ICFP – Soft Matter

Elasticity of a polymer gel – Solution

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1 Elasticity of a single chain

1. The probability $\psi_0(\boldsymbol{r}, N)$ is proportional to a number of configurations. The associated free energy is thus

$$A_c(\boldsymbol{r}) = -kT \log(\psi_0(\boldsymbol{r})) = \frac{3kTr^2}{2Nb^2}, \tag{1}$$

where we have discarded a $\boldsymbol{r}$ independent term. The restoring force $\boldsymbol{f}$ is thus given by

$$\boldsymbol{f} = -\nabla A_c(\boldsymbol{r}) = -\frac{3kT\boldsymbol{r}}{Nb^2}. \tag{2}$$

2 Elasticity of a gel

2. The average free energy of a chain (or partial chain) with length L is $\int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)A_c(\boldsymbol{r}, N)$. Taking into account the distribution of lengths $\phi_0(N)$, we arrive at

$$A = n_c \int_0^\infty \mathrm{d}N\phi_0(N) \int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)A_c(\boldsymbol{r}, N), \tag{3}$$

where we can add a term that does not depend on the stretching of the chains, $A_0(V, T)$.

3. The free energy becomes

$$A' = n_c \int_0^\infty \mathrm{d}N\phi_0(N) \int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)A_c(\boldsymbol{E} \cdot \boldsymbol{r}, N) + A_0(V', T). \tag{4}$$

4. Using the expression of the free energy of a chain, Eq. (1), we compute

$$\int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)A_c(\boldsymbol{E} \cdot \boldsymbol{r}, N) = \frac{3kT}{2Nb^2} \int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)(E \cdot \boldsymbol{r})^2 \tag{5}$$

$$= \frac{3kT}{2Nb^2} E_{\mu\nu} E_{\mu\sigma} \int \mathrm{d}\boldsymbol{r}\psi_0(\boldsymbol{r}, N)r_\nu r_\sigma \tag{6}$$

$$= \frac{3kT}{2Nb^2} E_{\mu\nu} E_{\mu\sigma} \times \frac{Nb^2}{3}\delta_{\nu\sigma} \tag{7}$$

$$= \frac{kT}{2} E_{\mu\nu} E_{\mu\nu}. \tag{8}$$

The total energy is thus

$$A' = \frac{kTn_c}{2} E_{\mu\nu} E_{\mu\nu} + A_0(V', T). \tag{9}$$

5. The volume change δV is given by

$$\frac{\delta V}{V} = \frac{\det(\boldsymbol{E} + \delta\boldsymbol{E})}{\det(\boldsymbol{E})} = \det(1 + \boldsymbol{\epsilon}) \simeq \mathrm{Tr}\,(\boldsymbol{\epsilon}). \tag{10}$$

6. The free energy change is

$$\delta A = kTn_c E_{\mu\nu}\delta E_{\mu\nu} + \frac{\partial A_0}{\partial V}\delta V. \tag{11}$$

Using $\delta E_{\mu\nu} = \epsilon_{\mu\sigma}E_{\sigma\nu}$ and the previous expression for the volume change,

$$\delta A = kTn_c E_{\mu\nu}\epsilon_{\mu\sigma}E_{\sigma\nu} + \frac{\partial A_0}{\partial V}V\epsilon_{\mu\mu}. \tag{12}$$

7. Upon a deformation ϵ, the change in free energy allows to identify the stress σ with

$$\delta A = V\sigma_{\mu\nu}\epsilon_{\mu\nu}, \tag{13}$$

hence here

$$\sigma_{\mu\nu} = kT\nu_c E_{\mu\sigma}E_{\nu\sigma} - P\delta_{\mu\nu}, \tag{14}$$

with $\nu_c = n_c/V$ the density of chains.

8. We deformation gradient tensor

$$\boldsymbol{E} = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix}. \tag{15}$$

We check that $\det(\boldsymbol{E}) = 1$, ensuring the conservation of volume.

9. From the equations above the stress is given by

$$\boldsymbol{\sigma} = kT\nu_c \begin{pmatrix} \lambda^{-1} & 0 & 0 \\ 0 & \lambda^{-1} & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix} - P\boldsymbol{1}. \tag{16}$$

Since the stress should be zero on the sides, $P = kT\nu_c/\lambda$, hence

$$\sigma_{zz} = kT\nu_c\left(\lambda^2 - \frac{1}{\lambda}\right). \tag{17}$$

10. The finite extensibility of the chains is not taken into account in the above theory. This can be traced back to the elasticity of a single chain, where any extension is allowed.

3   Freely jointed chain

11. In the freely jointed chain

$$\boldsymbol{R}_N = b\sum_{i=1}^{N} \boldsymbol{n}_i. \tag{18}$$

The partition function Z under a force $\boldsymbol{f}$ is given by

$$Z = \int \prod_i \mathrm{d}\boldsymbol{n}_i \exp\left(\frac{\boldsymbol{f}\cdot\boldsymbol{R}_N}{kT}\right) = z_1^N, \tag{19}$$

where

$$z_1 = \int \mathrm{d}\boldsymbol{n} \exp\left(\frac{b\boldsymbol{f}\cdot\boldsymbol{n}}{kT}\right) = \frac{4\pi\sinh(\lambda)}{\lambda}, \tag{20}$$

with

$$\lambda = \frac{bf}{kT}. \tag{21}$$

12. The average orientation of a bond can be obtained with

$$\langle\boldsymbol{n}\rangle = \frac{1}{z_1}\int \mathrm{d}\boldsymbol{n}\boldsymbol{n}\exp\left(\lambda\hat{\boldsymbol{f}}\cdot\boldsymbol{n}\right) = \hat{\boldsymbol{f}}\frac{\partial\log(z_1)}{\partial\lambda} = \hat{\boldsymbol{f}}\left[\coth(\lambda) - \frac{1}{\lambda}\right]. \tag{22}$$

The average position of the end monomer is thus

$$\langle \boldsymbol{R}_N \rangle = Nb\hat{\boldsymbol{f}} \left[\coth(\lambda) - \frac{1}{\lambda} \right]. \tag{23}$$

At small λ, we can use the Taylor expansion $\coth(\lambda) = \frac{1}{\lambda} + \frac{\lambda}{3} + \mathcal{O}(\lambda^3)$. In this limit

$$\langle \boldsymbol{R}_N \rangle = \frac{Nb^2}{3kT}\boldsymbol{f} : \tag{24}$$

we recover the behavior of the Rouse model. At large λ, $\coth(\lambda) \to 1$ so that

$$\langle \boldsymbol{R}_N \rangle \to Nb\hat{\boldsymbol{f}}. \tag{25}$$

13. The partition function of the polymer chain gives access to its free energy,

$$A(\boldsymbol{r}, \boldsymbol{f}) = -kTN \log \left(\frac{\sinh(\lambda)}{\lambda} \right) = A_0(\boldsymbol{r}) - \boldsymbol{r} \cdot \boldsymbol{f}, \tag{26}$$

where $A_0(\boldsymbol{r})$ is the entropy of a single chain. The difficulty in getting the expression for $A_0(\boldsymbol{r})$ is to invert the relation between $\boldsymbol{r} = \langle \boldsymbol{R}_N \rangle$ and λ. Once A_0 is known it can be used in Kuhn's gel theory.

References

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