Different Flavours of the Mean-Field Theory

Epifanio G. Virga

SMMM

Soft Matter Mathematical Modelling

Department of Mathematics

University of Pavia, Italy

Summary

Averages: Ex Multis Unum

N-Particle Ensemble

Gibbs-Bogolubov Inequalities

Minimum Principle

One-Particle Probability Function

Averages: ***Ex Multis Unum***

Mean-field theories embody ***averages*** of one kind or another.

They are variously regarded in the trade:

Averages: ***Ex Multis Unum***

Mean-field theories embody ***averages*** of one kind or another.

They are variously regarded in the trade:

- They are used to predict transitions between different collective molecular arrangements, mainly driven by changes in temperature.

Averages: ***Ex Multis Unum***

Mean-field theories embody ***averages*** of one kind or another.

They are variously regarded in the trade:

- They are used to predict transitions between different collective molecular arrangements, mainly driven by changes in temperature.
- They constitute a possible theoretical foundation of continuum theories of soft matter phases.

Averages: ***Ex Multis Unum***

Mean-field theories embody ***averages*** of one kind or another.

They are variously regarded in the trade:

- They are used to predict transitions between different collective molecular arrangements, mainly driven by changes in temperature.
- They constitute a possible theoretical foundation of continuum theories of soft matter phases.
- They bridge the scales between molecular and continuum levels.

Averages: *Ex Multis Unum*

Mean-field theories embody ***averages*** of one kind or another.

They are variously regarded in the trade:

- They are used to predict transitions between different collective molecular arrangements, mainly driven by changes in temperature.
- They constitute a possible theoretical foundation of continuum theories of soft matter phases.
- They bridge the scales between molecular and continuum levels.

Their rigorous formulation is still the source of mathematical interest.

Gartland & Virga (2010)

Upon average over the intermolecular vector, assumed to be ***isotropically distributed*** in space, the interaction energy between two molecules becomes the ***average Hamiltonian*** H, also called the ***pair-potential***, which is the basis of our theory.

Upon average over the intermolecular vector, assumed to be ***isotropically distributed*** in space, the interaction energy between two molecules becomes the ***average Hamiltonian*** H, also called the ***pair-potential***, which is the basis of our theory.

Steric effects may also be embodied in H, which result from the mutual hindrance of molecules. They introduce in H a subtle dependence on the relative molecular orientation. Sonnet & Virga (2008)

Upon average over the intermolecular vector, assumed to be ***isotropically distributed*** in space, the interaction energy between two molecules becomes the ***average Hamiltonian*** H, also called the ***pair-potential***, which is the basis of our theory.

Steric effects may also be embodied in H, which result from the mutual hindrance of molecules. They introduce in H a subtle dependence on the relative molecular orientation. Sonnet & Virga (2008)

average Hamiltonian

- H depends only on the state of the interacting molecules.

Upon average over the intermolecular vector, assumed to be ***isotropically distributed*** in space, the interaction energy between two molecules becomes the ***average Hamiltonian*** H, also called the ***pair-potential***, which is the basis of our theory.

Steric effects may also be embodied in H, which result from the mutual hindrance of molecules. They introduce in H a subtle dependence on the relative molecular orientation. Sonnet & Virga (2008)

average Hamiltonian

- H depends only on the state of the interacting molecules.
- For rigid molecules, H is ultimately a function of their relative orientation.

Upon average over the intermolecular vector, assumed to be ***isotropically distributed*** in space, the interaction energy between two molecules becomes the ***average Hamiltonian*** H, also called the ***pair-potential***, which is the basis of our theory.

Steric effects may also be embodied in H, which result from the mutual hindrance of molecules. They introduce in H a subtle dependence on the relative molecular orientation. Sonnet & Virga (2008)

average Hamiltonian

- H depends only on the state of the interacting molecules.
- For rigid molecules, H is ultimately a function of their relative orientation.
- For deformable molecules, H also depends on their conformations.

state space

H is a real-valued mapping over $\Omega \times \Omega$

$$(\omega, \omega') \mapsto H(\omega, \omega')$$

Ω state space

state space

H is a real-valued mapping over $\Omega \times \Omega$

$$(\omega, \omega') \mapsto H(\omega, \omega')$$

Ω state space

molecular exchange

All molecules are ***indistinguishable***

$$H(\omega, \omega') = H(\omega', \omega) \quad \forall\, \omega, \omega' \in \Omega$$

state space

H is a real-valued mapping over $\Omega \times \Omega$

$$(\omega, \omega') \mapsto H(\omega, \omega')$$

Ω state space

molecular exchange

All molecules are ***indistinguishable***

$$H(\omega, \omega') = H(\omega', \omega) \quad \forall\ \omega, \omega' \in \Omega$$

frame-indifference

Given a rotation $\mathbf{R} \in \mathsf{SO}(3)$, $R_{\mathbf{R}} : \Omega \to \Omega$ is the ***action*** of $\mathbf{R}$ upon Ω:

$$H(R_{\mathbf{R}}(\omega), R_{\mathbf{R}}(\omega')) = H(\omega, \omega') \quad \forall\ \omega, \omega' \in \Omega \text{ and } \forall\ \mathbf{R} \in \mathsf{SO}(3)$$

symmetry

A symmetry transformation $G : \Omega \to \Omega$ changes the state of the molecule in an ***equivalent*** one:

$$H(G(\omega), \omega') = H(\omega, G(\omega')) = H(\omega, \omega') \quad \forall\, \omega, \omega' \in \Omega \text{ and } G \in \mathsf{G}$$

G symmetry group

symmetry

A symmetry transformation $G : \Omega \to \Omega$ changes the state of the molecule in an ***equivalent*** one:

$$H(G(\omega), \omega') = H(\omega, G(\omega')) = H(\omega, \omega') \quad \forall\, \omega, \omega' \in \Omega \text{ and } G \in \mathsf{G}$$

G symmetry group

measurable space

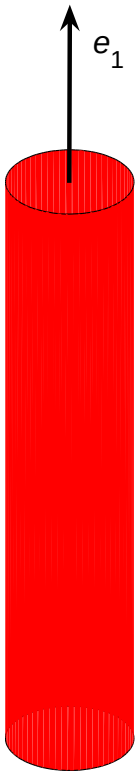
We envision Ω as a ***compact*** measurable space endowed with an appropriate ***measure*** μ

