

Self-Assembly Behavior of Monomers with Directional Interactions

Self-assembly is the spontaneous formation of complex, hierarchical structures from solutions of randomly oriented molecules¹. Molecular assemblies created in such a way are of great interest in materials science, as they represent a way to build complex structures from a “bottom-up” approach, as contrasted to the more typical “top-down” methodologies such as photolithography and chemical vapor deposition². The process of self-assembly also is of fundamental importance in the fields of biology and biotechnology¹. The goal of this work is to understand the physical process of self-assembly using mathematically simple models, and then to use these models to both interpret experimental data and to design new materials.

As a first step, a two-dimensional system consisting of monomers with directional interactions between two walls was modeled using the Ono-Kondo density functional theory (DFT)³, with the goal of studying the phase behavior of the system. The molecules were modeled as having two different sides, denoted as A and B. Nearest neighbor molecule-molecule and molecule-wall interactions were explicitly accounted for in the model.

Four different types of behavior were observed from these predictions. First, the system was studied under low interaction potentials. This regime is important because it allows for detailed comparisons to commonly made approximations in experimental studies. In this work we specifically consider the Langmuir and Frumkin approximations. It also allows the results of the DFT model to be compared to Monte Carlo machine simulation data, which is a good test of the ability of the theory to capture the essential physics of the system. The second type of behavior studied was condensation transitions, which were found to occur when the three molecule-molecule interactions (A-A, B-B, and A-B) were equal and larger than -1.0 kT. Next, the ordering behavior of the system was examined, which was found to occur when one of the molecule-molecule interactions (here the A-A interaction) was significantly larger than the other two. Finally, complex transitions in which all interactions were large were studied, which appeared to be a superposition of both ordering and condensation transitions.

In the low interaction limit, it was found that when molecule-molecule interactions were present in the system, there were significant deviations between the DFT predictions and the Langmuir and Frumkin approximations at moderate to high bulk concentrations of monomers. However, the DFT model predictions were closest to the machine simulation data. Of interest was the magnitude of the error in using the Frumkin approximation, which is commonly thought to be a good experimental model for real isotherm data. It was found that in cases where the final state of the system was ordered, the error in the Frumkin approximation was so large that even qualitative predictions of the system behavior were wrong.

The condensation transition was found to exist when the molecule-molecule interactions

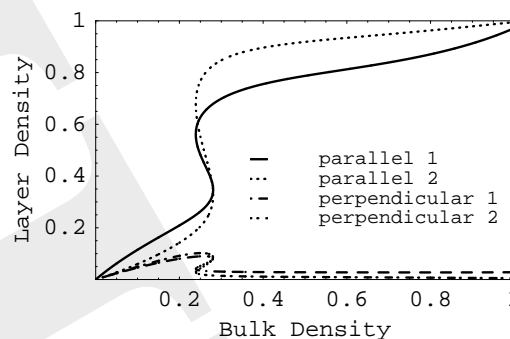


Figure 1: An order-disorder transition.

were relatively symmetric (almost equal to each other) and more attractive than -1.0 kT. Snapshots from Monte Carlo simulations in the two phase region showed that the condensed phase was liquid-like in the number of nearest neighbors and unordered.

For systems in which one of the molecule-molecule interactions was significantly larger than the other two, ordering was observed. It was found that when the largest interaction was less attractive than -2.4 kT, the system became more ordered as the bulk concentration was increased. However, when this interaction was -2.4 kT or more attractive, the system ordered itself as a first-order phase transition (Figure 1). This transition is an order-disorder transition. It was found that the magnitude of the molecule-surface interactions could be used to control the orientation of the molecules in the ordered state. Monte Carlo simulations in the two phase region showed that the order-disorder transition resulted in the formation of long chains of molecules in the system (Figure 2); the orientation of these chains can be controlled by adjusting the molecule-surface interaction. There is experimental evidence for the formation of these types of chain-like structures in real systems; one example is magnetorheological fluids that are exposed to a magnetic field^{4,5}.

Finally, by increasing all of the interactions in the system to large values, transitions can be observed which are a combination of both ordering and condensation. Similar to the order-disorder transitions, the molecule-surface interaction can be used to control the orientation of the ordered state. Monte Carlo simulation shows that the phase transition results in a condensed, liquid-like state, except that the final state is made of monomers which are all in the same orientation.

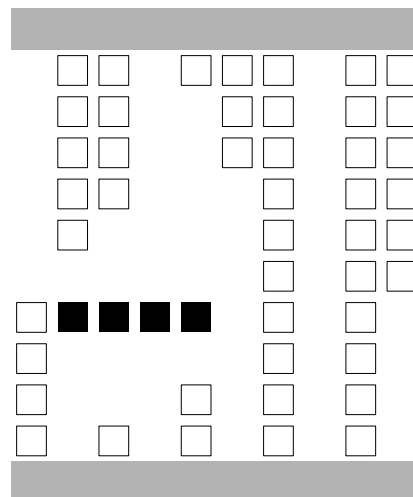


Figure 2: A Monte Carlo snapshot of a system with ten layers after an order disorder transition. The formation of chain-like structures is apparent. In the figure, the open squares represent monomers in the parallel orientation, while the filled squares are monomers in the perpendicular orientation.

¹Lindsey, J. S. *New. J. Chem.* **1991**, 15, 153.

²Gomez-Lopez, M.; Preece, J. A.; Stoddart, J. F. *Nanotech.* **1996**, 7, 183.

³*Molecular Theory of Surface Tension in Liquids*, Ono, S.; Kondo, S., Eds.; Elsevier: Amsterdam; 1960.

⁴Silva, A. S.; Wirtz, D. W. *Langmuir* **1998**, 14, 578.

⁵Lin, J.; Zhou, W.; Kumbhar, A.; Wiemann, J.; Fang, J.; Carpenter, E. E.; O'Conner, C. J. *Solid State Chem.*, in press.