

# Onsager theory of the isotropic-nematic transition

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The shape of the particles (molecules or colloids) in a fluid matter. Here we study how elongated particles may align at equilibrium: this is the isotropic-nematic phase transition. We consider hard cylinders with diameter  $d$  and length  $\ell \gg d$  and follow the approach of Onsager [1, 2]: we use the second virial coefficient to obtain the free energy of the distribution of the orientations. We show that this distribution undergoes a discontinuous isotropic-nematic transition at a critical density that we determine.

We study the system composed of  $N$  cylinders in a volume  $V$ , with density  $\bar{\rho} = N/V$ . We denote  $\mathbf{x}_i$  and  $\mathbf{n}_i$  the position and orientation of the particle  $i$ ; note that the particles are not polar, hence the unit vectors  $\mathbf{n}$  and  $-\mathbf{n}$  refer to the same orientation. The particles interact only through excluded volume interactions. Useful formulas are given in appendix A.

*Technical note:* questions requiring calculations are indicated with asterisks: no asterisk for less than three lines of calculations, one for less than 10 lines, and two for longer calculations.

## 1 Free energy for the orientations

We introduce the Mayer function  $\Phi(\mathbf{x} - \mathbf{x}', \mathbf{n}, \mathbf{n}')$  which is 0 if the particles located at  $(\mathbf{x}, \mathbf{n})$  and  $(\mathbf{x}', \mathbf{n}')$  in the position-orientation space do not overlap, and  $-1$  if they do.

1. Explain why the partition function is given by

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

2. From a simple geometric argument, give the excluded volume of the particles  $i$  and  $j$ ,

$$v(\mathbf{n}_i, \mathbf{n}_j) = - \int \Phi(\mathbf{x}, \mathbf{n}_i, \mathbf{n}_j) d\mathbf{x}, \quad (2)$$

at the leading order in  $\ell/d$ .

3. \* Perform a virial expansion: expand the partition function at the first order in  $\Phi$  and integrate over the positions in order to get the free energy for the orientations,  $F((\mathbf{n}_i))$ .

Instead of the individual orientations, we prefer to use the density of orientations  $\hat{\psi}(\mathbf{n})$  (normalized with  $\int \hat{\psi}(\mathbf{n}) d\mathbf{n} = N$ ), or the distribution  $\psi = \hat{\psi}/N$ .

4. \* Using the appropriate entropic and energetic terms, write the free energy for the density  $\hat{\psi}$ . Deduce the free energy per particle for the distribution  $\psi$ , which we write as

$$f[\psi] = \sigma[\psi] + \frac{A}{2} \rho[\psi], \quad (3)$$

where  $\sigma$  is the entropic term,  $\rho$  is the energetic term, and  $A$  is a coupling constant that depends on the density  $\bar{\rho}$ ,  $d$  and  $\ell$ .

5. Discuss the expression of  $A$ ; how does it compare to the volume fraction?

## 2 Phase transition

As it is difficult to find the distribution  $\psi(\mathbf{n})$  that minimizes the free energy, we use the following ansatz for an anisotropic distribution of the orientations:

$$\psi(\mathbf{n}) = \frac{1}{4\pi} \left( 1 + q \left[ (\mathbf{a} \cdot \mathbf{n})^2 - \frac{1}{3} \right] \right) = \frac{1}{4\pi} (1 + \mathbf{n}^T \mathbf{Q} \mathbf{n}), \quad (4)$$

where  $\mathbf{a}$  is a unit vector that indicates the direction of the anisotropy and  $q$  indicate its magnitude.  $\mathbf{Q} = q(\mathbf{a}\mathbf{a}^T - \mathbf{1}/3)$  is a traceless tensor. Since the rods are not polar, the distribution should be an even function of  $\mathbf{n}$ . As the system is isotropic, the free energy of the distribution  $\psi(\mathbf{n})$  depends only on  $q$ .

6. \* Compute the entropy  $\sigma[\psi]$  up to order 4 in  $q$ .

7. \* What powers of  $q$  are present in the energy  $\rho[\psi]$ ? Show that the term of order  $q$  is zero. Without any calculation, give the sign of the coefficient of  $q^2$ .

8. \*\* Show that

$$\rho[\psi] = \frac{\pi}{4} - \frac{\pi}{360} q^2. \quad (5)$$

9. At what value of the density  $\bar{\rho}$  does the isotropic state become unstable? What is the value of the anisotropy  $q$  after the transition?

## A Useful formulas

In this appendix we provide useful formulas for the calculations:

$$(1+x) \log(1+x) = x + \sum_{k=2}^{\infty} \frac{(-1)^k}{k(k-1)} x^k = x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{24} + \dots, \quad (6)$$

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

## References

- [1] Lars Onsager. The effects of shape on the interaction of colloidal particles. *Annals of the New York Academy of Sciences*, 51(4):627–659, 1949.
- [2] G J Vroege and H N W Lekkerkerker. Phase transitions in lyotropic colloidal and polymer liquid crystals. *Reports on Progress in Physics*, 55(8):1241–1309, aug 1992.