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 of 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/ℓ, a parallelogram with area $\ell^2|\boldsymbol{n}_i \times \boldsymbol{n}_j|$. Taking into account the direction perpendicular to this plane, we see that the forbidden area has a thickness $2d$, hence

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

3. At order 1 in Φ, the partition function is

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

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

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

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

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

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

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 $\hat{\psi}(\boldsymbol{n})$ is (discarding the orientation-independent term):

$$\frac{F[\hat{\psi}]}{T} = \int \hat{\psi}(\boldsymbol{n})\log\left(\hat{\psi}(\boldsymbol{n})\right)\mathrm{d}\boldsymbol{n} + \frac{1}{2V}\int v(\boldsymbol{n}, \boldsymbol{n}')\hat{\psi}(\boldsymbol{n})\hat{\psi}(\boldsymbol{n}')\mathrm{d}\boldsymbol{n}\mathrm{d}\boldsymbol{n}'. \tag{7}$$

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

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

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

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

with

$$\sigma[\psi] = \int \psi(\boldsymbol{n}) \log(\psi(\boldsymbol{n}))\mathrm{d}\boldsymbol{n}, \tag{10}$$

$$\rho[\psi] = \int |\boldsymbol{n} \times \boldsymbol{n}'|\psi(\boldsymbol{n})\psi(\boldsymbol{n}')\mathrm{d}\boldsymbol{n}\mathrm{d}\boldsymbol{n}' \tag{11}$$

$$A = 2\bar{\rho}d\ell^2. \tag{12}$$

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/ℓ. There may be a transition for A of order 1, hence for very low volume fractions.

2 Phase transition

6. For the entropic term,

$$\sigma[\psi] = \int \frac{1}{4\pi} \left(1 + \boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n}\right) \log \left(1 + \boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n}\right) \mathrm{d}\boldsymbol{n}, \tag{13}$$

$$= \frac{1}{4\pi} \int \left[\boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n} + \frac{1}{2} \left(\boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n}\right)^2 - \frac{1}{6} \left(\boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n}\right)^3 + \frac{1}{24} \left(\boldsymbol{n}^{\mathrm{T}}\boldsymbol{Q}\boldsymbol{n}\right)^4\right] \mathrm{d}\boldsymbol{n}. \tag{14}$$

We now use

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

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

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

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

7. The free energy term is

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

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

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

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

The interaction energy $v(\boldsymbol{n}, \boldsymbol{n}')$ 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

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

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

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

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

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

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

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

$$= -\frac{\pi}{360}. \tag{24}$$

Finally,

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

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

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

leading to

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

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

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

the transition is discontinuous.