$$\int_{\Sigma} g(\omega) d\mu(\omega)$$

$\Sigma \subset \Omega$ measurable subset

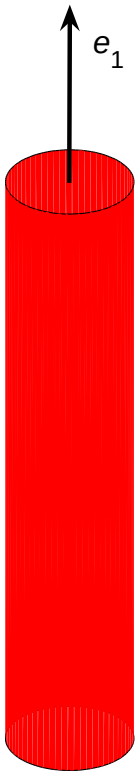
g measurable real-valued function

examples

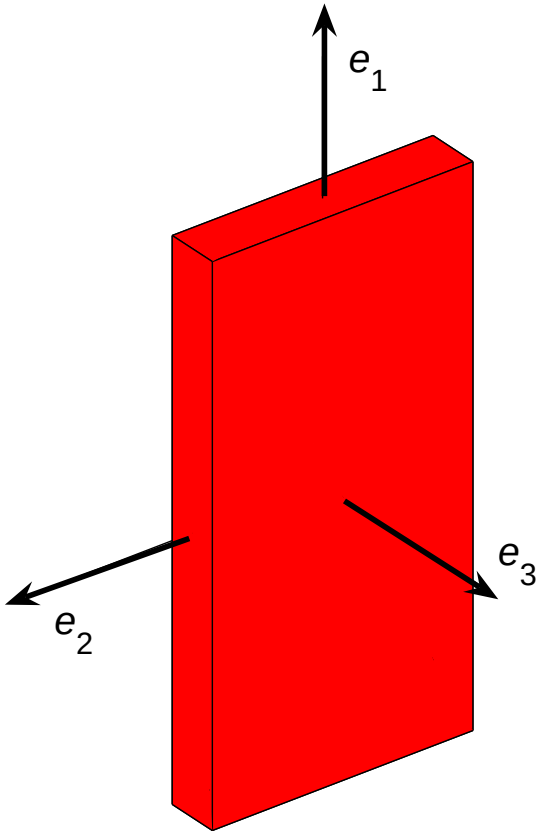


$\mathsf{G} = \mathsf{D}_{\infty h}$

examples

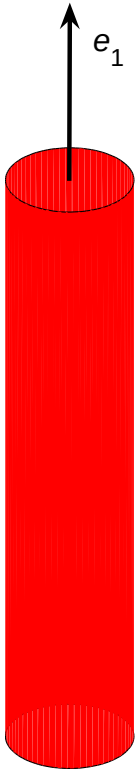


$\mathsf{G} = \mathsf{D}_{\infty h}$

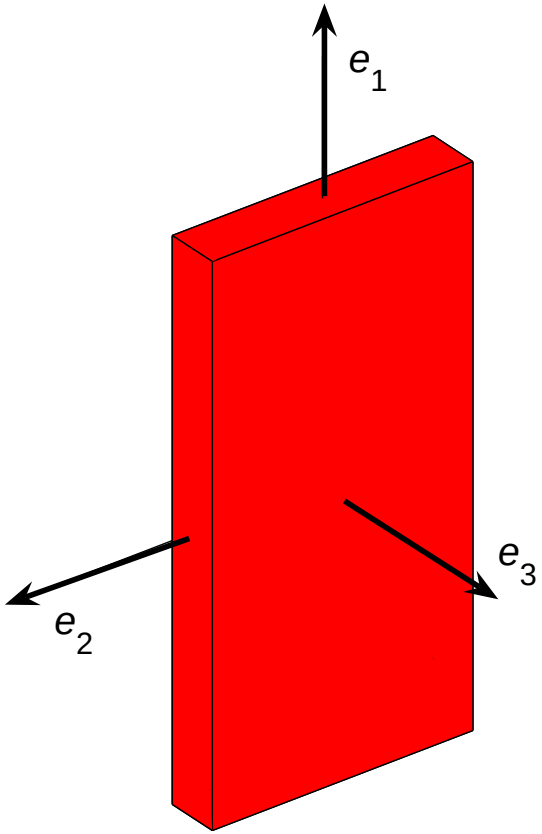


$\mathsf{G} = \mathsf{D}_{2h}$

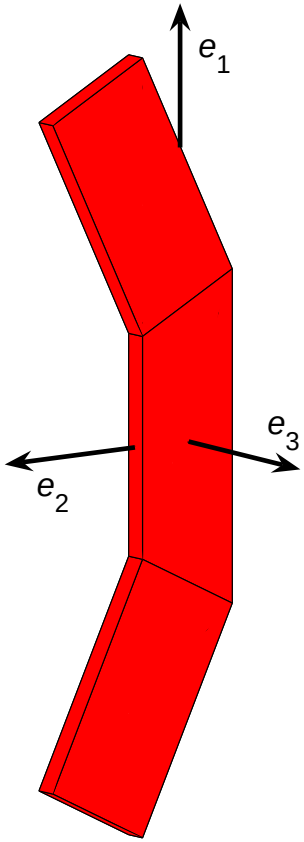
examples



$\mathsf{G} = \mathsf{D}_{\infty h}$



$\mathsf{G} = \mathsf{D}_{2h}$



$\mathsf{G} = \mathsf{C}_{2v}$

Bilinear Hamiltonians

The theory applies to a Hamiltonian H that can be expressed as a ***bilinear from*** of any number of ***molecular tensors*** living in a ***linear space***.

Bilinear Hamiltonians

The theory applies to a Hamiltonian H that can be expressed as a ***bilinear from*** of any number of ***molecular tensors*** living in a ***linear space***.

Though the Hamiltonian could involve tensors of any ***rank***, for simplicity here we shall consider the ***quadrupolar approximation*** only.

Bilinear Hamiltonians

The theory applies to a Hamiltonian H that can be expressed as a ***bilinear from*** of any number of ***molecular tensors*** living in a ***linear space***.

Though the Hamiltonian could involve tensors of any ***rank***, for simplicity here we shall consider the ***quadrupolar approximation*** only.

Maier-Saupe model for uniaxial nematics

$$H(\omega,\omega') = -U_0 \mathbf{q}(\omega)\cdot\mathbf{q}(\omega') =: \widehat{H}(\mathbf{q},\mathbf{q}')$$

Bilinear Hamiltonians

The theory applies to a Hamiltonian H that can be expressed as a ***bilinear from*** of any number of ***molecular tensors*** living in a ***linear space***.

Though the Hamiltonian could involve tensors of any ***rank***, for simplicity here we shall consider the ***quadrupolar approximation*** only.

Maier-Saupe model for uniaxial nematics

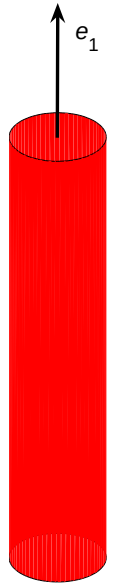
$$H(\omega,\omega') = -U_0 \mathbf{q}(\omega)\cdot\mathbf{q}(\omega') =: \widehat{H}(\mathbf{q},\mathbf{q}')$$

$$\mathbf{q}' := \mathbf{q}(\omega')$$

$$\mathbf{q}(\omega) := \boldsymbol{e}_1(\omega)\otimes\boldsymbol{e}_1(\omega) - \tfrac{1}{3}\mathbf{I}$$

U_0 scaling energy

$\Omega = \mathbb{S}^2$ orientation sphere



Straley model for biaxial nematics

$$\widehat{H} = -U_0[\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

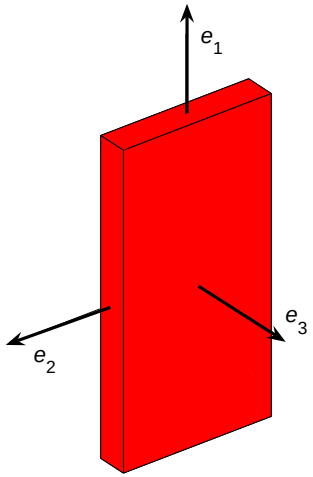
Straley model for biaxial nematics

$$\widehat{H} = -U_0[\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

$$\mathbf{q} := \boldsymbol{e}_1(\omega)\otimes\boldsymbol{e}_1(\omega) - \tfrac{1}{3}\mathbf{I}$$

$$\mathbf{b} := \boldsymbol{e}_2(\omega)\otimes\boldsymbol{e}_2(\omega) - \boldsymbol{e}_3(\omega)\otimes\boldsymbol{e}_3(\omega)$$

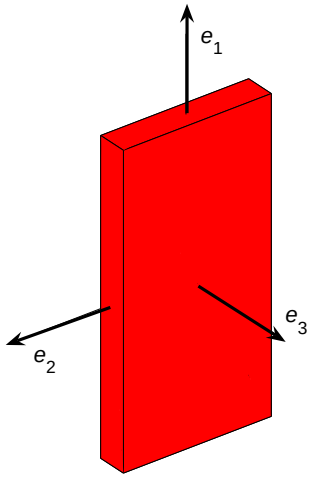
$\Omega = \mathbb{S}^1 \times \mathbb{S}^2$ orientation torus



Straley model for biaxial nematics

$$\widehat{H} = -U_0[\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

$$\mathbf{q} := \boldsymbol{e}_1(\omega)\otimes\boldsymbol{e}_1(\omega) - \tfrac{1}{3}\mathbf{I}$$
$$\mathbf{b} := \boldsymbol{e}_2(\omega)\otimes\boldsymbol{e}_2(\omega) - \boldsymbol{e}_3(\omega)\otimes\boldsymbol{e}_3(\omega)$$
$$\Omega = \mathbb{S}^1\times\mathbb{S}^2 \quad \text{orientation torus}$$



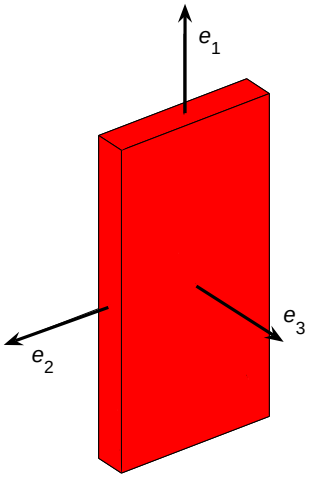
Quadrupolar model for C_{2v} molecules

$$\widehat{H} = -U_0[\varepsilon\boldsymbol{e}_2\cdot\boldsymbol{e}_2' + \mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

Straley model for biaxial nematics

$$\widehat{H} = -U_0[\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

$$\mathbf{q} := \boldsymbol{e}_1(\omega)\otimes\boldsymbol{e}_1(\omega) - \tfrac{1}{3}\mathbf{I}$$
$$\mathbf{b} := \boldsymbol{e}_2(\omega)\otimes\boldsymbol{e}_2(\omega) - \boldsymbol{e}_3(\omega)\otimes\boldsymbol{e}_3(\omega)$$
$$\Omega = \mathbb{S}^1\times\mathbb{S}^2 \quad \text{orientation torus}$$

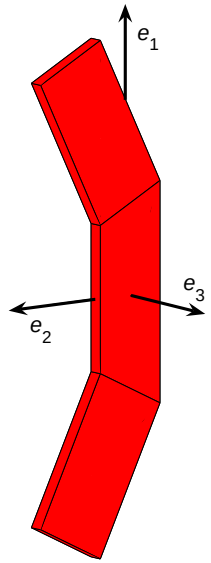


Quadrupolar model for C_{2v} molecules

$$\widehat{H} = -U_0[\varepsilon\boldsymbol{e}_2\cdot\boldsymbol{e}_2' + \mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b} + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}']$$

$\boldsymbol{e}_2$ molecular dipole

$$\boldsymbol{e}_2' := \boldsymbol{e}_2(\omega')$$



N-particle Ensemble

Consider a system with N identical particles.

