

Simulating mesoscopic order

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Abstract

Simulations of ordering transitions in mesoscopic systems are, at present, mainly of fundamental interest. It is argued that such simulations are potentially important for the design of novel materials.

1. Introduction

One of the attractive features of “nano-technology” is that it is now becoming possible to build materials atom-by-atom. Still, nobody in his or her right mind would try to build a silicon crystal (say) in this way. The reason is, of course, that nature already does this for us. In fact, crystal formation is such a common phenomenon that it is easy to forget that it is also something of a miracle. In order to form a crystal, the crystalline phase must be thermodynamically stable but, in addition, the kinetics of crystal formation must be such that the stable phase forms on a reasonable time scale. In fact, this is certainly not always the case: many mixtures will vitrify before they crystallize and this is also true for many pure substances, in particular those consisting of large molecules. Yet, many materials, even proteins and colloids, do form crystals and this has considerable relevance for materials science, as we all know that ordered phases have electrical, optical and mechanical properties that are completely

different from those of the corresponding disordered phase.

By contrast, if we use bricks to build a wall, we should not wait for these bricks spontaneously to assemble: we put them in place by hand. However, also when we build smaller ordered structures (e.g., memory chips), we *impose* the order. The lure of “nano-technology” is that it extends this form of manual control to the nanometer scale. However, as the example of crystal formation shows, some structures will form without our direct intervention, as long as we provide the correct building blocks and create the conditions such that ordering is not kinetically inhibited. It is for this reason that there is a great need to understand the physical factors that determine the spontaneous ordering of mesoscopic systems. In fact, in several instances, present-day technology exploits the spontaneous ordering of mesoscopic systems, for instance in the fabrication of high-strength fibers that are spun from liquid-crystalline solution in which the polymeric building blocks of the fibre are already partially

aligned. However, compared with the way in which nature exploits spontaneous ordering processes in biological systems, our efforts in this direction are still in their infancy. When it comes to preparing ordered patterns in electronic devices, we still rely on lithography, rather than on self-assembly. I believe that this will change but, in order for these changes to happen, we must be able to predict what building blocks to choose in order to achieve a specific type of mesoscopic order. Moreover, it is not enough to know that a particular mesoscopic structure is thermodynamically stable: the formation must also be kinetically allowed. In fact, kinetic factors are much more important in ordering transitions of mesoscopic systems than in microscopic (“atomic”) systems, because in the former systems vitrification (gelation) is never far away.

Computer simulations can be used to predict the structure and rate of formation of mesoscopically ordered systems. I shall not attempt to review the extensive literature in this field. Let me just indicate the three focal points of the simulation of mesoscopic systems, viz., (a) the computation of structure and phase stability, (b) the simulation of transport properties (including the study of gelation) and (c) the determination of free-energy barriers for activated processes (e.g., crystal nucleation). One feature that is common to all mesoscopic systems and that is very different from the corresponding atomic or simple molecular systems, is the important, often dominant, role that entropy plays in determining the physical properties. I shall illustrate this by discussing the spontaneous formation of AB_{13} (!) crystals in mixtures of essentially hard, repulsive colloidal particles. However, in order to explain why the formation of such crystalline superstructures is surprising, I must first briefly explain how our intuitive interpretation of entropy may conflict with the statistical mechanical definition.

2. Order through disorder

The second law of thermodynamics states that the entropy of an isolated system increases until it reaches a maximum. Statistical mechanics has

given a “microscopic” interpretation to this law: in suitable units, entropy is simply equal to the number of (quantum) states accessible to the system. If we constrain a system to be in a single state, its entropy will be zero. If we then release this constraint and allow the system to explore all other states with the same energy, the entropy will increase until the system is equally likely to be in any one of its accessible states. At that point the entropy attains its maximum value and the system has reached equilibrium. Of course, in the process, we have lost information about the system: initially, we knew exactly what state it was in, but after equilibration the system can be in any one of a large number of states. We have gone from an *ordered* initial situation to a more *disordered* final situation. In this sense, entropy is a measure for the amount of disorder in a system. Can we *see* order or disorder? Strictly speaking, the answer is no, because we cannot see the number of accessible states of a system. However, we have another, more intuitive notion of order and disorder based on things that we *can* see. We call a crystal ordered, because its constituent particles are constrained to be near specific points in space (lattice sites). A fluid, where no such constraints apply, is called disordered. Our intuitive notion about order and disorder suggests that a system with a given density and energy should have a higher entropy in the fluid phase than in the crystalline phase, and that freezing would result in a decrease of entropy. The second law of thermodynamics tells us that this can only happen if this decrease in entropy is offset by a larger increase in entropy of some other part of the universe. This can happen if the *energy* of the crystalline phase is lower than that of the liquid phase. In that case, the system releases heat on freezing, and thereby increases the entropy of the rest of the universe. This unsophisticated description of the thermodynamics of freezing explains why, for a long time, it was commonly thought that attractive forces between molecules are essential for crystallization: a crystal can form because the lowering of the potential energy of the system upon solidification pays the price for the decrease in entropy.

