Lyotropic Transition to Nematic Phase [pln75]

Rod-shaped molecules in solution with gradually increasing concentration undergo a lyotropic transition between an isotropic liquid and a nematic liquid crystal, described here in a much simplified version of Onsager's theory.

Specifications:

- rods of length L and circular cross section with diameter D,
- aspect ratio: L/D,
- volume of rod: $v_\mathrm{r} = \pi(D/2)^2 L$,
- concentration of rods: $c = N/V$,
- volume fraction of rods: $\phi = v_\mathrm{r} c$.

Configurational entropy originating from two sources of disorder.

(a) *Orientational disorder*:

- orientation function:[1] $g(\theta)$ (distribution of angles relative to director),
- entropy reduction: $\dfrac{\Delta S_\mathrm{a}}{Nk_\mathrm{B}} = -2\pi \displaystyle\int_0^\pi d\theta \sin\theta\, g(\theta) \ln\big(4\pi g(\theta)\big) \doteq -q\big[g(\theta)\big]$.

(b) *Translational disorder*:

- entropy of ideal gas: $\dfrac{S_\mathrm{icg}}{Nk_\mathrm{B}} = \ln\big(V/V_0\big) + f(T)$.
- entropy reduction due to exclusion volume caused by increasing numbers of rods and their partial misalignment:

$$\frac{\Delta S_\mathrm{b}}{Nk_\mathrm{B}} = \ln\left(\frac{V - Nb}{N}\right) = \ln\left(\frac{V}{N}\right) + \underbrace{\ln\left(1 - \frac{bN}{V}\right)}_{\simeq -bN/V} \simeq -\ln c - cb.$$

  - estimate of average exclusion volume: $b = DL^2\langle|\sin\gamma|\rangle$,
  - angle between rods neighboring rods: γ,
  - averaging carried out:

$$\langle|\sin\gamma|\rangle = \int_0^{2\pi} d\phi_1 \int_0^\pi d\theta_1 \sin\theta_1 \int_0^{2\pi} d\phi_2 \int_0^\pi d\theta_2 \sin\theta_2 \\ \times g(\theta_1) g(\theta_2) |\sin\gamma(\theta_1,\phi_1,\theta_2,\phi_2)| \doteq p\big[g(\theta)\big],$$

  - isotropic limit: $g(\theta) = \dfrac{1}{4\pi} \quad \Rightarrow \langle|\sin\gamma|\rangle = \dfrac{\pi}{4}$.

[1] Note the reduced molecular symmetry assumed here in comparison to [pln74].

Functional of entropy reduction:

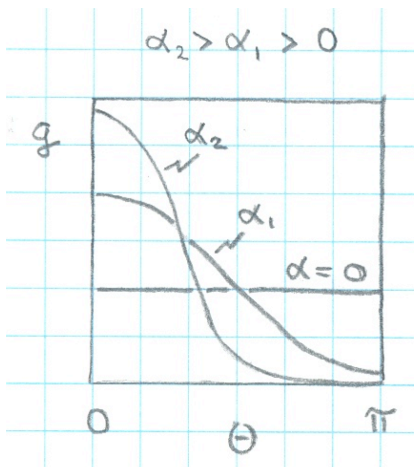
$$\frac{\Delta S}{Nk_{\mathrm{B}}} = \frac{\Delta S_{\mathrm{b}}}{Nk_{\mathrm{B}}} + \frac{\Delta S_{\mathrm{a}}}{Nk_{\mathrm{B}}} = -\ln c - cDL^2 p\big[g(\theta)\big] - q\big[g(\theta)\big], \tag{1}$$

- physically relevant parameter: $x \doteq \dfrac{\phi L}{D} \quad \Rightarrow cDL^2 = \dfrac{4x}{\pi}$,

$$\Rightarrow \frac{\Delta S}{Nk_{\mathrm{B}}} = -\ln x - \frac{4x}{\pi} p\big[g(\theta)\big] - q\big[g(\theta)\big]. \tag{2}$$

Phenomenological one-parameter orientation function:

$$g(\theta, \alpha) \doteq \frac{\alpha}{4\pi}\frac{\cosh\big(\alpha\cos\theta\big)}{\sinh\alpha} \quad \stackrel{\alpha\to 0}{\longrightarrow} \quad \frac{1}{4\pi}. \tag{3}$$



Parametrized versions of order parameter and entropy reduction:

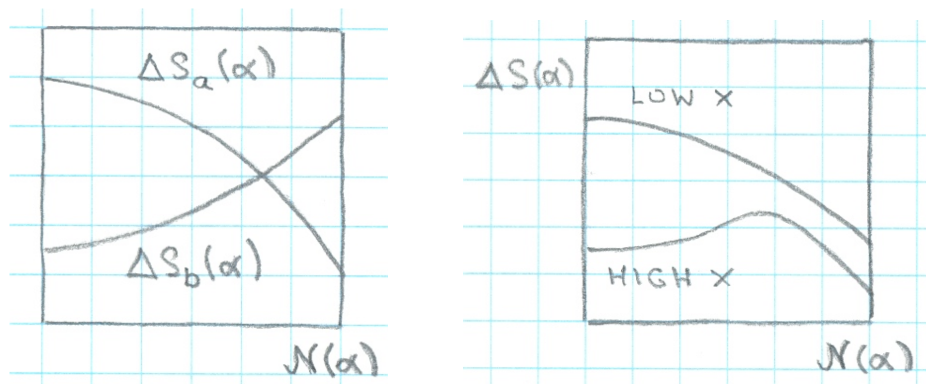
$$\mathcal{N}(\alpha) = \pi\int_0^\pi d\theta \sin\theta\big(3\cos^2\theta - 1\big)g(\theta, \alpha), \tag{4}$$

$$\Delta s(\alpha) \doteq \frac{\Delta S}{Nk_{\mathrm{B}}} = -\ln x - \frac{4x}{\pi}p(\alpha) - q(\alpha). \tag{5}$$

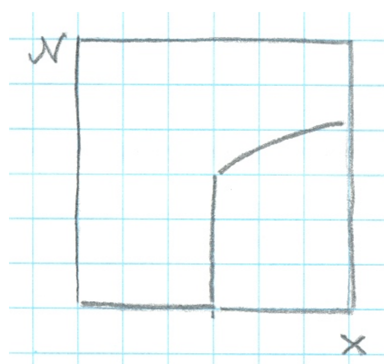
with functionals turned into functions of the parameter:

$$p(\alpha) = p\big[g(\theta, \alpha)\big], \quad q(\alpha) = q\big[g(\theta, \alpha)\big].$$

Graphical representations of entropy reduction versus order parameter:



- low x: Δs has a maximum at $\mathcal{N} = 0$,
- high x: Δs has a maximum at $\mathcal{N} \neq 0$,
- critical x: position of maximum switches from $\mathcal{N} = 0$ to $\mathcal{N} \neq 0$.



[adapted from Jones 2002]