Soft Matter Mathematical Modelling

Cortona 12th-16th September 2005

Biaxial Nematics

Fact, Theory and Simulation

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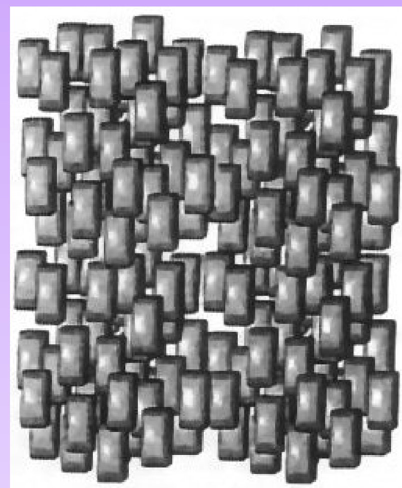
Fact

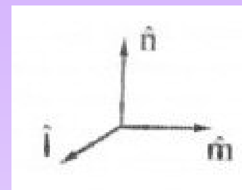
The elusive biaxial nematic

Claims to discovery

Recognition of the biaxial nematic

Biaxial Nematic N_B molecular organisation





Macroscopic definition

Frank

Symmetry of average tensorial property, **T**,

such as the dielectric susceptibility or the quadrupolar splitting in NMR is biaxial.

Principal components

$\tilde{T}_{XX} \neq \tilde{T}_{YY} \neq \tilde{T}_{ZZ}$ for N_B

$$\eta = 3(\tilde{T}_{XX} - \tilde{T}_{YY}) / \left(2\tilde{T}_{ZZ} - (\tilde{T}_{XX} + \tilde{T}_{YY})\right)$$

(n.b. $\tilde{T}_{XX} = \tilde{T}_{YY} \neq \tilde{T}_{ZZ}$ for N_U)

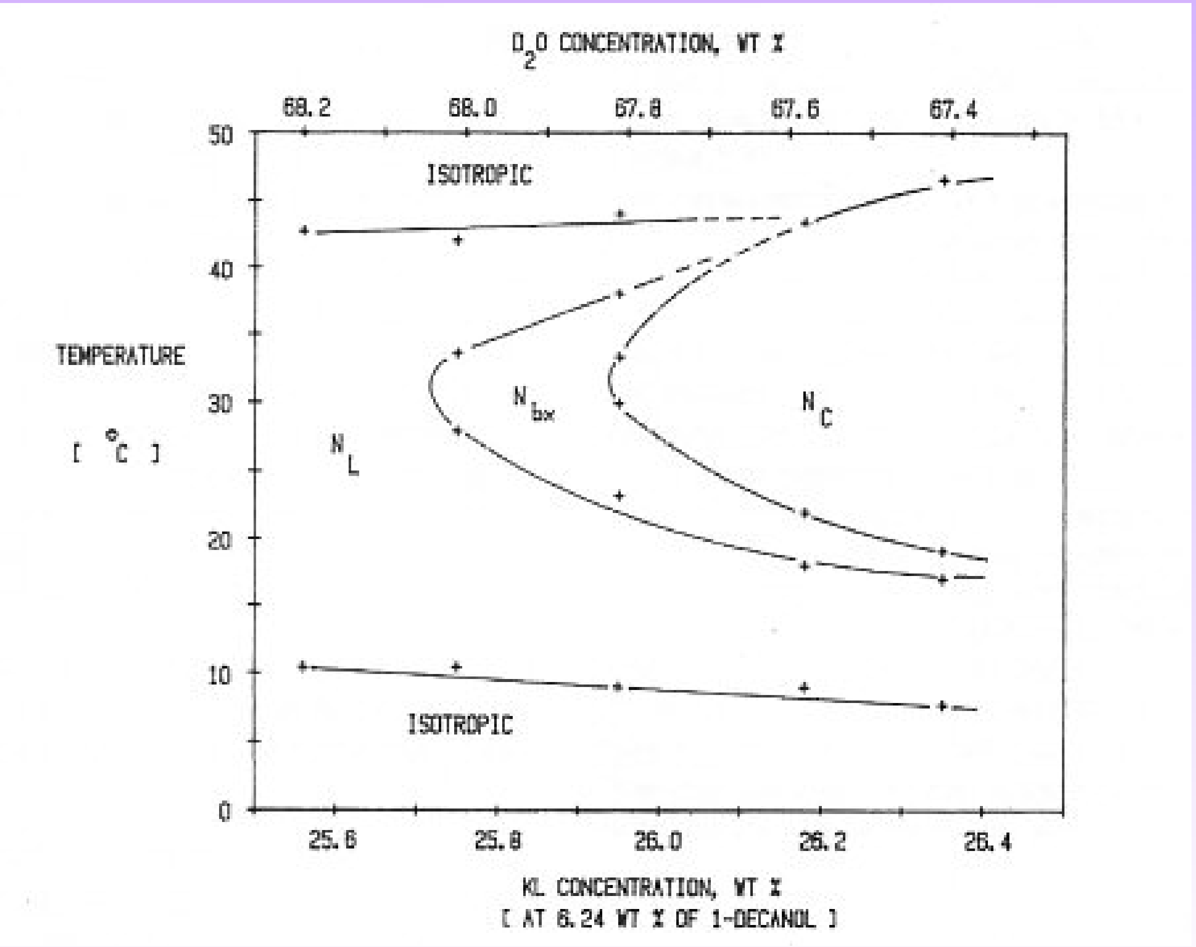
The directors, **n**, **l**, **m** are identified with the principal axes of $\tilde{T}$.

Lyotropic Biaxial Nematic

(potassium laurate (KL) , 1-decanol, D_2O)

