

MATHEMATICAL THEORIES OF LIQUID CRYSTALS

III. The Onsager Theory

EPIFANIO G. VIRGA

Mathematical Institute

University of Oxford

virga@maths.ox.ac.uk

on leave from

Department of Mathematics

University of Pavia, Italy

Summary

Introduction

Helmholtz Free Energy

Mayer's Cluster Expansion

Penrose's Tree Identity

Forest Cluster Expansion

Onsager's Functional

Phase Coexistence

Introduction

The celebrated paper by **ONSAGER (1949)** laid the premises for a theory of liquids (not only liquid crystals) based on purely **repulsive** intermolecular forces.

Canonical Ensemble

Suppose that N identical particles described by the coordinates

$$\mathbf{q} = (q_1, \dots, q_N) \in \mathcal{Q}^N$$

\mathcal{Q} single particle configurational space

are interacting via a **diverging**, steric pair-potential U .

partition function

$$Z_N := \frac{1}{N!} \int_{\mathcal{Q}^N} e^{-\frac{1}{kT} \mathcal{U}(\mathbf{q})} dq_1 \dots dq_N$$

k Boltzmann constant T absolute temperature
 $\mathcal{U}(\mathbf{q}) := \sum_{i < j=1}^N U(q_i, q_j)$ interaction energy $U(q_i, q_j) = U(q_j, q_i)$

Helmholtz Free Energy

The objective is to compute the free energy

$$F_N = -kT \ln Z_N$$

without even possibly dreaming of *averaging* over the diverging interactions.

Mayer functions

$$e^{-\frac{1}{kT}U(q_i, q_j)} = 1 + \Phi_{ij}$$

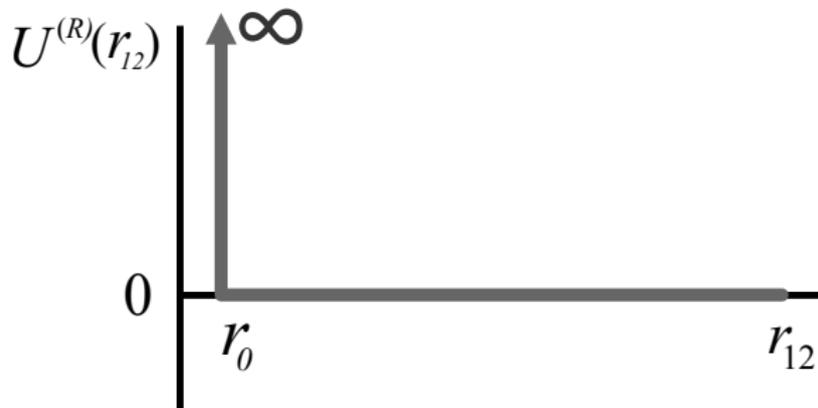
$$Z_N = \frac{1}{N!} G_N \quad \text{where} \quad G_N := \int_{\mathcal{Q}^N} \prod_{i < j}^N (1 + \Phi_{ij}) dq_1 \dots dq_N$$

For *hard* repulsion potentials

$\Phi_{ij} = 0$ when particles i and j are *not* in *contact*

$\Phi_{ij} = -1$ when particles i and j *overlap*

idealized case



$$\Phi_{12}(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} 0 & r_{12} > r_0 \\ -1 & r_{12} < r_0 \end{cases}$$

graph terminology

Rearranging terms,

$$\begin{aligned} G_N &= \int_{\mathcal{Q}^N} \prod_{i < j}^N (1 + \Phi_{ij}) dq_1 \dots dq_N \\ &= \int_{\mathcal{Q}^N} \sum_{G \in \mathcal{G}_N} \prod_{(i,j) \in G} \Phi_{ij} dq_1 \dots dq_N \end{aligned}$$

\mathcal{G}_N collection of graphs on N labeled vertices
 (i, j) edge joining vertices i and j

A *vertex* represents a *particle*
A *edge* represents a steric *interaction*

missing steps

Upon suitable rearrangement of the sum

$$e^{-w/kT} = 1 + \sum_{i>j} \Phi_{ij} + \sum \Phi_{ij} \Phi_{i'j'} + \dots \quad (19)$$

which now constitutes the integrand of EQUATION 4, Mayer and Mayer obtain an expansion for the integral in terms of the irreducible cluster integrals

$$\beta_1 = \frac{1}{V} \int \Phi_{12} d\tau_1 d\tau_2 \quad (20)$$

$$\beta_2 = \frac{1}{2V} \int \Phi_{12} \Phi_{23} \Phi_{31} d\tau_1 d\tau_2 d\tau_3$$

and these furnish the first two correction terms to the ideal gas laws in the expansion

$$\log B_p = N_p \{ 1 + \log (V/N_p) + \frac{1}{2} \beta_1 (N_p/V) + \frac{1}{3} \beta_2 (N_p/V)^2 + \dots \}. \quad (21)$$

ONSAGER (1949)

B_p the same as Z_N β_1 pair-excluded volume
 N_p the same as N $\rho := \frac{N}{V}$ number density

- ▶ In his paper **ONSAGER (1949)** endeavours to prove that for *slender rods* interacting via *excluded volume* the third virial coefficient β_2 is *negligible* compared to β_1 .
- ▶ Is the density *expansion* justified in the first place?
- ▶ When does the *first term* in this expansion suffice to estimate properly Z_N ?
- ▶ Could there possibly be a justification *not* requiring any *density expansion*?
- ▶ Once these questions are answered, we shall be able to write with confidence the Onsager free-energy functional in the *orientation distribution* density ϱ , akin in form to Maier-Saupe's, though quite different in content.

objective, in Onsager's own words

We introduce a distribution-function $f(\mathbf{a})$ for the directions \mathbf{a} of the axes of the cylindrical particles, normalized according to EQUATION 26. When we neglect the terms which depend on β_2 and higher cluster integrals in the expansion given by EQUATION 27, we arrive at the following formula for the configuration-integral

$$\begin{aligned} \log B_p = N_p \{ 1 + \log (V/N_p) \} - \int f(\mathbf{a}) \log 4\pi f(\mathbf{a}) d\Omega(\mathbf{a}) \\ + (N_p/2V) \int \beta_1 (\cos^{-1} (\mathbf{a} \cdot \mathbf{a}')) f(\mathbf{a}) f(\mathbf{a}') d\Omega d\Omega'. \end{aligned} \quad (61)$$

The function $f(\mathbf{a})$ is implicitly determined by the condition

$$B_p = \text{maximum}, \quad (62)$$

ONSAGER (1949)

Mayer's Cluster Expansion

ONSAGER (1949) referred to the celebrated book by J. E. MAYER & M. G. MAYER (1940), but the theory being invoked has an interesting history that started earlier and has not yet seen an end.

- ▶ URSELL (1927) computes $\ln Z_N$ for a gas of N impenetrable particles in a region \mathcal{B} of volume V .
- ▶ MAYER (1937) derives a formula for $\ln Z_N$, *assuming* it to be a *power series* in the number density $\rho = \frac{N}{V}$.

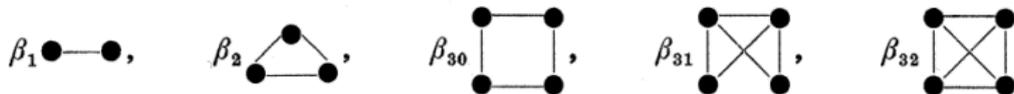
$$\frac{F_N}{N} = kT \left(\ln \rho - 1 + \sum_{\nu=1}^{\infty} \frac{1}{\nu+1} \beta_{\nu} \rho^{\nu} \right)$$
$$\beta_{\nu} := -\frac{1}{V} \frac{1}{\nu!} \int_{\mathcal{B}^{\nu}} \sum_{G \in \mathcal{G}_{\nu+1}^{(2)}} \prod_{(i,j) \in G} \Phi_{ij} dq_1 \dots dq_{\nu+1}$$

irreducible integrals

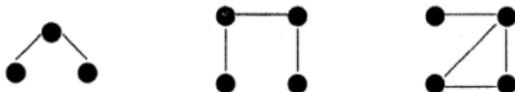
$$\beta_\nu := -\frac{1}{V} \frac{1}{\nu!} \int_{\mathcal{B}^\nu} \sum_{G \in \mathcal{G}_{\nu+1}^{(2)}} \prod_{(i,j) \in G} \Phi_{ij} dq_1 \dots dq_{\nu+1}$$

