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Branched amphiphilic molecules on a water surface:
a Monte Carlo simulation

Abstract Amphiphilic molecules consist of a hydrophilic head and one or more hydrophobic tails. The heads are strongly attracted by the water surface, whereas the tails can move in the upper half space. We investigated the behavior of a monomolecular film consisting of branched amphiphilic molecules in dependence on the head density and the side chain length. The Monte Carlo simulations were carried out on a simple cubic lattice using periodic boundary conditions in x- and y-direction.

Key words Lattice Monte Carlo simulations - amphiphilic molecules - surfaces/liquids - order behavior

Introduction

Assemblies of amphiphilic molecules are of fundamental interest. The possible application range extends from electronic and electro-optical devices to drug transport within the human body, and lipid mono- and bilayers serve as model membranes in biology. The molecules of these layers mainly consist of a hydrophilic head and two or more hydrophobic chains [1]. Extensive theoretical and experimental work has been carried out on liquid supported Langmuir films and on Langmuir–Blodgett films transferred onto solid surfaces. The standard method for investigations of amphiphilic molecules on liquid supported surfaces (usually water) is the estimation of \( \pi-A \) isothermes with a Langmuir trough [1,2].

Monomolecular films show a rich polymorphism with phase transitions in dependence on the temperature, lateral pressure, and the molecular species [2]. These effects require a statistical interpretation on a molecular level. Monomolecular layers have been studied by Monte Carlo simulations within several model systems [3–6]. Our athermal Monte Carlo simulations of branched chain molecules were carried out on a simple cubic lattice. The results are compared with simulations of linear (nonbranched) molecules on the same lattice [7]. Our goal is to study how a side chain connected near the head segment influences the behavior of linear molecules.

Model

We have used the cubic lattice model proposed by Harris and Rice [3]. A monolayer is built up from \( N \) amphiphilic chain molecules consisting of \( s = s_1 + s_2 \) segments. \( s_1 \) segments form the main chain. The first segment is the hydrophilic head which is strongly attracted to the liquid surface. All other units are hydrophobic. At the second unit a further hydrophobic chain is connected with \( s_2 \) segments (\( s_1 \geq s_2 \)). The number of segments in the main chain was maintained at \( s_1 = 10 \). The number of side chain segments was varied in \( 0 \leq s_2 \leq 8 \). For the simulations we
use an athermal version of the algorithm proposed by Harris and Rice. The constraint of chain connectivity requires that consecutive segments of a chain lie on adjacent sites and that no more than one segment can occupy a site. Within this model we already investigated linear molecules with varying chain length and molecules with a structured head. The surface is taken to be a square lattice with \( n \) surface sites. The head or molecular fraction \( \Phi = N/n \) (surface coverage) is a measure of the density of the system. It may vary in \( 0 < \Phi < 1 \).

**Calculated properties**

We are interested in calculating average values of the molecular geometrical properties, the associated order parameter, and the \( \pi-A \) isotherms. From end-to-end vectors \( r_{i,k} = (\Delta x_{i,k}, \Delta y_{i,k}, \Delta z_{i,k}) \) of the molecules several mean values have been estimated as the end-end distance of the main chains and of the side chains, as well as the total degree of order by taking into consideration all end-to-end vectors \([7]\). The index \( i \) labels the number of the molecules \( (1 \leq i \leq N) \), whereas \( k \) labels the main and the side chains \( (k = 1 \text{ for main chain, } k = 2 \text{ for side chain}) \). Furthermore, the radius of gyration was estimated which is a measure of the total mean molecular size:

\[
r_{\text{gyr}} = \left( \frac{1}{Ns} \sum_{i=1}^{N} \sum_{p=1}^{s} \left( r_{i,p} - r_{i, \text{com}} \right) \right)^{1/2},
\]

where \( r_{i,p} \) the chain vector (actually \( p \) vectors) containing all segment coordinates and \( r_{i, \text{com}} \) the center of mass of the \( i \)-th chain molecule. The angular brackets indicate the average of the property over at least \( 2 \cdot 10^3 \) system configurations.

The lateral pressure \( \pi \) can be estimated using the virial theorem of Clausius. Within an athermal lattice system there is only a contribution to the virial if two segments lie on adjacent lattice sites. For the lateral pressure, due to pure repulsive interactions, we have only to count the number of nearest neighbor segment pairs in \( x \) and \( y \) direction. Thus, we get Eq. (2) with \( K \) being the force between two neighbor segments (typically \( 10^{-10} \text{ N} \)) and \( L \) being the lattice constant (typically \( 5 \text{ Å} \)). The upper term counts the intermolecular nearest-neighbour segment pairs which lie in the same \( z \) plane, while the lower term counts the intramolecular nearest neighbor segment pairs.

\[
\pi A = K \cdot L \left( \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \sum_{p=1}^{s} \sum_{q=1}^{s} \delta(|r_{i,p} - r_{j,q}| - 1) \times \delta(z_{i,p} - z_{j,q}) \right)
+ K \cdot L \left( \sum_{i=1}^{N} \sum_{p=1}^{s} \sum_{q>p}^{s} \delta(|r_{i,p} - r_{i,q}| - 1) \times \delta(z_{i,p} - z_{i,q}) \right)
\]

\[(2)\]

**Results**

Every simulation was equilibrated by \( 10^6 \) attempted moves starting with uniformly stretched-out chains. Each of the values presented below is derived from an average of at least \( 2 \cdot 10^3 \) configurations with \( 500 \) attempted moves between configurations. For each move a molecule was selected randomly, both chains were erased from the lattice and a trial molecule was regrown using a self-avoiding walk. The trial molecule was accepted as the new one with a probability which equals the ratio of the Rosenbluth weights of the new and old molecules \([3, 4, 9]\). The head density was varied within \( 0.0025 \leq \Phi \leq 0.45 \).

Figure 1 shows a molecule with \( s_2 = 4 \). In the case of \( s_2 = 8 \) both chains would have the same length.

The mean end-to-end distance \( r_1(\Phi) \) of the main chains increases with growing head density \( \Phi \). The onset of \( r_1(\Phi) \) at small head density \( (\Phi \text{ nearly 0}) \) hardly depends on the number of side-chain segments. For \( 0 \leq s_2 \leq 6 \) holds: the more side-chain segments the greater is the end-to-end distance of the main chains at fixed head density. The end-to-end distance \( r_1 \) for \( s_2 = 8 \) has slightly diminished in comparison to molecules with \( s_2 = 6 \).

The mean end-to-end distance \( r_2(\Phi) \) of the side chains in dependence on the head density \( \Phi \) exhibits a different behavior. In general, the end-to-end distance \( r_2 \) is smaller than \( r_1 \). For \( s_2 = 1 \) the end-to-end distance weakly decreases with increasing \( \Phi \) \( (r_2(\Phi = 0.005) = 1.57, r_2(\Phi = 0.45) = 1.54) \). For \( s_2 = 4 \) \( r_2(\Phi) \) decreases till \( \Phi = 0.1 \) and