Variational Nonequilibrium Statistical Mechanics

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Blatt 10 - Hausaufgabe

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Aufgabe 1: Excluded area

(a) Sketch the excluded area between two hard rectangles of length L and width D at a relative angle ϕ.

(b) Demonstrate that the excluded area is

$$A_{\text{exc}}(\phi) = 2LD + (L^2 + D^2)|\sin\phi| + 2LD|\cos\phi|. \tag{1}$$

Aufgabe 2: Scaled particle theory for hard rectangles

Consider a system of hard rectangles of length-to-width aspect ratio L/D. For spatially homogeneous systems, $\rho(\mathbf{r}, \phi) = \rho f(\phi)$, the approximated excess free energy according to the scaled particle theory is

$$\psi_{\text{exc}} = \frac{\beta F_{\text{exc}}}{A} = \rho\left(-\ln(1-\eta) + \frac{\rho}{2(1-\eta)}\langle\langle A_{\text{exc}}^{(0)}\rangle\rangle\right). \tag{2}$$

Here $A = \int d\mathbf{r}$ is the total area of the system, $\eta = \rho LD$ is the packing fraction, $A_{\text{exc}}^{(0)} = A_{\text{exc}} - 2LD$, and $\langle\langle\cdot\rangle\rangle$ denotes a double angular average, that is

$$\langle\langle A_{\text{exc}}^{(0)}\rangle\rangle = \int_0^\pi d\phi_1 \int_0^\pi d\phi_2 f(\phi_1) f(\phi_2) A_{\text{exc}}^{(0)}(\phi), \tag{3}$$

with $\phi = \phi_1 - \phi_2$.

(a) At low density the stable phase is isotropic with the particles randomly oriented. Find the value of the orientational distribution function, $f(\phi)$, $\phi \in [0, \pi]$ for the isotropic phase.

(b) At sufficiently high density and aspect ratio, the system forms a uniaxial nematic phase in which the particles are oriented on average along a given direction (called the director). The orientational order around the director increases with density. Sketch the orientational distribution function $f(\phi)$ in the nematic phase for different densities (ϕ is the angle with respect to the director).

(c) Bifurcation analysis. Find the packing fraction at which the isotropic phase gets unstable with respect to the nematic phase and represent it as a function of the aspect ratio of the particles. Hint: assume that in the nematic phase the orientational distribution function is the isotropic one plus a perturbation compatible with the symmetry of the nematic phase, i.e. $f(\phi) = 1/\pi(1 + f_1\cos(2\phi))$, and compare the total free energy of the isotropic and nematic phases.

(d) For sufficiently small aspect ratio and high density, a tetratic phase can be stabilized. In the tetratic phase the particles are oriented along two directors perpendicular to each other. Sketch a microstate of a tetratic state together with the corresponding orientational distribution function.

(e) Repeat the bifurcation analysis (c) for the tetratic phase. In which range of aspect ratios can the tetratic phase be stable?

Further reading: Yuri Martínez-Ratón, Enrique Velasco, and Luis Mederos, J. Chem. Phys. **122**, 064903 (2005).