$\mathcal{G}_{\nu+1}^{(2)}$ collection of *irreducible* graphs on $\nu + 1$ vertices

irreducible graphs



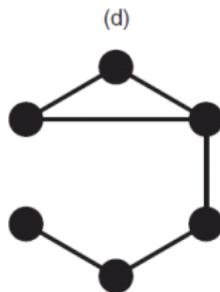
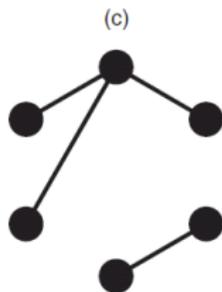
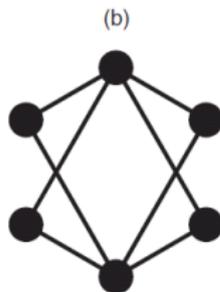
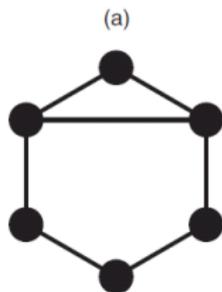
reducible graphs



“irreducible” means “bi-connected”

- ▶ A graph G on n vertices is said to be *connected*, if there is a *path* from any vertex to any other vertex.
- ▶ An *articulation* vertex of G is any vertex that, if removed (with all links emanating from it), would disconnect G . In such a case G is also said to be *articulated*.
- ▶ G is *bi-connected*, if it is connected and possesses *no* articulation vertex.

simple examples $\nu = 5$



(a) and (b) bi-connected

(c) disconnected

(d) articulated

Remarks

- ▶ Each irreducible integral β_ν encloses a **cluster** of $\nu + 1$ particles.
- ▶ For classical mass-point particles interacting in a region \mathcal{B} in space of volume V with a repulsive pair potential U

$$\beta_1 = \frac{1}{V} \int_{\mathcal{B}^2} \sum_{G \in \mathcal{G}_2^{(2)}} \prod_{(i,j) \in G} (1 - e^{-\frac{1}{kT} U(q_i, q_j)}) dq_1 dq_2 = V_{\text{exc}}^{(2)}$$

$$\beta_2 = \frac{1}{2V} \int_{\mathcal{B}^3} \sum_{G \in \mathcal{G}_3^{(2)}} \prod_{(i,j) \in G} (1 - e^{-\frac{1}{kT} U(q_i, q_j)}) dq_1 dq_2 dq_3 = \frac{1}{2} \left(V_{\text{exc}}^{(3)} \right)^2$$

$V_{\text{exc}}^{(2)}$ pair-excluded volume
 $V_{\text{exc}}^{(3)}$ triple-excluded volume

- ▶ In Mayer's theory the cluster integrals β_ν are scalars that only depend on the pair interaction potential U . In particular, they are independent of the density ρ .
- ▶ For *hard spheres* of volume V_0

$$V_{\text{exc}}^{(2)} = 8V_0 \quad V_{\text{exc}}^{(3)} = \sqrt{\frac{15}{32}} V_{\text{exc}}^{(2)} = \sqrt{30} V_0 \quad \frac{\beta_2}{\beta_1^2} = \frac{15}{64}$$

- ▶ For *hard cylinders* of diameter D and height L

$$\frac{\langle \beta_2 \rangle}{\langle \beta_1 \rangle^2} = O((D/L) \ln(L/D))$$

$\langle \cdot \rangle$ isotropic average

equation of state

$$\frac{PV}{RT} = 1 + \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+1} \beta_{\nu} \rho^{\nu}$$

$R = Nk$ gas constant

virial coefficients

$$\frac{P}{kT} = \rho + \sum_{\nu=1}^{\infty} B_{\nu+1} \rho^{\nu+1}$$

$$B_{\nu+1} := \frac{\nu}{\nu+1} \beta_{\nu}$$

B_m virial coefficients

rigorous proof

BORN (1937) and BORN & K. FUCHS (1938) gave a rigorous mathematical proof of Mayer's results.

- ▶ They used the method of *steepest descent* to estimate configurational integrals for a *large number* of particles N .
- ▶ The main issue remained the convergence of the series delivering F_N or P .
- ▶ The *lack* of convergence *was* interpreted as the *onset* of condensation, which the theory has the potential to detect, but not to describe.

- ▶ **LEBOWITZ & O. PENROSE (1964)** and **RUELLE (1969)** proved that Mayer's virial expansion converges uniformly *if*

$$\rho\beta_1 < \frac{[W(\frac{e}{2}) - 1]^2}{W(\frac{e}{2})} \doteq 0.1447$$

W Lambert function
 $x = W(x)e^{W(x)} \quad W(x) \geq -1$

This proof was *not* entirely phrased in the canonical ensemble, but required the proof of convergence of two ancillary series in the grand canonical *fugacity* (or *activity*), one for the pressure and the other for the density.

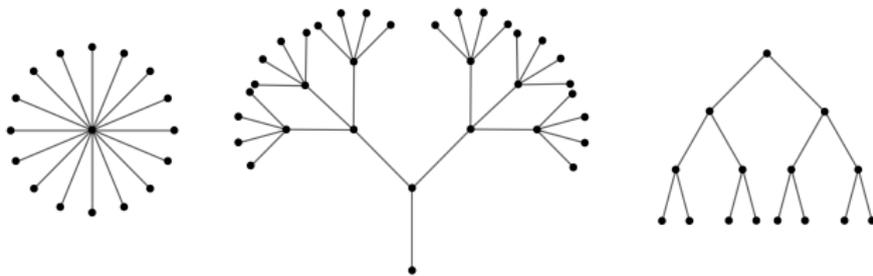
- ▶ **O. PENROSE (1967)** gave a proof of the same result based on a surprising graph identity.

Penrose's Tree Identity

$$\sum_{G \in \mathcal{G}_\nu^{(1)}} \prod_{(i,j) \in G} \Phi_{ij} = \sum_{T \in \mathcal{T}_\nu} \prod_{(i,j) \in T} \Phi_{ij} \prod_{(h,k) \in T^* \setminus T} (1 + \Phi_{hk})$$

- $\mathcal{G}_\nu^{(1)}$ set of all *connected* graph on ν vertices
 \mathcal{T}_ν collection of Cayley's trees on ν vertices
 T^* maximal graph *reducing* to T

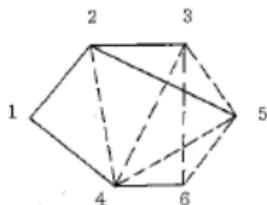
Cayley's trees



trees and forests

- ▶ A *tree* is a graph in which any *two* vertices are connected by *exactly one* path.
- ▶ A tree is a connected *acyclic* graph.
- ▶ A graph with a *single* vertex is also a (singular) *tree*.
- ▶ CAYLEY (1889) proved that there are $\nu^{\nu-2}$ trees on ν labeled vertices.
- ▶ A *forest* is a disjoint union of trees.

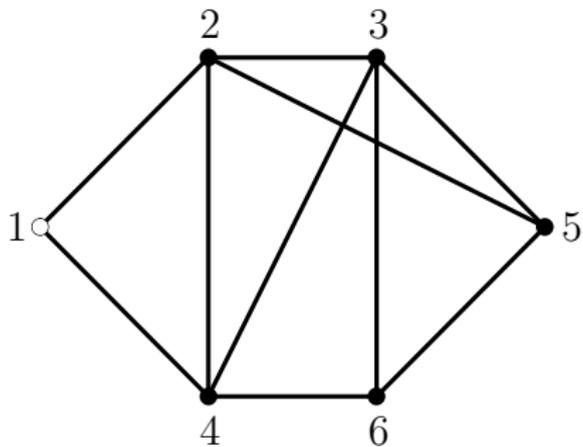
Penrose's reduction (partition scheme)



- ▶ Assign a **weight** w_i to every vertex $i \neq 1$ of a connected graph G , defined as the number of edges in the shortest path joining i to 1.
- ▶ Delete all edges between vertices of equal weight.
- ▶ Delete, for every vertex $i \neq 1$, all edges connecting vertex i to a vertex with weight $w_i - 1$, but the one connecting the vertex i to the vertex of weight $w_i - 1$ with least index.
- ▶ Each of these steps leaves all the indices w_i unchanged.

