Can shape-changing spheroids give you a biaxial nematic?

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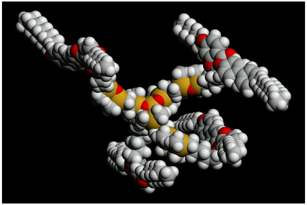
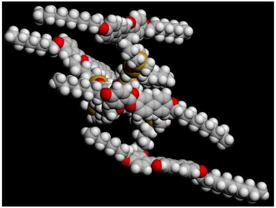
Introduction

- A basic model of a liquid crystal (LC) is a rigid rod or disc.
- But flexible molecules, e.g., tetrapodes, also exhibit LC phases [1,2].





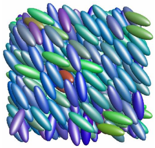
(C. Cruz)

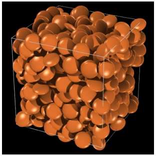
- These molecules are able to exist in several stable conformations: conformational disorder is sacrificed to achieve better packing.
- A thermotropic biaxial nematic phase could be stabilised thus [2].

[1] K. Merkel *et al.*, Phys. Rev. Lett. **93**, 237801 (2004).
[2] J. L. Figueirinhas *et al.*, Phys. Rev. Lett. **94**, 107802 (2005).

Model

- Particles can exist as prolate or oblate spheroids [3].





(D. J. Cleaver)

- The two states (conformers) are in chemical equilibrium and their energies differ by a prescribed amount.
- Interactions described by Hard Gaussian Overlap (HGO) model [4]:

$$U(12) = \begin{cases} 0 & \text{if } r_{12} \geq \sigma(12) \\ \infty & \text{if } r_{12} < \sigma(12) \end{cases}$$

$$\sigma(12) = \sigma_0 \left\{ 1 - \frac{1}{2}\chi \left[\frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\omega}_1 + \hat{\mathbf{r}}_{12} \cdot \hat{\omega}_2)^2}{1 + \chi(\hat{\omega}_1 \cdot \hat{\omega}_2)} + \frac{(\hat{\mathbf{r}}_{12} \cdot \hat{\omega}_1 - \hat{\mathbf{r}}_{12} \cdot \hat{\omega}_2)^2}{1 - \chi(\hat{\omega}_1 \cdot \hat{\omega}_2)} \right] \right\}^{-\frac{1}{2}}$$

$$\chi = \frac{\kappa^2 - 1}{\kappa^2 + 1} \quad , \quad \kappa = \frac{\sigma_L}{\sigma_0}$$

[3] A. G. Vanakaras *et al.*, Mol. Cryst. Liq. Cryst. **362**, 67 (2001).
[4] D. J. Cleaver *et al.*, Phys. Rev. E **54**, 559 (1996).

Theory

- Helmholtz free energy density (FED) of uniform mixture of interconverting rods (R) and plates (P) in Onsager approximation,

$$\begin{aligned}\beta f(\rho_R,\rho_P) &= \rho_R\left[\log\left(\Lambda^3\rho_R\right)-1\right]+\rho_P\left[\log\left(\Lambda^3\rho_P\right)-1\right] \\ &+\rho_R\int \hat{f}_R(\omega)\log\left[4\pi\hat{f}_R(\omega)\right]d\omega+\rho_P\int \hat{f}_P(\omega)\log\left[4\pi\hat{f}_P(\omega)\right]d\omega \\ &+\rho_R^2\int \hat{f}_R(\omega_1)B_{RR}(\omega_1,\omega_2)\hat{f}_R(\omega_2)\,d\omega_1 d\omega_2 \\ &+\rho_P^2\int \hat{f}_P(\omega_1)B_{PP}(\omega_1,\omega_2)\hat{f}_P(\omega_2)\,d\omega_1 d\omega_2 \\ &+2\rho_R\rho_P\int \hat{f}_R(\omega_1)B_{RP}(\omega_1,\omega_2)\hat{f}_P(\omega_2)\,d\omega_1 d\omega_2 \\ &+\epsilon_R\rho_R+\epsilon_P\rho_P.\end{aligned}$$

- Successfully applied to hard rod-plate mixtures [5].

