Phase behavior of a diluted model for biaxial nematics

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April 6, 2022

CNPq

Phase behavior of a lattice-gas model for biaxial nematics

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(Dated: April 1, 2022)

Abstract

We employ a lattice-gas extension of the Maier–Saupe model with discrete orientation states to study the phase behavior of a statistical model for biaxial nematogenic units in mean-field theory. The phase behavior of the system is investigated in terms of the strength of isotropic interaction between anisotropic objects, as well as the degree of biaxiality and the concentration of those units. We obtain phase diagrams with isotropic phases and stable biaxial and uniaxial nematic structures, various phase coexistences, many types of critical and multicritical behaviors, such as ordinary vapor-liquid critical points, critical end points and tricritical points, and distinct Landau-like multicritical points. Our results widen the possibilities of relating the phenomenological coefficients of the Landau–de Gennes expansion to microscopic parameters, allowing an improved interpretation of theoretical fittings to experimental data.

Molecular idealization (like-bricks)

- Orientation of a nematogen

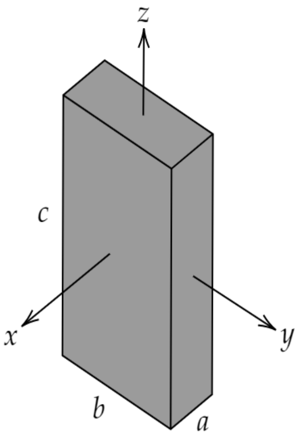
$$\mathbf{\Lambda} = \mathbf{I} - \frac{\mathrm{Tr}\{\mathbf{I}\}}{3}\mathbf{1} = \lambda \boldsymbol{\omega}_1,$$

where

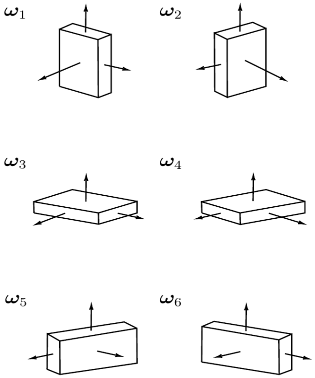
$$\boldsymbol{\omega}_1 = \frac{1}{2}\begin{pmatrix} -1-\Delta & 0 & 0 \\ 0 & -1+\Delta & 0 \\ 0 & 0 & 2 \end{pmatrix},$$

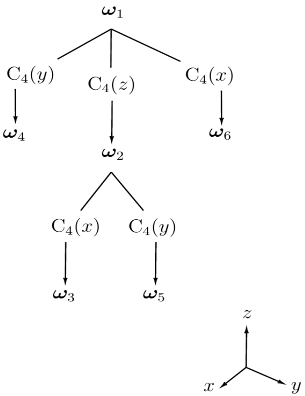
and

$$\Delta = \frac{b^2 - a^2}{a^2 + b^2 - 2c^2}.$$



Zwanzig approximation





The LGMSZ model

Hamiltonian

$$\mathcal{H} = -A \sum_{(i,j)} \gamma_i \mathbf{\Omega}_i : \gamma_j \mathbf{\Omega}_j + U \sum_{(i,j)} \gamma_i \gamma_j \quad \text{com} \quad A > 0,$$

Thermodynamic behavior of the system

$$\mathcal{Z} = \sum_{\{\mathbf{\Omega}_i\}} \sum_{\{\gamma_i\}} \exp\left(\beta A \sum_{(i,j)} \gamma_i \mathbf{\Omega}_i : \gamma_j \mathbf{\Omega}_j - U \sum_{(i,j)} \gamma_i \gamma_j \right).$$

(i) $\{\mathbf{\Omega}_i\} \longrightarrow$ Orientational degree of freedom.

(ii) $\{\gamma_i\} \longrightarrow$ Occupation degree of freedom.