*maximal reducing graph T^**

- ▶ Start with a *tree* T and assign weights w_i to its vertices.
- ▶ Join all pairs of vertices with the same weight.
- ▶ Join every vertex $i \neq 1$ to all vertices of weight $w_i - 1$ with labels greater than the largest label of the vertices of weight $w_i - 1$ to which it is already joined in T .
- ▶ Each of these steps leaves all the indices w_i unchanged.

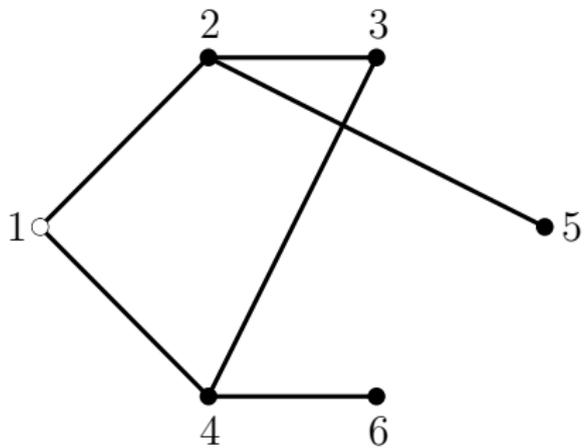


G

$$w_1 = 0$$

$$w_2 = w_4 = 1$$

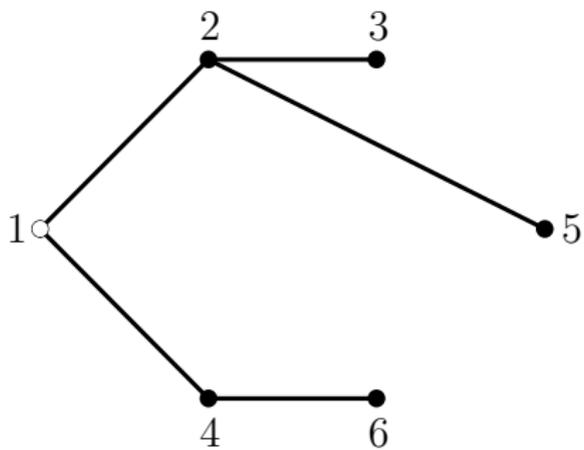
$$w_3 = w_5 = w_6 = 2$$



$$w_1 = 0$$

$$w_2 = w_4 = 1$$

$$w_3 = w_5 = w_6 = 2$$

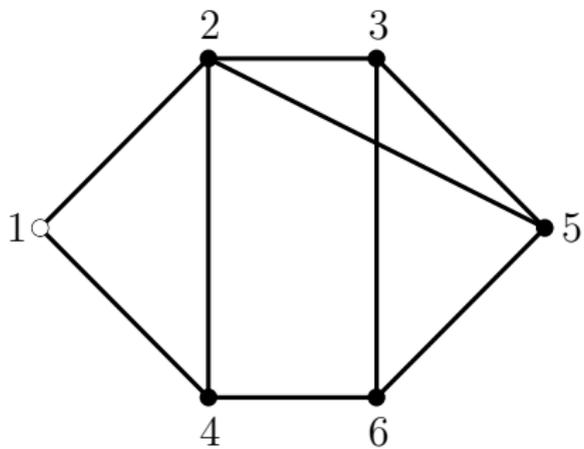


T

$$w_1 = 0$$

$$w_2 = w_4 = 1$$

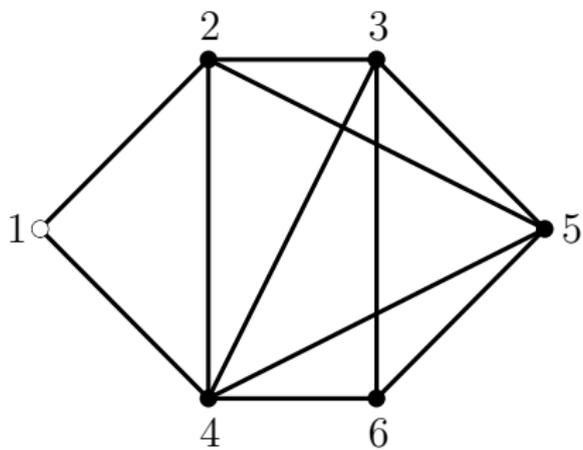
$$w_3 = w_5 = w_6 = 2$$



$$w_1 = 0$$

$$w_2 = w_4 = 1$$

$$w_3 = w_5 = w_6 = 2$$

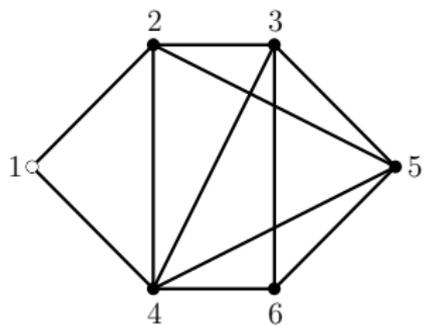


T^*

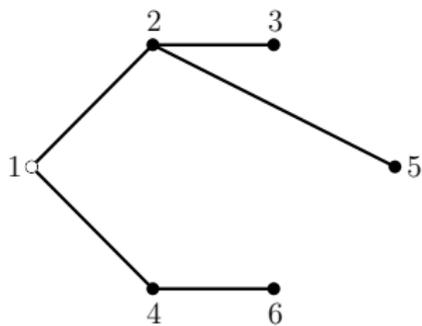
$$w_1 = 0$$

$$w_2 = w_4 = 1$$

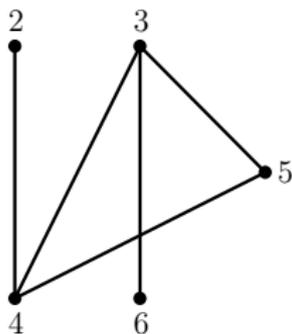
$$w_3 = w_5 = w_6 = 2$$



T^*



T



$T^* \setminus T$

proof of the identity

For a tree $T \in \mathcal{T}_\nu$, denote by $\mathcal{R}(T)$ the set of graphs in the family $\mathcal{G}_\nu^{(1)}$ of all **connected** graphs on ν vertices that can be **reduced** to T .

$$\begin{aligned}
 \sum_{G \in \mathcal{G}_\nu^{(1)}} \prod_{(i,j) \in G} \Phi_{ij} &= \sum_{T \in \mathcal{T}_\nu} \sum_{G \in \mathcal{R}(T)} \prod_{(i,j) \in G} \Phi_{ij} \\
 &= \sum_{T \in \mathcal{T}_\nu} \left\{ \prod_{(i,j) \in T} \Phi_{ij} + \prod_{(i,j) \in T} \Phi_{ij} \sum_{G^* \subset T^* \setminus T} \prod_{(h,k) \in G^*} \Phi_{hk} \right\} \\
 &= \sum_{T \in \mathcal{T}_\nu} \prod_{(i,j) \in T} \Phi_{ij} \left\{ 1 + \sum_{G^* \subset T^* \setminus T} \prod_{(h,k) \in G^*} \Phi_{hk} \right\} \\
 &= \sum_{T \in \mathcal{T}_\nu} \prod_{(i,j) \in T} \Phi_{ij} \prod_{(h,k) \in T^* \setminus T} (1 + \Phi_{hk})
 \end{aligned}$$

- ▶ E. PULVIRENTI & TSAGKAROGIANNIS (2012) recently gave a proof of the very same Lebowitz-Penrose convergence *sufficient* condition in the *canonical ensemble*.
- ▶ MORAIS & PROCACCI (2013) and PROCACCI & YUHJTMAN (2015), building on an improved tree identity, refined in general the Lebowitz-Penrose convergence condition.
- ▶ However, such a refinement does *not* apply to purely *repulsive* interactions, for which the old sufficient convergence condition is still unsurpassed (TATE 2013).

