

# STATISTICAL PHYSICS OF SIMPLE AND COMPLEX FLUIDS

## SOFT CONDENSED MATTER THEORY

### HOMEWORK #1

#### Entropic systems

## 1 Isotropic–nematic transition of liquid crystals: mean-field theory

We consider a fluid whose molecules are modeled as “hard-core” rods. To simplify, one assumes that the axis of a rod can only point along the 3 directions  $x$ ,  $y$  et  $z$ . We neglect any interaction other than steric repulsion. We note  $V$  the volume of the fluid and  $\rho = N/V$  the density.

1. Let  $v_{\parallel}$  be the excluded volume for two parallel rods, that is, the forbidden volume to one of the rod center because of the presence of the other rod. Let  $v_{\perp}$  the excluded volume for two perpendicular rods. With simple arguments, show that  $v_{\perp} > v_{\parallel}$ .
2. Compare the translational entropy with the rotational entropy, and explain qualitatively why one expects a disoriented liquid at low density (isotropic liquid), and an oriented liquid at high density (nematic liquid).

*A mean-field theory is constructed by treating the rods as uncorrelated systems, which can freely translate in space and each having the probability  $1 - 2r$  to point towards direction  $z$  (the common alignment direction), and probability  $r$  to point towards in each of  $x$  and  $y$  directions. Let  $F(r)$  be the mean-field free energy of the system. We have  $F(r) = \langle E \rangle - NT(s_{\text{rot}} + s_{\text{tr}})$ , where  $E$  is the actual energy of the system (taking excluded volume into account), and  $s_{\text{rot}}$  and  $s_{\text{tr}}$  are the rotational and translational entropies for an individual rod, respectively.*

3. Calculate  $s_{\text{rot}}$ .
4. Justify that  $\langle E \rangle = \frac{3}{2}Nk_{\text{B}}T$  (using classic approximation).
5. Express the mean volume  $V_z$  that a rod oriented towards  $z$  can access to, as a function of  $V$ ,  $\rho$ ,  $r$ ,  $v_{\parallel}$  and  $v_{\perp}$ . Same question for the mean volumes  $V_x$  and  $V_y$  that rods with orientation  $x$  and  $y$  can access to.
6. We consider the rods as three ideal gases evolving in three independent volume compartments. Using the classic expression of the entropy of an ideal gas (Sackur-Tetrode expression)

$$s_{\text{ST}}(T, V, N) = k_{\text{B}} \left[ \ln \left( \frac{V}{N\lambda^3} \right) + \frac{5}{2} \right], \quad (1)$$

calculate, to first order in  $\rho$ , the entropy  $s_z$  of a rod oriented along  $z$  and the entropies  $s_x$  and  $s_y$  of a rod oriented along  $x$  and  $y$ , respectively. Deduce  $s_{\text{tr}}$  by weighting these expressions with the corresponding probabilities.

7. Deduce  $F(r)$  and determine the “mean-field” value of  $r$ .
8. One defines the order parameter  $S = 1 - 3r$  : explain why and give the value range of  $S$ . Write the equation that gives  $S$ .

9. With help of the sign of the second derivative of the function

$$S \rightarrow \ln \frac{1+2S}{1-S} \quad (2)$$

at  $S = 0$ , show that there is a isotropic–nematic phase transition that appears when we increasing  $\rho$  and that it is a discontinuous transition (first order transition).

## 2 Entropic elasticity of rubber: Freely Jointed Chain (FJC) chain model

Rubber is made of long molecules (polymers). We study the strain-stress relation of a unique polymer chain lying in the plane. We suppose that the orientations of the  $N \gg 1$  monomers are uncorrelated, and the steric repulsions and interactions between monomers are neglected. The energy of the molecule is then composed exclusively of the kinetic energy of its monomers (purely entropic chain).

We first suppose that the polymer is attached at both ends. We note  $X$  the (fixed) abscissa difference between both ends,  $a$  the length of each monomer, and  $E$  the energy of the polymer chain.

A configuration of the polymer (“micro-state”) is described by the momentum and orientation of every monomer of the chain. Orientation of monomer  $i$  is given by polar angles  $(\theta_i, \varphi_i)$ , with  $\theta_i \in [0, \pi[$  and  $\varphi_i \in [0, 2\pi[$  (the angles are measured with respect to the  $x$  axis). Its momentum is denoted  $\mathbf{p}_i$ .

The system is in contact with a thermostat with temperature  $T$ .

1. Show that the probability distribution of the micro-states that satisfy the boundary conditions (attached ends) still follows the Gibbs statistics.
2. Explain why the chosen boundary conditions are not convenient to calculate the partition function  $Z$  of this system.

