Maier-Saupe Theory for Nematic Ordering [pln74]

Consider rod-like molecules with indistinguishable ends¹ at fixed concentration in solution. The nematic phase is isotropic in the plane perpendicular to the director.

The orientations of individual molecules relative to the director **n** of nematic ordering is described by a distribution $f(\theta)$, named *orientation function*. The normalization condition under the circumstances described is

$$\mathcal{M} = 2\pi \int_0^{\pi/2} d\theta \,\sin\theta \, f(\theta) = 1. \tag{1}$$

In the isotropic liquid phase, one end of each rod is equally likely to point in any direction on a hemisphere: $f_{\rm iso}(\theta) = 1/2\pi = \text{const.}$

The nematic order parameter,

$$\mathcal{N} = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle = \pi \int_0^{\pi/2} d\theta \, \sin\theta \, (3\cos^2\theta - 1) f(\theta), \tag{2}$$

is sensitive to any deviation of $f(\theta)$ from $f_{iso}(\theta)$ that reflects an alignment tendency of the rods.

The agents of nematic ordering are, in parts, *enthalpic* and *entropic* in nature:

- attractive van der Waals forces favor alignment,
- aligned rods are more loosely packed, i.e. less constrained in positioning and motion.

The equilibrium macrostate is the state of lowest free energy, here expressed relative to the isotropic state:

$$\Delta F = \Delta H - T \Delta S. \tag{3}$$

The enthalpy change in mean-field approximation is rendered as the following function of the order parameter:

$$\Delta H = -\frac{1}{2}u\mathcal{N}^2,\tag{4}$$

where u is a measure for the coupling strength of the van der Waals attraction.

¹The molecules are assumed to be symmetric when rotated 180° perpendicular to their long axis.

The entropy reduction relative to the (most disordered) isotropic macrostate depends on the orientation function as follows:

$$\Delta S = -k_{\rm B} 2\pi \int_0^{\pi/2} d\theta \sin \theta \left[f(\theta) \ln f(\theta) - \frac{1}{2\pi} \ln \left(\frac{1}{2\pi} \right) \right]$$
$$= -k_B \int_0^{\pi/2} d\theta \sin \theta \left[2\pi f(\theta) \right] \ln \left(2\pi f(\theta) \right). \tag{5}$$

The Maier-Saupe theory extracts a one-parameter orientation function from the variational problem that extremizes the following functional with two Lagrange multipliers:

$$J[f] = \Delta S + \lambda_1 \mathcal{N} + \lambda_2 \mathcal{M}.$$
 (6)

The solution of this variational problem,

$$f(\theta, b) = A(b) \exp\left(b \cos^2 \theta\right),\tag{7}$$

is worked out in [pex43] including an analytic expression for the amplitude function A(b).

The Maier-Saupe theory for the thermotropic transition between an isotropic liquid and nematic phase thus expresses the scaled free energy, $\Delta \hat{F} \doteq \Delta F/k_{\rm B}T$, as a function of the parameter b and the scaled coupling constant $\hat{u} \doteq u/k_{\rm B}T$:

$$\Delta \hat{F}(b,\hat{u}) = -\frac{1}{2}\hat{u}[\mathcal{N}(b)]^2 - \Delta \hat{S}(b), \qquad (8)$$

where $\Delta \hat{S} = \Delta S / k_{\rm B}$ is a dimensionless entropy.

Plotting $\Delta \hat{F}(b, \hat{u})$ versus $\mathcal{N}(b)$ at fixed \hat{u} , as worked out in [pex44], reveals the nature of the equilibrium state: for weak coupling (or high temperature) the minimum free energy is realized for vanishing order parameter.

There exists a critical coupling strength \hat{u}_c or a transition temperature $\hat{T}_c \doteq 1/\hat{u}_c$, where the location of that minimum switches to a location at nonzero order parameter.

The location of the free-energy minimum determines a function $\bar{\mathcal{N}}(\hat{T})$, which gradually decreases as \hat{T} increases from zero and then drops to zero at \hat{T}_{c} in a first-order phase transition. This function and the transition point are worked out quantitatively in [pex5].

[adapted from Jones 2002]