Forest Cluster Expansion

Irreducible cluster integrals have been used to compute the coefficients of Mayer's virial expansions. Much in the spirit of Penrose's proof of convergence, we propose a cluster expansion to compute the configurational integral G_N *without* assuming that it is a power series of ρ .

forest expansion

$$\begin{aligned} G_N &= \int_{\mathcal{B}^N} \sum_{G \in \mathcal{G}_N} \prod_{(i,j) \in G} \Phi_{ij} dq_1 \dots dq_N \\ &= \int_{\mathcal{B}^N} \sum_{F \in \mathcal{F}_N} \prod_{(i,j) \in F} \Phi_{ij} \prod_{(h,k) \in F^* \setminus F} (1 + \Phi_{hk}) dq_1 \dots dq_N \end{aligned}$$

\mathcal{F}_N collection of forests on N vertices

F^* maximal forest reducing to F

limited connectivity

Neglecting all clusters that are not forests (all including *cycles*),

$$\begin{aligned} G_N &\approx \int_{\mathcal{B}^N} \sum_{F \in \mathcal{F}_N} \prod_{(i,j) \in F} \Phi_{ij} dq_1 \dots dq_N \\ &= \int_{\mathcal{B}^N} \sum_{n=0}^{N-1} \sum_{F \in \mathcal{F}_N^{(n)}} (-1)^n \prod_{(i,j) \in F} f_{ij} dq_1 \dots dq_N \\ &= V^N \sum_{n=0}^{N-1} (-1)^n C(n, N) \left(\frac{\beta_1}{V} \right)^n \end{aligned}$$

$$V := |\mathcal{B}|$$

$$f_{ij} := -\Phi_{ij}$$

$$\beta_1 = \frac{1}{V} \int_{\mathcal{B}^2} f_{12}(q_1, q_2) dq_1 dq_2$$

$\mathcal{F}_N^{(n)}$

collection of forests on N vertices with n edges

$C(n, N)$ cardinality of $\mathcal{F}_N^{(n)}$

asymptotic estimates

For $N \rightarrow \infty$,

$$C(n, N) \approx \begin{cases} \binom{N}{n} \left(\frac{N-n}{2}\right)^n & n \text{ bounded} \\ \frac{N^{2n}}{n!2^n} \left(1 - \frac{2n}{N}\right)^{\frac{1}{2}} & 0 < \gamma < \frac{1}{2} \\ \frac{N^{N-2}}{2^{N-n-1}(N-n-1)!} \left(\frac{2n}{N} - 1\right)^{-\frac{5}{2}} & \frac{1}{2} < \gamma \leq 1 \end{cases}$$

$$\gamma := \lim_{N \rightarrow \infty} \frac{n(N)}{N}$$

BRITIKOV (1988)

neglecting large trees

Approximating $C(n, N)$ as

$$C(n, N) \approx \frac{N^{2n}}{2^n n!}$$

and neglecting *for the moment* all terms with $n > \lceil \frac{N}{2} \rceil - 1$ in G_N

$$\begin{aligned}
G_N &\approx V^N \sum_{n=0}^{\lceil \frac{N}{2} \rceil - 1} (-1)^n \frac{N^{2n}}{n! 2^n} \left(\frac{\beta_1}{V} \right)^n \\
&= V^N \sum_{n=0}^{\lceil \frac{N}{2} \rceil - 1} \frac{N^n}{n!} (-x)^n \\
&= V^N Q \left(\left\lceil \frac{N}{2} \right\rceil, -Nx \right) e^{-Nx}
\end{aligned}$$

$$x := \frac{1}{2} \frac{\beta_1 N}{V} = \frac{1}{2} \rho \beta_1$$

$$Q(a, z) := \frac{\Gamma(a, z)}{\Gamma(a)}$$

$\Gamma(a)$ Gamma function

$\Gamma(a, z)$ incomplete Gamma function

$Q(a, z)$ incomplete Gamma function ratio

TEMME (1979) proved the asymptotic estimate

$$Q(a, z) = \frac{1}{2} \operatorname{erfc} \left(\eta \sqrt{\frac{a}{2}} \right) + \left(\frac{1}{\lambda - 1} - \frac{1}{\eta} \right) \frac{e^{-\frac{1}{2}a\eta^2}}{\sqrt{2\pi a}} + O \left(\frac{1}{a} \right)$$

$$\lambda = \frac{z}{a} \quad \eta = \sqrt{2(\lambda - 1 - \ln \lambda)}$$

In the case of interest,

$$\lambda = -2x, \quad \eta = \alpha + i\beta, \quad \begin{cases} \frac{1}{2}(\alpha^2 - \beta^2) = -\mu, \\ \alpha\beta = -\pi \end{cases} \quad \mu(x) = 1 + 2x + \ln 2x$$

$$G_N \approx V^N \begin{cases} e^{-Nx} & 0 < x < x_0 \\ -e^{i\pi \lceil \frac{N}{2} \rceil} \frac{1}{2x+1} \frac{1}{\sqrt{\pi N}} e^{(\lceil \frac{N}{2} \rceil - \lfloor \frac{N}{2} \rfloor)x} (2ex)^{\frac{N}{2}} & x > x_0 \end{cases}$$

x_0 root of $\mu(x) = 0$

The *same* asymptotic estimate also holds for $n > \lfloor \frac{N}{2} \rfloor + 1$

- ▶ For $x > x_0$, G_N fails to be definite in sign, and our approximation breaks down.
- ▶ But, for $x < x_0$, computing F_N , we arrive at

$$\lim_{N \rightarrow \infty} \frac{F_N}{N} = kT \left(\ln \rho - 1 + \frac{1}{2} \beta_1 \rho \right)$$

PALFFY-MUHORAY, VIRGA & ZHENG (2017)

$$\begin{aligned} F_N &= -kT \ln \left(\frac{1}{N!} G_N \right) \approx -kT \ln \left(\frac{V^N}{N!} e^{-\frac{1}{2} N \rho \beta_1} \right) \\ &\approx kT \left(\ln N! - N \ln V + \frac{1}{2} N \rho \beta_1 \right) \\ &\approx kT \left(N \ln N - N - N \ln V + \frac{1}{2} N \rho \beta_1 \right) \\ &= kTN \left(\ln N - \ln V - 1 + \frac{1}{2} \rho \beta_1 \right) \end{aligned}$$

density compatibility requirement

$$x < x_0 \iff \rho\beta_1 < W\left(\frac{1}{e}\right) \doteq 0.2785$$

- ▶ Forest clusters reproduce Onsager's free energy functional in the limit of *limited connectivity* without assuming any *power series* in the density.
- ▶ The density compatibility requirement signals the density at which *connectivity* starts playing a role in the cluster expansion.

Onsager's Functional

Having established on a different basis the same approximation that Onsager derived from Mayer's cluster expansion, we use Onsager's very argument to construct the free-energy functional.

Multi-species argument

The ensemble of N particles is partitioned in M subsystems, the particles of each of which share one and the same orientation in space.

$$\begin{aligned} \Omega & \text{ orientation manifold} \\ \Omega^{(i)} & \text{ partition components} \\ \Omega & = \cup_{i=1}^M \Omega^{(i)} \\ \omega_i \in \Omega^{(i)} & \text{ core orientation in } \Omega^{(i)} \\ N_i & \text{ number of particles in } \Omega^{(i)} \\ & \sum_{i=1}^M N_i = N \\ \Delta\omega_i & \text{ measure of } \Omega^{(i)} \end{aligned}$$

$$N_i = N \varrho(\omega_i) \Delta\omega_i \quad \sum_{i=1}^M \varrho(\omega_i) \Delta\omega_i = 1$$