It was therefore a great surprise when, in the

1950s, computer simulations by Alder and Wainwright [1] and Wood and Jacobson [2] indicated that a fluid of hard spheres could freeze. In this case, the potential energy of the system is always zero. Hence, if crystallisation occurs, this can only mean that the entropy of the crystalline solid is *higher* than that of the fluid. Although, at present, the hard-sphere freezing transition is well-established and non-controversial, this was certainly not the case when it was first reported. In fact, during a round-table discussion on this topic held in 1957, the chairman (G.E. Uhlenbeck) asked the experts on the panel (including two Nobel laureates) to *vote* on the existence of the hard-sphere freezing transition, and the vote was even Uhlenbeck closed the discussion with the following words: "... I am quite sure that the transition goes a little bit against intuition: that is why so many people have difficulty with it, and surely I am one of those. But this transition – it still might be true, you know – and I don't think one can decide by general arguments" (the proceedings were published six (!) years later [3]). Yet, in retrospect, we can *understand* the hard-sphere freezing as follows: a naive picture of a solid is a cell model in which all molecules are confined to cells centered around lattice sites. Confining the molecules to cells *costs* entropy (we call this contribution to the entropy *configurational*). However, we also *gain* entropy, because a molecule has more free volume to move in this cell than it had in the fluid; in other words, there is more *jamming* of molecules in a dense fluid than in a solid of the same density. At sufficiently high densities, the gain in entropy due to the increase in free volume outweighs the loss in configurational entropy. When this happens, entropy will favour crystallization: an increase in macroscopic order is driven by an increase of microscopic disorder. In fact, it is now known that numerous ordering transitions can be driven by entropy alone. In particular, not only crystals, but also many kinds of liquid crystal can form in systems of hard repulsive particles [4].

The complexity of the order that can be induced by entropy has become clear only recently when Ottewill et al. [5] reported experiments on the crystallisation of a colloidal suspension of a

mixture "large" and "small" polymethylmethacrylate (PMMA) particles with a size ratio of 0.58. These mesoscopic particles have steep repulsive interaction, not unlike hard spheres. Bartlett et al. observed that this mixed colloid would form a crystal with a so-called AB_{13} structure. This structure is familiar in metal alloys (e.g., $NaZn_{13}$) and consists of a simple cubic lattice of A particles. In the middle of each A-cube, we find a B-particle surrounded by an icosahedral cluster of other Bs. The full unit cell consists of eight such sub-cells with neighbouring icosahedra alternating in orientation by $\pi/2$.

These findings immediately raised two questions: (1) is the observed AB_{13} phase stabilized by entropy alone or is the fact that PMMA particles are not hard spheres crucial? and (2) can we understand why this phase should form? A definitive answer to the first question can only come from computer simulations. In fact, the results of an extensive numerical study by Eldridge et al. [6] indicate that entropy alone can indeed account for the stability of the AB_{13} structure. In a recent publication, Xu and Baus [7] consider both questions from a different point of view. In their paper, Xu and Baus use classical density-functional theory, i.e., the best analytical theory of freezing to date, to estimate the stability of the AB_{13} phase in a mixture of large and small hard spheres. Their calculations confirm that, for a size ratio of 0.58, there is a density range where the AB_{13} structure is more stable than the fluid mixture, the pure A and B solids or the AB_2 compound. Why is AB_{13} the stable solid structure? Surprisingly, it turns out that, in this case, it is not the free volume that is responsible. In fact, both the pure A and B phases and the AB_2 structure can fill space more efficiently, and hence the free volume would favour those phases over AB_{13} . The AB_{13} phase is stable because it has a higher *configurational* entropy. In a mixture, this configurational entropy is closely related to the entropy of mixing. In the words of Xu and Baus "... the larger entropy of mixing of the AB_{13} structure relative to that of the competing structures is responsible for its stability". I guess that George Uhlenbeck would have found this observation more than a little *counter-intuitive*.

3. Discussion

I have included this discussion of the AB_{13} crystal to illustrate that quite complex colloidal structures are thermodynamically allowed. However, this is only part of the story, because I have not discussed the kinetics of crystal nucleation and growth. In fact, the experimental evidence strongly suggests that kinetic factors play an important role in determining which phase actually forms. In fact, we do have the techniques to compute both the free-energy barrier for crystal nucleation [8] and the rate at which this barrier is crossed (for a clear discussion, see ref. [9]). The latter calculations are non-trivial because the simulation of the dynamics of dense colloidal suspensions requires special techniques [10] that I will not go into here.

In summary, simulations of ordering in mesoscopic systems are, at present, still very much a technique to increase our fundamental understanding of the statistical mechanics of order-disorder transitions. However, in the near future, such simulations may play a crucial role in designing materials with tailor-made mesoscopic order.

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