L J Yu, A Saupe, *Phys.Rev.Lett.*, 1980, **45**, 1000-1003

Phase diagram

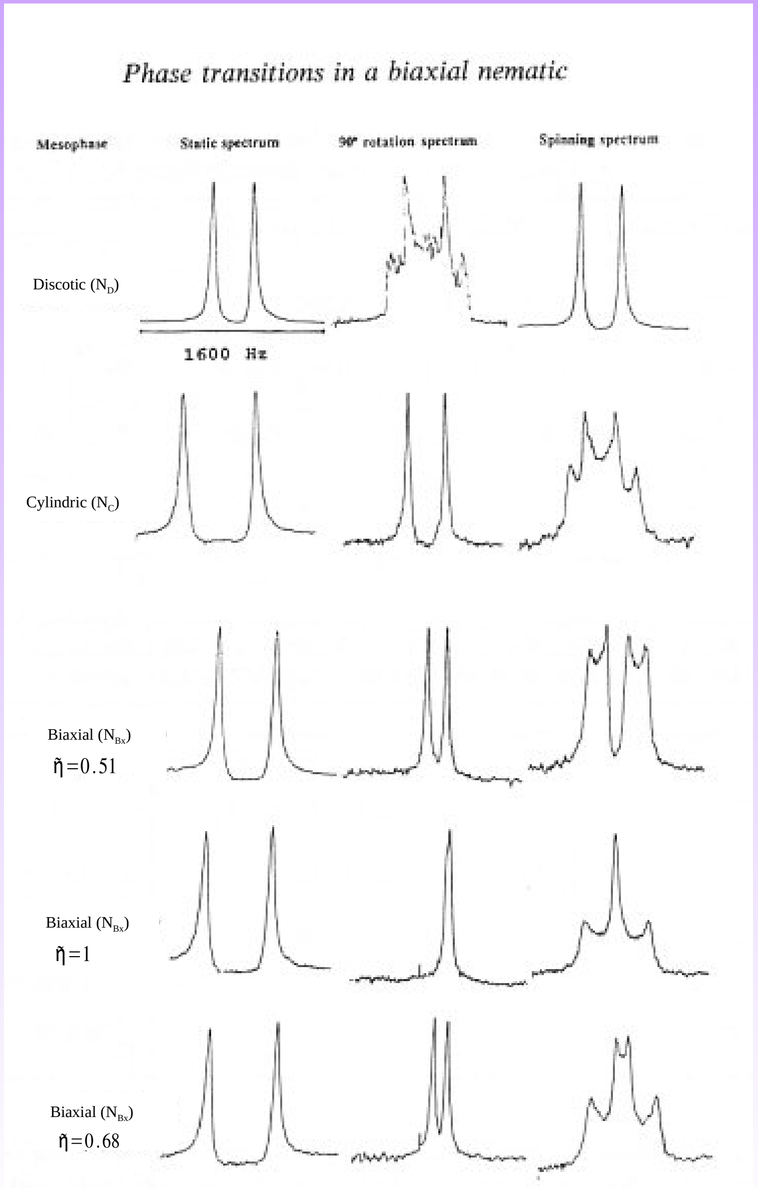


Identifying a Biaxial Nematic

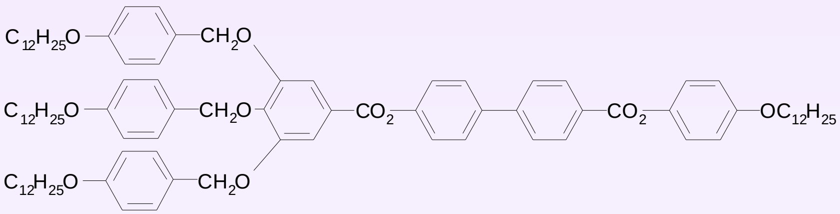
F P Nicoletta, G Chidichimo, A Golemme, P Picci, *Liq.Cryst.*, 1991, **10**, 665-674

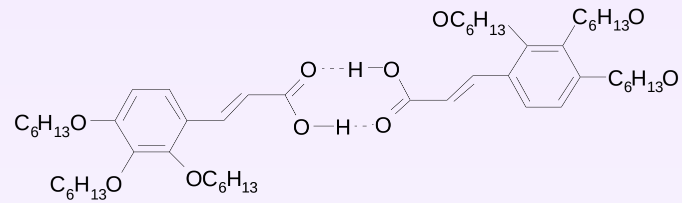
Another lyotropic biaxial nematic (potassium laurate,
decyl ammonium chloride, D_2O)

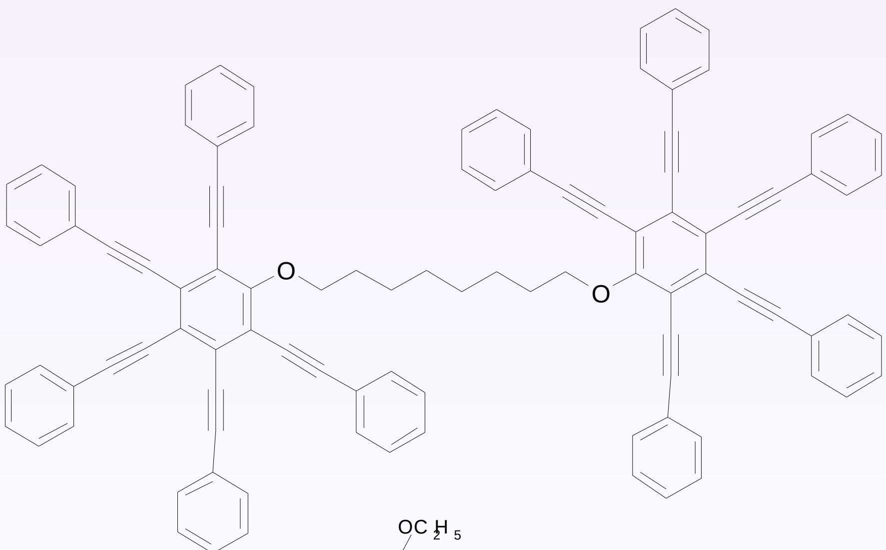
The primary ^2H NMR data

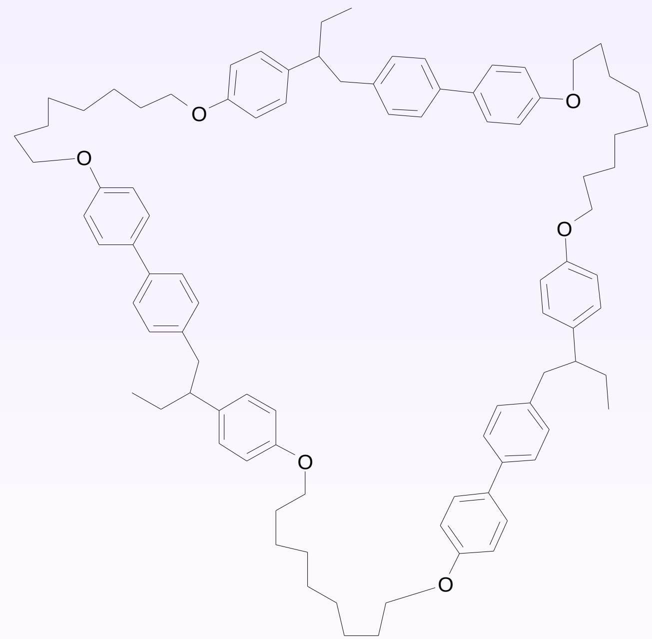


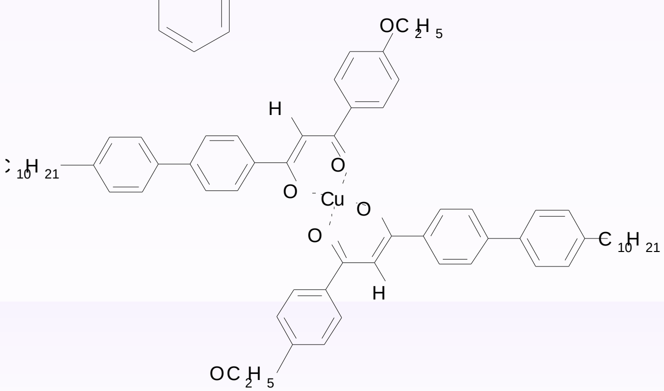
Thermotropic Biaxial Nematics?