ϱ orientational distribution density

free-energy component

$$F_N = NkT \left(\ln \frac{N}{V} - 1 \right) + kT \frac{1}{2} \frac{N^2}{V} \beta_1$$

$$F_{N_i} = N_i kT \left(\ln \frac{N_i}{V_i} - 1 \right) + kT \frac{1}{2V} \sum_{i,j=1}^M N_i N_j \beta_1(\omega_i, \omega_j)$$

$$V_i = V \Delta\omega_i \quad \beta_1(\omega_1, \omega_2) := \frac{1}{V} \int_{\mathcal{B}^2} f_{12}(\mathbf{x}_1, \omega_1; \mathbf{x}_2, \omega_2) d\mathbf{x}_1 d\mathbf{x}_2$$

composed free energy

$$\begin{aligned} F_N &= \sum_{i=1}^M F_{N_i} \\ &= \sum_{i=1}^M kTN_i \left(\ln \frac{N_i}{V_i} - 1 \right) + kT \frac{1}{2V} \sum_{i,k=1}^M N_i N_k \beta(\omega_i, \omega_k) \\ &= kTN \sum_{i=1}^M \varrho(\omega_i) \Delta\omega_i (\ln \rho_0 \varrho(\omega_i) - 1) \\ &\quad + \frac{1}{2} kTN \rho_0 \sum_{i,j=1}^M \varrho(\omega_i) \Delta\omega_i \varrho(\omega_j) \Delta\omega_j \beta_1(\omega_i, \omega_j) \end{aligned}$$

$$\rho_0 = \frac{N}{V} \quad \text{number density}$$

continuum limit

$$\frac{F_N}{kTN} = \int_{\Omega} \varrho(\omega) (\ln \rho_0 \varrho(\omega) - 1) d\omega + \frac{1}{2} \rho_0 \int_{\Omega^2} \beta_1(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'$$

$$\int_{\Omega} \varrho(\omega) d\omega = 1$$

(dimensionless) free energy per particle

$$\mathcal{F}_O[\varrho] := \int_{\Omega} \varrho(\omega) \ln \varrho(\omega) d\omega + \frac{1}{2} \rho_0 \int_{\Omega^2} \beta_1(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'$$

complete free energy

$$F_N = kTN (\ln \rho_0 - 1 + \mathcal{F}_O[\varrho])$$

equilibrium (integral) equation

$$\delta \mathcal{F}_O \varrho[\delta \varrho] = \int_{\Omega} \left\{ \ln \varrho(\omega) + 1 + \rho_0 \int_{\Omega} \beta_1(\omega, \omega') \varrho(\omega') d\omega' \right\} \delta \varrho(\omega) d\omega$$

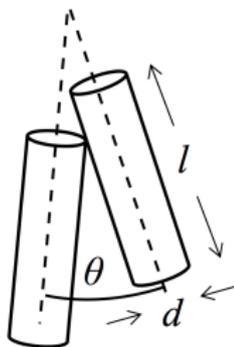
$$\delta \mathcal{F}_O(\varrho)[\delta \varrho] = \lambda \int_{\Omega} \delta \varrho(\omega) d\omega$$

$$\ln \varrho(\omega) + \rho_0 \int_{\Omega} \beta_1(\omega, \omega') \varrho(\omega') d\omega' = \lambda$$

$$\varrho(\omega) = \frac{e^{-\rho_0 \int_{\Omega} \beta_1(\omega, \omega') d\omega'}}{\int_{\Omega} e^{-\rho_0 \int_{\Omega} \beta_1(\omega, \omega') d\omega'} d\omega}$$

β_1 **effective** potential
 ρ_0 **effective** reciprocal temperature

Excluded volume of congruent cylinders



d diameter
 l height
 θ angle between axes

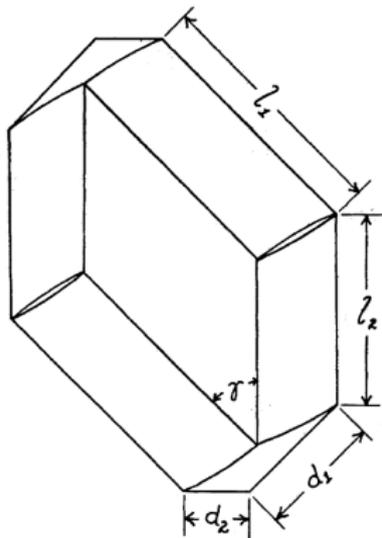
$$\beta_1(\theta) = l^2 d \left\{ 2 \sin \theta + \frac{d}{l} \left(\frac{\pi}{2} + \frac{\pi}{2} |\cos \theta| + 2E(\sin \theta) + \frac{d^2}{l^2} \frac{\pi}{2} \sin \theta \right) \right\}$$

$E(k) := \int_0^{\frac{\pi}{2}} \sqrt{1 - k^2 \sin^2 x} dx$
complete elliptic integral of the **second** kind

approximate formula

In the limit as $\frac{d}{l} \ll 1$,

$$\beta_1(\theta) \approx 2l^2 d \sin \theta$$



isotropic covolume

$$2b := \langle \beta_1 \rangle_{\text{iso}} = \frac{1}{2} \int_0^\pi \beta_1(\theta) \sin \theta d\theta = l^2 d \frac{\pi}{2} = 2v_0 \frac{l}{d}$$

v_0 particles' volume

volume fraction

$$\phi = \frac{Nv_0}{V} = \rho_0 v_0$$

dimensionless concentration

$$c := \rho_0 b = \phi \frac{l}{d}$$

Onsager's free-energy functional

$$\mathcal{F}_O[\varrho] = \int_{\mathbb{S}^2} \varrho(\omega) \ln \varrho(\omega) d\omega + c \frac{4}{\pi} \int_{\mathbb{S}^2 \times \mathbb{S}^2} \sin \theta(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'$$

Onsager's uniaxial trial density

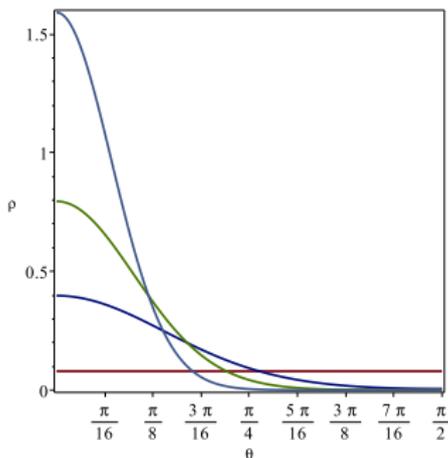
$$\varrho_{\text{O}}(\alpha; \vartheta) := \frac{1}{4\pi} \frac{\alpha}{\sinh \alpha} \cosh(\alpha \cos \vartheta)$$

$\alpha > 0$ parameter

$\omega = (\varphi, \vartheta)$ polar coordinates on \mathbb{S}^2

ϱ_{O} is symmetric about the *polar axis*

$d\omega = \sin \vartheta d\vartheta d\varphi$ measure on \mathbb{S}^2



$\alpha = 0, 5, 10, 20$

$$\mathcal{F}_O[\varrho_O] = \ln \left(\frac{\alpha \coth \alpha}{4\pi} \right) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha} + \frac{2c}{\sinh^2 \alpha} I_2(2\alpha)$$

I_2 Bessel function of order 2

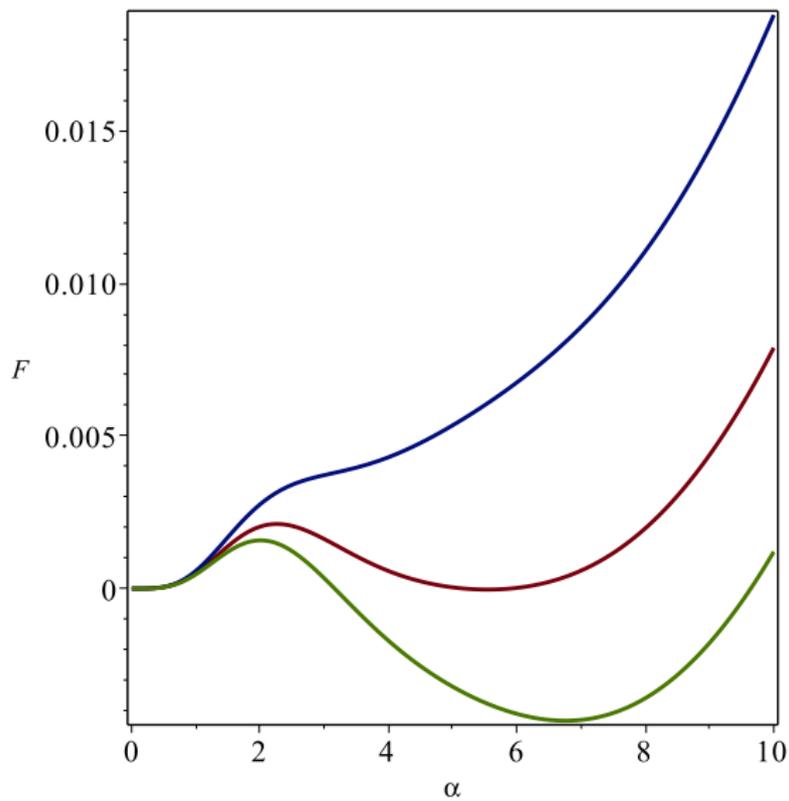
scaled free energy

As $\alpha \rightarrow 0$, $\mathcal{F}_O[\varrho_O] \rightarrow c - \ln 4\pi$. Taking the free energy of the *isotropic* state as a *reference*,

$$\begin{aligned} F(c, \alpha) &:= \mathcal{F}_O[\varrho_O] + \ln 4\pi - c \\ &= \ln(\alpha \coth \alpha) - 1 + \frac{\arctan(\sinh \alpha)}{\sinh \alpha} + c \left(\frac{2}{\sinh^2 \alpha} I_2(2\alpha) - 1 \right) \end{aligned}$$