[5] R. van Roij and B. Mulder, J. Physique II **4**, 1763 (1994).

The excluded volume of two different HGOs

- This is an analytical result:

$$B_{RP}(\omega_1, \omega_2) = \frac{4\pi}{3} \frac{\left[\frac{1}{2}\left(\sigma_R^2 + \sigma_P^2\right)\right]^{3/2}}{1 + a_{11} + a_{22} + a_{11}a_{22} + a_{12}a_{21}}$$

$$a_{11} = \frac{c_x\left(1 + c_y \cos^2\theta_{12}\right)}{1 - c_x c_y \cos^2\theta_{12}} \quad , \quad a_{12} = \frac{c_x \cos\theta_{12}\left(1 + c_y\right)}{1 - c_x c_y \cos^2\theta_{12}}$$

$$a_{21} = \frac{c_y \cos\theta_{12}\left(1 + c_x\right)}{1 - c_x c_y \cos^2\theta_{12}} \quad , \quad a_{22} = \frac{c_y\left(1 + c_x \cos^2\theta_{12}\right)}{1 - c_x c_y \cos^2\theta_{12}}$$

$$c_x = \frac{\sigma_R^2\left(1 - \kappa_R^{'\,2}\right)}{\sigma_P^2 + \sigma_R^2 \kappa_R^{'\,2}} \quad , \quad c_y = \frac{\sigma_P^2\left(1 - \kappa_P^{'\,2}\right)}{\sigma_R^2 + \sigma_P^2 \kappa_P^{'\,2}}$$

- Shape non-additivity may be introduced through ν:

$$\kappa_R^{'} = \nu\kappa_R \quad , \quad \kappa_P^{'} = \nu^{-1}\kappa_P$$

i.e., a rod (plate) sees another rod (plate) with elongation κ_R (κ_P), but a rod (plate) sees a plate (rod) with elongation $\kappa_P^{'}$ ($\kappa_R^{'}$).

Stability of I relative to N: bifurcation analysis I

- Find at what density I becomes unstable wrt N [5]:

$$\rho^* = \frac{5}{4}\left[\frac{-\left(x_R B_{RR}^{(2)} + x_P B_{PP}^{(2)}\right) - \sqrt{\left(x_R B_{RR}^{(2)} - x_P B_{PP}^{(2)}\right)^2 + 4 x_R x_P {B_{RP}^{(2)}}^2}}{x_R x_P \left(B_{RR}^{(2)} B_{PP}^{(2)} - {B_{RP}^{(2)}}^2\right)}\right].$$

- Instability is wrt $\mathrm{N_B}$ if:

$$1 + \frac{2}{5}\rho^* \left(x_R B_{RR}^{(2)} - x_P B_{RP}^{(2)}\right) = 0$$

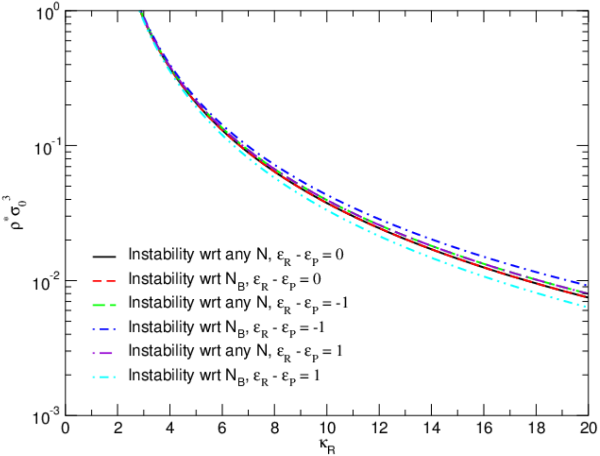
- $B_{ij}^{(l)}$ are the expansion coefficients of $B_{ij}(\omega_1, \omega_2)$:

$$B_{ij}(\omega_1, \omega_2) = \sum_{l=0} B_{ij}^{(l)} P_l(\cos\theta_{12})$$

[6] B. Mulder, Phys. Rev. A **39**, 360 (1989).