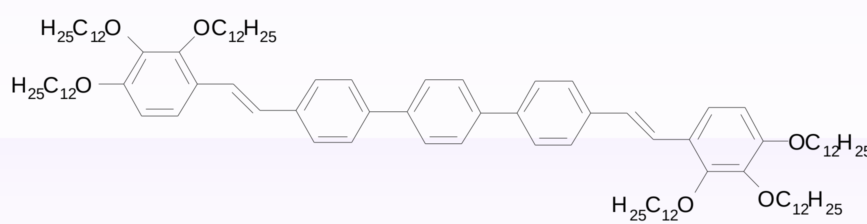








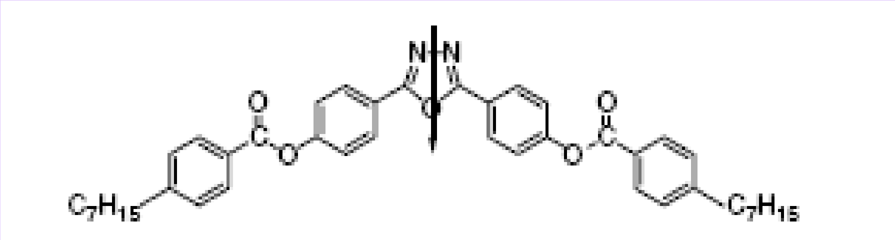


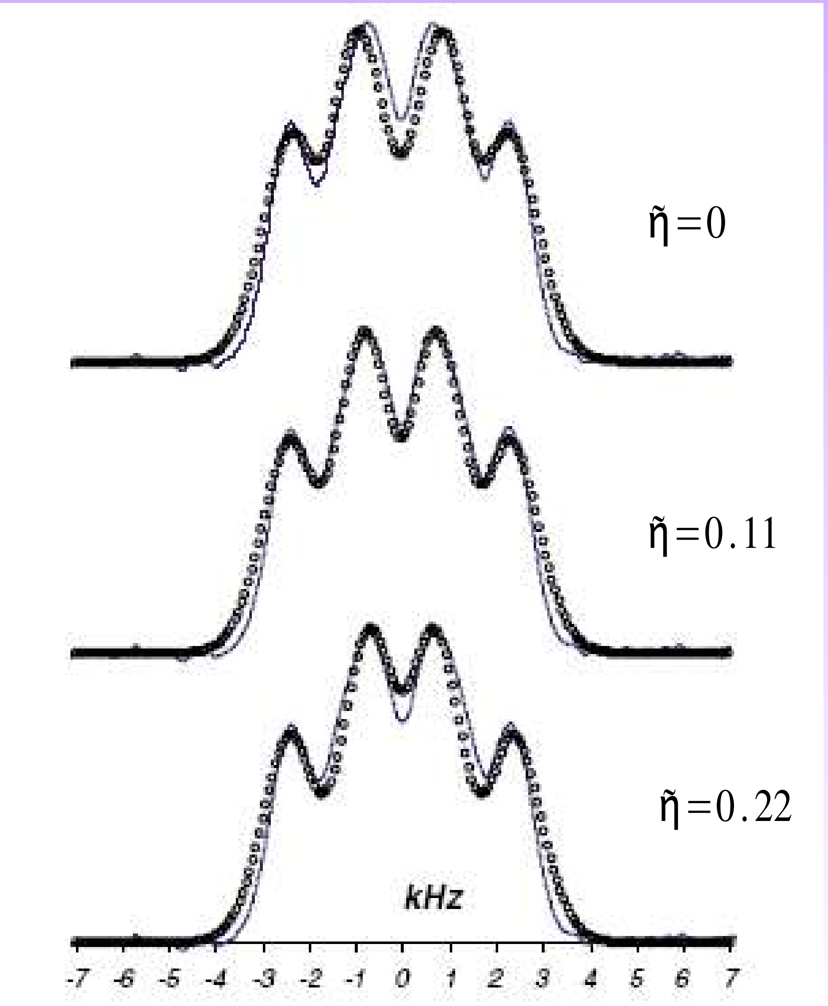


Thermotropic Biaxial Nematics 2004

V-shaped molecules

L A Madsen, T J Dingemans, M Nakata, and E T Samulski, *Phys. Rev. Lett.*, 2004, **92**, 145505