N-particle Ensemble

Consider a system with N identical particles.

ensemble state

$$\boldsymbol{\omega} = (\omega_1, \ldots, \omega_N) \in \Omega^N$$

N-particle Ensemble

Consider a system with N identical particles.

ensemble state

$$\boldsymbol{\omega} = (\omega_1, \ldots, \omega_N) \in \Omega^N$$

interaction set

$$\mathscr{I} = \{(i,j) | i,j \in \{1,\ldots,N\}, i < j, \text{particles } i \text{ and } j \text{ interact}\}$$

n cardinality of $\mathscr{I}$

$n \geq \lceil \frac{N}{2} \rceil$ least integer $\geq \frac{N}{2}$

ensemble Hamiltonian

$$\mathscr{H}(\boldsymbol{\omega}) := \sum_{(i,j)\in\mathscr{I}} H(\omega_i, \omega_j)$$

ensemble Hamiltonian

$$\mathscr{H}(\boldsymbol{\omega}) := \sum_{(i,j)\in\mathscr{I}} H(\omega_i, \omega_j)$$

Boltzmann distribution

$$\rho(\boldsymbol{\omega}, \beta) := \frac{1}{\mathscr{Z}(\beta)} \mathrm{e}^{-\beta\mathscr{H}(\boldsymbol{\omega})}$$

$$\beta := \frac{1}{k_B T}$$

k_B Boltzmann constant

ensemble Hamiltonian

$$\mathscr{H}(\boldsymbol{\omega}) := \sum_{(i,j)\in\mathscr{I}} H(\omega_i, \omega_j)$$

Boltzmann distribution

$$\rho(\boldsymbol{\omega}, \beta) := \frac{1}{\mathscr{Z}(\beta)} \mathrm{e}^{-\beta\mathscr{H}(\boldsymbol{\omega})}$$

$$\beta := \frac{1}{k_B T}$$

partition function

$$\mathscr{Z}(\beta) := \int_{\Omega^N} \mathrm{e}^{-\beta\mathscr{H}(\boldsymbol{\omega})} d\mu(\boldsymbol{\omega})$$

k_B Boltzmann constant

ensemble free energy

$$\mathscr{F}(\beta) := -\frac{1}{\beta} \ln \mathscr{Z}(\beta) = \mathscr{U}(\beta) - \frac{1}{\beta k_B} \mathscr{S}(\beta)$$

ensemble free energy

$$\mathscr{F}(\beta) := -\frac{1}{\beta} \ln \mathscr{Z}(\beta) = \mathscr{U}(\beta) - \frac{1}{\beta k_B} \mathscr{S}(\beta)$$

ensemble internal energy

$$\mathscr{U}(\beta) := -\frac{\partial}{\partial \beta} \ln \mathscr{Z}(\beta)$$

ensemble free energy

$$\mathscr{F}(\beta) := -\frac{1}{\beta} \ln \mathscr{Z}(\beta) = \mathscr{U}(\beta) - \frac{1}{\beta k_B} \mathscr{S}(\beta)$$

ensemble internal energy

$$\mathscr{U}(\beta) := -\frac{\partial}{\partial \beta} \ln \mathscr{Z}(\beta)$$

ensemble entropy

$$\mathscr{S} = -k_B \int_{\Omega^N} \rho(\boldsymbol{\omega}, \beta) \ln \rho(\boldsymbol{\omega}, \beta) d\mu(\boldsymbol{\omega})$$

ensemble average

$$\mathscr{U}(\beta) = \int_{\Omega^N} \mathscr{H}(\boldsymbol{\omega})\rho(\boldsymbol{\omega},\beta))d\mu(\boldsymbol{\omega}) =: \langle \mathscr{H} \rangle_\rho$$

$$\langle f \rangle_\rho := \int_{\Omega^N} f(\boldsymbol{\omega})\rho(\boldsymbol{\omega},\beta)d\mu(\boldsymbol{\omega})$$

ensemble average

$$\mathscr{U}(\beta) = \int_{\Omega^N} \mathscr{H}(\boldsymbol{\omega})\rho(\boldsymbol{\omega},\beta))d\mu(\boldsymbol{\omega}) =: \langle \mathscr{H} \rangle_\rho$$

$$\langle f \rangle_\rho := \int_{\Omega^N} f(\boldsymbol{\omega})\rho(\boldsymbol{\omega},\beta)d\mu(\boldsymbol{\omega})$$

per-particle potentials

$$F := \frac{1}{N}\mathscr{F} \qquad U := \frac{1}{N}\mathscr{U} \qquad S := \frac{1}{N}\mathscr{S}$$

Gibbs-Bogolubov Inequalities

Consider two ensemble Hamiltonians $\mathscr{H}$ and $\mathscr{H}'$ for the same N-particle system, with associated Boltzmann distributions ρ and ρ'. The corresponding free energies $\mathscr{F}$ and $\mathscr{F}'$ obey the inequalities

$$\langle \mathscr{H} - \mathscr{H}' \rangle_\rho \leq \mathscr{F} - \mathscr{F}' \leq \langle \mathscr{H} - \mathscr{H}' \rangle_{\rho'}$$

Gibbs-Bogolubov Inequalities

Consider two ensemble Hamiltonians $\mathscr{H}$ and $\mathscr{H}'$ for the same N-particle system, with associated Boltzmann distributions ρ and ρ'. The corresponding free energies $\mathscr{F}$ and $\mathscr{F}'$ obey the inequalities

$$\langle \mathscr{H} - \mathscr{H}' \rangle_\rho \leq \mathscr{F} - \mathscr{F}' \leq \langle \mathscr{H} - \mathscr{H}' \rangle_{\rho'}$$

Mean-field approximation

Conceptually, the mean field approximation replaces the interaction between particles with the action exerted by a ***mean-field***, at the same time produced and felt by all particles.

Gibbs-Bogolubov Inequalities

Consider two ensemble Hamiltonians $\mathscr{H}$ and $\mathscr{H}'$ for the same N-particle system, with associated Boltzmann distributions ρ and ρ'. The corresponding free energies $\mathscr{F}$ and $\mathscr{F}'$ obey the inequalities

$$\langle \mathscr{H} - \mathscr{H}' \rangle_\rho \leq \mathscr{F} - \mathscr{F}' \leq \langle \mathscr{H} - \mathscr{H}' \rangle_{\rho'}$$

Mean-field approximation

Conceptually, the mean field approximation replaces the interaction between particles with the action exerted by a ***mean-field***, at the same time produced and felt by all particles.

Mathematically, the mean-field approximation replaces the two particle Hamiltonian H with a ***one-particle*** Hamiltonian H_0 depending on the mean field.

collective tensor

We denote by **q** the ***collection*** of all molecular tensors in an individual molecule.

collective tensor

We denote by $\mathbf{q}$ the ***collection*** of all molecular tensors in an individual molecule.

$$\mathbf{q} = \mathbf{q} \quad \text{Maier-Saupe model}$$
$$\mathbf{q} = (\mathbf{q}, \mathbf{b}) \quad \text{Straley model}$$
$$\mathbf{q} = (e_2, \mathbf{q}, \mathbf{b}) \quad \mathsf{C}_{2v} \text{ model}$$

collective tensor

We denote by $\mathbf{q}$ the ***collection*** of all molecular tensors in an individual molecule.

$\mathbf{q} = \mathbf{q}$ Maier-Saupe model

$\mathbf{q} = (\mathbf{q}, \mathbf{b})$ Straley model

$\mathbf{q} = (e_2, \mathbf{q}, \mathbf{b})$ C_{2v} model

$$\widehat{H} = \widehat{H}(\mathbf{q}, \mathbf{q}')$$

$$\mathbf{q} = \mathbf{q}(\omega) \quad \mathbf{q}' = \mathbf{q}(\omega')$$

$$\omega, \omega' \in \Omega$$

$$H(\omega, \omega') = \widehat{H}(\mathbf{q}(\omega), \mathbf{q}(\omega'))$$

one-particle Hamiltonian

$$H_0(\omega; \mathbf{Q}) := \langle H(\omega, \cdot) \rangle_{\rho_0} - \frac{1}{2} \langle H(\cdot, \cdot) \rangle_{\rho_0^2}$$

Palffy-Muhoray (2002)

one-particle Hamiltonian

$$H_0(\omega;\mathbf{Q}) := \langle H(\omega,\cdot)\rangle_{\rho_0} - \frac{1}{2}\langle H(\cdot,\cdot)\rangle_{\rho_0^2}$$

