

Hypermolecular Liquids - A new route to the formation of colloidal gels: short range attraction and long range repulsion.

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Cluster phases tend to appear when bulk phase separation is frustrated. This happens for instance in systems containing amphiphilic molecules: if the heads and tails of such molecules could move independently, the polar head-groups and the non-polar tails would demix. However, as the two parts of the molecules are connected, bulk phase separation is impossible and the system undergoes microphase separation, forming micellar solutions, micro-emulsions or lamellar structures. Something similar (and, in fact closely related [1, 2]) may happen in solutions of charged species: bulk phase separation of the positive and negative charges is excluded (because of charge neutrality) and, again, micro-phase separation results [2].

In some cases, the nature of the frustration that preempts phase separation is less obvious. A recent paper by Sciortino et al. suggest that a new kind of micro-phase separation may take place in colloidal systems [3]. Here the competition is between short-ranged attraction and long-ranged repulsion. An example is the behavior of (like) charged colloids with short-ranged attraction (dispersion or depletion). An interesting discussion of the optimal cluster size in such systems can be found in ref. [4]. In the absence of the long-ranged repulsion, increasing the strength of the attraction will lead to a liquid-vapor-like demixing. However, long-ranged repulsion interferes with this transition. This is most easily understood by considering a simplified potential that contains a narrow attractive well of depth ϵ_1 and a broad repulsive shoulder of height $\epsilon_2 \ll \epsilon_1$. For small clusters, the repulsive interaction is negligible. However, as the clusters become larger (but still small compared to the range of the repulsion), the number of repulsive interaction scales with square of the number of particles in the cluster, unlike the attractive interaction that is linear in the number of particles. As a consequence, there is a size beyond which further growth of the cluster decreases its stability.

Sciortino et al. consider how the interaction between such clusters may affect the resulting phase behavior. In their analysis, the clusters are considered to be the building blocks of the phases that form. If we use the terminology where colloidal suspensions are denoted as "supra-molecular" liquids, then cluster phases should be called "hyper-molecular". Depending on the circumstances, we may expect to see a cluster liquid, a cluster glass or a cluster crystal. A different (but related) scenario had been proposed earlier by Kroy et al. [5] who considered the phase behavior of clusters that form by irreversible aggregation. There the small clusters are in a state of structural arrest. However, as the clusters grow, their attractive interaction becomes weaker and, at some point, they reach the stage where either the cluster phase "melts" or the fluid of clusters undergoes a glass transition. A difference with the scenario of ref. [3] is that, in that case,

the clusters are compact whereas Kroy et al. consider fractal aggregates that are less dense.

To conclude, I should point out that there is a very different mechanism by which clusters can be the building blocks of dense phases. This scenario was discussed some time ago in a paper by Likos et al. [6]. These authors discussed a kind of clustering that can occur in systems of particles with a soft core. Depending on the nature of the soft, repulsive potential, a dense system may lower its free energy by putting several soft particles on top of each other. Such a scenario could not work for colloids (that tend to repel strongly at short distances), but it may be relevant for softer objects, such as star polymers.

In summary, non-trivial structures may appear in soft-matter systems on length scales between the mesoscopic and the macroscopic. As the clusters outgrow the mesoscopic domain, the structure and dynamics of cluster phases is no longer determined by equilibrium statistical mechanics.

References

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