Stability of I relative to N: bifurcation analysis II

- Rods and plates have the same volume and $\kappa_P = 1/\kappa_R$.



- If $\epsilon_R = \epsilon_P$, the instability is always wrt $\mathrm{N_B}$.
- If $\epsilon_R \neq \epsilon_P$, the instability is always wrt $\mathrm{N_U}$.

Numerical results for the I–N transition

- Minimise FED with respect to $\hat{f}_R(\omega)$, $\hat{f}_P(\omega)$.
- Find order parameters:

$$\begin{aligned} S_R &= \langle P_2(\cos\theta)\rangle_R \\ \Delta_R &= \langle \sin^2\theta \cos 2\phi\rangle_R, \\ S_P &= \langle P_2(\cos\theta)\rangle_P \\ \Delta_P &= \langle \sin^2\theta \cos 2\phi\rangle_P \end{aligned}$$

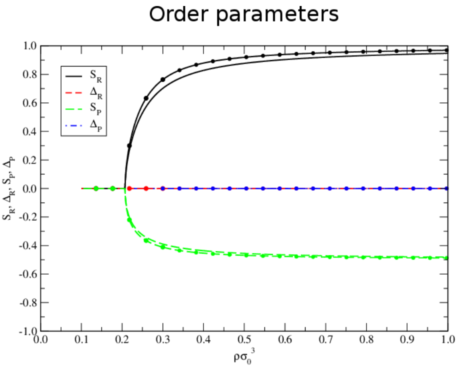
- Identify phases [7]:

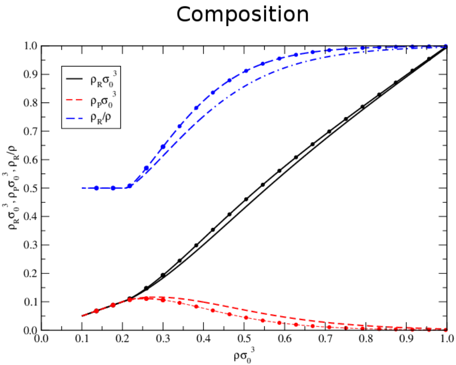
Phase	Symbol	S_R	Δ_R	S_P	Δ_P
Isotropic	I	0	0	0	0
Uniaxial nematic	$\mathrm{N_U^+}$	1	0	$-1/2$	0
Uniaxial nematic	$\mathrm{N_B^-}$	$1/4$	$1/2$	$-1/2$	-1
Biaxial	$\mathrm{N_B}$	1	0	$-1/2$	-1

- Start with L2 approximation: expand $B_{ij}(\omega_1, \omega_2)$ to second order as for bifurcation analysis. Next do full numerical solution.

[7] P. J. Camp *et al.*, J. Chem. Phys. **105**, 9270 (1997).

I–N_U^+ transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), additive ($\nu = 1$) shapes

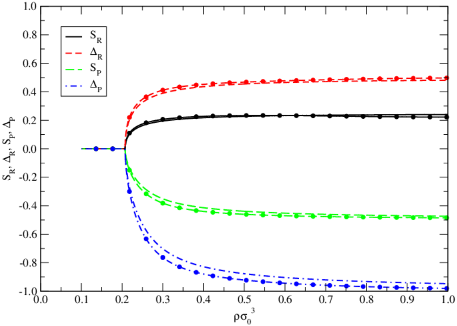




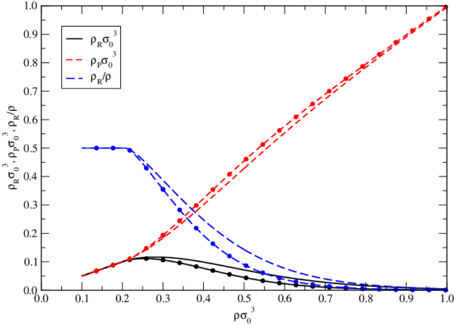
- Rods align along z-axis, plates are in-plane disordered..
- Very strong composition shift, with rods dominating N_U^+ phase.