PALFFY-MUHORAY (2002)

$$\rho_0(\omega;\beta,\mathbf{Q}) := \frac{1}{Z_0(\beta,\mathbf{Q})}\mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})}$$

$$Z_0(\beta,\mathbf{Q}) := \int_\Omega \mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})} d\mu(\omega)$$

one-particle Hamiltonian

$$H_0(\omega;\mathbf{Q}) := \langle H(\omega,\cdot)\rangle_{\rho_0} - \frac{1}{2}\langle H(\cdot,\cdot)\rangle_{\rho_0^2}$$

PALFFY-MUHORAY (2002)

$$\rho_0(\omega;\beta,\mathbf{Q}) := \frac{1}{Z_0(\beta,\mathbf{Q})}\mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})}$$

$$Z_0(\beta,\mathbf{Q}) := \int_\Omega \mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})} d\mu(\omega)$$

consistency condition

$$\mathbf{Q} := \langle \mathbf{q}\rangle_{\rho_0}$$

one-particle Hamiltonian

$$H_0(\omega;\mathbf{Q}) := \langle H(\omega,\cdot)\rangle_{\rho_0} - \frac{1}{2}\langle H(\cdot,\cdot)\rangle_{\rho_0^2}$$

PALFFY-MUHORAY (2002)

$$\rho_0(\omega;\beta,\mathbf{Q}) := \frac{1}{Z_0(\beta,\mathbf{Q})}\mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})}$$

$$Z_0(\beta,\mathbf{Q}) := \int_\Omega \mathrm{e}^{-\beta H_0(\omega;\mathbf{Q})} d\mu(\omega)$$

consistency condition

$$\mathbf{Q} := \langle \mathbf{q}\rangle_{\rho_0}$$

Since ρ_0 depends on H_0, strictly speaking, the above definition for H_0 is ***implicit***.

extension

Though H_0 is meaningful only for a self-consistent $\mathbf{Q}$, its definition can be formally ***extended*** to the whole space where $\mathbf{Q}$ lives.

extension

Though H_0 is meaningful only for a self-consistent $\mathbf{Q}$, its definition can be formally ***extended*** to the whole space where $\mathbf{Q}$ lives.

For the extended H_0,

$$F_0(\beta, \mathbf{Q}) := -\frac{1}{\beta} \ln Z_0(\beta, \mathbf{Q})$$

extension

Though H_0 is meaningful only for a self-consistent $\mathbf{Q}$, its definition can be formally ***extended*** to the whole space where $\mathbf{Q}$ lives.

For the extended H_0,

$$F_0(\beta, \mathbf{Q}) := -\frac{1}{\beta} \ln Z_0(\beta, \mathbf{Q})$$

F_0 has the meaning of ***one-particle free energy*** just for the consistent $\mathbf{Q}$'s

extension

Though H_0 is meaningful only for a self-consistent $\mathbf{Q}$, its definition can be formally ***extended*** to the whole space where $\mathbf{Q}$ lives.

For the extended H_0,

$$F_0(\beta, \mathbf{Q}) := -\frac{1}{\beta} \ln Z_0(\beta, \mathbf{Q})$$

F_0 has the meaning of ***one-particle free energy*** just for the consistent $\mathbf{Q}$'s

free energy gradient

$$\frac{\partial F_0}{\partial \mathbf{Q}} = \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0}$$

bilinear Hamiltonians

$$\left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} = \mathbf{0} \quad \Leftrightarrow \quad \langle \mathbf{q} \rangle_{\rho_0} = \mathbf{Q} \quad \Leftrightarrow \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

In this class of two-particle Hamiltonians, the ***consistency*** condition for Q is equivalent to ***criticality*** condition for the ***extended*** F_0.

ensemble mean-field Hamiltonian

$$\mathscr{H}_0(\boldsymbol{\omega};\mathbf{Q}) := \sum_{i=1}^{N} H_0(\omega_i;\mathbf{Q})$$

ensemble mean-field Hamiltonian

$$\mathscr{H}_0(\boldsymbol{\omega};\mathbf{Q}) := \sum_{i=1}^{N} H_0(\omega_i;\mathbf{Q})$$

ensemble mean-field free energy

$$\mathscr{F}_0(\beta,\mathbf{Q}) := -\frac{1}{\beta}\ln \mathscr{Z}_0(\beta,\mathbf{Q})$$

$$\mathscr{Z}_0(\beta,\mathbf{Q}) := \int_{\Omega^N} \mathrm{e}^{-\beta\mathscr{H}_0(\boldsymbol{\omega};\mathbf{Q})} d\mu(\boldsymbol{\omega}) = Z_0(\beta,\mathbf{Q})^N$$

ensemble mean-field Hamiltonian

$$\mathscr{H}_0(\boldsymbol{\omega};\mathbf{Q}) := \sum_{i=1}^{N} H_0(\omega_i;\mathbf{Q})$$

ensemble mean-field free energy

$$\mathscr{F}_0(\beta,\mathbf{Q}) := -\frac{1}{\beta}\ln \mathscr{Z}_0(\beta,\mathbf{Q})$$

$$\mathscr{Z}_0(\beta,\mathbf{Q}) := \int_{\Omega^N} \mathrm{e}^{-\beta\mathscr{H}_0(\boldsymbol{\omega};\mathbf{Q})} d\mu(\boldsymbol{\omega}) = Z_0(\beta,\mathbf{Q})^N$$

$$\mathscr{F}_0(\beta,\mathbf{Q}) = NF_0(\beta,\mathbf{Q})$$

Minimum Principle

We apply the right side of Gibbs-Bogolubov inequality to

$$\mathscr{F}' = \mathscr{F}_0 \qquad \mathscr{H}' = \mathscr{H}_0 \qquad \rho' = \rho_0^N$$

$$\mathscr{F}(\beta) - N F_0(\beta, \mathbf{Q}) \leq \langle \mathscr{H} - \mathscr{H}_0 \rangle_{\rho_0^N}$$

Minimum Principle

We apply the right side of Gibbs-Bogolubov inequality to

$$\mathscr{F}' = \mathscr{F}_0 \qquad \mathscr{H}' = \mathscr{H}_0 \qquad \rho' = \rho_0^N$$

$$\mathscr{F}(\beta) - N F_0(\beta, \mathbf{Q}) \leq \langle \mathscr{H} - \mathscr{H}_0 \rangle_{\rho_0^N}$$

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) + \frac{1}{N} \langle \mathscr{H}_0 - \mathscr{H} \rangle_{\rho_0^N}$$

Minimum Principle

We apply the right side of Gibbs-Bogolubov inequality to

$$\mathscr{F}' = \mathscr{F}_0 \qquad \mathscr{H}' = \mathscr{H}_0 \qquad \rho' = \rho_0^N$$

$$\mathscr{F}(\beta) - N F_0(\beta, \mathbf{Q}) \leq \langle \mathscr{H} - \mathscr{H}_0 \rangle_{\rho_0^N}$$

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) + \frac{1}{N} \langle \mathscr{H}_0 - \mathscr{H} \rangle_{\rho_0^N}$$

$\mathscr{H}_0$ is regarded as an approximating ***trial*** Hamiltonian depending on the parameter $\mathbf{Q}$ to be chosen so as to make the corresponding free energy per particle $F_0(\beta, \mathbf{Q})$ as close as possible to the ***true*** free energy per particle $F(\beta)$.

inequality

Whenever H is ***bounded***, possibly upon an appropriate rescaling, it satisfies the inequality

$$\langle \mathscr{H}_0 - \mathscr{H} \rangle_{\rho_0^N} \geq 0$$

inequality

Whenever H is ***bounded***, possibly upon an appropriate rescaling, it satisfies the inequality

$$\langle \mathscr{H}_0 - \mathscr{H} \rangle_{\rho_0^N} \geq 0$$

Thus

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) + \frac{1}{N} \langle \mathscr{H}_0 - \mathscr{H} \rangle_{\rho_0^N} \geq F(\beta)$$

minimum principle

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) \quad \& \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

minimum principle

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) \quad \& \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

Among all ***critical*** points $\mathbf{Q}$ of $F_0(\beta, \cdot)$, the ***best*** approximation of $F(\beta)$ is the one that makes F_0 attains its ***minimum***.

minimum principle

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) \quad \& \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

Among all ***critical*** points $\mathbf{Q}$ of $F_0(\beta, \cdot)$, the ***best*** approximation of $F(\beta)$ is the one that makes F_0 attains its ***minimum***.

But there is ***no guarantee*** that the global minimum of F_0 exists.

minimum principle

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) \quad \& \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

Among all ***critical*** points $\mathbf{Q}$ of $F_0(\beta, \cdot)$, the ***best*** approximation of $F(\beta)$ is the one that makes F_0 attains its ***minimum***.

But there is ***no guarantee*** that the global minimum of F_0 exists.

