Elastic modulus of an entangled solution of semiflexible polymers

2020-2021 Biophysics exam – Physics of Complex Systems M2

No documents, calculators or phones allowed.

The exam is composed of short questions collectively worth 25% of the total grade, followed by a problem within which all individual questions are worth the same number of points. The problem is long, and it is possible to obtain a perfect grade without completing all questions: focus on quality, not quantity. Bold characters denote vectors, and hats denote unit vectors.

Short questions

- Briefly explain the central dogma of molecular biology (about half a page or one large schematic).

- Let us write the master equation for the probability to have n monomers in the filament in the Brownian ratchet model as $\partial_t p(n,t) = \bar{k}_{\mathrm{on}} p(n-1,t) + k_{\mathrm{off}} p(n+1,t) - (\bar{k}_{\mathrm{on}} + k_{\mathrm{off}}) p(n,t)$. In the most general case, the transition rates $\bar{k}_{\mathrm{on}}$ and k_{off} may both depend on the applied force F. Nevertheless these expression are constrained by the detailed balance condition. Briefly sketch the brownian ratchet model and express this constraint.

- Consider a two-dimensional active matter model with anisotropic particles making an angle θ with the horizontal axis and moving with a velocity $\mathbf{v}$. A general form for the evolution of the angular order parameter is $\partial_t \theta = A_{ij} \nabla_i \nabla_j \theta + B_{ij} \nabla_i v_j$, where A and B are matrices of unknown phenomenological coefficients. Using the invariance of the system under mirror symmetry, show that four out of the eight entries of these matrices must be equal to zero.

Problem

Over long time scales, a collection of semiflexible polymers (*e.g.*, actin filaments) in solution without crosslinks behaves as a liquid. If the filaments are long, such behavior might however only manifest over exceedingly long time scales as each filament is trapped in a tube-like cage formed by its neighbors. To escape the tube and change neighbors as required for liquid-like behavior, the filament must diffuse longitudinally over a distance of the order of its own length, a very slow process known as reptation. On shorter time scales, each semiflexible polymer is effectively trapped within its own tube, and the system as a whole responds as an elastic medium. In this problem, we set out to determine the shear modulus of this medium as a function of the properties of the filaments through an effective medium approach inspired by Refs. [1, 2, 3].

The tube-induced confinement squeezes the polymer and prevents it from straying far from its original conformation. In Sec. 1, we discuss the extent to which this hinders the transverse fluctuations of the polymer and assess how often it "bumps" the walls of the tube. In Sec. 2, we show that this restriction of the filament's fluctuations affects its entropic elasticity and thus modifies the elastic response of the network as a whole. Finally, Sec. 3 constitutes the key step of our approach: having showed in the previous sections that the strength of the confinement affects the network's elasticity, we show that the confinement of an individual filament reciprocally stems from the elasticity of the elastic medium formed by its peers. This reciprocal relation allows us to determine the network's modulus self-consistently.

1 Entanglement length and tube radius

We consider an infinitely long single polymer confined in a tube of fixed radius R. We assume that the polymer lies along the z axis on average with small transverse deviations described by $\mathbf{U} = (x(z), y(z))$. To lowest order in $\mathbf{U}$ the filament's energy functional reads

$$\mathcal{E} = \int \left[\frac{\kappa}{2} \left(\partial_z^2 \mathbf{U} \right)^2 + \frac{\sigma}{2} \left(\partial_z \mathbf{U} \right)^2 + \frac{\lambda}{2} \mathbf{U}^2 \right] \mathrm{d}z, \tag{1}$$

where σ is the tension of the filament. Rather than implementing an impenetrable wall around the polymer, this expression represents the confinement of the polymer of interest by its neighbors through a more easily tractable harmonic potential with stiffness λ. In this section we relate the value of λ to the physical radius R associated with the confinement. We also determine the "entanglement length" L_e, which is the typical distance between two points where the polymer bumps the wall of the tube.