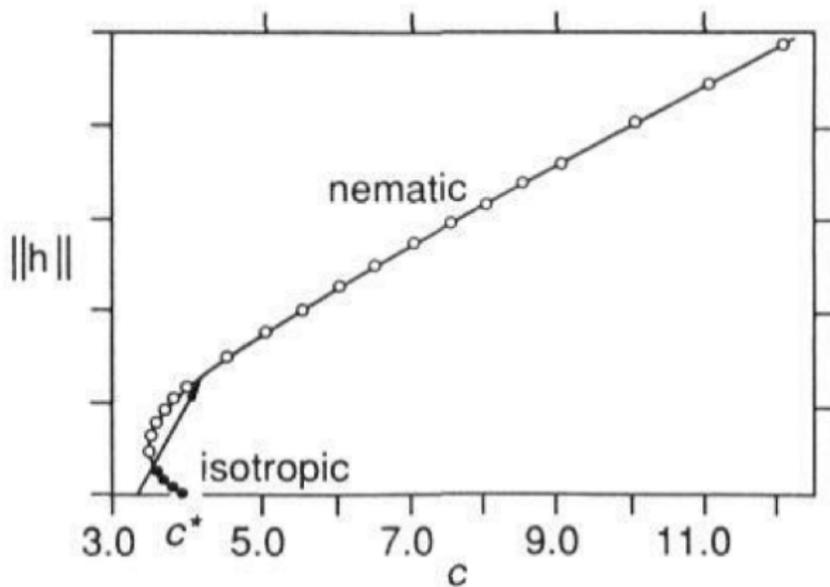
$$F(c, \alpha) = \frac{1}{90} \left(1 - \frac{c}{4} \right) \alpha^4 + O(\alpha^6)$$

Free-energy landscape



$$c_c \doteq 3.681$$

Bifurcation analysis



KAYSER & RAVECHÉ (1978)

- ▶ Computing the *nematic* scalar order parameter S for the minimizer α_m of $F(c, \alpha)$, we obtain a function of c :

$$S(c) := 3\pi \int_0^\pi \left(\cos^2 \vartheta - \frac{1}{3} \right) \varrho_O(\alpha_m; \vartheta) \sin \vartheta d\vartheta$$

- ▶ $S(c_c) \doteq 0.41$
- ▶ KAYSER & RAVECHÉ (1978) considered only solutions to the nonlinear integral equation for ϱ that bifurcate from the *isotropic* solution $\frac{1}{4\pi}$ and preserve the *uniaxial* symmetry.
- ▶ They adopted *two* strategies:
 1. Expand ϱ in a series of *Legendre polynomials* and solve for the coefficients of the expansion;
 2. Solve numerically by an *iterative* scheme the nonlinear integral equation for a *uniaxial* density ϱ .
- ▶ They proved analytically that $c = 4$ is a *transcritical* bifurcation point.

recent results

Recently, VOLLMER (2017) studied a class of functionals that include Onsager's free-energy functional as a special case. For the latter, the bifurcation analysis in the parameter

$$\lambda := \frac{\pi}{8c}$$

shows that

- ▶ The *first* bifurcation from the *isotropic* solution $\frac{1}{4\pi}$ is *transcritical* and it occurs at

$$\lambda_2 = \frac{\pi}{32} \quad (c = 4)$$

- ▶ *All* other bifurcations from the isotropic solution occur at

$$\lambda_s = \frac{\Gamma\left(\frac{s}{2} + \frac{1}{2}\right) \Gamma\left(\frac{s}{2} - \frac{1}{2}\right)}{\Gamma\left(\frac{s}{2} + 1\right) \Gamma\left(\frac{s}{2} + 2\right)}$$

Γ Euler's function

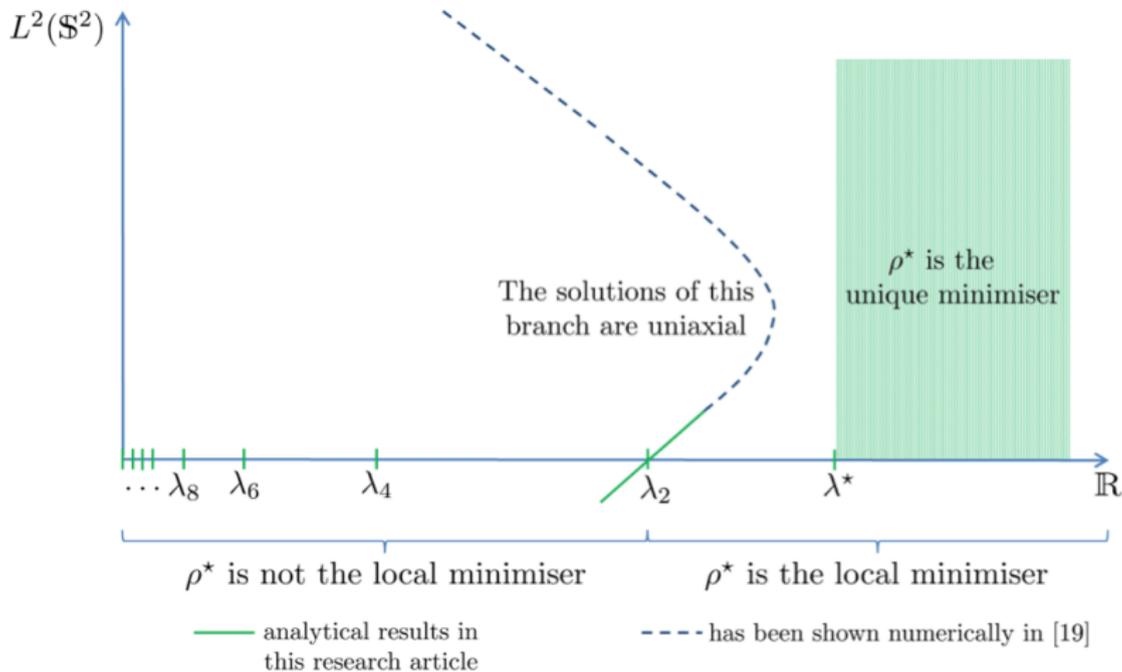
- ▶ The *nontrivial* critical points ϱ of Onsager's free-energy functional are *uniaxial* in the *vicinity* of the isotropic solution in a neighbourhood of $c = 4$.
- ▶ The *isotropic* solution is the *only* solution for

$$\lambda \geq \frac{16}{W\left(\frac{2}{\pi}\right)} \quad (c \leq 0.010)$$

W Lambert function

- ▶ *Every* critical point ϱ is *bounded*.
- ▶ *All* bifurcation branches either meet *infinity* or they meet *another* bifurcation branch.

bifurcation scenario



VOLLMER (2017)

Entropy competition

The Onsager theory is *athermal*: temperature plays no role in it. There is no exchange between kinetic and potential energies. The ordering transition that gives rise to the nematic phase results from the competition between *two* forms of *entropies*:

$$\mathcal{F}_O[\varrho] = \underbrace{\int_{\Omega} \varrho(\omega) \ln \varrho(\omega) d\omega}_{\text{orientational}} + \frac{1}{2} \rho_0 \underbrace{\int_{\Omega^2} \beta_1(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'}_{\text{positional or packing}}$$

Packing particles more closely, thus *minimising* their *excluded volume*, increases the volume they can explore by sliding one over the other: this *maximises* their *free volume*.