Hessian form

$$\mathbb{H} := \frac{\partial^2 F_0}{\partial \mathbf{Q}^2} = \left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^2} \right\rangle_{\rho_0} - \beta \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \otimes \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} + \beta \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} \otimes \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0}$$

minimum principle

$$F_0(\beta, \mathbf{Q}) \geq F(\beta) \quad \& \quad \frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0}$$

Among all ***critical*** points $\mathbf{Q}$ of $F_0(\beta, \cdot)$, the ***best*** approximation of $F(\beta)$ is the one that makes F_0 attains its ***minimum***.

But there is ***no guarantee*** that the global minimum of F_0 exists.

Hessian form

$$\mathbb{H} := \frac{\partial^2 F_0}{\partial \mathbf{Q}^2} = \left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^2} \right\rangle_{\rho_0} - \beta \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \otimes \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} + \beta \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} \otimes \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0}$$

$$\frac{\partial F_0}{\partial \mathbf{Q}} = \mathbf{0} \quad \Rightarrow \quad \mathbb{H} := \frac{\partial^2 F_0}{\partial \mathbf{Q}^2} = \left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^2} \right\rangle_{\rho_0} - \beta \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \otimes \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0}$$

repulsive order tensors

$$\mathbf{Q} = (\mathbf{Q}^{-}, \mathbf{Q}^{+}) \in \mathscr{V}^{-} \times \mathscr{V}^{+}$$

$$\dim \mathscr{V}^{-} + \dim \mathscr{V}^{+} = m^{-} + m^{+}$$

repulsive order tensors

$$\mathbf{Q} = (\mathbf{Q}^-, \mathbf{Q}^+) \in \mathscr{V}^- \times \mathscr{V}^+$$

$$\dim \mathscr{V}^- + \dim \mathscr{V}^+ = m^- + m^+$$

$\mathscr{V}^-$ repulsive space

m^- repulsive dimension

repulsive order tensors

$$\mathbf{Q} = (\mathbf{Q}^-, \mathbf{Q}^+) \in \mathscr{V}^- \times \mathscr{V}^+$$

$$\dim \mathscr{V}^- + \dim \mathscr{V}^+ = m^- + m^+$$

$\mathscr{V}^-$ repulsive space

m^- repulsive dimension

$\mathbf{Q}^-$ is ***repulsive*** if

$$\left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^{-2}} \right\rangle_{\rho_0} < 0 \quad \text{whenever} \quad \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} = \mathbf{0}$$

repulsive order tensors

$$\mathbf{Q} = (\mathbf{Q}^-, \mathbf{Q}^+) \in \mathscr{V}^- \times \mathscr{V}^+$$

$\mathscr{V}^-$ repulsive space

$$\dim \mathscr{V}^- + \dim \mathscr{V}^+ = m^- + m^+$$

m^- repulsive dimension

$\mathbf{Q}^-$ is ***repulsive*** if

$$\left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^{-2}} \right\rangle_{\rho_0} < 0 \quad \text{whenever} \quad \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} = \mathbf{0}$$

$$\mathbf{Q}^- \text{ repulsive} \quad \Rightarrow \quad \frac{\partial^2 F_0}{\partial \mathbf{Q}^{-2}} < 0 \quad \text{at all critical points of } F_0$$

repulsive order tensors

$$\mathbf{Q} = (\mathbf{Q}^-, \mathbf{Q}^+) \in \mathscr{V}^- \times \mathscr{V}^+$$

$$\dim \mathscr{V}^- + \dim \mathscr{V}^+ = m^- + m^+$$

$\mathscr{V}^-$ repulsive space

m^- repulsive dimension

$\mathbf{Q}^-$ is ***repulsive*** if

$$\left\langle \frac{\partial^2 H_0}{\partial \mathbf{Q}^{-2}} \right\rangle_{\rho_0} < 0 \quad \text{whenever} \quad \left\langle \frac{\partial H_0}{\partial \mathbf{Q}} \right\rangle_{\rho_0} = \mathbf{0}$$

$$\mathbf{Q}^- \text{ repulsive} \quad \Rightarrow \quad \frac{\partial^2 F_0}{\partial \mathbf{Q}^{-2}} < 0 \quad \text{at all critical points of } F_0$$

repulsive molecular tensors

Repulsive ***order*** tensors $\mathbf{Q}^-$ stem from repulsive ***molecular*** tensors $\mathbf{q}^-$. These are the components of $\mathbf{q}$ (or linear combinations of them) that would minimize $\widehat{H}$ when they are ***not*** the same in both interacting molecules.

Mountain Pass Lemma

If $\frac{\partial^2 F_0}{\partial \mathbf{Q}^{-2}} < 0$ at all critical points of $F_0(\beta, \mathbf{Q}^+, \cdot)$ and $F_0(\beta, \mathbf{Q}^+, \cdot)$ is ***negatively coercive***

$$F_0(\beta, \mathbf{Q}^+, \mathbf{Q}^-) \to -\infty \quad \text{as} \quad |\mathbf{Q}^-| \to +\infty$$

then, for every $(\beta, \mathbf{Q}^+)$, there is a ***unique*** critical point of $F_0(\beta, \mathbf{Q}^+, \cdot)$, which is necessarily a ***maximum***. COURANT (1950)

Mountain Pass Lemma

If $\frac{\partial^2 F_0}{\partial \mathbf{Q}^{-2}} < 0$ at all critical points of $F_0(\beta, \mathbf{Q}^+, \cdot)$ and $F_0(\beta, \mathbf{Q}^+, \cdot)$ is ***negatively coercive***

$$F_0(\beta, \mathbf{Q}^+, \mathbf{Q}^-) \to -\infty \quad \text{as} \quad |\mathbf{Q}^-| \to +\infty$$

then, for every $(\beta, \mathbf{Q}^+)$, there is a ***unique*** critical point of $F_0(\beta, \mathbf{Q}^+, \cdot)$, which is necessarily a ***maximum***. COURANT (1950)

minimax principle

The Mountain Pass Lemma ensures that the equation

$$\frac{\partial F_0}{\partial \mathbf{Q}^-}(\beta, \mathbf{Q}^+, \mathbf{Q}^-) = \mathbf{0}$$

has a ***unique solution*** in $\mathbf{Q}^-$

$$\mathbf{Q}^- = G(\beta, \mathbf{Q}^+)$$

The minimum principle then reduces to minimizing in $\mathbf{Q}^+$ the function

$$f_0(\beta, \mathbf{Q}^+) := F_0(\beta, \mathbf{Q}^+, G(\beta, \mathbf{Q}^+))$$

The global minimizer of f_0 is the ***least saddle*** of F_0.

Bogolubov Jr. (1972)

The minimum principle then reduces to minimizing in $\mathbf{Q}^+$ the function

$$f_0(\beta, \mathbf{Q}^+) := F_0(\beta, \mathbf{Q}^+, G(\beta, \mathbf{Q}^+))$$

The global minimizer of f_0 is the ***least saddle*** of F_0.

Bogolubov Jr. (1972)

minimality criterion

- The minimality criterion for f_0 eventually reduces to $\mathbb{H}$ having precisely m^- negative eigenvalues and m^+ positive eigenvalues.

The minimum principle then reduces to minimizing in $\mathbf{Q}^+$ the function

$$f_0(\beta, \mathbf{Q}^+) := F_0(\beta, \mathbf{Q}^+, G(\beta, \mathbf{Q}^+))$$

The global minimizer of f_0 is the ***least saddle*** of F_0.

Bogolubov Jr. (1972)

minimality criterion

- The minimality criterion for f_0 eventually reduces to $\mathbb{H}$ having precisely m^- negative eigenvalues and m^+ positive eigenvalues.

- This conclusion remains true even when $(\mathbf{Q}^-, \mathbf{Q}^+)$ are subject to any non-singular linear transformations. In this sense it is intrinsic, that is, independent of the choice of $\mathbf{Q}$.