Annealed case

System with N sites and N_m nematogens such that $(N \leq N_m)$

$$\mathcal{Z}_A = \sum_{\{\boldsymbol{\Omega}_i\}} \sum_{\{\gamma_i\}}{}' \exp\left(\beta A \sum_{(i,j)} \gamma_i \boldsymbol{\Omega}_i : \gamma_j \boldsymbol{\Omega}_j - U \sum_{(i,j)} \gamma_i \gamma_j\right).$$

where

$$\frac{1}{N}\sum_{i=1}^{N} \gamma_i = \frac{N_m}{N} = \phi \longrightarrow \text{concentration.}$$

Grand canonical ensemble

$$\Xi_A = \sum_{\{\boldsymbol{\Omega}_i\}} \sum_{\{\gamma_i\}} \exp\left(\beta A \sum_{(i,j)} \gamma_i \boldsymbol{\Omega}_i : \gamma_j \boldsymbol{\Omega}_j - U \sum_{(i,j)} \gamma_i \gamma_j + \beta\mu \sum_{i=1}^{N} \gamma_i\right).$$

MEAN-FIELD SOLUTION

Integral representation of Ξ_A

$$\Xi_A \propto \int_{\mathbb{R}^4} \exp\left[-N\beta\Psi(\boldsymbol{Q}, \phi; \{\boldsymbol{\alpha}_i\}) \right] d[\boldsymbol{Q}]\, d\phi.$$

where $\{\boldsymbol{\alpha}_i\} := \{\beta, \Delta, \mu\}$ and

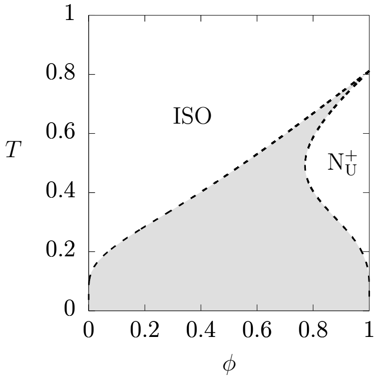
$$\boldsymbol{Q} = \langle \boldsymbol{\Omega}_i \rangle = \frac{1}{2} \begin{pmatrix} -S-\eta & 0 & 0 \\ 0 & -S+\eta & 0 \\ 0 & 0 & 2S \end{pmatrix}$$

(i) $S = \eta = 0 \longrightarrow$ isotropic phase (ISO),

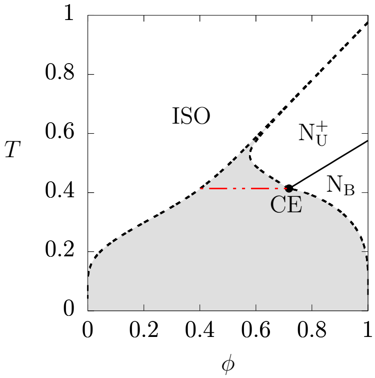
(ii) $S \neq 0$ e $\eta = 0$ (or $\eta = \pm 3S$) $\longrightarrow$ uniaxial nematic phase ($N_U^{\pm}$),

(iii) $\eta \neq 0 \longrightarrow$ biaxial nematic phase (N_B).

Intrinsically biaxial nematogens ($U = 0$)

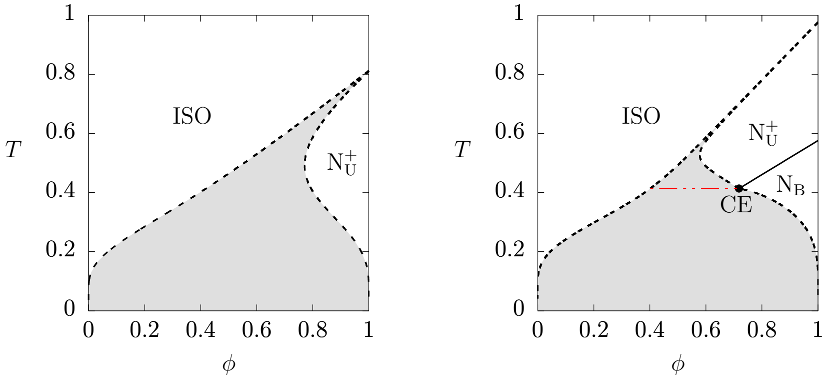


(a) $\Delta = 0$



(b) $\Delta = 19/20$

INTRINSICALLY BIAXIAL NEMATOGENS ($U = 0$)



