

Should entropy always drive a system to disorder?

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It is one of the accepted tenets of physics that entropy is intimately associated with the degree of disorder present in a system. Therefore it follows that an increase in entropy in any given system should lead to an increase in disorder. This has become an important topic for discussion in recent times. Surprisingly, theorists and experimentalists have come up with systems that behave very differently. In these systems an increase in entropy drives them from a state of positional disorder to a state of positional order. There is also one other possibility of going to a relatively ordered state. For example a homogeneous mixture of two components may also be driven, by entropy, to a state in which the two components get separated spatially resulting in a phase separation. In fact, it was this problem that first attracted the attention of theorists.

The early work of Labowitz and Rowlinson¹ on multicomponent hard sphere fluids indicated that in the Percus-Yevick (PY) approximation a complete miscibility results between the various components. There were no indications whatever of a phase separation at all concentrations and particle size ratios. This led to the generally accepted idea that binary hard-sphere fluids never phase-separate. It is in this context, that the work of Biben and Hansen² acquires a lot of significance. They studied a binary mixture of large (*A*) and small (*B*) hard spheres having diameter ratios (σ_A/σ_B) $\gg 1$, on the basis of Rogers and Young³ and Ballone *et al.*⁴ theories, which differ from that of

PY. They found the interesting result that the mixture phase separates at packing fractions typical of liquids. This is very important in view of the fact that there are no real attractive interactions between the components of the fluid. The effect is entirely due to an increase in the entropy of the phase-separated system relative to that of the homogeneous binary mixture. These authors attribute this feature to an effective 'attraction' between the large spheres *A*. This attraction which is entropic in origin leads to an aggregation of large spheres *A* in a solvent of small spheres *B*.

On the experimental side it is worth recalling the important results found in two totally different systems. It is quite well known⁵ that in a compound of sodium and zinc one can have a crystal with a complex structure AB_{13} with *A* representing Zn, the larger atom and *B* representing Na, the smaller of the two species. Interestingly an exactly similar structure has recently been seen by Bartlett *et al.*^{6,7} in a binary mixture of colloidal particles *A* and *B* in suspension with two different diameters σ_A and σ_B respectively ($\sigma_A > \sigma_B$). The structure AB_{13} is indeed very complex (Figure 1). It consists of a body-centred

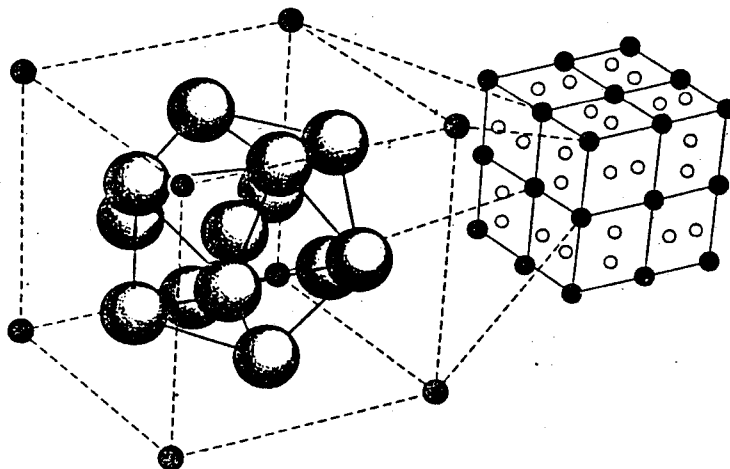


Figure 1. Schematic representation of AB_{13} structure. In the unit cell (right) 'closed' circles represent *A* and 'open' circles represent *B*. In the sub-cell (left), the small 'closed' circles represent *A* and the 'shaded' spheres represent *B* (After Eldridge *et al.*¹⁰).