Biaxiality in $\tilde{q}$

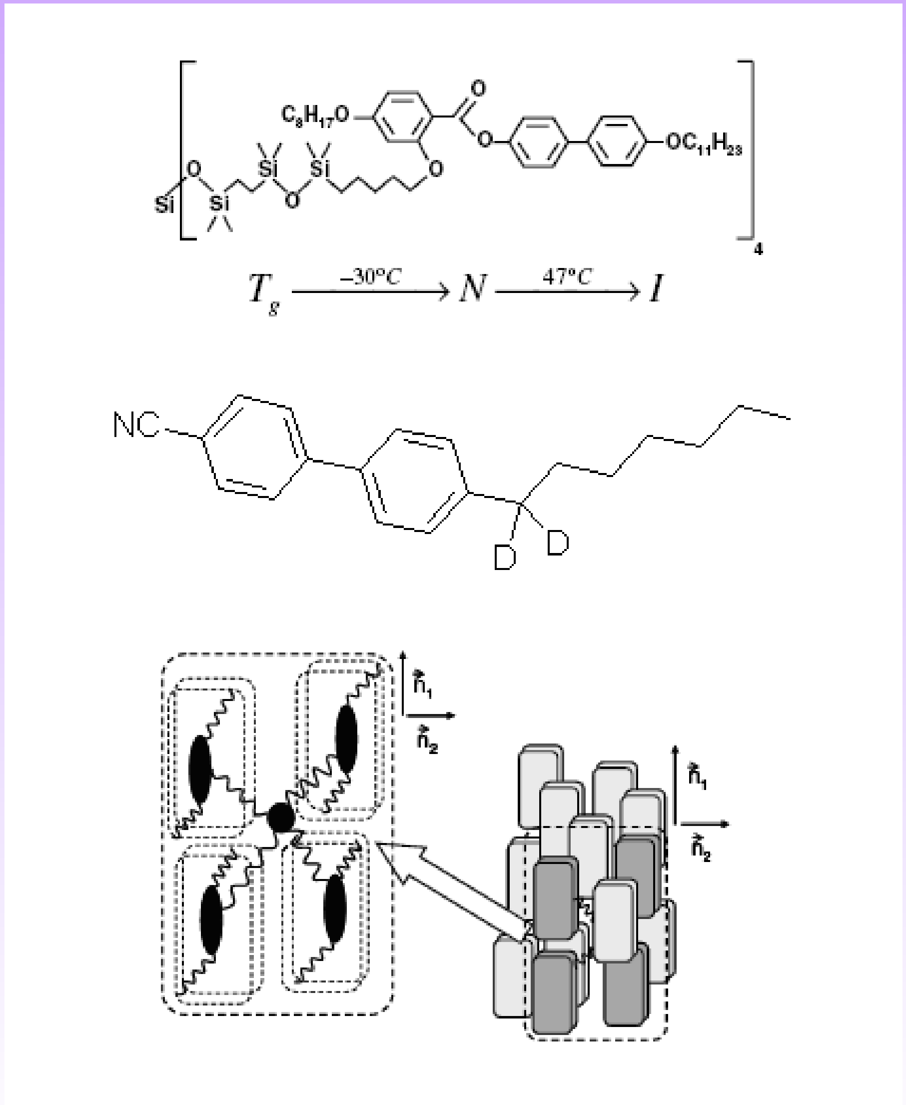
$$\tilde{\eta}=0.11$$

n.b. for lyotropic biaxial nematics

$$\tilde{\eta}\approx 0.7-1.0$$

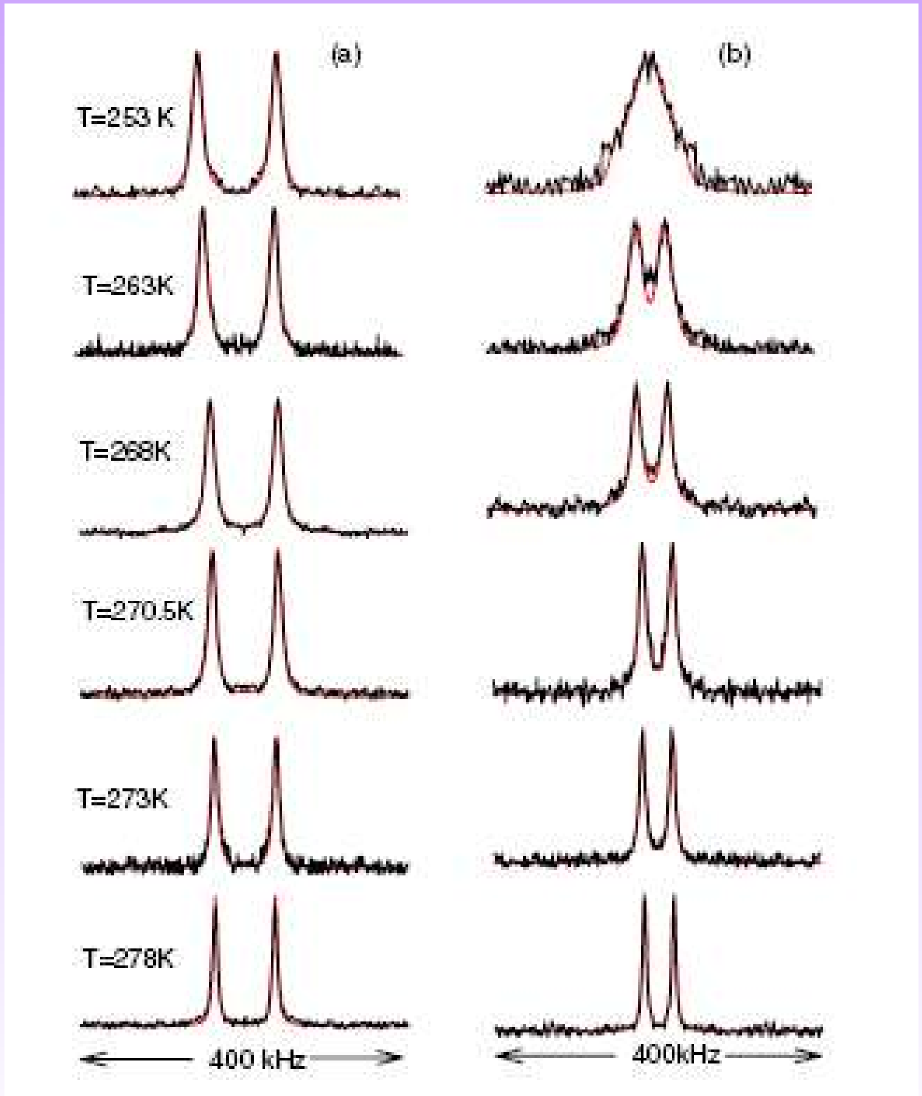
Thermotropic Biaxial Nematics 2005

Tetrapodes:



J L Figueirinhas, C Cruz,
D Filip, G Feio, A C Ribeiro,
Y Frère and T Meyer, G H Mehl
Phys. Rev. Lett., 2005, **94**, 107802

Tetrapodes: the NMR Evidence



Theory

Molecular field approach

Landau approach

Molecular Field Theory

General Notation

Single molecule potential

$$U = -\sum u_{2mn}(1+\delta_{m2})(1+\delta_{n2})(1+\delta_{p2})\langle R^2_{pm}\rangle R^2_{pn}(\Omega)$$

Symmetry adapted functions

Dependence on Euler angles

$$R^2_{00}(\Omega) = \left(3\cos^2\beta - 1\right)/2$$

$$R^2_{02}(\Omega) = \sqrt{3/8}\,\sin^2\beta\,\cos^2\gamma$$

$$R^2_{20}(\Omega) = \sqrt{3/8}\,\sin^2\beta\,\cos^2 2\alpha$$

$$R^2_{22}(\Omega) = 1/2\left(1/2\left(1+\cos^2\beta\right)\cos 2\alpha\cos 2\gamma - \cos\beta\,\sin 2\alpha\sin 2\gamma\right)$$

Order parameters are averages of R^2_{mn}

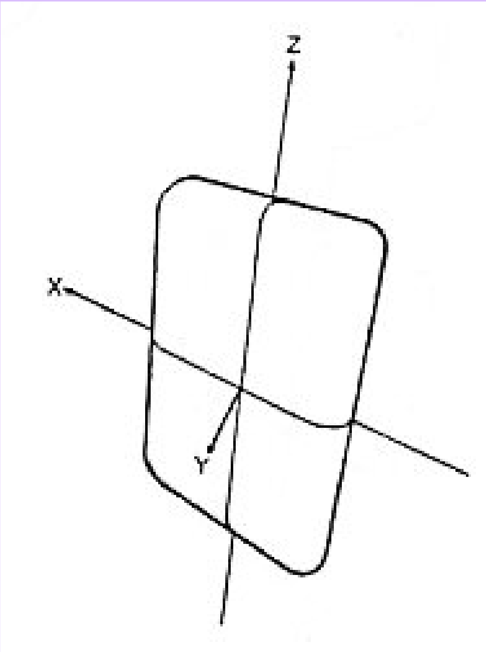
Strength parameters

u_{200} $\quad u_{220}(\equiv u_{202})$ $\quad u_{222}$

Orientational Order Parameters

Axes: molecular xyz and space XYZ

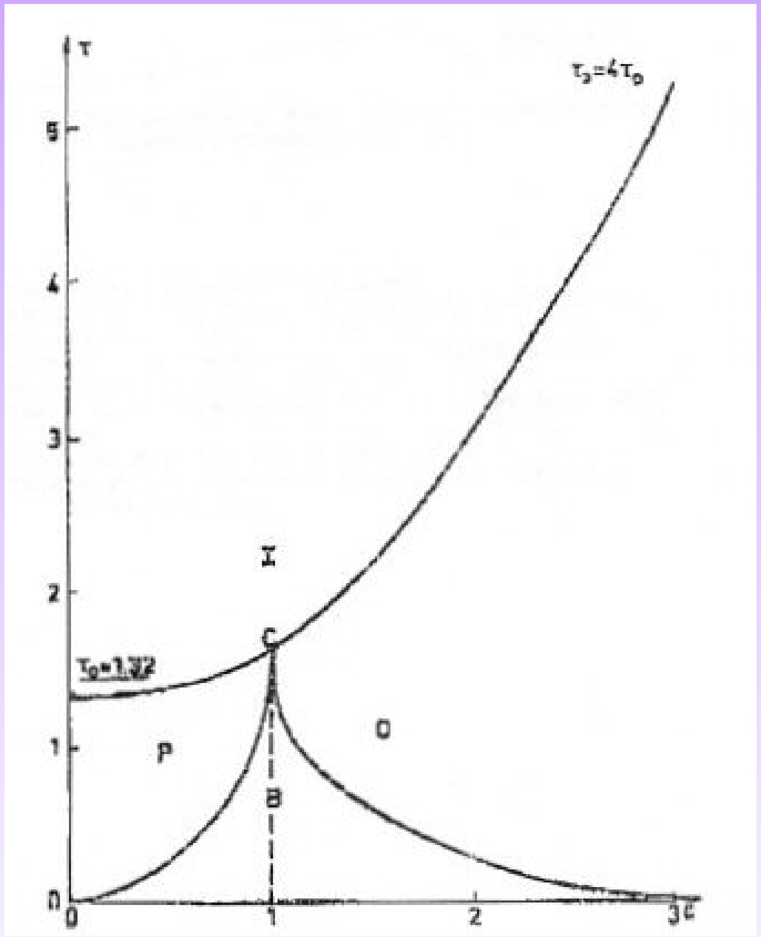
Biaxial molecule in biaxial phase	Limit	
major $S_{zz}^{ZZ} = \langle(3l_{zZ}^2 - 1)/2\rangle$	1	$\langle R^2_{00}\rangle$
molecular biaxial $S_{xx}^{ZZ} - S_{yy}^{ZZ} = \langle 3(l_{xZ}^2 - l_{yZ}^2)/2\rangle$	0	$\sqrt{\frac{8}{3}}\langle R^2_{02}\rangle$
phase biaxial $S_{zz}^{XX} - S_{zz}^{YY} = \langle 3(l_{zX}^2 - l_{zY}^2)/2\rangle$	0	$\sqrt{\frac{8}{3}}\langle R^2_{20}\rangle$
phase biaxial $(S_{xx}^{XX} - S_{xx}^{YY}) - (S_{yy}^{XX} - S_{yy}^{YY}) =$ $\langle 3\{(l_{xX}^2 - l_{xY}^2) - (l_{yX}^2 - l_{yY}^2)/2\}\rangle$	3	$6\langle R^2_{22}\rangle$