(a) $\Delta = 0$ (b) $\Delta = 19/20$

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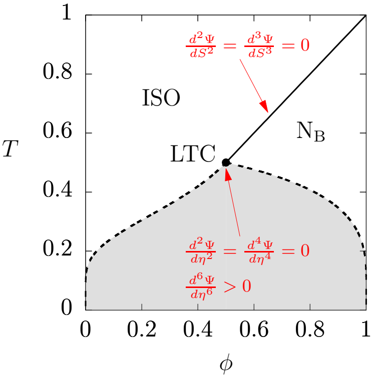
- M. A. Bates, Physical Review E **64**, 051702 (2001).

Intrinsically biaxial nematogens ($U = 0$)

- Landau Point
  - $\Delta = 1.$
  - $(\beta A - 1)e^{\beta\mu} - 1 = 0.$
  - $\beta A = 1/\phi.$

- Landau Tricritical Point
  - $(\phi, \beta, \mu, \Delta) = (\frac{1}{2}, \frac{2}{A}, 0, 1)$



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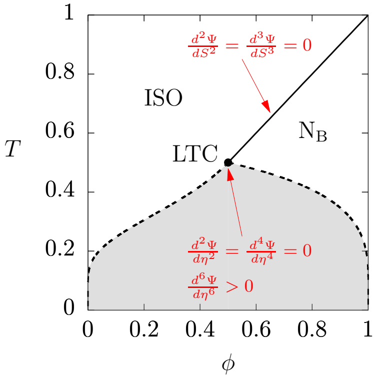
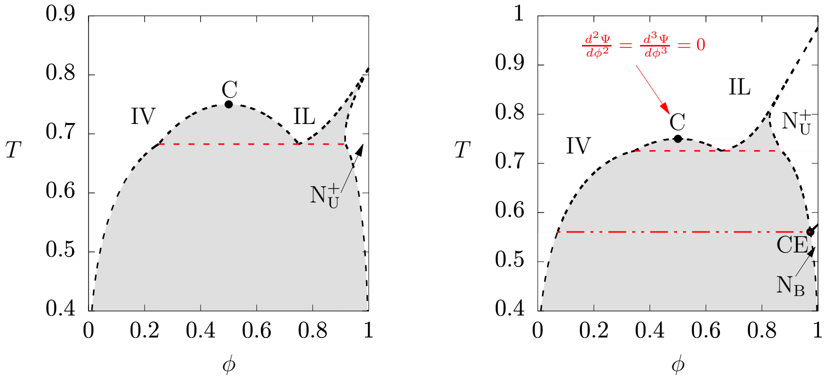


- D. D. Rodrigues, A. P. Vieira, and S. R. Salinas, Crystals **10**, 632 (2020).

