"Phase behavior of Langmuir monolayers with ionic molecular heads"

Authors: Guillermo Ramírez-Santiago & Carlos A. González Castro

Affiliation: Instituto de Matemáticas, UNAM Campus Juriquilla

ABSTRACT

We have carried out Monte Carlo simulations of a Langmuir monolayer coarse-grained molecular model. Taking into account that the hydrophilic groups can be ionized by modulating acid-base interactions, we have studied the phase behavior of a molecular model that incorporates the short-range steric and long-range ionic interactions. The simulations were carried out in the temperature range where there is a competition of these interactions. Different order parameters were calculated and analyzed for several values of the reduced surface pressure and temperature. For most of the surface pressures two directions of molecular tilt were found: (i) towards the nearest neighbor (NN) at low temperatures and (ii) towards next-nearest neighbors (NNN) at higher temperatures. We also found the coexistence of the NN and NNN at intermediate temperatures and high surface pressure values. A low-temperature reentrant disorder-order-disorder transition in the positions of the molecular heads and in the tails collective tilt was found for all the surface pressure values. It was also encountered that the molecular tails arranged forming “rotating patterns” at intermediate temperatures and at intermediate surface pressures. We estimated the monolayer’s surface pressure versus temperature and the temperature versus area per molecule phase diagrams. It was found that the Liquid Expanded (LE) ↔ Liquid Condensed (LC) phase transition shifts to smaller temperatures when the molecular heads carry an ion, in qualitative agreement with experimental observations of fatty acid monolayers with ionic head groups. Two surface pressure versus area per molecule isotherms were also calculated. One at low temperatures near the LC-NN ↔ LC-NNN transitions and the other at higher temperatures close to the LE ↔ LC transitions. From these isotherms the monolayer’s area compression modulus was obtained and its variation ranges in the LE and LC phases were found to be consistent with the experimental values.