Phase Coexistence

Onsager's theory is not only able to explain the isotropic-to-nematic transition. It is perhaps the first example of *density functional* theory, as it also describes phase *separation* and the *coexistence* of nematic and isotropic phases.

motivation

Onsager's original motivation was indeed to explain the phase separation of *tobacco mosaic viruses* in diluted solutions.

again in Onsager's own words

not nearly enough to explain why a solution of 2 per cent tobacco virus in 0.005 normal *NaCl* forms two phases.

tobacco mosaic virus

N. tabacum

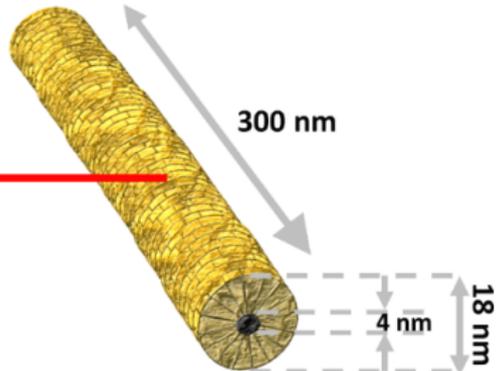
Uninfected leaf



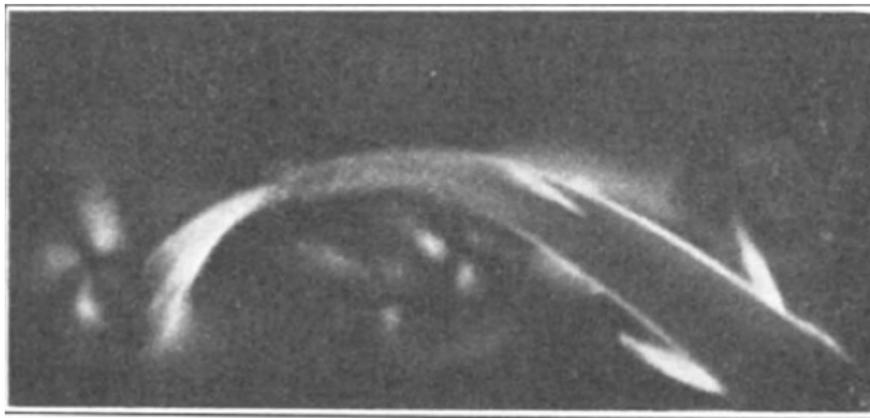
TMV-infected leaf



TMV particle

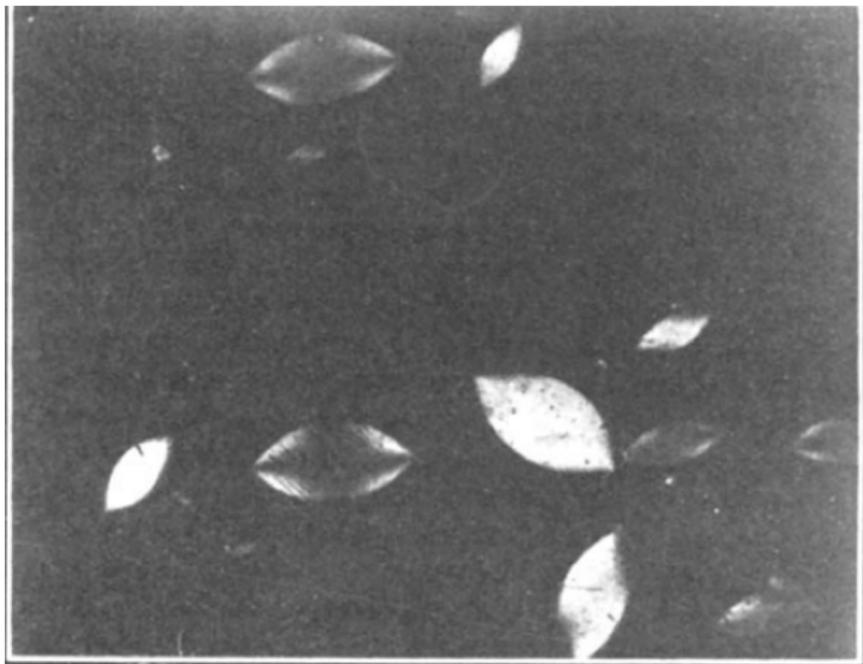


what Onsager might have seen



BAWDEN, PIRIE, BERNAL & FANKUCHEN (1936)

tactoids



BAWDEN, PIRIE, BERNAL & FANKUCHEN (1936)

complete free energy

$$F_N = kTN (\ln \rho_0 - 1 + \mathcal{F}_O[\varrho])$$

N number of particles

V volume occupied by the system

$\rho_0 = \frac{N}{V}$ number density

\mathcal{F}_O density functional

$$\mathcal{F}_O[\varrho] = \int_{\Omega} \varrho(\omega) \ln \varrho(\omega) d\omega + \frac{1}{2} \rho_0 \int_{\Omega^2} \beta_1(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'$$

chemical potential

At *equilibrium*,

$$\mu = \frac{\partial F_N}{\partial N}$$

pressure

$$P = -\frac{\partial F_N}{\partial V}$$

free energy density

In a *homogenous* system,

$$F_N = V f_e \quad f_e := kT \rho_0 (\ln \rho_0 - 1 + \mathcal{F}_O[\varrho])$$

$$\begin{aligned} \mu &= \frac{\partial f_e}{\partial \rho_0} \\ &= kT \left(\ln \rho_0 + \int_{\Omega} \varrho_{\text{eq}}(\omega) \ln \varrho_{\text{eq}}(\omega) d\omega + \rho_0 \int_{\Omega^2} \beta_1(\omega, \omega') \varrho_{\text{eq}}(\omega) \varrho_{\text{eq}}(\omega') d\omega d\omega' \right) \\ P &= \rho_0 \frac{\partial f_e}{\partial \rho_0} - f_e \\ &= kT \rho_0 \left(1 + \frac{1}{2} \rho_0 \int_{\Omega^2} \beta_1(\omega, \omega') \varrho_{\text{eq}}(\omega) \varrho_{\text{eq}}(\omega') d\omega d\omega' \right) \end{aligned}$$

ϱ_{eq} equilibrium density, which makes \mathcal{F}_O *stationary*

Phase Coexistence Criterion

$$[[\mu]] = 0 \quad [[P]] = 0$$

rods' density functional

$$\mathcal{F}_O[\varrho] = \int_{\mathbb{S}^2} \varrho(\omega) \ln \varrho \omega d\omega + c \frac{4}{\pi} \int_{\mathbb{S}^2 \times \mathbb{S}^2} \sin \theta(\omega, \omega') \varrho(\omega) \varrho(\omega') d\omega d\omega'$$

$$c = \rho_0 b = \phi \frac{l}{d} \quad \text{dimensionless concentration}$$

coexistence equations

$$\left[\ln c + \int_{\mathbb{S}^2} \varrho_{\text{eq}}(\omega) \ln \varrho_{\text{eq}}(\omega) d\omega + c \frac{8}{\pi} \int_{\mathbb{S}^2 \times \mathbb{S}^2} \sin(\omega, \omega') \varrho_{\text{eq}}(\omega) \varrho_{\text{eq}}(\omega') d\omega d\omega' \right] = 0$$

$$\left[c \left(1 + c \frac{4}{\pi} \int_{\mathbb{S}^2 \times \mathbb{S}^2} \sin(\omega, \omega') \varrho_{\text{eq}}(\omega) \varrho_{\text{eq}}(\omega') d\omega d\omega' \right) \right] = 0$$

- ▶ The two possibly coexisting phases are the *isotropic* phase and the *aligned* phase.
- ▶ Onsager found a solution to the coexistence equations in his class of *trial* equilibrium densities.

