ICFP M2 – SOFT MATTER PHYSICS
Tutorial 10. The sol-gel transition

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Gelation is the process by which a network of subunits, with bonds progressively created between them, becomes sufficiently connected that there appears at least one macroscopic joint path crossing the entire sample. By this so-called "sol-gel" transition, one goes from a liquid state – the "sol" – to a material with non-zero elastic shear modulus – the "gel". There are many examples of such a transition, depending on the network, the subunits and the type of bonds used, but there are also some universal features associated to them. Here, we would like to revisit the Flory-Stockmayer percolation model, that is the classical mean-field theory of gelation. For that purpose, we consider an infinite Bethe lattice (or Cayley tree) where each site (or subunit, or monomer) has z neighbouring sites – 1 "parent" and $z-1$ "children". Each link between sites can be turned into a bond (a reacted link, or crosslink) with probability p, thus creating an assembly of connected paths (or polymers) of various sizes N. We note $n(p, N)$ the average number of N-mers per site, and p_c the percolation (or gelation) threshold.

I Preliminaries

1 What are the limitations of this model ?

2 Define the average number $n_\mathrm{tot}(p)$ of finite-size polymers per monomer.

3 Define the probability of a given finite-size polymer to be a N-mer.

4 Define the weight density, *i.e.* the probability of a monomer to be part of a N-mer.

5 What is the sol fraction P_sol, *i.e.* the fraction of monomers belonging to finite-size polymers ?

6 Define the gel fraction P_gel. How are P_sol and P_gel related ? Discuss their general behaviours as a function of p.

7 Define the number-average polymerization index $N_\mathrm{n}(p)$, the weight-average one $N_\mathrm{w}(p)$, and the polydispersity index.

II Sol and gel fractions

1 Find the expression of the gelation point p_c.

2 Let Q be the probability that a given monomer is not connected to the gel through one of its neighbouring links. Define Q recursively.

3 Express P_sol from Q.

4 What is the equation satisfied by $P_{\rm sol}$? Comment on its solutions.

5 Study the $z = 3$ case, and plot $P_{\rm sol}$ and $P_{\rm gel}$.

III Polymerization index below gelation

1 Provide the average number of bonds per monomer.

2 What is the value of $n_{\rm tot}(0)$?

3 For $p < p_{\rm c}$, explain the effect of adding one bond and deduce $n_{\rm tot}(p)$.

4 Obtain $N_{\rm n}(p)$ for $p < p_{\rm c}$.

5 Let R be the average number of monomers connected to a given monomer through one of its neighbouring links. Define R recursively for $p < p_{\rm c}$, and provide its expression.

6 Deduce $N_{\rm w}(p)$ for $p < p_{\rm c}$, and characterize the polydispersity at gelation.

IV Distribution and critical behaviour

On can view each monomer as a unit molecule containing z groups that can react with neighbouring molecules to form bonds.

1 How many unreacted groups are there in a given N-mer ?

2 How many links (bonds + unreacted groups) are there in a given N-mer ?

3 What is the probability that an unreacted group belongs to a N-mer ?

4 Obtain the average number of N-mers per unreacted group, and deduce $n(p, N)$.

Homework : For $z > 2$, near the gel point, and at large N, show that one has the following asymptotic cut-off behaviour :

$$n(p, N) \sim N^{-\nu} \exp\left[-\frac{N}{N^*(p)}\right] , \tag{1}$$

by considering the limit $\epsilon^{-1}, N \to \infty$ at finite $N\epsilon^2$, where $\epsilon = (p - p_{\rm c})/p_{\rm c}$. Specify the value of ν, and show that $N^*(p) = 2(z-2)\epsilon^{-2}/(z-1)$. Compare the result to critical phenomena.