

WHAT ARE PHYSICAL GELS?

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A solution of associating molecules can transform to a gel state upon changes in temperature and/or other solution conditions (such as pH). While the case of chemical (irreversible) gelation is relatively simple and is well described by percolation theory, there has been a longstanding controversy about the thermodynamic nature of reversible physical gels. In this talk, I will describe a new approach to this problem based on the analogy between gelation and glass transition. I will show that gelation can occur through two principal mechanisms: in the single-phase region, gelation occurs as a result of proliferation of free energy minima each corresponding to a spatially inhomogeneous but nonperiodic distribution of the associating molecules – this is the same physics underlying glass transition; in the two-phase region, gelation can be viewed as the continuation of glass transition into the two-phase region, or equivalently as an incomplete phase separation arrested by the onset of glass transition. In both cases the transition is connected with an underlying spinodal of the uniform solution phase.

We have applied our new approach to two simple model systems capable of forming physical gels. The first system is a simple AB diblock copolymer melt, where a gel state can form as a result of the self-assembly of the diblocks into random microphase separated domains. A key result is that the gelling line approaches the spinodal line of the disordered state in the limit of long chain length, suggesting that spinodal is the mean-field signature for gelation. Another important result is the finding that, for very asymmetric diblocks, gelation can occur above the transition temperature to the body-centered-cubic phase. This is in contrast to normal molecular glass forming liquids where glass transition always occurs as a result a supercooling below the melting point and probably reflects the self-assembling nature of the system.

The second model we studied is a lattice model of anisotropic molecules. The model mimics systems where association is due to directional bonded interactions but also captures qualitatively the reduced number of nearest neighbor contacts in colloidal suspensions with short-ranged attractions and long-ranged repulsions. Using a mean-field phase diagram we calculated as a guide, we have examined the morphological behavior of the model through a dynamic mean-field simulation. Our simulation reveals a plethora of gel structures, such as foams, networks, and fibrils, in the two-phase region predicted by the mean-field phase diagrams. These structures show many features that resemble gels formed in colloidal suspensions studied in David Weitz's group at Harvard.