

ICFP – Soft Matter

Onsager theory of the isotropic-nematic transition

Anke Lindner, Vincent Démery

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 ℓ/d .

3. * Perform a virial expansion: expand the partition function at the first order in Φ 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 ψ , which we write as

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

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

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:

$$(1+x) \log(1+x) = x + \sum_{k=2}^{\infty} \frac{(-1)^k}{k(k-1)} x^k = x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{12} + \dots, \quad (6)$$

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.