

Homework 8
Polymer Physics 2024

Due Tuesday March 5 at noon

(**pdf** file should be called: **HW 4 Group x Last Name _Name _Name _Name.pdf**)

A polymer network immersed in a compatible solvent swell into a gel. Flory considered at equilibrium a balance between the osmotic swelling and rubber elasticity of the stretching chains between crosslinks to yield the Flory-Rehner equation,

$$-\left[\ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2\right] = \frac{V_1}{\bar{v}M_c} \left(1 - \frac{2M_c}{M}\right) \left(\nu_2^{\frac{1}{3}} - \frac{\nu_2}{2}\right)$$

Where ν_2 is the volume fraction of polymer, χ_1 is the chi parameter between polymer and solvent, M_c is the molecular weight between crosslinks, M is the molar mass of a Kuhn unit, V_1 is the molar volume of the solvent, \bar{v} is the specific molar volume of the polymer. This can be used to

determine the interaction parameter or to determine the molecular weight between crosslinks as shown in Flory's first book in some detail. The Flory-Rehner equation is based on Gaussian chains.

<https://www.eng.uc.edu/~beaucag/Classes/Properties/Books/%28George%20Fisher%20Baker%20Non-Resident%20Lec%29%20Paul%20J.%20Flory%20-%20Principles%20of%20Polymer%20Chemistry%20-%20Cornell%20University%20Press%20%281953%29.pdf> pages 576-584.

deGennes revisited this system for a good solvent with the concept of concentration blobs in his book on polymer physics chapter V V.3 pages 152-160.

<https://www.eng.uc.edu/~beaucag/Classes/Properties/Books/Pierre-giles%20De%20Gennes%20-%20Scaling%20concepts%20in%20polymer%20physics-%20Cornell%20University%20Press%20%281979%29.pdf>

deGennes' Figures below show the c^* - model and the makeup of polymer networks. The c^* - model involves considering the chains between crosslinks in an equilibrium swollen gel as chains at exactly c^* concentration and this governs the values of the swollen volume fraction.

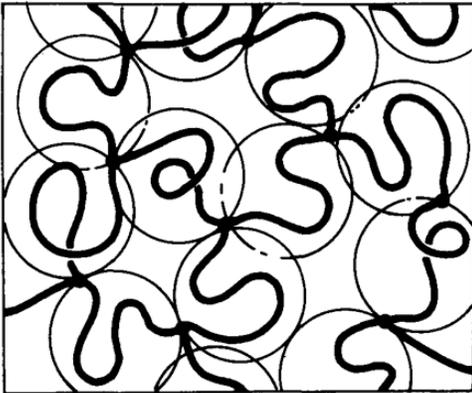


Figure V.15.

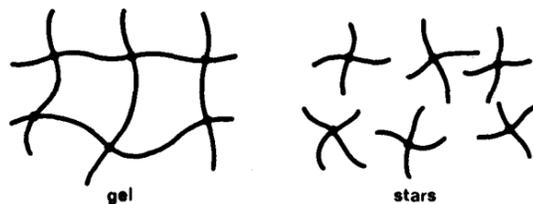


Figure V.17.

The structure of equilibrium swollen gels has been debated extensively since the work of Flory and Rehner. Recently, a group at the Institut Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden, Germany has published four papers based on coarse grain Monte Carlo simulations and synthesis of end-linked tetrafunctional star polymers (deGennes' last figure above), Scholz R, Lang M *Structural Characterization of Model Gels under Preparation*

Conditions and at Sewlling Equilibrium Macromolecules in press (2024) (<https://pubs.acs.org/action/showCitFormats?doi=10.1021/acs.macromol.3c02607&ref=pdf>).

Many literature studies have focused on neutron scattering using deuterium tagged networks following the schemes shown in Scholz's Figure 1. Scholz's simulations were performed in another 2024 publication, in this paper he reanalyzes those results by varying the tagging schemes of Figure 1, and Fourier transforming the simulated structure to generate scattered intensity versus scattering vector q , in the graphical abstract, Figures 2, 3, and 5. One advantage of simulation is that the tagging can be performed after the simulation is completed. Scholz uses star polymers of type A and type B differing in contrast which he manipulates. A stars bond only with B stars.

- a) In equation 3 Scholz assumes that you can linearly sum the scattering contribution of type A and type B stars. This ignores correlations between stars which could be either organized, specific interactions, or random, mean field interactions. Specific interactions can be modeled using a structure factor as is done in diffraction and would result in peaks in the scattering data while mean field interactions are modeled using the random phase approximation (RPA). Slide 43 of Slides 3 gives the RPA equation where $S(q)$ is $I(q)$ for Scholz and χ is the Schultz's χ_1 . N is the molecular weight and ϕ is the volume fraction.

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_U(q, R_{g1})} + \frac{1}{\phi_2 N_2 S_U(q, R_{g2})} - 2\chi \quad (9)$$

Work out how the resulting intensity would differ at low and high- q compared to Scholz's equation 3 considering that the $S(q)$ values are proportional to the contrast. Comment on the implications for the conclusions of this paper. (The RPA is a harmonic mean while the linear sum of Scholz is an arithmetic mean of the component scattering.)

- b) Figure 2 shows the effect of increasing concentration relative to c^* on the star polymer and star polymer networks. What is the impact of concentration on the correlation length (concentration blob size) expected from the scaling theory in class? Derive this expression. Does the data show this behavior?
- c) Why do the network stars show different scattering compared to the free stars? Figure 4 shows the behavior of correlation length with concentration for the free and networked stars. Why do they differ? Figure 8 shows how the network scaling changes with molecular weight of the star arms. Explain this behavior.
- d) Figure 9 shows Scholz's consideration of clustering of monomers near the crosslink sites which he says gives rise to "static" scattering due to its relative lack of motion compared to "dynamic" features (*by my understanding*). The scattering is fit summing two terms one for static and one for dynamic (which implies that the two are independent of each other) resulting in two correlation lengths (*the way I understand it*). The ratio of the static, I_G , to the dynamic chain scattering I_F is a measure of the reduction in the importance of this clustering as the concentration increases, as shown in Figure 11. Explain the origin of the $1/(3\nu-1)$ scaling factor on the bottom of page K, and the meaning of the x and y axis in figure 11.

- e) One point that Scholz misses is the emergence of large-scale structures (that cannot be simulated in his finite simulation box). For example, if the chains linking a crosslink point are entangled or are polydisperse, some short linkages exist which will necessarily sustain the majority of the tension on swelling from a crosslink site. These short chains or entangled chains will form a short-chain pathway through the network which will dominate the mechanical properties and swelling and structure in any real rubber or gel. Comment on the value of Schulz's studies in this context, that is, how much can you say about a bulk gel or rubber based on a box of 512 mer units per side.