Física Estatística de Fluidos Complexos

modelos estatísticos elementares para o comportamento termodinâmicos de fluidos complexos

... a física estatística dos líquidos é reconhecidamente difícil ....
... as física estatística dos cristais líquidos é mais difícil ainda ...
... portanto, modelos simples são sempre benvindos ...

Study of a magnetically oriented lyotropic mesophase

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(Received 11 April 1979; accepted 22 June 1979)

A study of a magnetically oriented lyomesophase formed by a quaternary system (Na decyl sulfate/water/decanol/Na sulfate) is reported. Small angle x-ray diffraction measurements have been performed on unoriented samples and samples previously subjected to the action of magnetic fields (**H**). Diffraction patterns show a diffuse inner halo at 80–140 Å and a sharp outer ring at 38 Å. They reduce to spots in the equator for oriented samples with the x-ray beam parallel to **H**; no diffraction figure is produced for the x-ray beam perpendicular to **H**. NMR spectra indicate that the director of the phase orients perpendicular to **H**. These results show that this lyomesophase has a structure not previously encountered. A model of finite planar micelles surrounded by water is proposed. In this model the micelles consist of a bilayer in the form of platelets, probably disk shaped. These platelets align in presence of magnetic fields, with their plane parallel to **H**, and further orientational restrictions are imposed by the container; they tend to be parallel and some periodicity appears in the direction of the director of the phase, perpendicular to the plane of polar heads. The mesophase satisfies the definition for nematics taking into account periodicities induced in nematic phases by magnetic fields.

J. Chem. Phys. **71**, 2940 (1979)

... mistura quaternária ....

Mol. Cryst. Liq. Cryst., 1981, Vol. 74, pp. 109–119
0026-8941/81/7404–0109 $06.50/0

Study of Type I Lyomesophases by X-ray Diffraction†

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(*Received July 25, 1980; in final form January 20, 1981*)

Type I lyomesophase LK (K laureate/KCl/water) and CDS (Cs decyl sulfate/$CsNO_3$/water) were studied by small angle X-ray diffraction and polarized optical microscopy. Different containers were used and samples studied under the influence of applied magnetic and electric fields. Residual magnetic orientation, obtained in thicker LK samples, gave diffraction results compatible with a model of finite cylinders for the amphiphilic micelles; only an inner band in the region of 140 Å is presented in this case. The same sample in presence of an electric field of 14 kV/cm presents a weak outer band at 43 Å. Surface effects in thinner samples correspond to the strengthening of the outer band, which has been associated with clustering of the cylinders and segregation of water. Surface effects are stronger in LK than in CDS. These results indicate that the interaction with the surface is of electrostatic origin.

Mol. Cryst. Liq. Cryst. 74, 109 (1981)
Misturas quaternárias ....

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 129–141
0026-8941/83/9502–0129/$18.50/0

Study of a Phase Transition in a Lyotropic Liquid Crystal of Potassium Laurate/KCl/ Water by X-ray Diffraction and Optical Microscopy

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(Received December 15, 1983)

