

# Statistical Theories of Liquid Crystals: Onsager, Maier-Saupe and Beyond

François Genoud

OxPDE, Mathematical Institute

University of Oxford

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where  $f : \mathbb{S}^2 \rightarrow \mathbb{R}_+$  is the distribution of orientations
- The order parameter  $\overline{P_2} := \langle P_2(\cos \theta) \rangle_f$  measures the anisotropy of the system

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order parameter too large, jump in concentration too high
- Athermal model: the critical concentration at phase transition is temperature independent

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$$W_{ij} \equiv W(X_i, X_j) = \begin{cases} \infty & \text{if particle } i \text{ intersects particle } j \\ 0 & \text{otherwise} \end{cases}$$

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It is convenient to introduce

$$\Phi_{ij} := \exp(-\beta W_{ij}) - 1 = \begin{cases} -1 & \text{if particle } i \text{ intersects particle } j \\ 0 & \text{otherwise} \end{cases}$$

# Cluster Expansion

Cluster expansion for  $N$  (spherical) particles of the same type:

$$\log Z = N \left\{ 1 + \log(V/N) + \frac{1}{2} b_1(N/V) + \frac{1}{3} b_2(N/V)^2 + \dots \right\}$$

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For  $N_1, \dots, N_n$  particles of **different species**  $1, \dots, n$ :

$$\log Z = \sum_k N_k \{1 + \log(V/N_k)\} + \frac{1}{2V} \sum_{k,k'} b_1(k, k') N_k N_{k'} + \dots$$

where now  $b_1(k, k')$  is computed only on particles of types  $k$  and  $k'$

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$$\simeq -2L^2 d \sin(\alpha) \quad \text{for very long cylinders } (L/d \rightarrow \infty)$$

# From Sums to Integrals

For a continuous distribution of orientations  $d\mu(\Omega) = f(\Omega)d\Omega$ :

$$\begin{aligned}\log Z \simeq & \int_{\mathbb{S}^2} N f(\Omega) \left\{ 1 + \log \left( \frac{V}{4\pi N f(\Omega)} \right) \right\} d\Omega \\ & + \frac{1}{2V} \int_{\mathbb{S}^2} \int_{\mathbb{S}^2} b_1(\Omega, \Omega') N f(\Omega) N f(\Omega') d\Omega d\Omega'\end{aligned}$$

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$$\begin{aligned} \Rightarrow N^{-1}\beta F &\simeq -1 + \int_{\mathbb{S}^2} f(\Omega) \log[4\pi f(\Omega) \rho] d\Omega \\ &\quad - \frac{\rho}{2} \int_{\mathbb{S}^2} \int_{\mathbb{S}^2} b_1(\Omega, \Omega') f(\Omega) f(\Omega') d\Omega d\Omega' \end{aligned}$$

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- Maier-Saupe interactions:
  - good prediction of order parameter** at phase transition
  - no short-range forces** taken into account
  - inconsistency of physical parameters dependence (volume)** with experiment/thermodynamic principles

# Distribution Functions

**Notations:**  $N$  rod-like particles in  $\Lambda \subset \mathbb{R}^3$ ,  $X_i = (x_i, \Omega_i) \in \Lambda \times \mathbb{S}^2$   
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**$k$ -particle distribution functions:**

$$P^{(k)}(X_1^k) = \int_{\Gamma^{N-k}} G(X_1^N) dX_{k+1}^N, \quad k = 1, \dots, N-1, \quad P^{(N)} = G$$

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This generalizes to the  $k$ -particle distributions:

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This generalizes to the  $k$ -particle distributions:

$$\begin{aligned} \nabla_1 P^{(k)}(X_1^k) &= -\beta \sum_{j=2}^k \partial_1 W(X_1, X_j) P^{(k)}(X_1^k) \\ &\quad -\beta(N-k) \int_{\Gamma} \partial_1 W(X_1, X_{k+1}) P^{(k+1)}(X_1^k, X_{k+1}) dX_{k+1} \end{aligned}$$

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This is the molecular field approximation.

## Self-Consistent Equation for the Orientational Distribution

Using this *Ansatz* in

$$\nabla_1 P^{(1)}(X_1) = -\beta(N-1) \int_{\Gamma} \partial_1 W(X_1, X_2) P^{(2)}(X_1, X_2) dX_2 \rightsquigarrow$$

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where we have set  $x_1 = 0$  and  $z$  is chosen so that  $\int f(\Omega) d\Omega = 1$

# Interpretation

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and  $z = \int_{\mathbb{S}^2} \exp[-\beta u(\Omega)] d\Omega$  the **1-particle partition function**

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Pair potential consistent with the Maier-Saupe theory:

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## Literature

Development, predictions and discussions can be found in:

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 W. Maier & A. Saupe, 3 papers in Z. Naturforsch. (1958-60), translation in *Dynamics and Defects in Liquid Crystals*