

# ICFP – Soft Matter

## Onsager theory of the isotropic-nematic transition – Solution

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### 1 Free energy for the orientations

**1.** With the Mayer functions, the integrand is zero if two cylinders overlap and one otherwise: the integral counts the allowed configurations.

**2.** In the plane of the two orientations, the forbidden area is, at the leading order in  $d/\ell$ , a parallelogram with area  $\ell^2|\mathbf{n}_i \times \mathbf{n}_j|$ . Taking into account the direction perpendicular to this plane, we see that the forbidden area has a thickness  $2d$ , hence

$$v(\mathbf{n}_i, \mathbf{n}_j) = 2d\ell^2|\mathbf{n}_i \times \mathbf{n}_j|. \quad (1)$$

**3.** At order 1 in  $\Phi$ , the partition function is

$$Z = \frac{1}{N!} \int \prod_i d\mathbf{x}_i d\mathbf{n}_i \prod_{i < j} [1 + \Phi(\mathbf{x}_i - \mathbf{x}_j, \mathbf{n}_i, \mathbf{n}_j)] \quad (2)$$

$$\simeq \frac{1}{N!} \int \prod_i d\mathbf{x}_i d\mathbf{n}_i \left[ 1 + \sum_{i < j} \Phi(\mathbf{x}_i - \mathbf{x}_j, \mathbf{n}_i, \mathbf{n}_j) \right] \quad (3)$$

$$= \frac{V^N}{N!} \int \prod_i d\mathbf{n}_i \left[ 1 - \frac{v(\mathbf{n}_i, \mathbf{n}_j)}{V} \right]. \quad (4)$$

The free energy for the orientations  $(\mathbf{n}_i)$  is thus

$$F((\mathbf{n}_i)) = -T \log \left[ \frac{V^N}{N!} \left( 1 - \frac{1}{V} \sum_{\langle ij \rangle} v(\mathbf{n}_i, \mathbf{n}_j) \right) \right] \quad (5)$$

$$\simeq -TN \log(\rho) + \frac{T}{V} \sum_{\langle ij \rangle} v(\mathbf{n}_i, \mathbf{n}_j). \quad (6)$$

The free energy thus describes a system of  $N$  orientations interacting through the pair potential (1).

**4.** The free energy of the density of orientations  $\hat{\psi}(\mathbf{n})$  is (discarding the orientation-independent term):

$$\frac{F[\hat{\psi}]}{T} = \int \hat{\psi}(\mathbf{n}) \log(\hat{\psi}(\mathbf{n})) d\mathbf{n} + \frac{1}{2V} \int v(\mathbf{n}, \mathbf{n}') \hat{\psi}(\mathbf{n}) \hat{\psi}(\mathbf{n}') d\mathbf{n} d\mathbf{n}'. \quad (7)$$

The free energy per particle  $f = F/N$  of the distribution  $\psi = \hat{\psi}/N$  is

$$\frac{f[\psi]}{T} = \int \psi(\mathbf{n}) \log(\psi(\mathbf{n})) d\mathbf{n} + \bar{\rho} d\ell^2 \int |\mathbf{n} \times \mathbf{n}'| \psi(\mathbf{n}) \psi(\mathbf{n}') d\mathbf{n} d\mathbf{n}', \quad (8)$$

where we have omitted a constant term. It is of the form

$$\frac{f[\psi]}{T} = \sigma[\psi] + \frac{A}{2} \rho[\psi], \quad (9)$$

with

$$\sigma[\psi] = \int \psi(\mathbf{n}) \log(\psi(\mathbf{n})) d\mathbf{n}, \quad (10)$$

$$\rho[\psi] = \int |\mathbf{n} \times \mathbf{n}'| \psi(\mathbf{n}) \psi(\mathbf{n}') d\mathbf{n} d\mathbf{n}' \quad (11)$$

$$A = 2\bar{\rho}d\ell^2. \quad (12)$$

5. The volume fraction is given by  $\phi = \bar{\rho} \times \pi d^2 \ell / 4 \ll A$ : the coupling constant is much larger than the volume fraction, the ratio scales as  $d/\ell$ . There may be a transition for  $A$  of order 1, hence for very low volume fractions.

## 2 Phase transition

6. For the entropic term,

$$\sigma[\psi] = \int \frac{1}{4\pi} (1 + \mathbf{n}^T \mathbf{Q} \mathbf{n}) \log(1 + \mathbf{n}^T \mathbf{Q} \mathbf{n}) d\mathbf{n}, \quad (13)$$

$$= \frac{1}{4\pi} \int \left[ \mathbf{n}^T \mathbf{Q} \mathbf{n} + \frac{1}{2} (\mathbf{n}^T \mathbf{Q} \mathbf{n})^2 - \frac{1}{6} (\mathbf{n}^T \mathbf{Q} \mathbf{n})^3 + \frac{1}{12} (\mathbf{n}^T \mathbf{Q} \mathbf{n})^4 \right] d\mathbf{n}. \quad (14)$$

We now use

$$\int (\mathbf{n}^T \mathbf{Q} \mathbf{n})^k d\mathbf{n} = 4\pi q^k \int_0^1 \left( u^2 - \frac{1}{3} \right)^k du. \quad (15)$$

With  $\int_0^1 (u^2 - \frac{1}{3})^2 du = 4/45$ ,  $\int_0^1 (u^2 - \frac{1}{3})^3 du = 16/945$  and  $\int_0^1 (u^2 - \frac{1}{3})^4 du = 16/945$ , we arrive at

$$\sigma[\psi] = \int \psi(\mathbf{n}) \log(\psi(\mathbf{n})) d\mathbf{n} = \alpha_2 q^2 + \alpha_3 q^3 + \alpha_4 q^4 + \mathcal{O}(q^5) \quad (16)$$

with  $\alpha_2 = 2/45$ ,  $\alpha_3 = -8/2835$  and  $\alpha_4 = 4/2835$ .