Example: Biaxial Nematics

Rigid molecules enjoying the D_{2h}-symmetry interact through the Hamiltonian first introduced by Straley.

$$\widehat{H} = -U_0 \left\{ \mathbf{q} \cdot \mathbf{q}' + \gamma(\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}' \right\}$$

Example: Biaxial Nematics

Rigid molecules enjoying the D_{2h}-symmetry interact through the Hamiltonian first introduced by Straley.

$$\widehat{H} = -U_0 \left\{ \mathbf{q} \cdot \mathbf{q}' + \gamma(\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}' \right\}$$

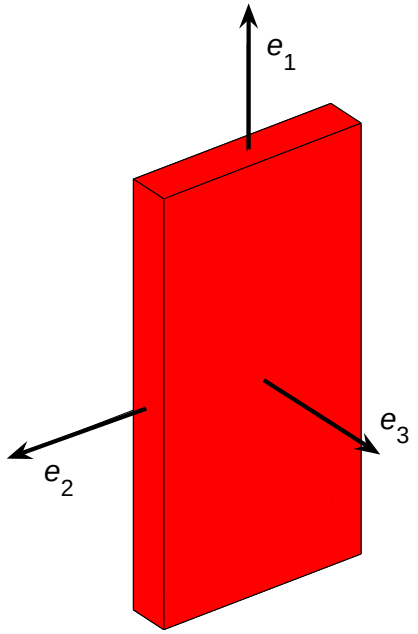
$$\mathbf{q} = \boldsymbol{e}_1 \otimes \boldsymbol{e}_1 - \tfrac{1}{3}\mathbf{I}$$
$$\mathbf{b} = \boldsymbol{e}_2 \otimes \boldsymbol{e}_2 - \boldsymbol{e}_3 \otimes \boldsymbol{e}_3$$

Example: Biaxial Nematics

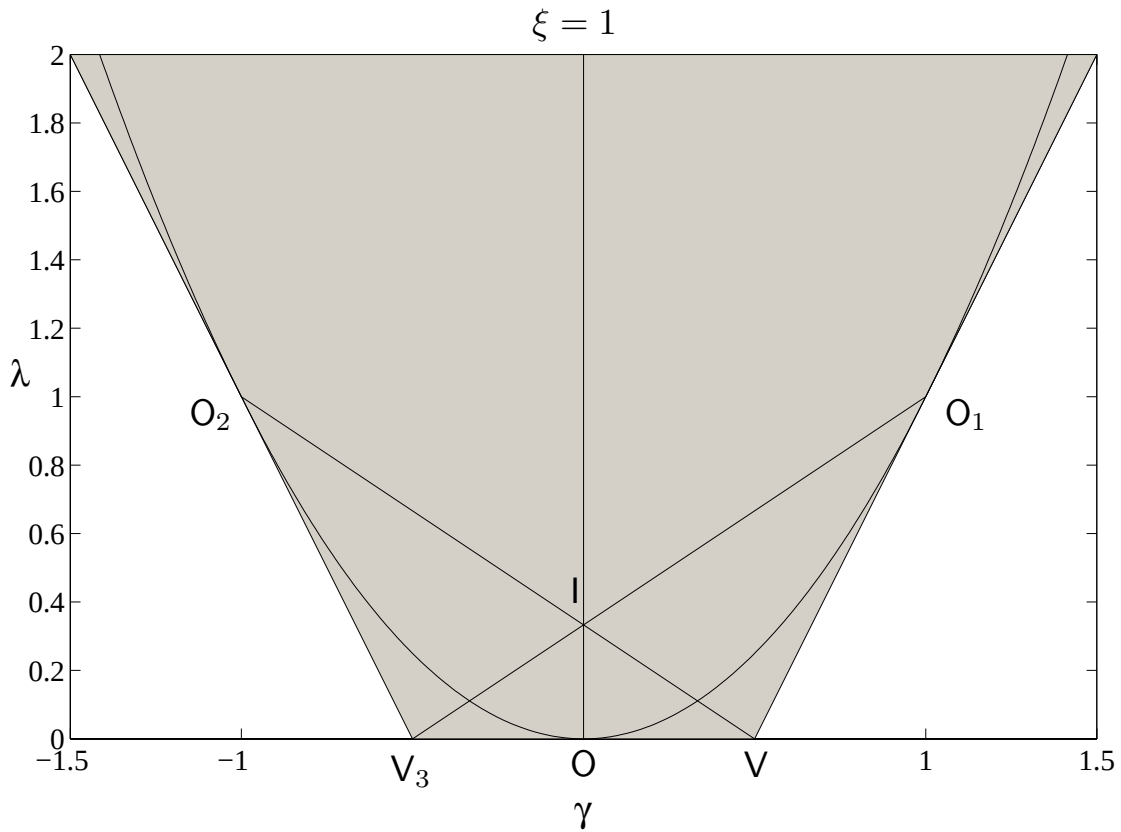
Rigid molecules enjoying the D_{2h}-symmetry interact through the Hamiltonian first introduced by Straley.

$$\widehat{H} = -U_0 \left\{ \mathbf{q} \cdot \mathbf{q}' + \gamma(\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}' \right\}$$

$$\mathbf{q} = \boldsymbol{e}_1 \otimes \boldsymbol{e}_1 - \tfrac{1}{3}\mathbf{I}$$
$$\mathbf{b} = \boldsymbol{e}_2 \otimes \boldsymbol{e}_2 - \boldsymbol{e}_3 \otimes \boldsymbol{e}_3$$



parameter space



Bisi, De Matteis, Durand, Gartland, Sonnet & Virga (2006)

order tensors

$$\mathbf{Q} := \langle \mathbf{q} \rangle = S \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

$$\mathbf{B} := \langle \mathbf{b} \rangle = S' \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P'}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

order tensors

$$\mathbf{Q} := \langle \mathbf{q} \rangle = S \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

$$\mathbf{B} := \langle \mathbf{b} \rangle = S' \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P'}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

$S,\ S'$ uniaxial order parameters

$P,\ P'$ biaxial order parameters

order tensors

$$\mathbf{Q} := \langle \mathbf{q} \rangle = S \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

$$\mathbf{B} := \langle \mathbf{b} \rangle = S' \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P'}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

$S,\ S'$ uniaxial order parameters

$P,\ P'$ biaxial order parameters

modal decomposition

In this case $\mathbf{q} = (\mathbf{q}, \mathbf{b})$. To identify the repulsive components of $\mathbf{q}$, we decompose $\widehat{H}$

$$\widehat{H} = \alpha^{+} \mathbf{q}^{+} \cdot \mathbf{q}^{+\prime} + \alpha^{-} \mathbf{q}^{-} \cdot \mathbf{q}^{-\prime}$$

repulsive variables

All the interactions represented by points below the parabola $\lambda = \gamma^2$ are ***partly repulsive***

$$\widehat{H} = \alpha^{+}\mathbf{q}^{+} \cdot \mathbf{q}^{+\prime} + \alpha^{-}\mathbf{q}^{-} \cdot \mathbf{q}^{-\prime}$$

repulsive variables

All the interactions represented by points below the parabola $\lambda = \gamma^2$ are ***partly repulsive***

$$\widehat{H} = \alpha^+ \mathbf{q}^+ \cdot \mathbf{q}^{+\prime} + \alpha^- \mathbf{q}^- \cdot \mathbf{q}^{-\prime}$$

$$\mathbf{q}^\pm = \mathbf{q} + \gamma^\pm \mathbf{b}$$

$$\gamma^\pm = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

$$\alpha^+ = U_0 \frac{\gamma - \gamma^-}{\gamma^- - \gamma^+} \qquad \alpha^- = U_0 \frac{\gamma^+ - \gamma}{\gamma^- - \gamma^+}$$

repulsive variables

All the interactions represented by points below the parabola $\lambda = \gamma^2$ are ***partly repulsive***

$$\widehat{H} = \alpha^+ \mathbf{q}^+ \cdot \mathbf{q}^{+\prime} + \alpha^- \mathbf{q}^- \cdot \mathbf{q}^{-\prime}$$

$$\mathbf{q}^\pm = \mathbf{q} + \gamma^\pm \mathbf{b}$$

$$\gamma^\pm = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

$$\alpha^+ = U_0 \frac{\gamma - \gamma^-}{\gamma^- - \gamma^+} \qquad \alpha^- = U_0 \frac{\gamma^+ - \gamma}{\gamma^- - \gamma^+}$$

$$\lambda < \gamma^2 \quad \Rightarrow \quad \alpha^+ \alpha^- < 0$$

repulsive variables

All the interactions represented by points below the parabola $\lambda = \gamma^2$ are ***partly repulsive***

$$\widehat{H} = \alpha^+ \mathbf{q}^+ \cdot \mathbf{q}^{+\prime} + \alpha^- \mathbf{q}^- \cdot \mathbf{q}^{-\prime}$$

$$\mathbf{q}^\pm = \mathbf{q} + \gamma^\pm \mathbf{b}$$

$$\gamma^\pm = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

$$\alpha^+ = U_0 \frac{\gamma - \gamma^-}{\gamma^- - \gamma^+} \qquad \alpha^- = U_0 \frac{\gamma^+ - \gamma}{\gamma^- - \gamma^+}$$

$$\lambda < \gamma^2 \quad \Rightarrow \quad \alpha^+ \alpha^- < 0$$

$$\mathbf{Q}^- := \langle \mathbf{q}^- \rangle \qquad \frac{\partial^2 H_0}{\partial \mathbf{Q}^{-2}} < 0$$

repulsive dimension

$$\mathbf{Q}^- := S^- \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P^-}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

(S^-, P^-) are linear combinations of (S, P, S', P') depending on the interaction parameters (γ, λ).