I–N_U^- transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), additive ($\nu = 1$) shapes

Order parameters

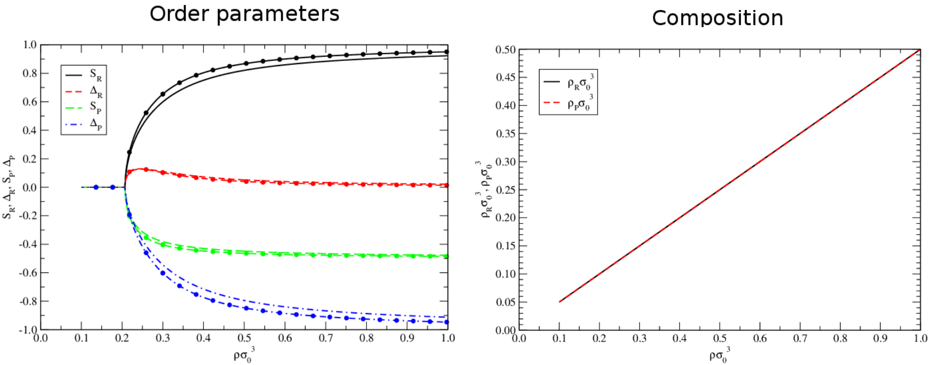


Composition



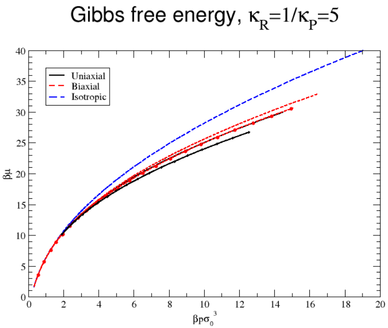
- Plates align along z-axis, rods are in-plane disordered.
- Very strong composition shift, with plates dominating N_U^- phase.

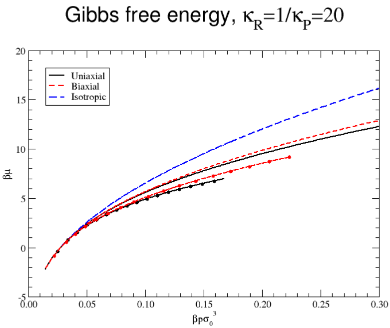
I–N_B transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), additive ($\nu = 1$) shapes



- WE FOUND IT! Rods align along *z*-axis, plates along *x*-axis.
- No composition shift, both phases equimolar.

Relative stability of N_U and N_B phases
Unbiassed ($\Delta\epsilon = 0$), additive ($\nu = 1$) shapes

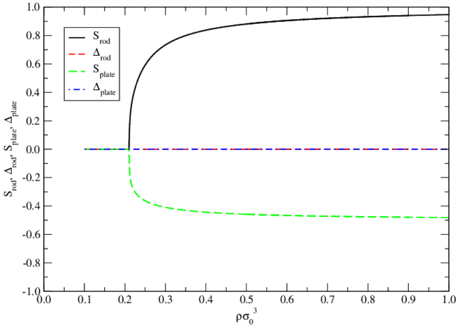




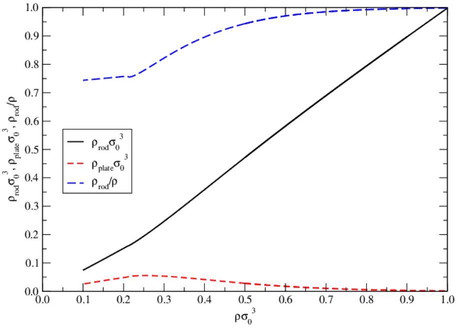
- BUT N_B is metastable!!!
- Even going to $\kappa_R = 20$ will not help...