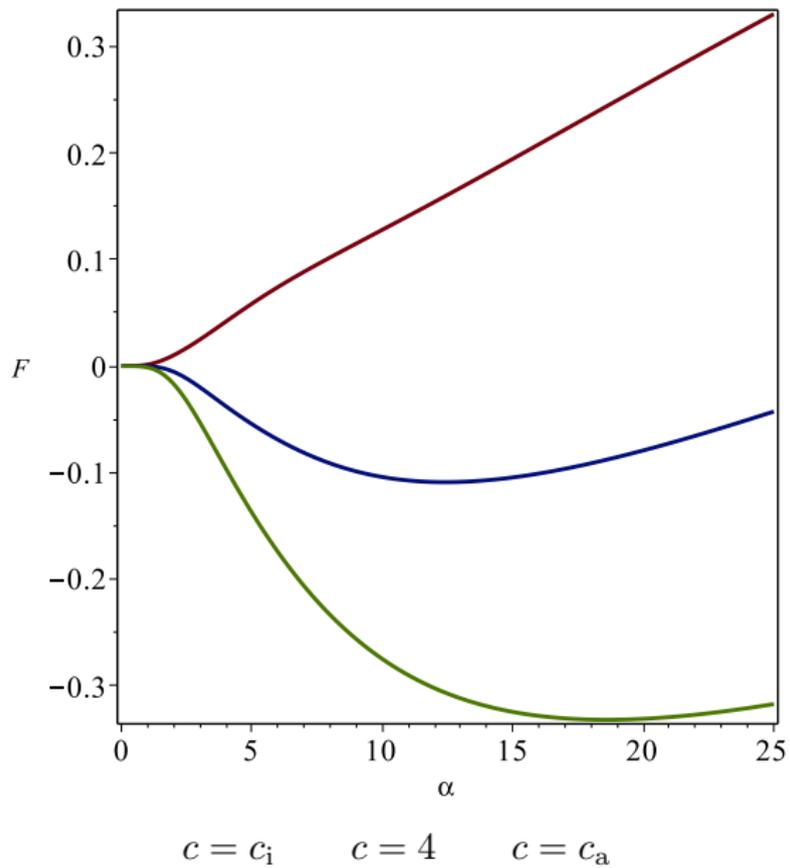
$$c_i \doteq 3.340 \quad c_a \doteq 4.486$$

- ▶ The *scalar order parameter* in the aligned *coexisting* phase is *larger* than the scalar order parameter at the transition

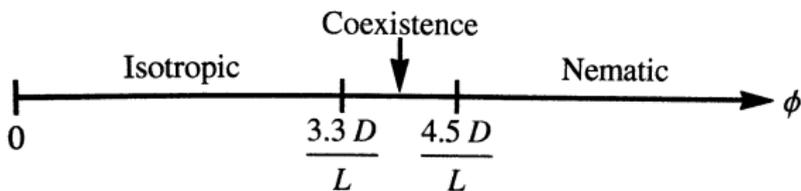
$$S(c_a) \doteq 0.84$$

- ▶ The concentration ratio is also *larger* than expected from experiment

$$\frac{c_a}{c_i} \doteq 1.34$$



volume fraction



lever rule

Suppose that the solution is prepared with a (dimensionless) concentration $c_i \leq c \leq c_a$. Let V_i and V_a be the volumes occupied by the two coexisting phases. Let N_i and N_a be the corresponding numbers of particles.

$$V_i + V_a = V \quad N_i + N_a = N$$

The solutions to these equations are

$$\frac{V_i}{V} = \frac{c_a - c}{c_a - c_i} \quad \frac{V_a}{V} = \frac{c - c_i}{c_a - c_i}$$

$$\frac{N_i}{N} = \frac{c_i}{c} \frac{c_a - c}{c_a - c_i} \quad \frac{N_a}{N} = \frac{c_a}{c} \frac{c - c_i}{c_a - c_i}$$

Sources

- ▶ F.C. BAWDEN, N.W. PIRIE, J.D. BERNAL & I. FANKUCHEN, Liquid crystalline substances from virus-infected plants, *Nature*, **138**, 1936, 1051–1052.
- ▶ M. BORN, The statistical mechanics of condensing systems, *Physica*, **4**, 1937, 1034–1044.
- ▶ M. BORN & K. FUCHS, The statistical mechanics of condensing systems, *Proc. R. Soc. Lond. A*, **166**, 1938, 391–414.
- ▶ V.E. BRITIKOV, Asymptotic number of forests from unrooted trees, *Mat. Zametki*, **43**, 1988, 672–684.
- ▶ A. CAYLEY, A theorem on trees, *Quart. J. Pure Appl. Math.*, **23**, 1889, 376–378. (The Collected Mathematical Papers of Arthur Cayley, Vol. XIII, pp. 26–28, Cambridge Univ. Press, Cambridge, 1897).

- ▶ **R.F. KAYSER & H.J. RAVECHÉ**, Bifurcation in Onsager's model of the isotropic-nematic transition, *Phys. Rev. A*, **17**, 1978, 2067—2072.
- ▶ **J.L. LEBOWITZ & O. PENROSE**, Convergence of virial expansions, *J. Math. Phys.*, **5**, 1964, 841–847.
- ▶ **J.E. MAYER**, The statistical mechanics of condensing systems I, *J. Chem. Phys.*, **5**, 1937, 67–73.
- ▶ **J.E. MAYER & M.G. MAYER**, *Statistical Mechanics*. Wiley, New York, 1940.
- ▶ **L. MEDEROS, E. VELASCO & Y. MARTÍNEZ-RATÓN**, Hard-body models of bulk liquid crystals, *J. Phys.: Condens. Matter*, **26**, 2014, 463101.
- ▶ **T. MORAIS & A. PROCACCI**, Continuous particles in the canonical ensemble as an abstract polymer gas, *J. Stat. Phys.*, **151**, 2013, 830–849.

- ▶ **L. ONSAGER**, Anisotropic solutions of colloids, *Phys. Rev.*, **62**, 1942, 558.
- ▶ **L. ONSAGER**, The effects of shape on the interaction of colloidal particles, *Ann. N.Y. Acad. Sci.*, **51**, 1949, 627–659.
- ▶ **P. PALFFY-MUHORAY, M.Y. PEVNYI, E.G. VIRGA & X. ZHENG**, The effects of particle shape in orientationally ordered soft materials, in *Mathematics and Materials*, vol. **23**, PCMS Series, AMS, 2017, *in press*.
- ▶ **P. PALFFY-MUHORAY, E.G. VIRGA & X. ZHENG**, Toward Onsager's density functional via Penroses tree identity, *to be submitted*, 2017.
- ▶ **O. PENROSE**, Convergence of fugacity expansions for classical systems, in T.A. BAK, Editor, *Statistical Mechanics, Foundations and Applications*, pp. 101–109, New York, 1967. I.U.P.A.P. Meeting (Copenhagen 1966), Benjamin, Inc.

- ▶ **A. PROCACCI & S. A. YUHJTMAN**, Convergence of Mayer and virial expansions and the Penrose tree-graph identity, *Lett. Math. Phys.*, **107**, 2017, 31–46.
- ▶ **E. PULVIRENTI & D. TSAGKAROGIANNIS**, Cluster expansion in the canonical ensemble, *Comm. Math. Phys.*, **316**, 2012, 289–306.
- ▶ **D. RUELLE**, *Statistical Mechanics: rigorous results*, World Scientific–Imperial College Press, Singapore, 1969.
- ▶ **J.V. SELINGER**, *Introduction to the Theory of Soft Matter: From Ideal Gases to Liquid Crystals*, Springer, Cham, 2016.
- ▶ **S.J. TATE**, Virial expansion bounds, *J. Stat. Phys.*, **153**, 2013, 325–338.
- ▶ **N.M. TEMME**, The asymptotic expansion of the incomplete Gamma functions, *SIAM J. Math. Anal.*, **10**, 1979, 757–766.
- ▶ **H.D. URSELL**, The evaluation of the Gibbs' phase-integral for imperfect gases, *Proc. Camb. Phil. Soc.*, **23**, 1927, 685–697.

- ▶ **M.A.C. VOLLMER**, Critical points and bifurcations of the three-dimensional Onsager model for liquid crystals, *submitted*, 2017.
- ▶ **G.J. VROEGE & H.N.W LEKKERKERKER**, Phase transitions in lyotropic colloidal and polymer liquid crystals, *Rep. Prog. Phys.*, **55**, 1992, 1241–1309.

MATHEMATICAL THEORIES OF LIQUID CRYSTALS

EPIFANIO G. VIRGA

Mathematical Institute

University of Oxford

virga@maths.ox.ac.uk

on leave from

Department of Mathematics

University of Pavia, Italy

Ideal Course Outline

I. Fundamentals

II. The Maier-Saupe Theory

III. The Onsager Theory

IV. The Oseen-Frank Theory

V. The Landau-deGennes Theory

VI. The Ericksen-Leslie Theory