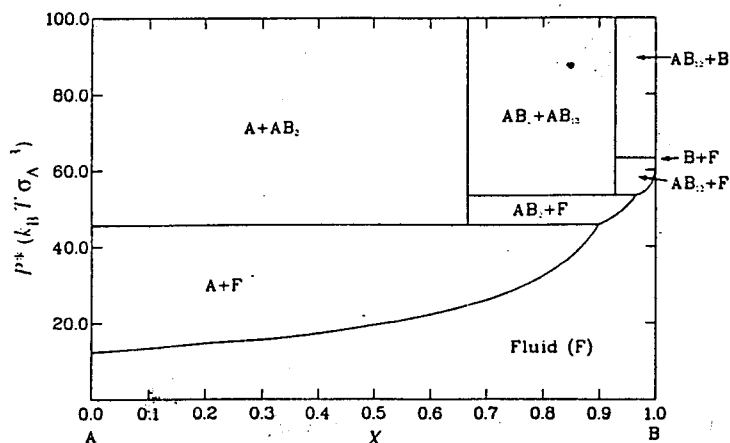


Figure 2. Theoretical, pressure (P^*)-composition (X) phase diagram of a binary A , B mixture for $\sigma_B/\sigma_A = 0.58$. P^* is in the reduced units $k_B T \sigma_A^{-3}$ where k_B is the Boltzmann constant and T is the absolute temperature. F is the fluid phase of AB mixture. A and B are crystalline phases of atoms A and atoms B respectively (after Eldridge *et al.*¹⁰).

icosahedra of 13 small particles B in a simple cubic sub-cell of the larger particles A . The unit cell is made up of eight such sub-cells with neighbouring icosahedra alternating in orientation by $\pi/2$. That such complex structures exist in two entirely different systems suggested that factors other than inter-particle attractions are probably involved in the formation of the AB_{13} structure.

Interestingly, even in one-component colloidal particles, Pusey *et al.*⁸ found an unusual crystallization. In these systems crystallization occurs at a particular concentration of the colloidal particles. This result is intriguing since there are only steep repulsive inter-particle interactions, i.e., the system can be approximated to a collection of hard spheres. An analysis⁹ indicated that at this concentration, the loss of entropy in the system associated with the appearance of the long-range order is more than offset by the gain in entropy associated with the motions of the hard spheres in the extra free volume available to them in the ordered spatial structure. In two-component systems also the formation of complex structures like AB_{13} can be interpreted on similar lines. Recently Eldridge *et al.*¹⁰, through computer simulations, worked out the phase diagram for a mixture of two particles A and B with a diameter ratio of $\sigma_B/\sigma_A = 0.58$. They found that at low densities a binary fluid is stable. For compositions of A up to 90%, as the

pressure is increased, an f.c.c. crystal of large spheres A is seen. At higher pressures, a hexagonal structure AB_2 forms and this coexists with either the crystalline phase of A or the binary fluid of A and B . At still higher pressures AB_{13} crystal structure forms, interestingly, around a composition value of 13 atoms of A to 14 atoms of B . Their theoretical phase diagram is shown in Figure 2. To compare their results with the experimental observations of Bartlett *et al.*⁷ they also worked out the phase diagram of the same system at a constant volume. In general, there is a broad agreement between the theory and the experiment.

In summary, we notice that there is a strong evidence in support of entropy being the driving force in the formation of the ordered structures. In other words, entropy which is generally regarded as a driving force for disorder, can in some systems lead to the formation of crystal structures with very complex order¹⁰. These structures are quite 'open' and hence the atoms have a large room for translatory motion. This increase in local entropy more than compensates for the decrease in global entropy due to the formation of the lattice-order.

In this context, we may consider some phase transitions where we may again suspect the role of entropy. For example we consider the phenomenon of reentrance¹¹ in liquid crystalline phases. On heating a nematic liquid crystal

which has no lattice order, sometimes, we get a smectic liquid crystal which has a one-dimensional lattice order. This lattice formation, in all probability, is partly due to molecular interactions and is partly entropy-driven. Our second example pertains to the studies on phase transitions in two-dimensional systems. Interestingly in a binary mixture of hard discs, studies have shown^{12,13} that a fluid phase of a particular composition can go over to a demixed state where one has two fluid phases of two different compositions. At least some of these transformations could be entropic in origin. Finally there is another possible system¹⁴, where entropy is likely to induce phase separation. This is a fluid mixture of nearly non-interacting (inert) atoms of the elements like argon, krypton, etc. It should be very interesting to look for the possible existence of entropy driven phase separation and ordered structures (on freezing) in these systems.

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