Molecular Field Theory

N Boccara, R Medjani, L de Seze, *J.Phys.*, 1977, **38**, 149-151

Phase diagram
(molecular biaxiality $\epsilon = \lambda\sqrt{6}$



Geometric mean approximation

$$u_{220} = \left(u_{200} u_{222}\right)^{1/2}$$

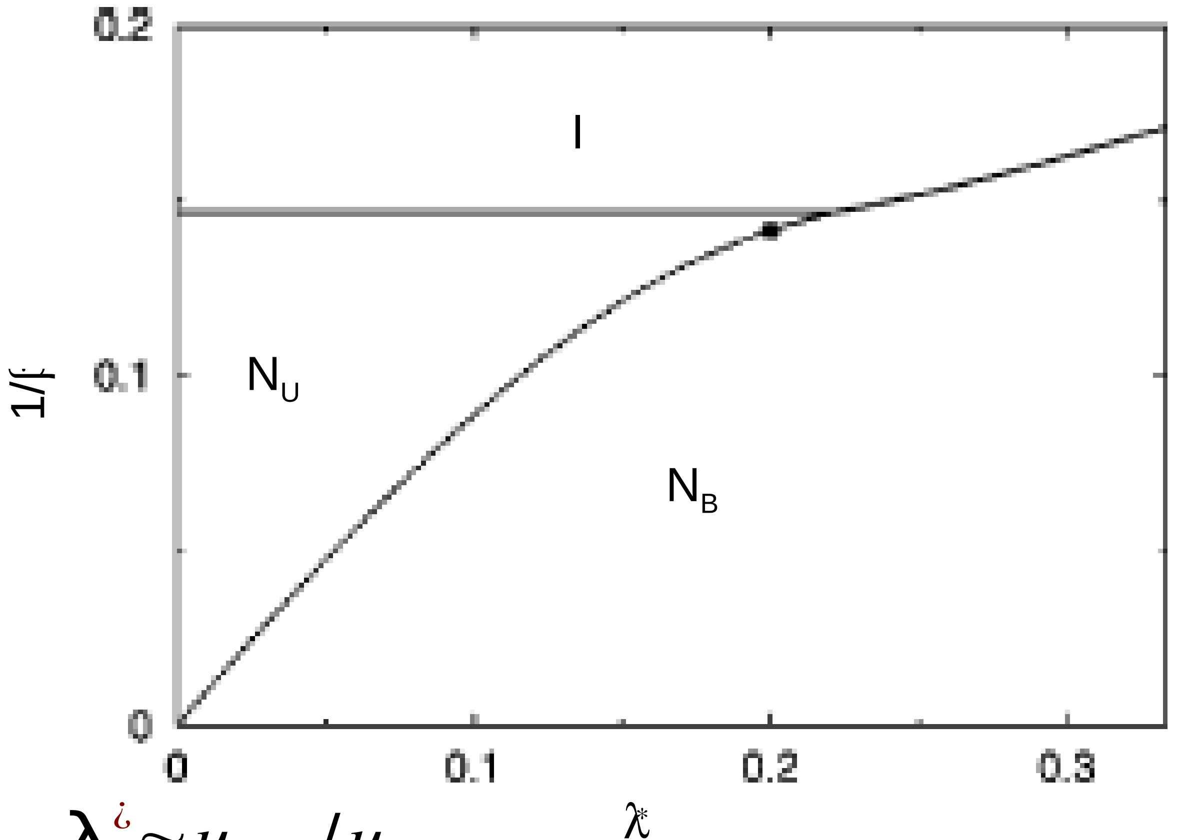
$$\lambda = \left(u_{222} / u_{200} \right)^{1/2}$$

Bounds on ϵ of 0 and 3 correspond to uniaxial molecules
$\epsilon = 1$is the maximum biaxiality giving the Landau point

Molecular Field Theory

A M Sonnet, E G Virga and G E Durand, *Phys. Rev., E*, 2003, **67**, 061701

Phase Diagram



$u_{220}=0 \quad \lambda^{¿} \sim u_{222}/u_{200}$

Landau Theory

Uniaxial nematic of uniaxial molecules

Key order parameter for nematic-isotropic transition: S

$$A = A_0 + BS^2 + CS^3 + DS^4$$

Free energy expansion of invariants

Assumption:

$$B = b(T - T^{¿})$$

Dependence on S and magnitude of other coefficients related to experimental quantities

Landau Theory

Biaxial phase of biaxial molecules

Order parameters

Major

$$S = \langle 3\cos^2\beta - 1/2 \rangle \qquad = \langle R^2_{00} \rangle$$

Molecular biaxial

$$T = \langle \sin^2\beta \cos^2\gamma \rangle \qquad = \sqrt{\frac{8}{3}} \langle R^2_{02} \rangle$$

Phase biaxial

$$U = \langle \sin^2\beta \cos 2\alpha \rangle \qquad = \sqrt{\frac{8}{3}} \langle R^2_{20} \rangle$$

Landau Theory

Phase / molecular biaxial

$$V = \langle {}^{1}\!/_{2} (1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma - \cos \beta \sin 2\alpha \sin 2\gamma \rangle = 2 \langle R_{22} \rangle$$

Uniaxial nematic

$$S \neq 0 \qquad T \neq 0 \qquad U = 0 \qquad V = 0$$

Biaxial nematic

$$S \neq 0 \qquad T \neq 0 \qquad U \neq 0 \qquad V \neq 0$$

Landau Theory

D W, Allender, M A Lee, N Hafiz, *Mol. Cryst. Liq. Cryst.*, 1985, **124**, 45-52

Free energy

$$A_N - A_I = A(S^2/2 + T^2 + U^2 + V^2/18)$$

$$+B(S^3/4 - 3SU^2/2 - 3ST^2/2 + SV^2/12 + TUV)$$

$$+C_1(S^2/2 + T^2 + U^2 + V^2/18)^2$$

$$+C_2(VS/2 - 2TU)^2$$

$$+D_1(S^2/2 + T^2 + U^2 + V^2/18)$$

$$\text{¿}(S^3/4 - 3ST^2/2 - 3SU^2/2 + SV^2/12 + TUV)$$

$$+D_2(SV/3 - 2TU)(SV^2/4 - TV^2/2 - U^2V/2 + V^3/108)$$

$$+\dots$$

Landau Theory

Free energy (continued)

$$\ldots + E_1 (S^2/2 + T^2 + U^2 + V^2/18)^3$$
$$+ E_2 (S^2/2 + T^2 + U^2 + V^2/18)(SV/3 - 2TU)^2$$
$$+ E_3 (S^3/4 - ST^2/2 - 3SU^2/2 + TUV + SV^2/12)^2$$
$$+ E_4 (S^2 V/4 - U^2 V/2 - T^2 V/2 - 3STU + V^3/108)^2$$
$$+ E_5 (\ldots\ldots)$$

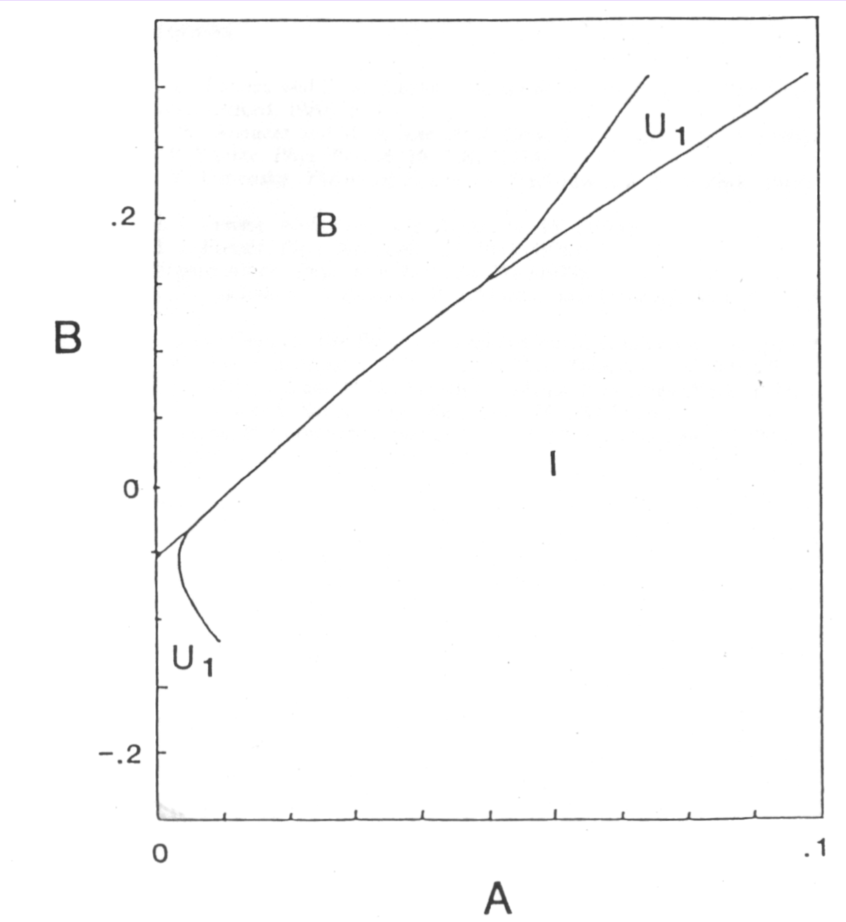
Assumptions

A is linear in temperature ~ ($T - T^*$)

B , C_1 , C_2, D_1 , D_2 , E_1 , E_2 , E_3 , E_4 , E_5 are temperature independent.