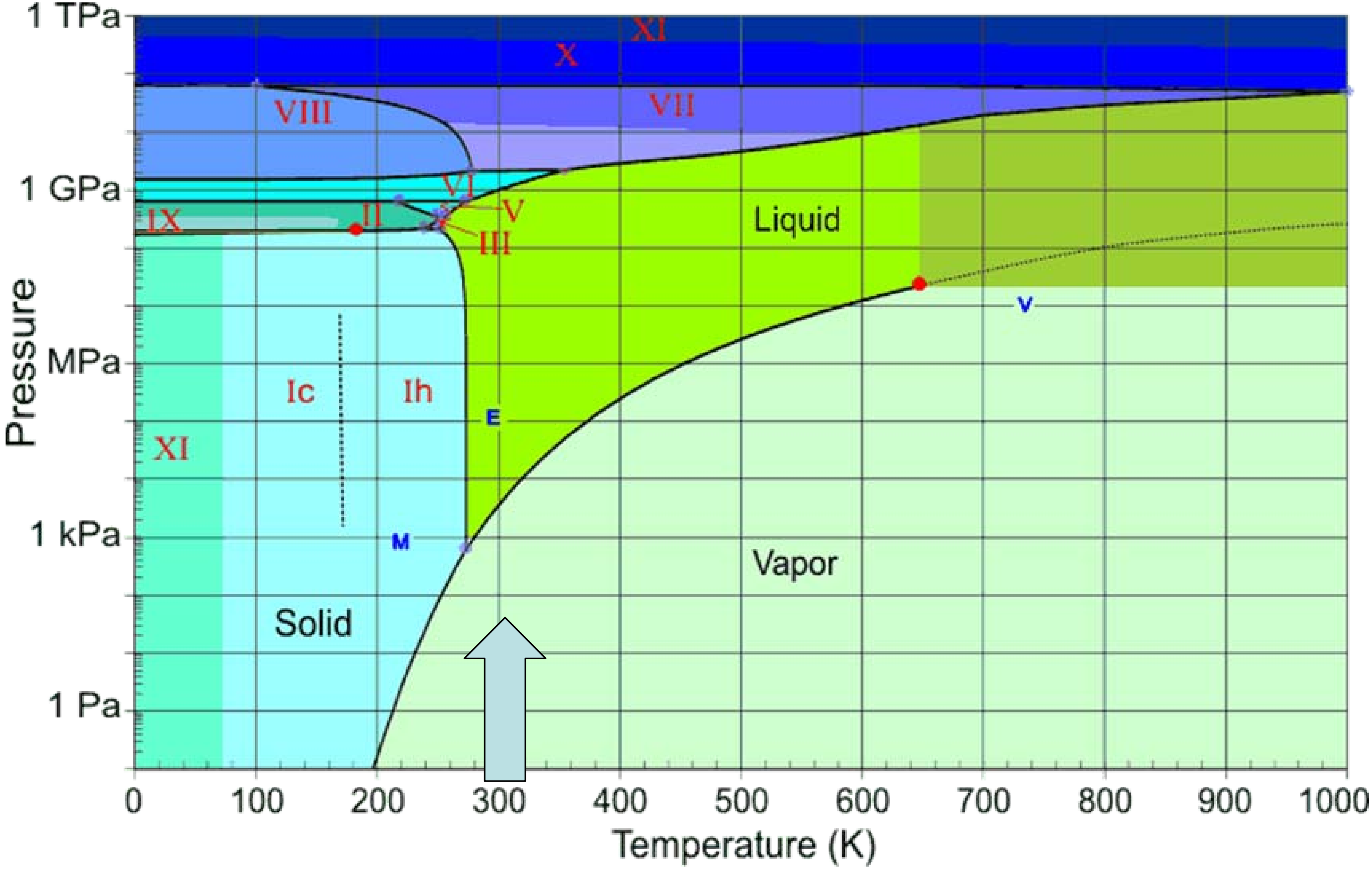
Type I lyomesophase of potassium laurate was studied by X-ray diffraction and optical microscopy techniques with temperature variation. For increasing temperatures from 22°C to about 54°C only a nematic phase (N) was observed. For temperatures between 60°C and 74°C it was observed coexistence of an isotropic (I) and hexagonal (H_α) phase with lattice parameter (47 ±1) Å. For temperatures between 54°C and 60°C, in some experiments, it was observed the coexistence of phases N and H_α. A binary system of potassium laurate/water (H_α phase) was also studied by both techniques at room temperature; the lattice parameter is (44.9 ±0.5) Å. Possible models for the N phase are discussed and compared with the obtained lattice parameters and associated micellar radius.