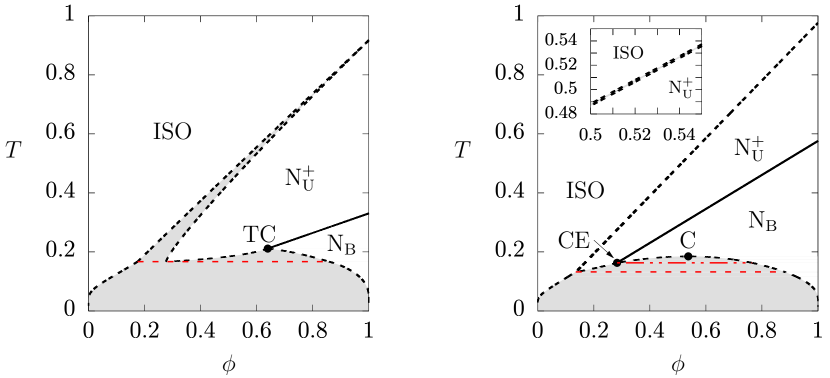
Intrinsically biaxial nematogens



(a) $\Delta = 0 \quad U = -3$

(b) $\Delta = 19/20 \quad U = -3$

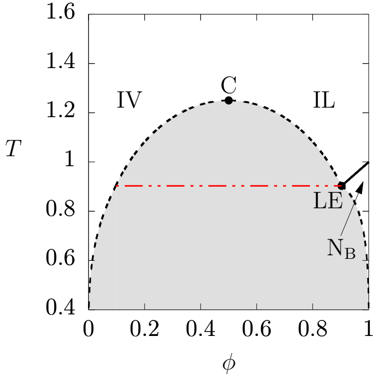
Intrinsically biaxial nematogens



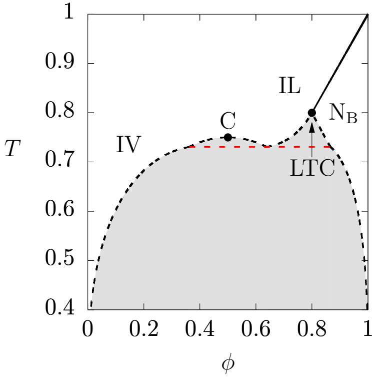
(a) $\Delta = 4/5 \quad U = 1$

(b) $\Delta = 19/20 \quad U = 13/10$

Maximum degree of biaxiality ($\Delta = 1$)

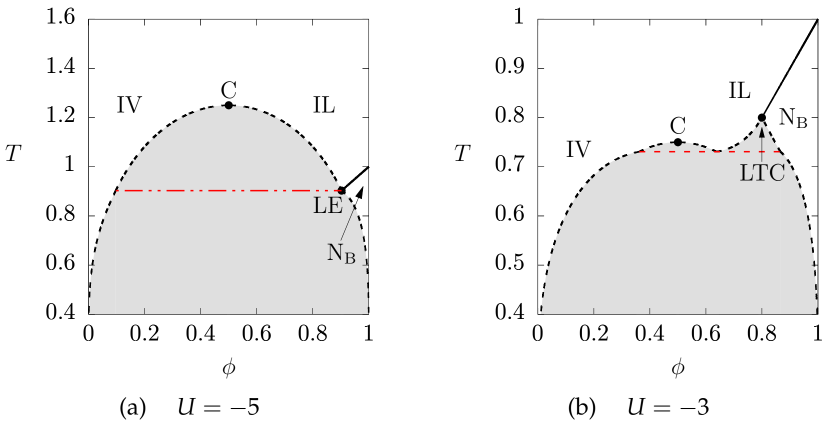


(a) $U = -5$



(b) $U = -3$

MAXIMUM DEGREE OF BIAXIALITY ($\Delta = 1$)



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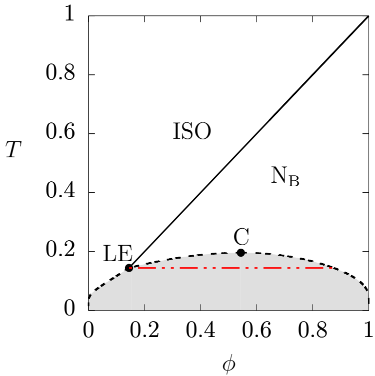
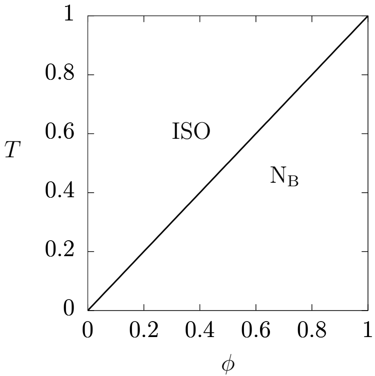
Maximum degree of biaxiality ($\Delta = 1$)