Landau Theory for Biaxial Nematics

Phase diagram



$C_1 = 0$, $C_2 = 1$, $D_1 = 1$, $D_2 = 1$, $E_1 = 1$, $E_2 = 1$, $E_3 = 1$, $E_4 = 1$, $E_5 = -7$

Landau Theory for Biaxial Nematics

Problems:

(b) Large number of unknown parameters

(c) Single characteristic temperature, might have expected more

(d) Four nematic phases are predicted

Phase	Order	Parameter
I	0	-
N_{U1}	1	S
N_{U2}	2	S, T
N_B	2	S, U
N_B*	4	S, T, U, V

Strategy of Katriel *et al.*

J Katriel, G F Kventsel, G R Luckhurst, T J Sluckin, *Liq. Cryst.*, 1986, **1,** 337-355

(1) Free energy

$$A = -\frac{1}{2} u_{200} \langle P_2 \rangle^2 + k_B T \int f(\beta) \ln 2 f(\beta) \sin\beta d\beta$$
$$= U - TS$$

(4) Order parameter

$$\langle P_2 \rangle = \int P_2(\cos\beta) f(\beta) \sin\beta d\beta$$

(6) Entropy a functional of distribution function *f*(β)

$$S = S[f(\beta)]$$

But *A* is not yet a function of OP !

Strategy of Katriel *et al.*

$$A = k_B T \int f(\beta) \ln 2 f(\beta) \sin\beta d\beta - \frac{1}{2} u_{200} \langle P_2 \rangle^2 = U - TS$$

Maximise entropy term subject to given OP

(1) f(β) a function of auxiliary parameter η

$$f(\beta) = \frac{1}{Z(\eta)} \exp \eta P_2(\cos\beta)$$

(3) Partition function

$$Z(\eta) = \int \exp \eta P_2(\cos\beta) \sin\beta d\beta$$

(5) OP a function of η

$$\langle P_2 \rangle = \frac{\partial \ln Z(\eta)}{\partial \eta}$$

A is now a function of η and OP

Strategy of Katriel *et al.*

$$A = k_B T \int f(\beta) \ln 2 f(\beta) \sin \beta d\beta - \frac{1}{2} u_{200} \bar{P}_2^{\,2} = U - TS$$

(1) Invert equation:

$$\bar{P}_2 = \frac{\partial \ln Z(\eta)}{\partial \eta}$$

(3) *A was* a function of OP and η

Expand $\langle P_2 \rangle$ in a power series in η

Invert power series to required order

(6) *A* is *now* a function of OP

Expand A in power series in OP

$$A = A\left(\langle P_2 \rangle\right)$$

Result

$$A=\frac{5}{2}k_B\left(T-T^{¿}\right)\langle P_2\rangle^2-\frac{25}{21}k_BT\langle P_2\rangle^3+\frac{425}{196}k_BT\langle P_2\rangle^4+\ldots.$$

$$T^{¿}=u_{200}/5k_B$$

Landau Theory for Biaxial Nematics

A molecular field approach

Energy

$$U_N = {}^{-1}\!/_{2} \sum u_{2mn} (1+\delta_{m2})(1+\delta_{n2})(1+\delta_{p2}) \langle R^2_{pm} \rangle \langle R^2_{pn} \rangle$$

$$U_N = {}^{-1}\!/_{2} \left(u_{200}(S^2+2U^2)+4u_{220}(ST+2UV)+4u_{222}(T^2+2V^2) \right)$$