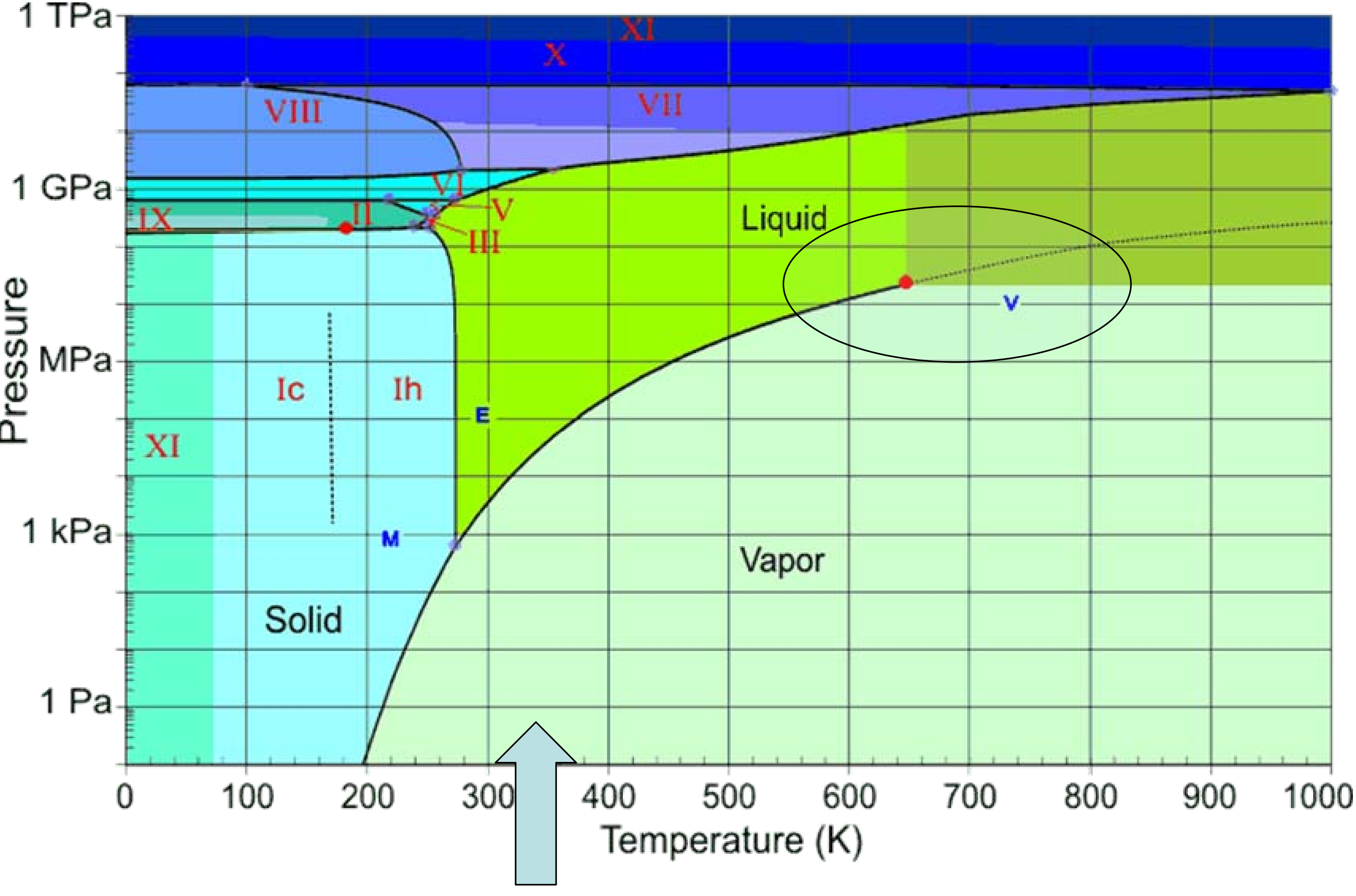
Mol. Cryst. Liq. Cryst. 95, 129 (1983)
... mistura ternária ....

Diagrama de fases da água

A “fase sólida” é complexa (onze fases sólidas diferentes!). A pressões mais altas a situação é complicada (talvez haja um segundo ponto crítico). Muitas fases sólidas permanecem metaestáveis a pressões baixas

(**1 atm = 0,1 MPa**; note a escala logarítmica do eixo das pressões)





1 TPa
1 GPa
MPa
1 kPa
1 Pa
Pressure
XI
X
VIII
VII
VI
V
II
IX
III
Liquid
V
Ic
Ih
E
XI
M
Vapor
Solid
0
100
200
300
400
500
600
700
800
900
1000
Temperature (K)

VOLUME 92, NUMBER 25 PHYSICAL REVIEW LETTERS week ending 25 JUNE 2004

Phase Diagram of Water from Computer Simulation

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(Received 18 November 2003; published 22 June 2004)