1.1 What is the physical meaning of the κ term in Eq. (1)?

1.2 Give the name and explain the physical meaning of $\ell_p = \kappa/k_B T$.

1.3 Defining the one-dimensional Fourier transform through

$$\mathbf{U}(z) = \int \tilde{\mathbf{U}}(q) e^{iqz} \frac{\mathrm{d}q}{2\pi}, \qquad \tilde{\mathbf{U}}(q) = \int \mathbf{U}(z) e^{-iqz} \, \mathrm{d}z, \tag{2}$$

which implies

$$\delta(z) = \int e^{iqz} \frac{\mathrm{d}q}{2\pi}, \qquad 2\pi \delta(q) = \int e^{-iqz} \, \mathrm{d}z, \tag{3}$$

write down the energy E as a sum over Fourier components.

1.4 Show that

$$\left\langle \tilde{U}_i(q) \tilde{U}_j(q') \right\rangle = \frac{2\pi k_B T}{H(q) + \sigma q^2} \delta_{ij} \delta(q + q'), \tag{4}$$

where $\langle \cdot \rangle$ denotes the thermal average and where $H(q)$ is a function to be specified (you can use the same quick and dirty proof previously used in the tutorials).

1.5 In the absence of an external stress on the polymer solution, each polymer has the time to relax its tension, implying $\sigma = 0$. In that case, show that we have

$$\left\langle U_x^2(0) \right\rangle = A \frac{k_B T}{\lambda^{3/4} \kappa^{1/4}} \tag{5}$$

where A is a dimensionless coefficient to be specified. You may use $\int_{-\infty}^{\infty} (1 + a^4)^{-1} \mathrm{d}a = \pi/\sqrt{2}$.

1.6 To determine the value of λ, we must impose that the typical lateral displacement of the polymer inside the tube is equal to the confinement radius R. In the case $\sigma = 0$, give the scaling of λ as a function of R and other parameters of the problem.

1.7 In the case $\sigma = 0$, argue for the existence of a characteristic wavevector q_e at which the energy crosses over between two different physical regimes. Explain the nature of these regimes.

1.8 Infer the scaling of the entanglement length L_e as a function of R and ℓ_p from your result.

2 Linear elastic response

Here we study of the response of the polymer solution to an external stress at the single-polymer level, then at the continuum level. We first consider a single polymer under a tension $\sigma \neq 0$. We denote by ϵ the extensional strain of our infinite polymer. To clarify its physical meaning, we may temporarily consider a polymer with a finite length L_0 in the absence of stress and with final length $L_0 + \Delta L$ in its presence; then $\epsilon = \Delta L/L_0$. As shown in the tutorials, the extensional strain is given by

$$\epsilon = \frac{\phi(\sigma) - \phi(0)}{2} \qquad \text{where} \qquad \phi(\sigma) = \iint qq' \left\langle \tilde{\mathbf{U}}(q) \tilde{\mathbf{U}}(q') \right\rangle \frac{\mathrm{d}q}{2\pi} \frac{\mathrm{d}q'}{2\pi}. \tag{6}$$

Equation (6) does not make a reference to polymer length and is directly applicable to our infinite polymer.

2.1 Using Eq. (4), show that to lowest order in σ we can write

$$\sigma = k\epsilon, \qquad \text{where} \qquad k_B T/k \propto \int_{-\infty}^{\infty} \left[\frac{H(q)}{k_B T q^3} \right]^n \frac{\mathrm{d}q}{q^2}. \tag{7}$$

You will specify the exponent n and the proportionality coefficient in Eq. (7). This result implies that for small deformations, the energy per unit length of a single polymer can be expressed as a function of its extensional strain as

$$e = \frac{k\epsilon^2}{2} \tag{8}$$

2.2 Our isotropic solution is a mixture of filaments with all possible orientations. We first consider a straight (apart from thermal fluctuations) filament with an end-to-end vector $\mathbf{R}$, and subject it to an affine deformation which takes it to a new end-to-end vector $\mathbf{R}+\delta\mathbf{R}$. Write down the new length of the filament as a function of $\mathbf{R}$ and $\delta\mathbf{R}$ to first order in $\delta\mathbf{R}$. We now assume that the affine deformation takes any point of the system with position $\mathbf{r}$ to $\mathbf{r}+\mathbf{u}$, where the displacement vector is given by $u_i = \Gamma_{ij}r_j$. Denoting $\hat{\mathbf{R}} = \mathbf{R}/|\mathbf{R}|$, write the extensional strain $\epsilon(\hat{\mathbf{R}})$ of the polymer as a function of Γ and $\hat{\mathbf{R}}$ to first order in Γ.