7. The free energy term is

$$\rho[\psi] = \int |\mathbf{n} \times \mathbf{n}'| \psi(\mathbf{n}) \psi(\mathbf{n}') d\mathbf{n} d\mathbf{n}' = \frac{1}{(4\pi)^2} \int |\mathbf{n} \times \mathbf{n}'| \left( 1 + q \left[ (\mathbf{a} \cdot \mathbf{n})^2 - \frac{1}{3} \right] \right) \left( 1 + q \left[ (\mathbf{a} \cdot \mathbf{n}')^2 - \frac{1}{3} \right] \right) d\mathbf{n} d\mathbf{n}', \quad (17)$$

it contains a constant term and  $q$  and  $q^2$  terms. The constant term does not play a role in the analysis.

The terms of order  $q$  vanish: the integral

$$\frac{1}{(4\pi)^2} \int |\mathbf{n} \times \mathbf{n}'| \left[ (\mathbf{a} \cdot \mathbf{n})^2 - \frac{1}{3} \right] d\mathbf{n} d\mathbf{n}' \quad (18)$$

can be integrated over  $\mathbf{n}'$  first, which reduces the  $|\mathbf{n} \times \mathbf{n}'|$  term to a constant, and then the weight  $(\mathbf{a} \cdot \mathbf{n})^2 - \frac{1}{3}$  integrates to zero.

The interaction energy  $v(\mathbf{n}, \mathbf{n}')$  is lower if the orientations are aligned. Hence the energetic term  $\rho[\psi]$  should be lower if the distribution is more polarized, meaning that  $q$  is larger. We thus expect the  $q^2$  to have a negative prefactor, that we denote  $-r$ .

8. The  $q$  independent term is

$$\frac{1}{(4\pi)^2} \int |\mathbf{n} \times \mathbf{n}'| d\mathbf{n} d\mathbf{n}' = \frac{\pi}{4}. \quad (19)$$

The term of order  $q^2$  can be calculated by using the vector  $\mathbf{n}$  as a reference in polar coordinates for the vector  $\mathbf{n}'$ :

$$\int |\mathbf{n} \times \mathbf{n}'| \left[ (\mathbf{a} \cdot \mathbf{n}')^2 - \frac{1}{3} \right] d\mathbf{n}' = \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin(\theta)^2 \left( [\cos(\theta) \cos(\theta_a) + \sin(\theta) \sin(\theta_a) \cos(\phi)]^2 - \frac{1}{3} \right) \quad (20)$$

$$= -\frac{\pi^2}{8} \left[ \cos(\theta_a)^2 - \frac{1}{3} \right]. \quad (21)$$

where  $\theta_a$  is the angle between  $\mathbf{n}$  and  $\mathbf{a}$  and  $\phi$  is the azimuthal angle between  $\mathbf{a}$  and  $\mathbf{n}'$ . Then, integrating over  $\mathbf{n}$  amounts to integrate over  $\theta_a$  with a weight  $2\pi \sin(\theta_a)$ :

$$\frac{1}{(4\pi)^2} \int |\mathbf{n} \times \mathbf{n}'| \left[ (\mathbf{a} \cdot \mathbf{n}')^2 - \frac{1}{3} \right] \left[ (\mathbf{a} \cdot \mathbf{n})^2 - \frac{1}{3} \right] d\mathbf{n}' d\mathbf{n} = -\frac{1}{(4\pi)^2} \int_0^\pi 2\pi \sin(\theta_a) \frac{\pi^2}{8} \left[ \cos(\theta_a)^2 - \frac{1}{3} \right]^2 d\theta_a \quad (22)$$

$$= -\frac{\pi}{32} \int_0^1 \left( u^2 - \frac{1}{3} \right)^2 du \quad (23)$$

$$= -\frac{\pi}{360}. \quad (24)$$

Finally,

$$\rho[\psi] = \frac{\pi}{4} - \frac{\pi}{360} q^2. \quad (25)$$

**9.** The isotropic state  $q = 0$  is stable when the  $q^2$  term is positive, which is the case for

$$\alpha_2 = \frac{2}{45} > \frac{Ar}{2} = \frac{\pi}{360} \bar{\rho} d\ell^2, \quad (26)$$

leading to

$$(\bar{\rho} d\ell^2) < (\bar{\rho} d\ell^2)^* = \frac{16}{\pi} \quad (27)$$

At the transition, as  $\alpha_3 < 0$ , the order parameter jumps to

$$q^* = -\frac{3\alpha_3}{4\alpha_4} = \frac{3}{2} : \quad (28)$$

the transition is discontinuous.