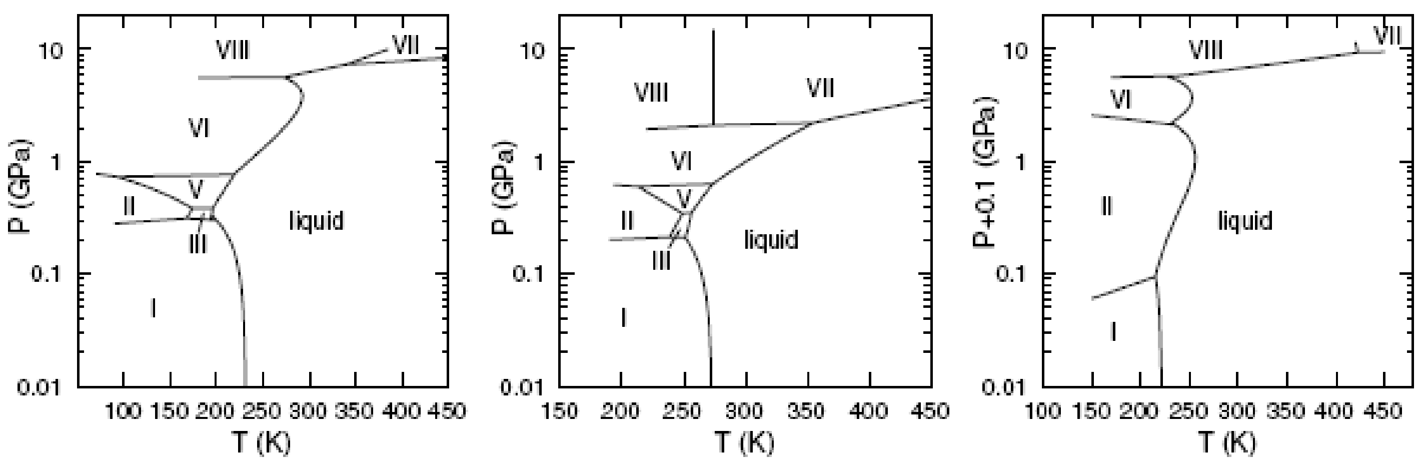
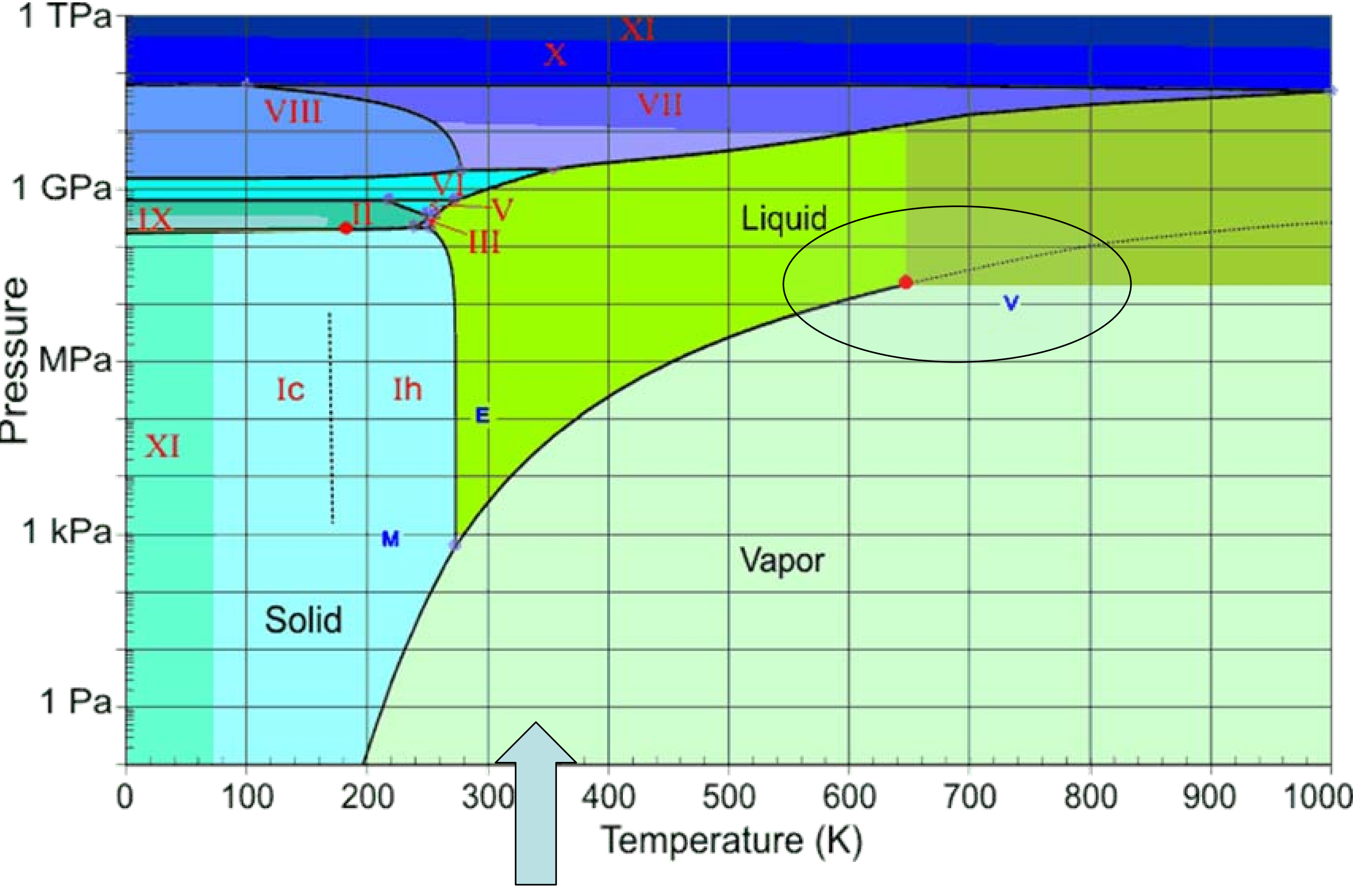
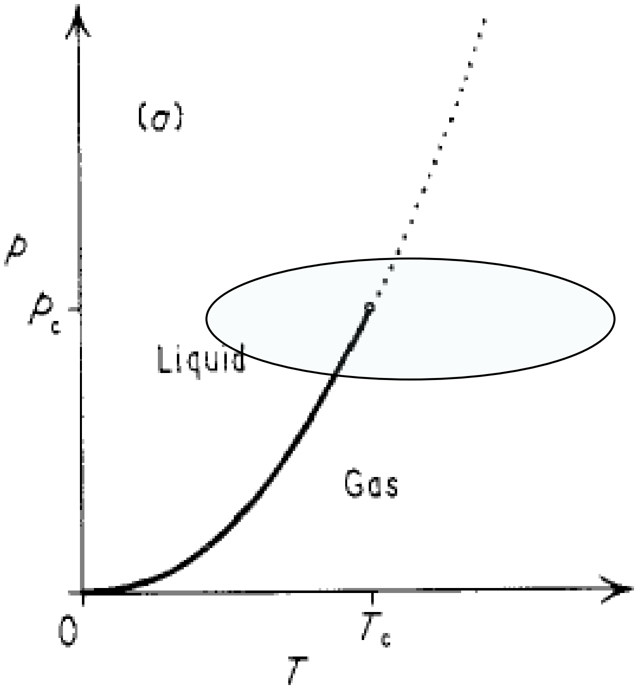