I–N_U^+ transition for $\kappa_R = 1/\kappa_P = 5$
Biassed ($\Delta\epsilon = -1$), additive ($\nu = 1$) shapes

Order parameters

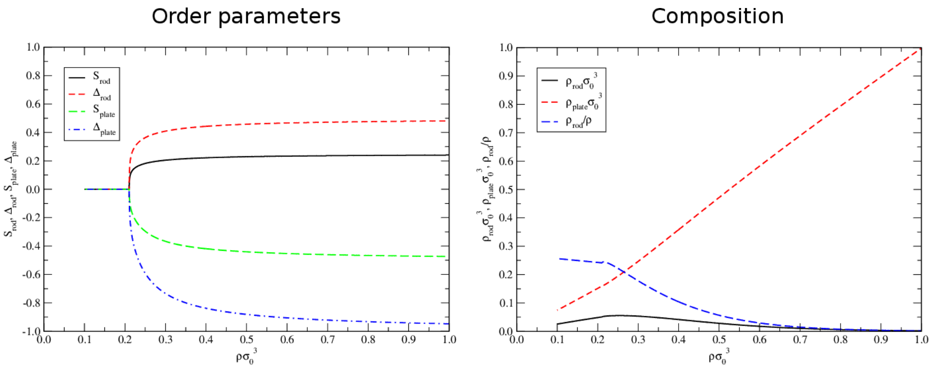


Composition



- If rods favoured ($\Delta\epsilon < 0$), transition is I–N_U^+.
- BOTH N_U^+ AND I phases rod-rich.
- NO I–N_B transition.

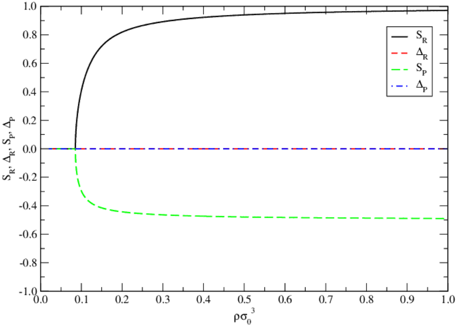
I–N_U^- transition for $\kappa_R = 1/\kappa_P = 5$
Biassed ($\Delta\epsilon = 1$), additive ($\nu = 1$) shapes



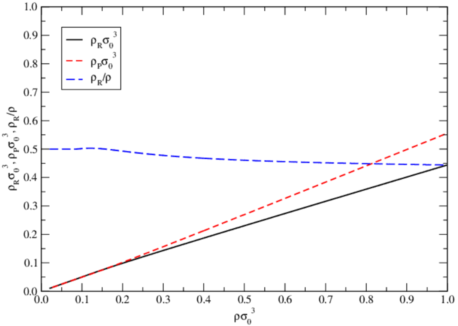
- If plates favoured ($\Delta\epsilon > 0$), transition is I–N_U^-.
- BOTH N_U^- AND I phases plate-rich.
- NO I–N_B transition.

I–N_U^+ transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), non-additive ($\nu = 3$) shapes

Order parameters

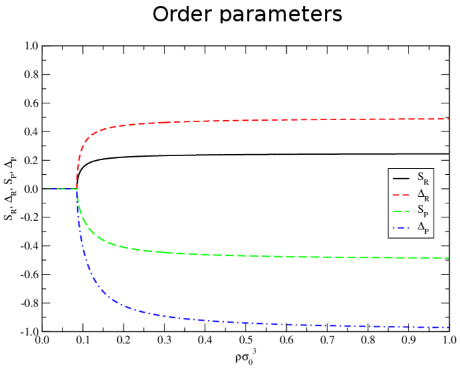


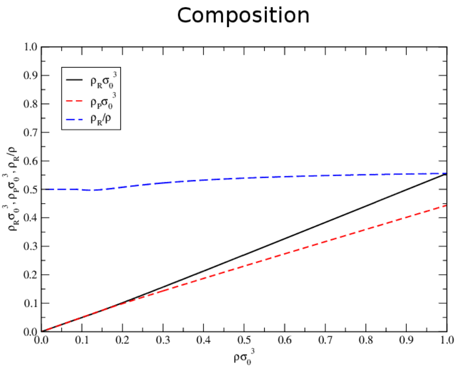
Composition



- I–N_U^+ transition at lower density than for additive shapes.
- N_U^+ phase can be plate-rich!!!