We now replace one of the boundary condition: we suppose that one of the extremities of the molecule is attached to a spring with length at rest  $l_0$  and spring constant  $k_{sp}$ , while the other extremity is fixed. We suppose the spring can extend only in the  $x$  direction:

$$\mathbf{F}_{sp} = -k_{sp}(l - l_0)\mathbf{e}_x,$$

where  $l > 0$  is the length of the spring,  $l_0$  its length at rest,  $k_{sp}$  the spring constant, and  $\mathbf{e}_x$  the unit vector pointing in the  $x$  direction. We consider that the beads can freely move in the  $y$  and  $z$  directions.

*Experimentally, such a “spring” can be done by grafting the polymer extremity to a dielectric bead and applying a non-uniform external electric field on it: then the bead experiences an attractive force (optical tweezers), which can be idealized by a hookean spring (see Fig. 1).*

We note  $X$  the (fluctuating) abscissa difference between both ends of the polymer (*projected length*).

3. Write down the potential energy of the spring  $E_{sp}$  as a function of  $X$ ,  $l_0$  and  $L$ , the (fixed) distance between the two attached extremities of the system (see Figure 1).
4. Let  $\langle X \rangle$  be the average projected length of the polymer. Show that when the fluctuations  $\delta X = X - \langle X \rangle$  are small, the potential energy of the spring becomes:

$$E_{sp} = E_0 - \tau X,$$

where  $E_0$  is a constant and  $\tau$  is the tension exerted by the chain, which you will express as a function of  $k_{sp}$ ,  $L$ ,  $\langle X \rangle$  and  $l_0$ . What is the physical interpretation of this relation ?

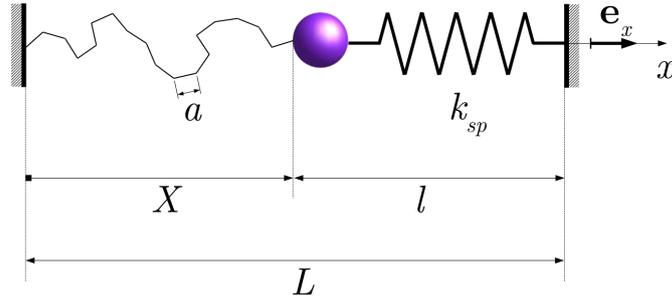


Figure 1: polymer with one end fixed, and the other attached to a spring.

5. Justify that the above approximation becomes increasingly accurate at high tensions.
6. Show that within this approximation, the partition function of the system is:

$$\mathcal{Z} = \mathcal{Z}_{kinetic} z^N,$$

where  $\mathcal{Z}_{kinetic}$  denotes the kinetic part of the partition function – **which we will not try to evaluate** – and

$$z = \int \sin \theta d\theta d\varphi e^{\beta \tau a \cos \theta} = 4\pi \frac{\sinh(\beta \tau a)}{\beta \tau a}.$$

7. Calculate the free energy  $F = -k_B T \ln \mathcal{Z}$ , and show that  $F = \langle E \rangle - TS - \tau \langle X \rangle$ , where  $E$  and  $S$  are the kinetic energy and entropy of the system (polymer + spring), respectively.
8. What are the variables that describe the macroscopic state of the polymer alone? Define the thermodynamic potential adapted to the corresponding thermodynamic ensemble (i.e. the one which is minimized).
9. Express the average chain elongation  $\langle X \rangle$  as a function of  $N$ ,  $a$ ,  $T$  and  $\tau$ .
10. Show that when  $\tau \ll k_B T/a$ , the chain behaves like an hookean spring, and give the associate spring constant.
11. What is the value of  $\langle X \rangle$  in the limit  $\tau \rightarrow \infty$ ?
12. What happens when a rubber elastic is heated (does it contract or dilate)?
13. We now come back to the initial boundary conditions (both ends attached). A very general way to take constraints into account in the evaluation of  $\mathcal{Z}$  is by introducing appropriate Dirac delta and then use its Fourier transform representation:  $\delta(\mathbf{R} - \sum_k \mathbf{a}_k) = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{-i\mathbf{q} \cdot (\mathbf{R} - \sum_k \mathbf{a}_k)} d^3 \mathbf{q}$ , where  $\mathbf{R} = (X, Y, Z)$  is the relative vector position between the two ends. With help of this technique, show that:

$$\mathcal{Z} = C \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{-i\mathbf{q} \cdot \mathbf{R}} \left( 4\pi \frac{\sin qa}{qa} \right)^N d^3 \mathbf{q},$$

where  $C$  is a constant.