2.3 We define the polymer density ρ as the length of polymer in a unit volume of the solution (ρ thus has units of m^{-2}). Assuming that the filaments in the solution are oriented isotropically, the energy per unit volume of the solution under our affine deformation reads

$$E = \rho \left\langle e(\hat{\mathbf{R}}) \right\rangle_{\hat{\mathbf{R}}} = \frac{\rho k}{2} \left\langle \epsilon(\hat{\mathbf{R}})^2 \right\rangle_{\hat{\mathbf{R}}}, \tag{9}$$

where $\langle \cdot \rangle_{\hat{\mathbf{R}}} = \iint \cdot \sin\theta\, d\theta\, d\phi/4\pi$ is the average over all possible orientations of $\hat{\mathbf{R}}$ on the unit sphere. For a simple shear deformation characterized by

$$\Gamma = \begin{pmatrix} 0 & 0 & \eta \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{10}$$

show that

$$E = B\rho k\eta^2 \propto \frac{\rho(k_B T)^{n+1}\eta^2}{\int H(q)^n q^{-(3n+2)}\, dq} \tag{11}$$

and give the value of the dimensionless coefficient B. Note that the simplified approach used here does not take into account the curvature stresses induced by Γ.

2.4 From a continuum medium perspective, the energy per unit volume of an elastic medium is

$$E = 2\mu \left(\gamma_{ij} - \frac{\delta_{ij}}{3}\gamma_{kk} \right) \left(\gamma_{ij} - \frac{\delta_{ij}}{3}\gamma_{kk} \right) + \frac{K}{2}(\gamma_{kk})^2, \tag{12}$$

where $\gamma_{ij} = (\partial_i u_j + \partial_j u_i)/2$ is the linearized strain tensor. Under what name is the elastic modulus K known? What type of deformations of the medium is it associated with?

2.5 Write E for the deformation of Eq. (10), then use Eq. (11) to express the shear modulus as a function of the filaments' microscopic parameters.

3 Self-consistent determination of the shear modulus

Here we consider the collection of polymers surrounding the polymer of interest not as a harmonic confining potential with rigidity λ, but as a deformable, continuum elastic medium. Any deformation of the central polymer induces a deformation in this medium, implying an elastic energy cost. We compute this cost, then assimilate it to the confinement energy introduced in Sec. 1. This then enables our self-consistent conclusion.

The mechanical equilibrium of the medium is described by

$$\partial_j \sigma_{ij} = -f_i, \tag{13}$$

where f_i is the density of body forces exerted by the polymer on the medium. The stress tensor reads

$$\sigma_{ij} = 2\mu \left(\gamma_{ij} - \frac{\delta_{ij}}{3}\gamma_{kk} \right). \tag{14}$$

Indeed the deformations described by K in Eq. (12) turn out to be irrelevant in the following, and so we set $K = 0$ in Eq. (14) to simplify the notation.

3.1 Write down the mechanical equilibrium equation as a set of three scalar linear differential equations expressing the three components of $\mathbf{f}$ as functions of the components of the displacement field $\mathbf{u}$ introduced in Sec. 2. You may find it convenient to write the divergence with the compact notation $\nabla \cdot \mathbf{u}$ where applicable.

3.2 Fourier transform these equations and invert them to show that

$$\tilde{\mathbf{u}}(\mathbf{k}) = \frac{\tilde{\mathbf{f}}(\mathbf{k})}{k^2} - C\frac{[\mathbf{k} \cdot \tilde{\mathbf{f}}(\mathbf{k})]}{k^4}\mathbf{k}, \qquad (15)$$

where C is a numerical coefficient to be specified and $\mathbf{k}$ is the three-dimensional wavevector. Here tildes denote three-dimensional Fourier transforms.