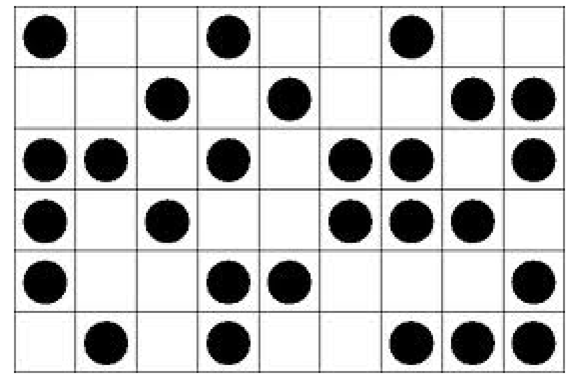
diagrama experimental

Falar com Sylvio Canuto, Kaline Coutinho, ...



1 TPa
1 GPa
MPa
1 kPa
1 Pa
Pressure
0
100
200
300
400
500
600
700
800
900
1000
Temperature (K)
XI
X
VIII
VII
VI
V
II
III
IX
Liquid
V
Ic
Ih
E
XI
M
Vapor
Solid





Gás de rede: V células e N partículas

configuração microscópica do sistema:

$$\{t_i\} = \{t_1, t_2, ..., t_V\}\ , \text{ com } t_i = 0 \text{ ou } 1$$

energia de um par i, j:

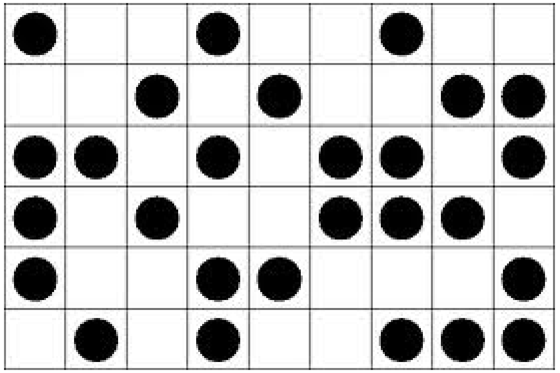
$$-\epsilon t_i t_j$$

energia da configuração $\{t_i\}$:

$$H(\{t_i\}) = \sum_{(i,j)} -\epsilon t_i t_j$$

probabilidade da configuração $\{t_i\}$:

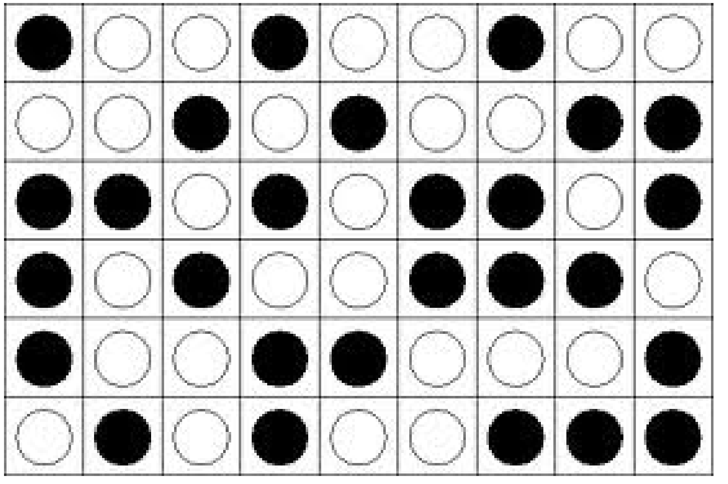
$$p(\{t_i\}) = \frac{1}{Z} \exp\left[-\beta H(\{t_i\})\right], \quad \beta = \frac{1}{k_B T}$$



V células
N partículas

justificativa da equação de van der Waals

Mistura binária (concentrada)



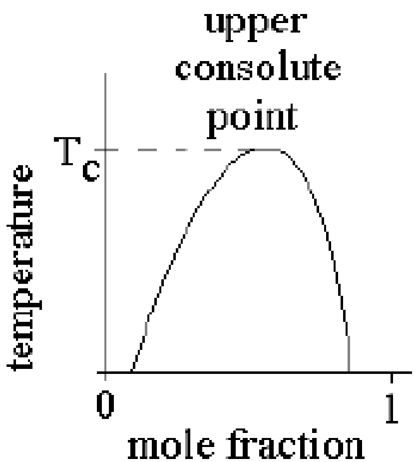
Mistura binária $\longrightarrow \lambda_i = +1$ (tipo A) ou $\lambda_i = -1$ (tipo B)

energia da configuração microscópica $\{\lambda_i\}$:

$$\mathcal{H} = -\sum_{(i,j)} \left[A\lambda_i\lambda_j + \frac{1}{2}B\left(\lambda_i + \lambda_j\right) + C \right]$$

então

$$\begin{aligned} w_{AA} &= A + B + C \\ w_{BB} &= A - B + C \\ w_{AB} &= w_{BA} = -A + C \end{aligned}$$



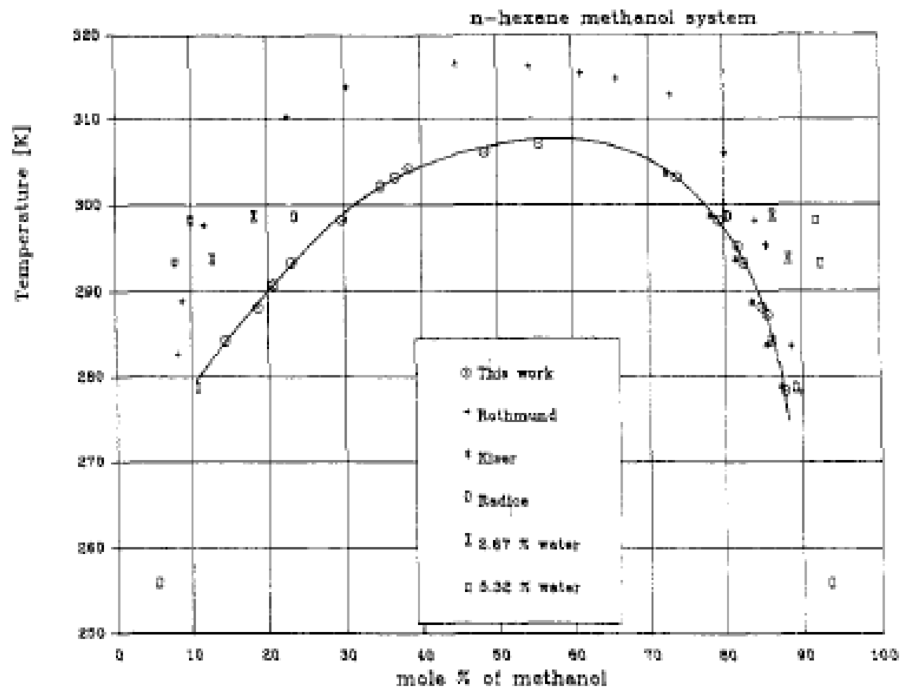


Figure 2. Binary LLE data for the *n*-hexane–methanol system as a function of temperature: comparison with literature data.