repulsive dimension

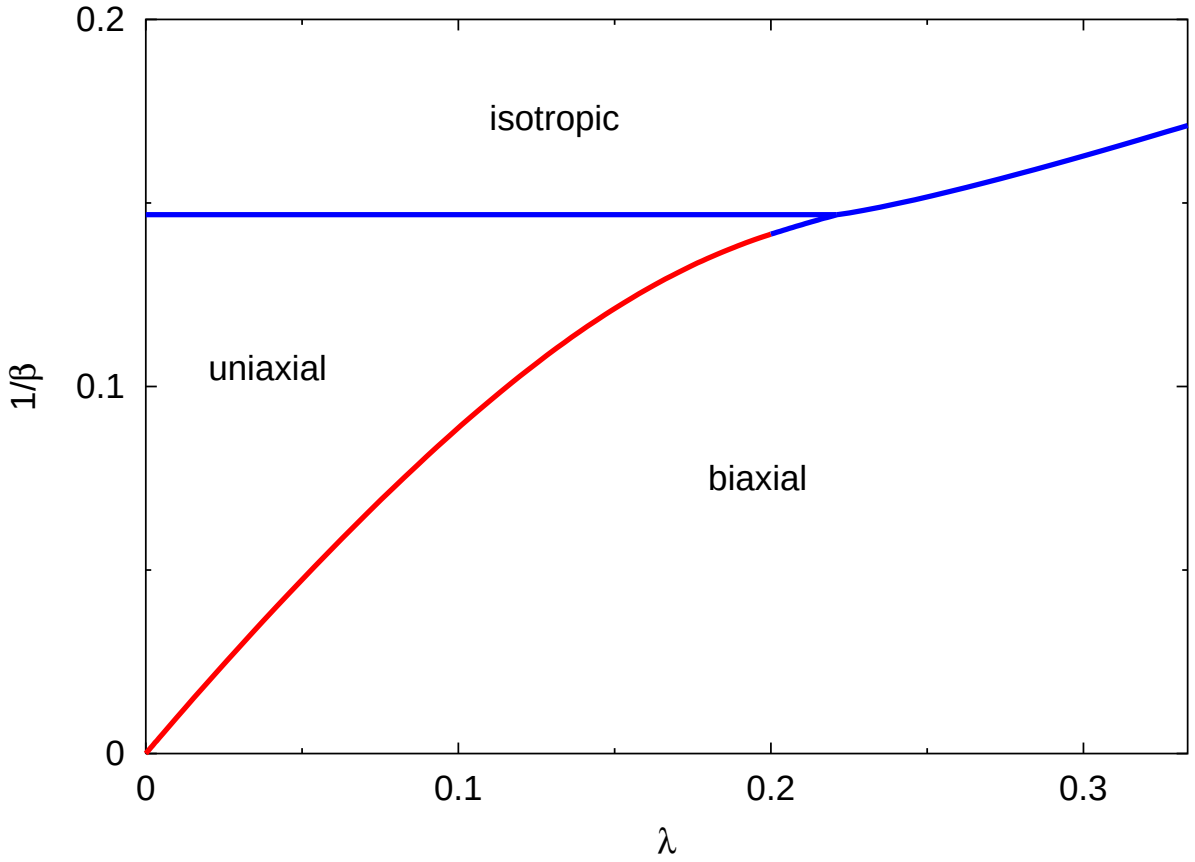
$$\mathbf{Q}^- := S^- \left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I} \right) + \frac{P^-}{3} \left(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y \right)$$

(S^-, P^-) are linear combinations of (S, P, S', P') depending on the interaction parameters (γ, λ).

$$m^- = \begin{cases} 2 & \text{if } \lambda < \gamma^2 \\ 0 & \text{if } \lambda \geq \gamma^2 \end{cases}$$

universal phase diagram

The mean-field theory predicts that the phase diagram obtained for $\gamma = 0$ and $0 \leq \lambda \leq \frac{1}{3}$ is indeed ***universal***.



$\frac{1}{\beta} := \frac{U_0}{k_B T}$

Durand, Sonnet & Virga (2003)

One-Particle Probability Function

An alternative way to take ***averages*** is to assume that all particles obey the ***same*** probability law

$$\rho(\omega_1, \ldots, \omega_N) = \prod_{i=1}^{N} \varrho(\omega_i)$$

One-Particle Probability Function

An alternative way to take ***averages*** is to assume that all particles obey the ***same*** probability law

$$\rho(\omega_1, \ldots, \omega_N) = \prod_{i=1}^{N} \varrho(\omega_i)$$

$$\int_\Omega \varrho(\omega) d\mu(\omega) = 1 \qquad \Rightarrow \qquad \int_{\Omega^N} \rho(\boldsymbol{\omega}) d\mu(\boldsymbol{\omega}) = 1$$

One-Particle Probability Function

An alternative way to take ***averages*** is to assume that all particles obey the ***same*** probability law

$$\rho(\omega_1, \ldots, \omega_N) = \prod_{i=1}^{N} \varrho(\omega_i)$$

$$\int_\Omega \varrho(\omega) d\mu(\omega) = 1 \qquad \Rightarrow \qquad \int_{\Omega^N} \rho(\boldsymbol{\omega}) d\mu(\boldsymbol{\omega}) = 1$$

ensemble free-energy functional

$$\mathscr{F}[\rho; \beta] := \int_{\Omega^N} \mathscr{H}(\boldsymbol{\omega}) \rho(\boldsymbol{\omega}) d\mu(\boldsymbol{\omega}) + \frac{1}{\beta} \int_{\Omega^N} \rho(\boldsymbol{\omega}) \ln \rho(\boldsymbol{\omega}) d\mu(\boldsymbol{\omega})$$

$\beta = \frac{1}{k_B T}$ Boltzmann factor

$$\mathscr{F}[\rho;\beta] = n\int_{\Omega\times\Omega} H(\omega,\omega')\varrho(\omega)\varrho(\omega')d\mu(\omega)d\mu(\omega') + \frac{N}{\beta}\int_{\Omega}\varrho(\omega)\ln\varrho(\omega)d\mu(\omega)$$

n cardinality of $\mathscr{I}$

$\mathscr{I}$ interaction set

$$\mathscr{F}[\rho;\beta] = n\int_{\Omega\times\Omega} H(\omega,\omega')\varrho(\omega)\varrho(\omega')d\mu(\omega)d\mu(\omega') + \frac{N}{\beta}\int_{\Omega}\varrho(\omega)\ln\varrho(\omega)d\mu(\omega)$$

n cardinality of $\mathscr{I}$

$\mathscr{I}$ interaction set

free energy per particle

$$F[\varrho;\beta] := \frac{1}{N}\mathscr{F}[\varrho;\beta] = \frac{1}{2}\int_{\Omega\times\Omega} H(\omega,\omega')\varrho(\omega)\varrho(\omega')d\mu(\omega)d\mu(\omega) + \frac{1}{\beta}\int_{\Omega}\varrho(\omega)\ln\varrho(\omega)d\mu(\omega)$$

$$\mathscr{F}[\rho;\beta] = n\int_{\Omega\times\Omega} H(\omega,\omega')\varrho(\omega)\varrho(\omega')d\mu(\omega)d\mu(\omega') + \frac{N}{\beta}\int_{\Omega}\varrho(\omega)\ln\varrho(\omega)d\mu(\omega)$$

n cardinality of $\mathscr{I}$

$\mathscr{I}$ interaction set

free energy per particle

$$F[\varrho;\beta] := \frac{1}{N}\mathscr{F}[\varrho;\beta] = \frac{1}{2}\int_{\Omega\times\Omega} \mathfrak{z} H(\omega,\omega')\varrho(\omega)\varrho(\omega')d\mu(\omega)d\mu(\omega) + \frac{1}{\beta}\int_{\Omega}\varrho(\omega)\ln\varrho(\omega)d\mu(\omega)$$

$\mathfrak{z} := \frac{2n}{N}$ coordination parameter

$1 \le \mathfrak{z} \le N-1$

example: Maier-Saupe Hamiltonian

Of all quadrupolar bilinear interactions, the simplest is Maier and Saupe's

$$H(\omega, \omega') = -U_0 \mathbf{q}(\omega) \cdot \mathbf{q}(\omega') = \widehat{H}(\mathbf{q}, \mathbf{q}')$$

example: Maier-Saupe Hamiltonian

Of all quadrupolar bilinear interactions, the simplest is Maier and Saupe's

$$H(\omega, \omega') = -U_0 \mathbf{q}(\omega) \cdot \mathbf{q}(\omega') = \widehat{H}(\mathbf{q}, \mathbf{q}')$$

Maier-Saupe Hamiltonian has (repeatedly) been treated within this formalism. Katriel, Kventsel, Luckhurst & Sluckin (1986)
(Fatkullin & Slastikov 2005)
Ball & Majumdar (2010)

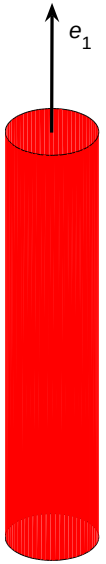
example: Maier-Saupe Hamiltonian

Of all quadrupolar bilinear interactions, the simplest is Maier and Saupe's

$$H(\omega, \omega') = -U_0 \mathbf{q}(\omega) \cdot \mathbf{q}(\omega') = \widehat{H}(\mathbf{q}, \mathbf{q}')$$

