ICFP – Soft Matter

Elasticity of a polymer gel

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A polymer gel is a network of polymer chains jointed together at connection sites by covalent chemical bonds or physical interactions such as hydrogen bonds or electrostatic forces [1]. These bonds turn the liquid polymer melt in the solid gel; this process is called gelation. The polymer gel is a solid in the sense that it resists shear forces; however its structure looks like the one of a liquid. The polymer gel can be very homogeneous if the gelation is fast, or heterogeneous if gelation is slow; we restrict ourselves to homogeneous gels in the following.

The elasticity of a polymer gel such as rubber is very different from that of crystalline solids. The elastic modulus of a polymer gel is rather low, but they can hold deformations of order one without breaking. Moreover, the elastic modulus of gels are approximately proportional to the temperature. In this tutorial, we introduce the Kuhn's theory for the elasticity of a polymer gel, which is based on the thermal motion of the polymer chains.

We start by calculating the elasticity of a single chain. Then we use this result to construct the elasticity of the gel. Recognizing that our result does not take into account the finite extensibility of the chain, we introduce a refined model, the freely jointed chain.

Technical note: questions requiring calculations are indicated with asterisks: no asterisk for less than three lines of calculations, one for less than 10 lines, and two for longer calculations.

1 Elasticity of a single chain

We recall that the probability density of the end-to-end vector $\boldsymbol{r}$ of a polymer made of N segments of length b on a square lattice is given by

$$\psi_0(\boldsymbol{r}, N) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2Nb^2}\right). \tag{1}$$

1. What is the free energy $A_c(\boldsymbol{r}, N)$ of a configuration with the end-to-end vector $\boldsymbol{r}$? What is the restoring force $\boldsymbol{f}$ on the end monomer?

2 Elasticity of a gel

A gel is composed of cross-linked chains: chains are attached at some points, leading to $n_c = V\nu_c$ partial chains in a volume V, with a distribution of lengths $\phi_0(N)$. At rest, we assume that the distribution of end-to-end vector of a partial chain is given by the equilibrium distribution for ideal chains, $\psi_0(\boldsymbol{r}, N)$.

2. Explain that the total free energy of the gel is given by

$$A = n_c \int_0^\infty \mathrm{d}N \phi_0(N) \int \mathrm{d}\boldsymbol{r} \psi_0(\boldsymbol{r}, N) A_c(\boldsymbol{r}, N) + A_0(V, T), \tag{2}$$

where $A_0(V, T)$ does not depend on the stretching of the chains.

We assume that the deformation is affine at the scale of the polymer chains. Upon deformation, the vector $\boldsymbol{R}$ moves to $\boldsymbol{R}' = \boldsymbol{E} \cdot \boldsymbol{R}$, where $\boldsymbol{E}$ is the deformation gradient tensor.

3. How is the free energy (2) modified upon deformation?

4. * Show that the free energy of the deformed gel is given by

$$A' = \frac{kTn_c}{2} E_{\mu\nu} E_{\mu\nu} + A_0(V', T). \tag{3}$$

In order to compute the stress $\boldsymbol{\sigma}$, we need to determine the free energy change upon an infinitesimal change in the deformation gradient tensor, $\boldsymbol{E} \to \boldsymbol{E} + \delta\boldsymbol{E}$ (we thus consider an arbitrary deformation followed by an infinitesimal one). The deformation associated to this change can be encoded in the deformation tensor $\boldsymbol{\epsilon}$ such that $\boldsymbol{E} + \delta\boldsymbol{E} = (\mathbf{1} + \boldsymbol{\epsilon})\boldsymbol{E}$ (we ignore the symmetry of $\boldsymbol{\epsilon}$ at this stage).

5. What is the change in volume δV associated with this small deformation? Express it with the trace of the deformation.

6. Express the change in free energy, δA, as a function of the deformation tensor $\boldsymbol{\epsilon}$.

The free energy change is related to the deformation through the stress tensor $\boldsymbol{\sigma}$ as

$$\delta A = V \sigma_{\mu\nu} \epsilon_{\mu\nu}. \tag{4}$$

7. Write down the stress tensor $\boldsymbol{\sigma}$ for an arbitrary deformation $\boldsymbol{E}$. You can introduce the pressure $P = -\partial A_0/\partial V$.

As liquids, polymer gels are almost incompressible: their volume is constant and their pressure is set by external conditions.

We consider a piece of rubber stretched along z. The boundaries in the perpendicular directions are free.

8. What is the deformation gradient tensor $\boldsymbol{E}$ in this state?

9. What is the stress $\boldsymbol{\sigma}$?

10. Does our theory take into account the finite extensibility of the chains? Where does this comes from?

3 Freely jointed chain

In the freely jointed chain model, each bond has a length b and an orientation $\boldsymbol{n}_i$; the orientations of the different bonds are independent.

11. * Write and compute the partition function Z_N of a chain of N bonds when an external force $\boldsymbol{f}$ is applied on the end monomer.

12. * What is the average extension under the force $\boldsymbol{f}$? How does it compare with the behavior of the Rouse chain?

13. Sketch the steps needed to incorporate this single chain model in the Kuhn's gel theory.

References

[1] Masao Doi. *Introduction to polymer physics.* Oxford university press, 1996.