P. Alessi et al. J. Chem. Eng. Data 1989

Mistura binária de ferrofluidos (de spin ½)

$$\mathcal{H} = -\sum_{(i,j)} \left[A\lambda_i\lambda_j + \frac{1}{2}B\left(\lambda_i + \lambda_j\right) + C \right] \sigma_i\sigma_j$$

dois conjuntos de graus de liberdade:

posicionais: $\{\lambda_i\}$ com $\lambda_i = +1$ (tipo A) ou $\lambda_i = -1$ (tipo B)
orientacionais: $\{\sigma_i\}$ com $\sigma_i = +1$ (spin para cima) ou $\sigma_i = -1$ (spin para baixo)

função canônica de partição

$$Z = \sum_{\{\lambda_i\}} \sum_{\{\sigma_i\}} \exp\left[-\beta\mathcal{H}\right]$$

Modelo de Maier-Saupe-Zwanzig com discos e cilindros

$$\mathcal{H} = -\sum_{(i,j)} \left[A\lambda_i\lambda_j + \frac{1}{2}B\left(\lambda_i + \lambda_j\right) + C \right] \sum_{\mu,\nu} S_i^{\mu\nu} S_j^{\mu\nu}$$

dois conjuntos de graus de liberdade:

posicionais: $\{\lambda_i\}$ com $\lambda_i = +1$ (tipo A) ou $\lambda_i = -1$ (tipo B)

orientacionais: $\{S_i^{\mu\nu}\}$, com três possibilidades para cada $S_i^{\mu\nu}$

$$S_i = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \text{ ou } S_i = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \text{ ou } S_i = \begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

objetos intrinsecamente uniaxiais

Observation of a Biaxial Nematic Phase in Potassium Laurate-1-Decanol-Water Mixtures

L. J. Yu and A. Saupe

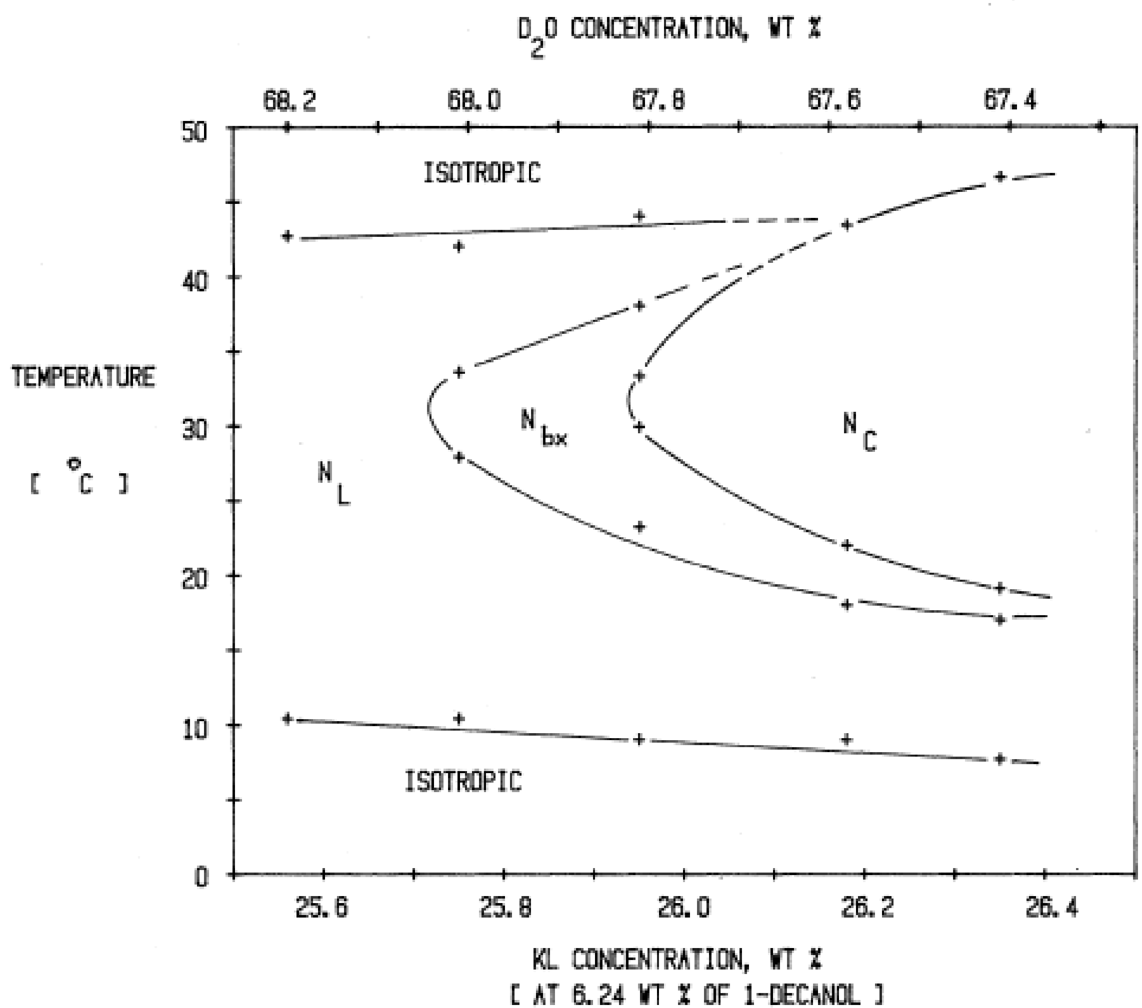


FIG. 1. Phase diagram of the potassium laurate (KL)–1-decanol–D_2O system.