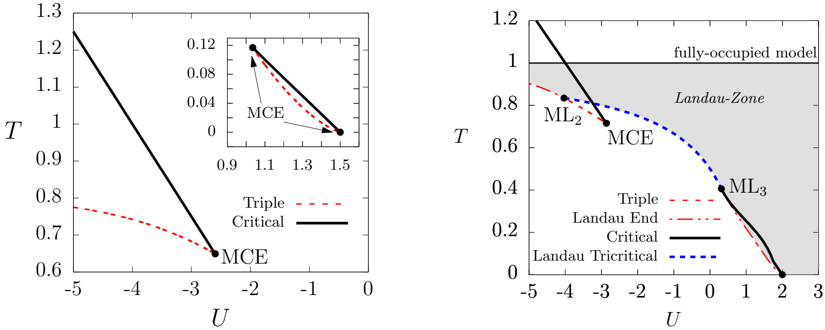


(a) $U = 13/10$



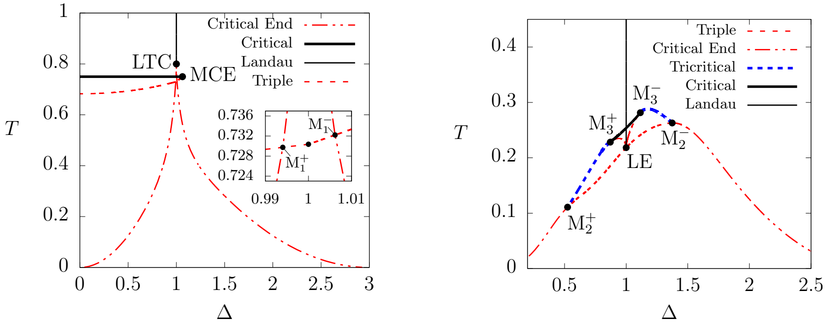
(b) $U > 2A$

Multicritical lines (Isotropic Interaction)



(a) $\Delta = 0$ (b) $\Delta = 1$

Multicritical lines (Degree of Biaxiality)



(a) $U = -3$

(b) $U = 1$

Conclusions

- We considered a lattice-gas version of the Maier–Saupe model for biaxial nematics with discrete orientations, in addition to an energetic term that described an isotropic interaction.
- We find different types of high-density–low-density transitions (off-lattice models).
- Large number of critical phenomena, mainly for the maximum degree of biaxiality of nematogens (all analytically described).
- Our results widen the possibilities of relating the phenomenological coefficients of the Landau–de Gennes expansion to microscopic parameters.

The End

Mean-field free-energy functional

$$\Psi(S,\eta,\phi;\{\boldsymbol{\alpha}_i\}) = \frac{A}{4}(3S^2+\eta^2) + \frac{U}{2}\phi^2 - \mu\phi + \frac{1}{\beta}\left[(1-\phi)\ln\left(\frac{1-\phi}{6}\right) + \phi\ln(\phi)\right] - \frac{\phi}{\beta}\ln[\Lambda(S,\eta)]$$

where

$$\Lambda(S,\eta) = 2e^{\frac{3\beta A}{2}S}\cosh\left(\frac{3\beta A}{2}\eta\Delta\right) + 2e^{-\frac{3\beta A}{4}(S+\eta)}\cosh\left[\frac{3\beta A}{4}\left(S-\frac{\eta}{3}\right)\Delta\right] + 2e^{-\frac{3\beta A}{4}(S-\eta)}\cosh\left[\frac{3\beta A}{4}\left(S+\frac{\eta}{3}\right)\Delta\right].$$