3.3 We consider a central polymer whose center line lies along the z axis, as in the previous sections. The polymer is constrained to follow the motion of the surrounding elastic medium, and so

$$u_x(0,0,z) = U_x(z) \qquad u_y(0,0,z) = U_y(z) \qquad u_z(0,0,z) = 0. \qquad (16)$$

We assume a simple sinusoidal deformation profile in the x direction only, namely $\mathbf{U}(z) \propto \hat{\mathbf{x}}\cos(qz)$. Note that this is not a serious restriction, as a superposition of such sinusoids allows to reconstruct any polymer deformation profile in the usual Fourier transform way. Since we are faced with a linear problem, the force field exerted by the polymer onto the elastic medium must also be a sinusoid. We use

$$\mathbf{f}(\mathbf{r}) = f_0\frac{\cos(qz)}{2\pi L_e^2}\exp\left(-\frac{x^2+y^2}{2L_e^2}\right)\hat{\mathbf{x}}, \qquad (17)$$

where f_0 has dimensions of force per unit length. The dependence of this force on x and y manifests the discrete nature of the network. As a result of this discreteness, the continuum description holds only down to length scales of the order of the entanglement length L_e defined in Sec. 1. Thus L_e acts as an ultraviolet cutoff for our description and the force $\mathbf{f}$ is effectively "smudged" over that length scale. Write down the Fourier transform $\tilde{\mathbf{f}}(\mathbf{k})$

3.4 Remembering the back Fourier transform formula

$$\mathbf{u}(\mathbf{r}) = \iint \tilde{\mathbf{u}}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}, \qquad (18)$$

show that the Fourier transform of the polymer displacement field satisfies

$$\mathbf{U}(z) = \frac{f_0\cos(qz)\hat{\mathbf{x}}}{\mu g(qL_e)}, \qquad (19)$$

where you show that the dimensionless function $g(\xi)$ is a function only of the variable ξ. You will express it as a two-dimensional integral (do not attempt to perform the integration).

3.5 Why does the product $\mu g(qL_e)$ play the same role as trap stiffness λ introduced in Sec. 1? In the following we assume that the results of Secs. 1 and 2 still hold for such a q-dependent confining potential $\lambda(q)$.

3.6 The expression of μ derived in Sec. 2 was derived under an assumption of affine deformation. A different calculation allowing non-affine deformations and the bending of the filaments under strain yields

$$\mu = \frac{7\rho k_B T}{5}\int_{-\infty}^{\infty}\frac{\lambda(q)}{\kappa q^4 + \lambda(q)}\frac{\mathrm{d}q}{2\pi}. \qquad (20)$$

A simple scaling reasoning regarding the average distance between two neighboring filaments yields $\rho = DR^{-2}$ where D is a numerical coefficient of order one. Using this result, compare the scaling of μ according to Eq. (20) as a function of $k_B T$, R and ℓ_p to the one extracted from Eq. (11).

3.7 In the regime $R \ll \ell_p$ implicitly considered throughout this problem, which of the two is the largest? As a result, which of the two should we consider and why?

3.8 Combine this result with the results from the previous section into a nonlinear algebraic equation for the quantity $\tilde{\mu} = \mu L_e^4/\kappa$. Conclude as to the scaling of μ with $k_B T$, ρ and ℓ_p.

References

[1] Theo Odijk. On the statistics and dynamics of confined or entangled stiff polymers. *Macromolecules*, 16:1340, 1983.

[2] David C. Morse. Viscoelasticity of concentrated isotropic solutions of semiflexible polymers. 1. model and stress tensor. *Macromolecules*, 31(20):7030, September 1998.

[3] David C. Morse. Tube diameter in tightly entangled solutions of semiflexible polymers. *Phys. Rev. E*, 63(3):031502, February 2001.