n.b. expansion coefficients are components of supertensor and not scalars

Simulation

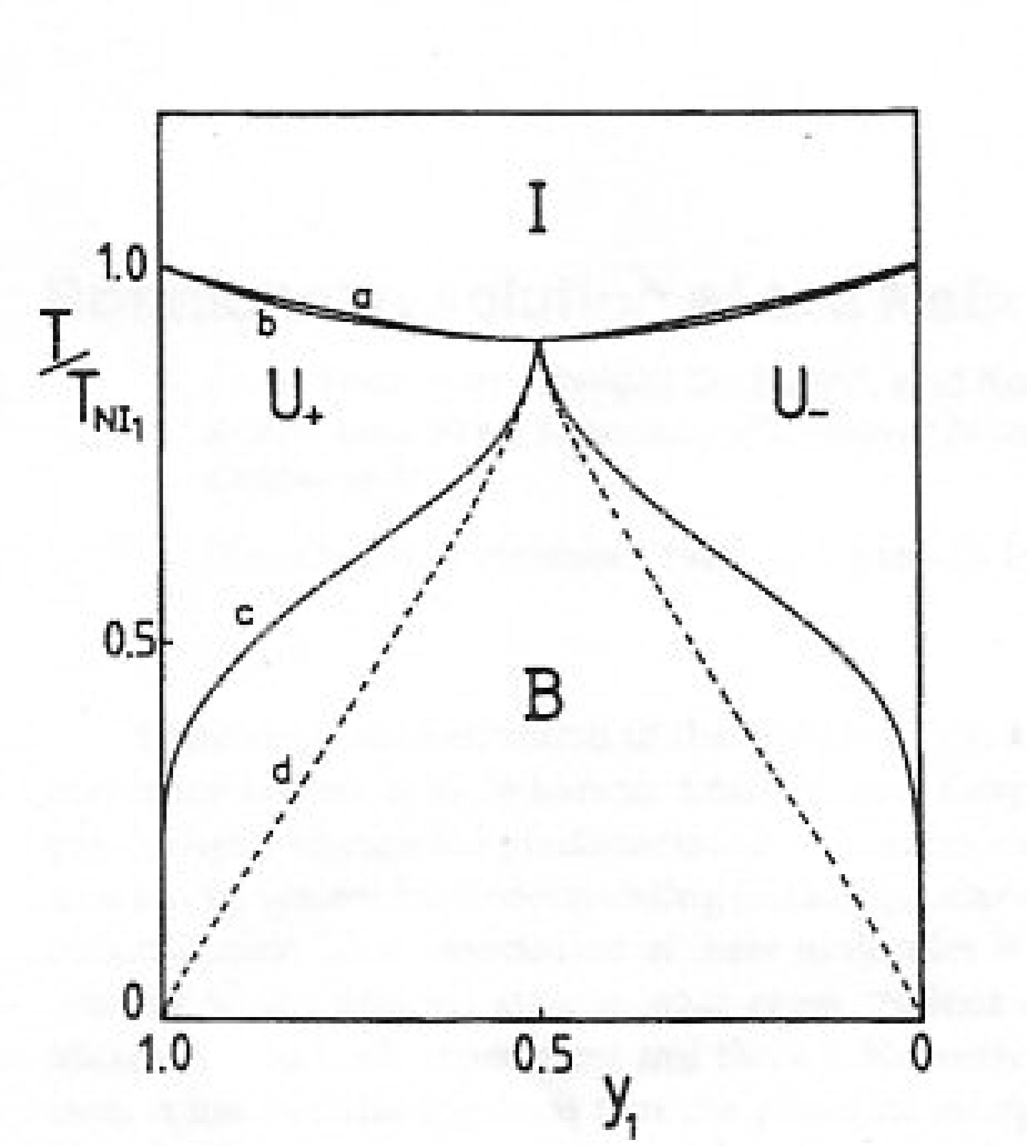
Rod-Disc Mixtures

Rod-Disc Dimers

Flexibility

Mixtures of rods and discs

The phase diagram

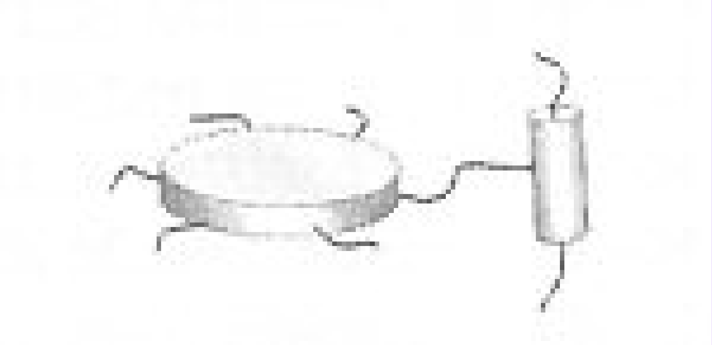


P Palffy-Muhoray, J R Bruyn,
D A Dunmur,
J.Chem.Phys., 1985, **82**, 5294-5295

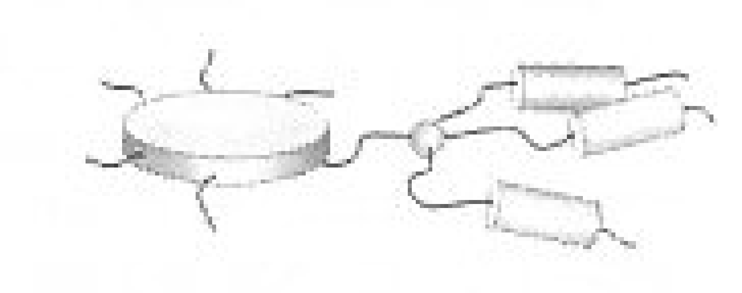
Rod – Disc Dimers

I D Fletcher, G R Luckhurst, *Liq.Cryst.*, 1995, **18**, 175-183

J J Hunt, R W Date, B A Timimi, G R Luckhurst, D W Bruce, *J.Am.Chem.Soc.*, 2001, **123**, 10115-10116



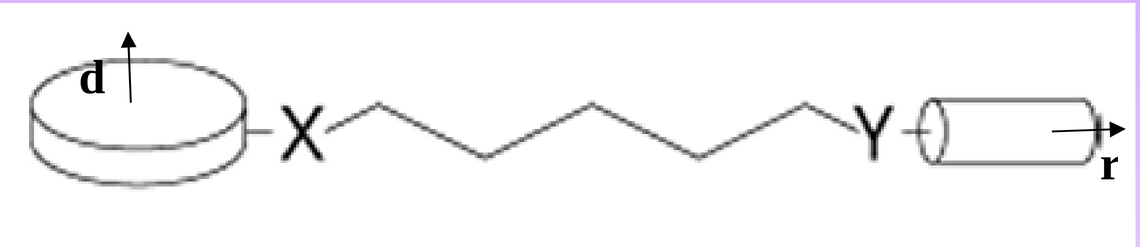
P H J Kouwer, G H Mehl., *Mol.Cryst.Liq.Cryst.*, 2003, **397**, 301-316



The Phase Behaviour of Rod-Disc Dimers

M A Bates, G R Luckhurst, *PCCP*, 2005, **7**, 2821-2829

The Lebwohl-Lasher lattice Model



Anisotropic interactions

$$U_{ij}^{RR} = -\epsilon_{RR} P_2(r_i \cdot r_j)$$

$$U_{ij}^{RD} = \epsilon_{RD} P_2(r_i \cdot d_j)$$

$$U_{ij}^{RD} = \epsilon_{RD} P_2(d_i \cdot r_j)$$

$$U_{ij}^{DD} = -\epsilon_{DD} P_2(d_i \cdot d_j)$$

Torsional potential

$$U_{tors}^{RD} = \epsilon_a P_2(r_i \cdot d_i)$$

$\varepsilon_a > 0$ symmetry axes orthogonal

$\varepsilon_a < 0$ symmetry axes parallel

Parameterisation

Scaling Parameter

$$\epsilon_{RR} \qquad \text{e.g.} \qquad T^{¿} = k_B T / \epsilon_{RR}$$

Relative anisotropy

$$\epsilon^{¿} = \epsilon_{DD} / \epsilon_{RR}$$

Controls the molecular biaxiality

Geometric mean or Berthelot approximation

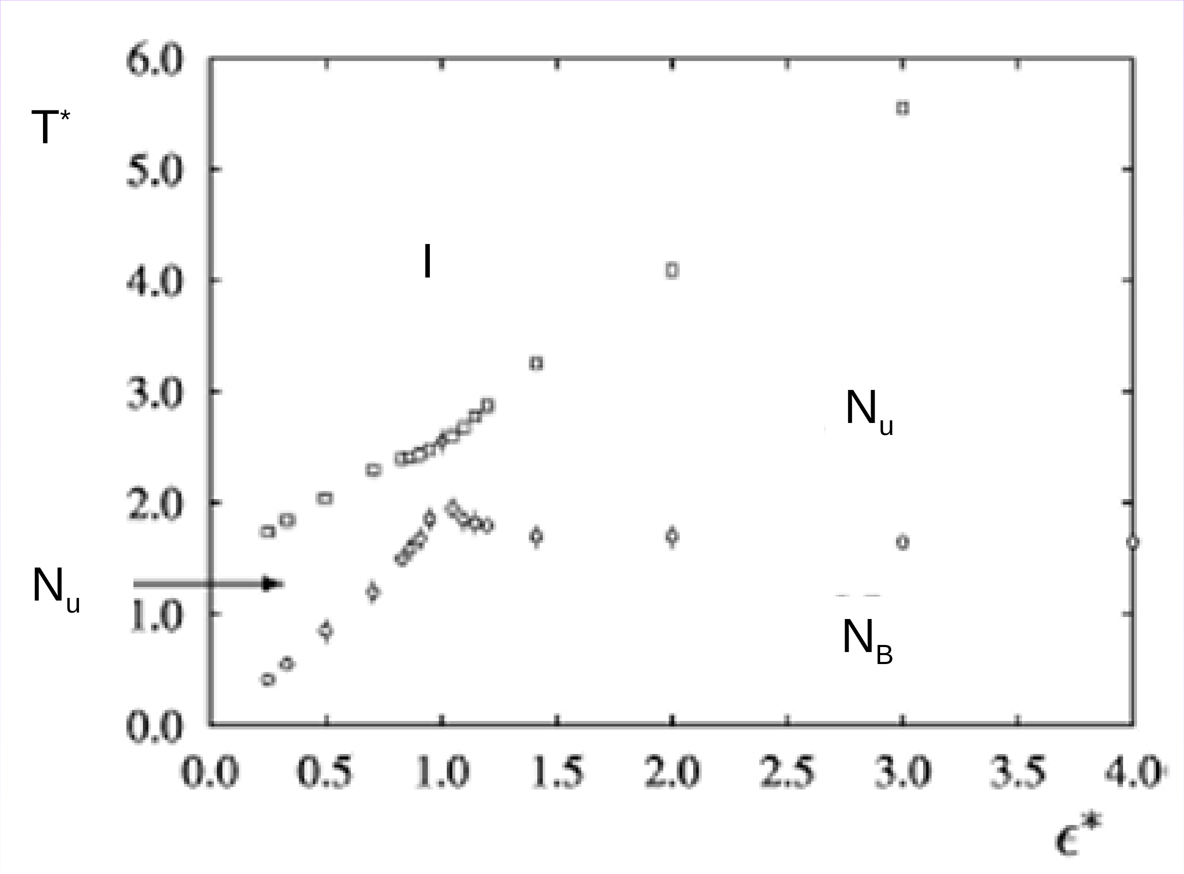
$$\epsilon_{RD} = \left(\epsilon_{DD} \epsilon_{RR} \right)^{½}$$