Maier-Saupe Hamiltonian has (repeatedly) been treated within this formalism. Katriel, Kventsel, Luckhurst & Sluckin (1986)
(Fatkullin & Slastikov 2005)
Ball & Majumdar (2010)

$$\mathbf{q}(\omega) = \boldsymbol{e}_1(\omega) \otimes \boldsymbol{e}_1(\omega) - \tfrac{1}{3}\mathbf{I}$$
$$\omega \in \Omega = \mathbb{S}^2$$



minimizing F

The Euler-Lagrange equation for F translates into a ***fixed-point*** problem for ϱ

$$\varrho(\omega) = \frac{1}{Z} \mathrm{e}^{-\beta H_\varrho(\omega)}$$

$$Z := \int_\Omega \mathrm{e}^{-\beta H_\varrho(\omega)} d\mu(\omega) \qquad H_\varrho(\omega) := \int_\Omega \mathfrak{z} H(\omega, \omega') \varrho(\omega') d\mu(\omega')$$

Z partition function

H_ϱ average Hamiltonian

minimizing F

The Euler-Lagrange equation for F translates into a ***fixed-point*** problem for ϱ

$$\varrho(\omega) = \frac{1}{Z} \mathrm{e}^{-\beta H_\varrho(\omega)}$$

$$Z := \int_\Omega \mathrm{e}^{-\beta H_\varrho(\omega)} d\mu(\omega) \qquad H_\varrho(\omega) := \int_\Omega \mathfrak{z} H(\omega, \omega') \varrho(\omega') d\mu(\omega')$$

Z partition function

H_ϱ average Hamiltonian

parameterizing H_ϱ

$$H(\omega, \omega') = -U_0 \mathbf{q}(\omega) \cdot \mathbf{q}(\omega')$$
$$H_\varrho(\omega) = -\mathfrak{z} U_0 \mathbf{q}(\omega) \cdot \mathbf{Q}$$

minimizing F

The Euler-Lagrange equation for F translates into a ***fixed-point*** problem for ϱ

$$\varrho(\omega) = \frac{1}{Z} \mathrm{e}^{-\beta H_\varrho(\omega)}$$

$$Z := \int_\Omega \mathrm{e}^{-\beta H_\varrho(\omega)} d\mu(\omega) \qquad H_\varrho(\omega) := \int_\Omega \mathfrak{z} H(\omega, \omega') \varrho(\omega') d\mu(\omega')$$

Z partition function

H_ϱ average Hamiltonian

parameterizing H_ϱ

order tensor

$$H(\omega, \omega') = -U_0 \mathbf{q}(\omega) \cdot \mathbf{q}(\omega')$$

$$H_\varrho(\omega) = -\mathfrak{z} U_0 \mathbf{q}(\omega) \cdot \mathbf{Q} \qquad \mathbf{Q} := \langle \mathbf{q} \rangle_\varrho = \int_\Omega \mathbf{q}(\omega) \varrho(\omega) d\mu(\omega)$$

self-consistency

The fixed-point equation for H_ϱ reduces to a fixed-point equation for $\mathbf{Q}$

$$\varrho_{\mathbf{Q}}(\omega) = \frac{\mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega) \cdot \mathbf{Q}}}{\int_\Omega \mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega) \cdot \mathbf{Q}} d\mu(\omega)}$$

self-consistency

The fixed-point equation for H_ϱ reduces to a fixed-point equation for $\mathbf{Q}$

$$\varrho_{\mathbf{Q}}(\omega) = \frac{\mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega)\cdot\mathbf{Q}}}{\int_\Omega \mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega)\cdot\mathbf{Q}} d\mu(\omega)}$$

$$\mathbf{Q} = \int_\Omega \mathbf{q}(\omega)\varrho_{\mathbf{Q}}(\omega) d\mu(\omega)$$

self-consistency

The fixed-point equation for H_ϱ reduces to a fixed-point equation for $\mathbf{Q}$

$$\varrho_{\mathbf{Q}}(\omega) = \frac{\mathrm{e}^{U_0 \jmath \beta \mathbf{q}(\omega)\cdot\mathbf{Q}}}{\int_\Omega \mathrm{e}^{U_0 \jmath \beta \mathbf{q}(\omega)\cdot\mathbf{Q}} d\mu(\omega)}$$

$$\mathbf{Q} = \int_\Omega \mathbf{q}(\omega)\varrho_{\mathbf{Q}}(\omega) d\mu(\omega)$$

H_ϱ formalism

- One can easily generalize to all bilinear Hamiltonians $\widehat{H}(\mathbf{q}, \mathbf{q}')$ the Maier-Saupe parametrization of H_ϱ.

self-consistency

The fixed-point equation for H_ϱ reduces to a fixed-point equation for $\mathbf{Q}$

$$\varrho_{\mathbf{Q}}(\omega) = \frac{\mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega)\cdot\mathbf{Q}}}{\int_\Omega \mathrm{e}^{U_0 \mathfrak{z} \beta \mathbf{q}(\omega)\cdot\mathbf{Q}} d\mu(\omega)}$$

$$\mathbf{Q} = \int_\Omega \mathbf{q}(\omega)\varrho_{\mathbf{Q}}(\omega) d\mu(\omega)$$

H_ϱ *formalism*

- One can easily generalize to all bilinear Hamiltonians $\widehat{H}(\mathbf{q}, \mathbf{q}')$ the Maier-Saupe parametrization of H_ϱ.
- The general formalism based on the average Hamiltonian H_ϱ is in principle also applicable to ***non-bilinear*** interaction Hamiltonmians H.

- For bilinear Hamiltonians, it has the advantage of being applicable to ***non-attractive*** Hamiltonians, that is, to Hamiltonians that do not attain their ground state when all molecules are in the one and the same state, such as the ones for dipolar interactions.

Piastra & Virga (2012)
Gartland & Virga (2013)

- For bilinear Hamiltonians, it has the advantage of being applicable to ***non-attractive*** Hamiltonians, that is, to Hamiltonians that do not attain their ground state when all molecules are in the one and the same state, such as the ones for dipolar interactions.

Piastra & Virga (2012)
Gartland & Virga (2013)

perspectives

Apply the ***fixed-point theory*** to predict phase transitions: ***phases*** then become analogs of ***defects***.

- For bilinear Hamiltonians, it has the advantage of being applicable to ***non-attractive*** Hamiltonians, that is, to Hamiltonians that do not attain their ground state when all molecules are in the one and the same state, such as the ones for dipolar interactions.

Piastra & Virga (2012)
Gartland & Virga (2013)

perspectives

Apply the ***fixed-point theory*** to predict phase transitions: ***phases*** then become analogs of ***defects***.
Phase transitions could be envisioned as defect ***nucleations*** or ***annihilations***.

- For bilinear Hamiltonians, it has the advantage of being applicable to ***non-attractive*** Hamiltonians, that is, to Hamiltonians that do not attain their ground state when all molecules are in the one and the same state, such as the ones for dipolar interactions.

Piastra & Virga (2012)
Gartland & Virga (2013)

perspectives

Apply the ***fixed-point theory*** to predict phase transitions: ***phases*** then become analogs of ***defects***.
Phase transitions could be envisioned as defect ***nucleations*** or ***annihilations***.
The theory of ***topological degree*** would assign a ***charge*** to each ***phase***, which must ***conserved*** in the transitions.

Acknowledgements

Discussion

G.E. Durand

E.C. Gartland, Jr.

M. Osipov

A.M. Sonnet

C. Zannoni

Acknowledgements

Discussion

G.E. Durand

E.C. Gartland, Jr.

M. Osipov

A.M. Sonnet

C. Zannoni

Financial Support

Italian MIUR through grant PRIN 2009N5JH4F

Isaac Newton Institute through the Programme on ***The Mathematics of Liquid Crystals***

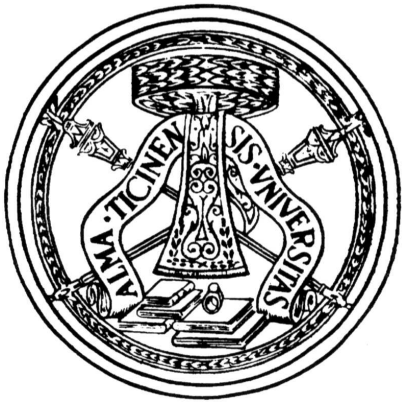
Acknowledgements

Discussion

G.E. Durand
E.C. Gartland, Jr.
M. Osipov
A.M. Sonnet
C. Zannoni

Financial Support

Italian MIUR through grant
PRIN 2009N5JH4F
Isaac Newton Institute through
the Programme on
The Mathematics of Liquid Crystals



Soft Matter Mathematical Modelling
Department of Mathematics
University of Pavia, Italy

http://smmm.unipv.it