14. Justify that we can safely replace  $(\sin qa/qa)^N$  with its expansion around its max ( $q = 0$ ) in the thermodynamic limit. Give the corresponding analytic expression for  $\mathcal{Z}$ . We recall that, for any  $\alpha, \beta \in \mathbb{C}$  with  $\Re(\alpha) > 0$ :

$$\int_{-\infty}^{+\infty} e^{-\frac{\alpha}{2} x^2 + \beta x} dx = \sqrt{\frac{2\pi}{\alpha}} e^{\frac{\beta^2}{2\alpha}}.$$

15. Calculate the average tension  $\langle \tau \rangle = \partial F / \partial X$  of the chain. Compare the relationship between tension and extension with the one obtained in 10.
16. We now consider the situation where only one end is fixed, the other one if free. Relate the probability density  $P_N(\mathbf{R})$  that this end points at position  $\mathbf{R}$  to the partition function defined in 13.
17. Deduce the analytic expression of  $P_N(\mathbf{R})$  when  $Na \gg |\mathbf{R}|$ . Could we have obtained this expression with almost no calculus ?
18. *Bonus question:* calculate the exact partition function of the system (polymer+spring) – ie without linearization of the spring energy obtained in question 3 – using Hubbard-Stratonovich transformation.

## Answers

### Correction: Rubber elasticity

1. Let  $p_l$  be the probability distribution of any configuration  $l$  of the polymer, satisfying or not the boundary conditions. The probability distribution for the configurations that satisfy the boundary conditions is:

$$p'_l = \frac{p_l}{\sum_{l \text{ satisfying b.c.}} p_l}.$$

It is then clear that if  $p_l$  follows Gibbs statistics, so it is for  $p'_l$ .

2. The orientations of the monomers are not independent, as they must satisfy:  $\sum_i a \cos \theta_i = X$ .
3. The energy is:

$$E = E_{kinetic} + \frac{k}{2} (L - X - l_0)^2,$$

where  $E_{kinetic}$  is the kinetic energy of the polymer.

4. If  $|\delta X| \ll L - \langle X \rangle - l_0$ :

$$E_{sp} = \frac{k}{2} (L - \langle X \rangle - \delta X - l_0)^2 \simeq \frac{k}{2} (L - \langle X \rangle - l_0)^2 - k (L - \langle X \rangle - l_0) \delta X.$$

Since  $\delta X = X - \langle X \rangle$ :  $E_{sp} = E_0 - \tau X$  with  $\tau = k (L - \langle X \rangle - l_0)$ .

Physical meaning: the projected length of the polymer is free to fluctuate, but it experiences a **constant** tension  $\tau$ .

5. The condition  $|\delta X| \ll L - \langle X \rangle - l_0$  is equivalent  $k|\delta X| \ll \tau$ . Therefore the approximation becomes increasingly accurate as  $\tau$  increases.
6. Partition function:

$$Z = \sum_{\text{configs } l} e^{-\beta(E_l - \tau X_l)} = Z_{kin} \times \int d^2 \Omega_1 \dots d^2 \Omega_N e^{\beta \tau a \sum_i \cos \theta_i}.$$

Introducing  $z = \int \sin \theta d\theta d\varphi e^{\beta \tau a \cos \theta} = 4\pi \frac{\sinh(\beta \tau a)}{\beta \tau a}$ , one gets  $Z = Z_{kinetic} z^N$ .

Note that we integrated over all possible angles, while we required small  $\Delta X$ . This is justified by the fact that the exponential term is sharply peaked around its max.

7.  $F(T, \tau, N) = -k_B T \ln Z = F_0(T) - N k_B T \ln \left( \frac{\sinh(\beta \tau a)}{\beta \tau a} \right)$ .

8.  $\langle X \rangle = -\frac{\partial F}{\partial \tau}$ . Thus:

$$\langle X \rangle = Na \left( \coth(\beta\tau a) - \frac{1}{\beta\tau a} \right).$$

By definition  $S = -k_B \sum_l p_l \ln p_l$ , with here  $p_l = e^{-\beta(E_l - \tau X_l)} / Z$ . It comes:  $-TS = -\langle E \rangle + \tau \langle X \rangle - k_B T \ln Z$ , or equivalently,  $F = \langle E \rangle - TS - \tau \langle X \rangle$ .

9. Since  $\coth \epsilon \simeq \epsilon^{-1} + \epsilon/3$ , one gets:

$$\langle X \rangle = \frac{Na^2}{3k_B T} \tau.$$

The spring constant is  $k = \frac{3k_B T}{Na^2}$ .

10. When  $\tau \rightarrow \infty$ ,  $\langle X \rangle \rightarrow Na$ . That is the maximal length of the chain.

11. When  $T$  increases, the spring constant increases. For a given tension applied on the chain, the rubber contracts. (this is counter-intuitive: most materials dilate when heated).