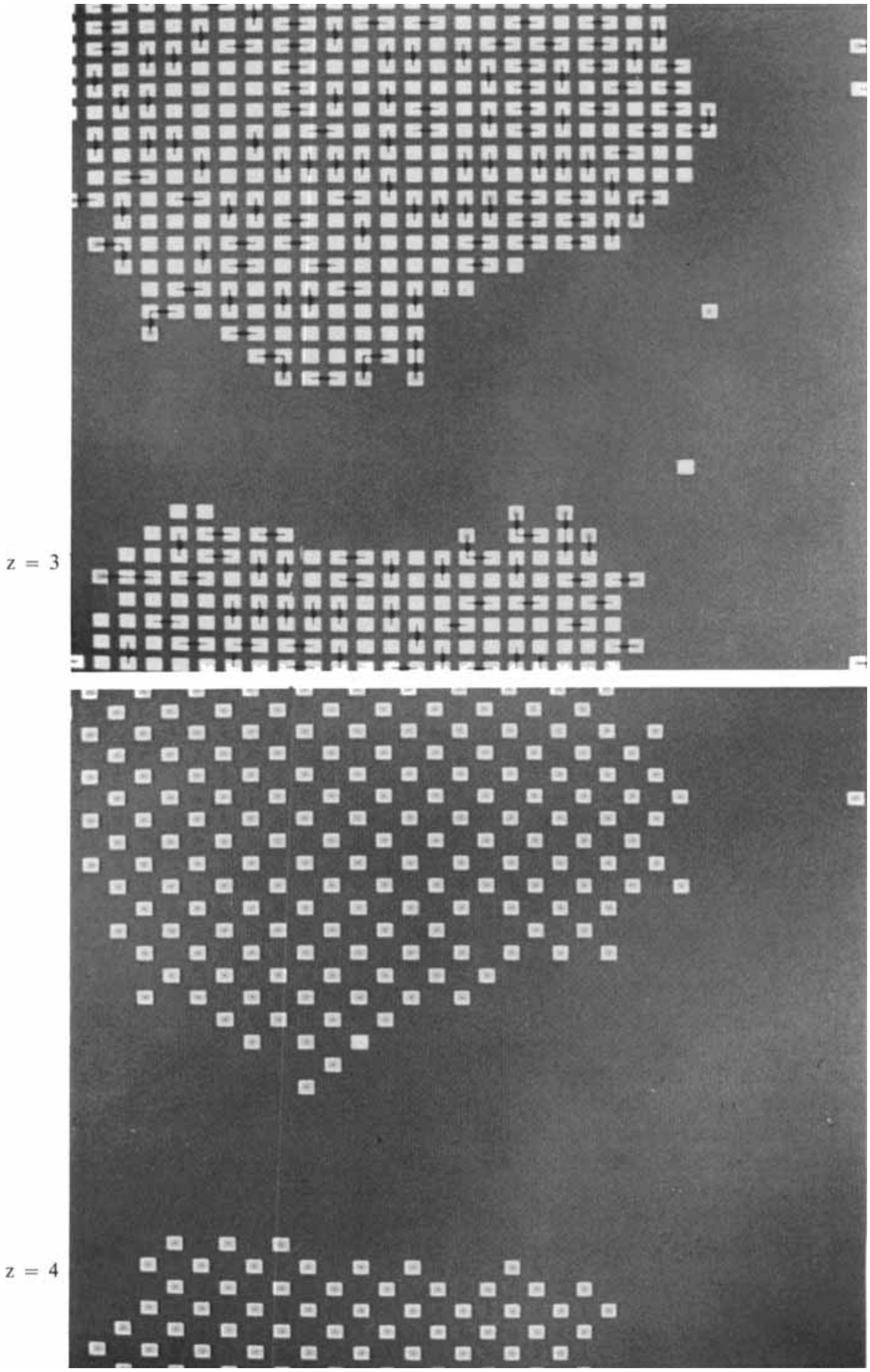

Figure 2 (*Continued*) (*See* colour plate XI).

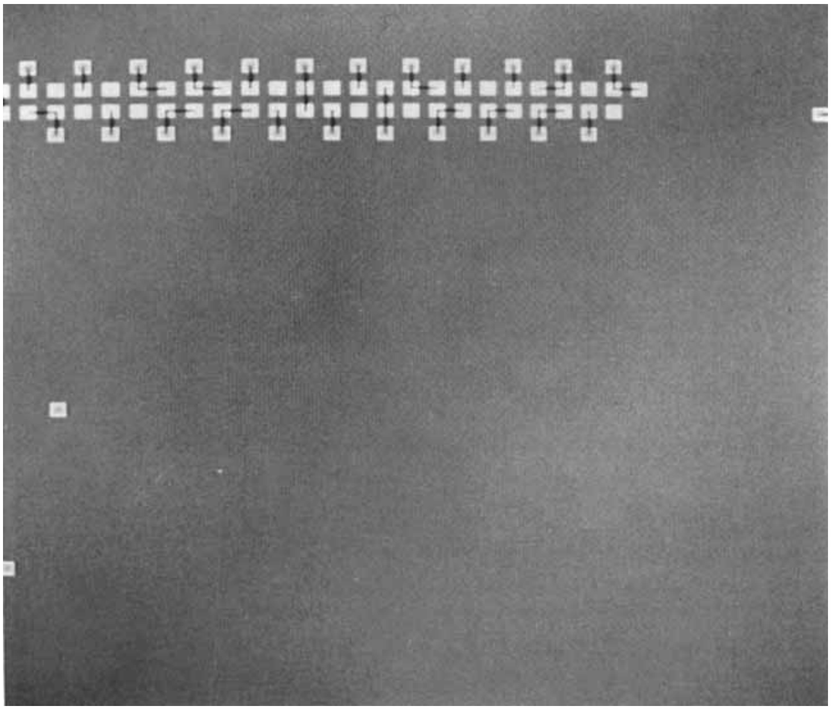

Figure 3 (*See* colour plate XII). Cross section through bilayer. Note random ordering of flexible tails.

Early results for $s = 4$ and $s = 6$ simulations also show the self assembly of bilayers for $\gamma = -1.6$ at low temperatures. It is interesting that in these cases the minimum in the cluster size distribution in the micellar region appears deeper than for $s = 3$.

The results presented in this paper are preliminary and we are currently determining the full phase diagram for the model. It is intended to establish if there is a sharp transition to bilayers, the order of this transition and the dependence of the bilayer structures on temperature, amphiphile concentration, head-solvent interaction and chain length. The presence of a minimum in the cluster size distribution is often used as the criterion for micellar behaviour [12] and it is intended to investigate if the observed minimum becomes stronger as the chain length is increased and also if the model shows a critical micelle concentration.

In conclusion we have established that a chain type lattice model of amphiphilic materials can exhibit self assembly into structures which are analogous to those exhibited by real amphiphilic materials. A detailed study of this model and its extensions should yield greater understanding of the process of self assembly.

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