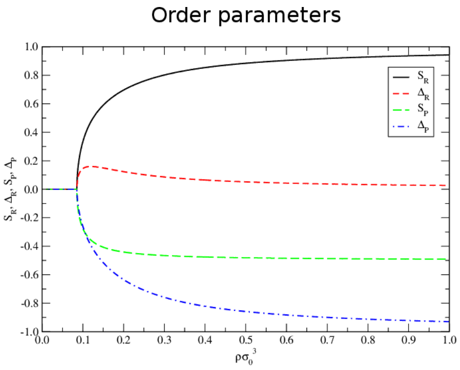
I–N_U^- transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), non-additive ($\nu = 3$) shapes

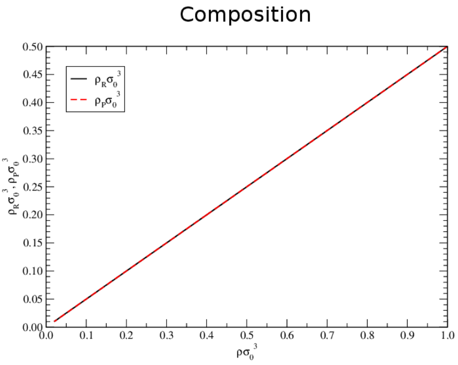




- I–N_U^- transition at lower density than for additive shapes.
- N_U^- phase can be rod-rich!!!

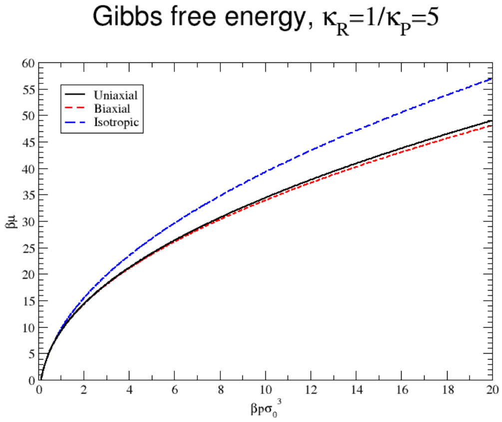
I–N$_B$ transition for $\kappa_R = 1/\kappa_P = 5$
Unbiassed ($\Delta\epsilon = 0$), non-additive ($\nu = 3$) shapes





- WE FOUND IT!
- Non-additivity favours biaxiality: unlike particles can pack more effectively.

Relative stability of N_U and N_B phases
Unbiassed ($\Delta\epsilon = 0$), non-additive ($\nu = 3$) shapes



- N_B is stable for non-additive shapes.
- Maybe not easy to realise experimentally, but can be simulated.

Summary and outlook

- We have obtained an analytical expression for the excluded volume of two different HGOs, and generalised Onsager theory to binary mixtures of interconverting prolate and oblate HGOs.
- There is a density-driven I–N transition. The N phase can be rod-like uniaxial ($N_{\rm U}^{+}$), plate-like uniaxial ($N_{\rm U}^{-}$), or biaxial ($N_{\rm B}$).
- The uniaxial nematic phase is dramatically rod-rich ($N_{\rm U}^{+}$) or plate-rich ($N_{\rm U}^{-}$).
- If there is no penalty for changing shape ($\Delta\epsilon = 0$), the $N_{\rm B}$ phase is unstable with respect to the $N_{\rm U}$ phases.
- If there is a penalty for changing shape ($\Delta\epsilon \neq 0$), the transition is always I–$N_{\rm U}^{+}$ or I–$N_{\rm U}^{-}$.
- The biaxial nematic seems to be stabilised by non-additive shapes.
- We have not considered any other possible competing phases, such as smectics of crystals.
- The Gibbs free energies of $N_{\rm U}$ and $N_{\rm B}$ phases are very close at the I–N transition, hence one might observe a metastatble $N_{\rm B}$ phase.
- Need to consider effects of third- or higher-order virial coefficients?

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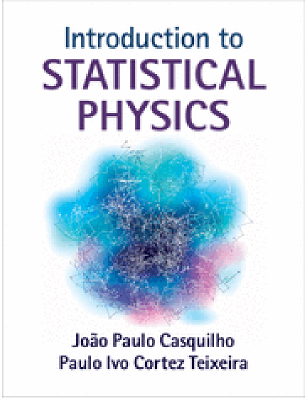
Shameless publicity plug



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