Scaled torsional strength

$$\epsilon_a^{¿} = \epsilon_a / \epsilon_{RR}$$

Rigid Rod-Disc Dimer

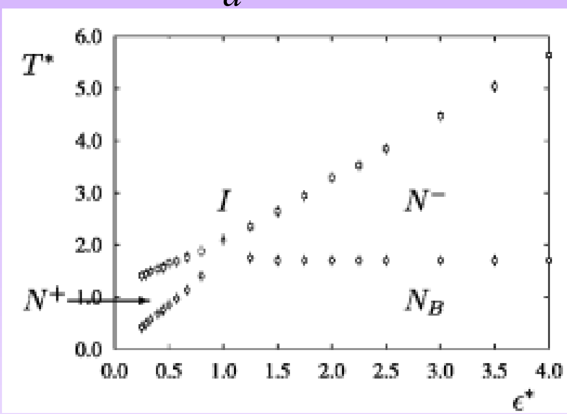
Phase diagram as function of relative anisotropy $\left(\equiv \epsilon_{DD} / \epsilon_{RR}\right)$



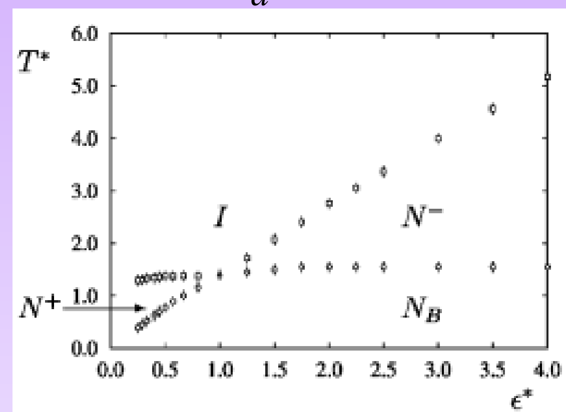
Flexible Rod-Disc Dimers

Phase diagram for different torsional strengths $\epsilon_a^{¿}(\equiv \epsilon_a/\epsilon_{RR})$

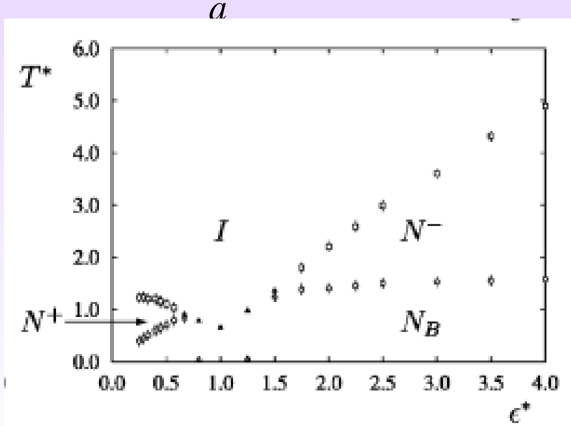
$\epsilon_a^{¿}=0$



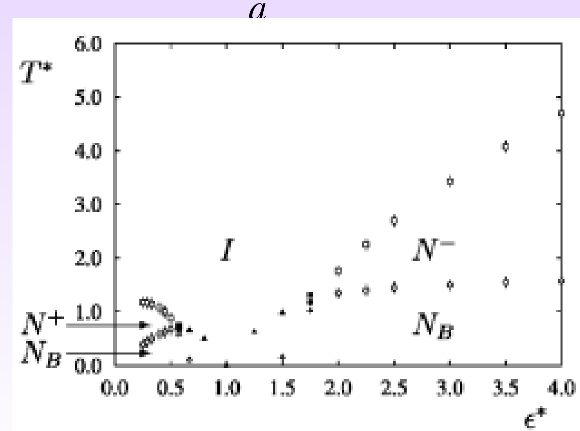
$\epsilon_a^{¿}=-4$



$\epsilon_a^{¿}=-6$



$\epsilon_a^{¿}=-7$



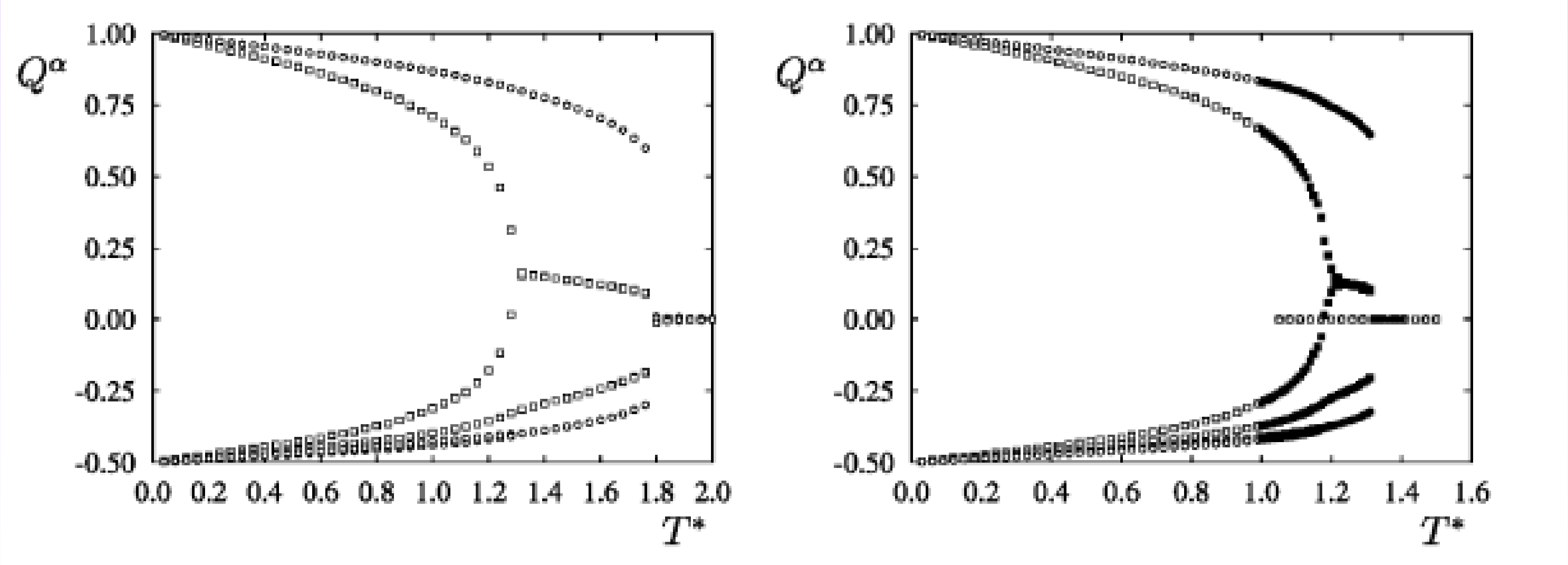
Flexible Rod-Disc Dimers

Orientational order parameters

Q^{R}_{AA} and Q^{D}_{AA} $[\equiv S^{\alpha}_{XX}, S^{\alpha}_{YY}, S^{\alpha}_{ZZ}]$ α= R or D

$\epsilon^{¿}_{a} = -7$

$\epsilon^{¿} = 2.0$ $\epsilon^{¿} = 1.75$



Acknowledgements

Fact

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Theory

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Simulation

Martin Bates (York)
Silvano Romano (Pavia)