Observation of a Biaxial Nematic Phase in Potassium Laurate–1-Decanol–Water Mixtures

L. J. Yu and A. Saupe

VOLUME 45, NUMBER 12 PHYSICAL REVIEW LETTERS 22 SEPTEMBER 1980

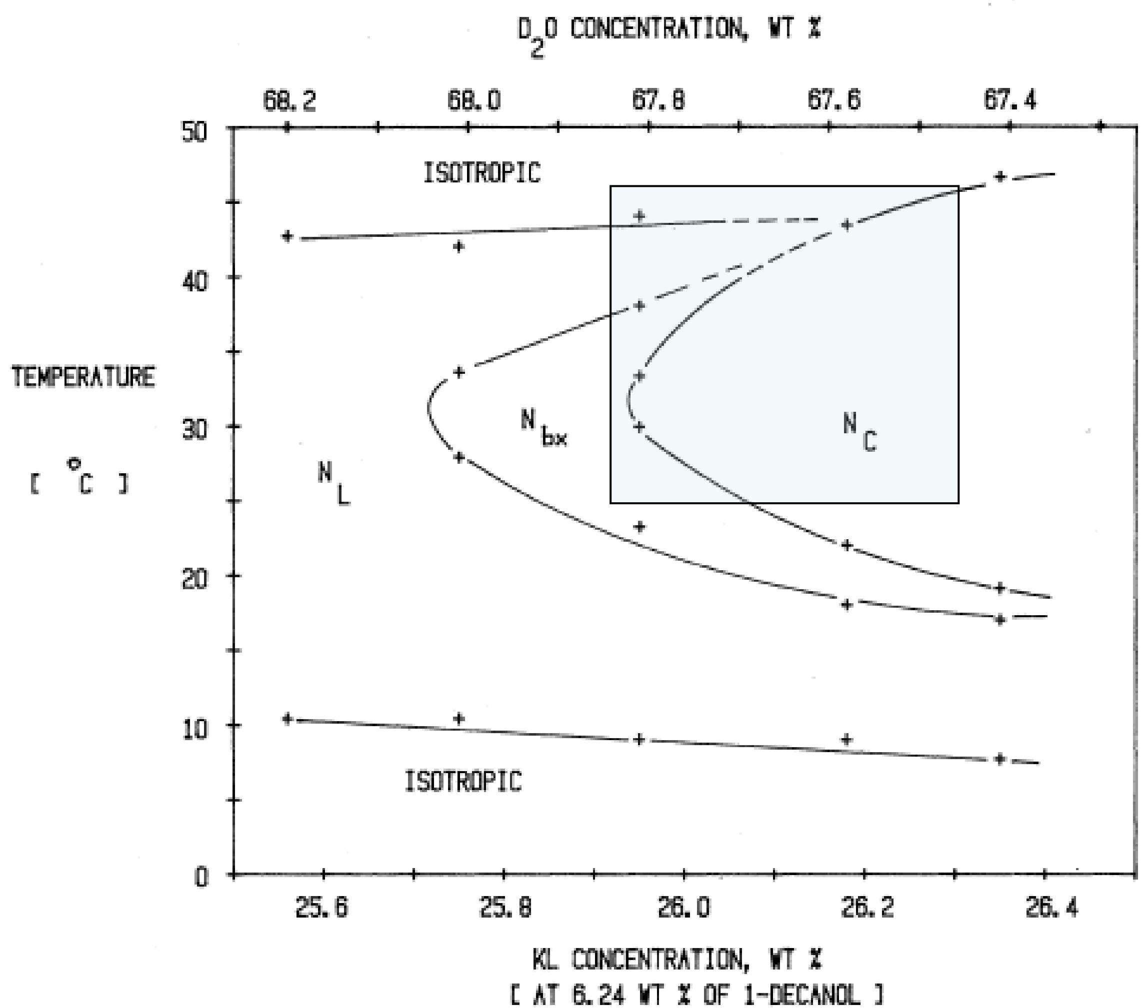
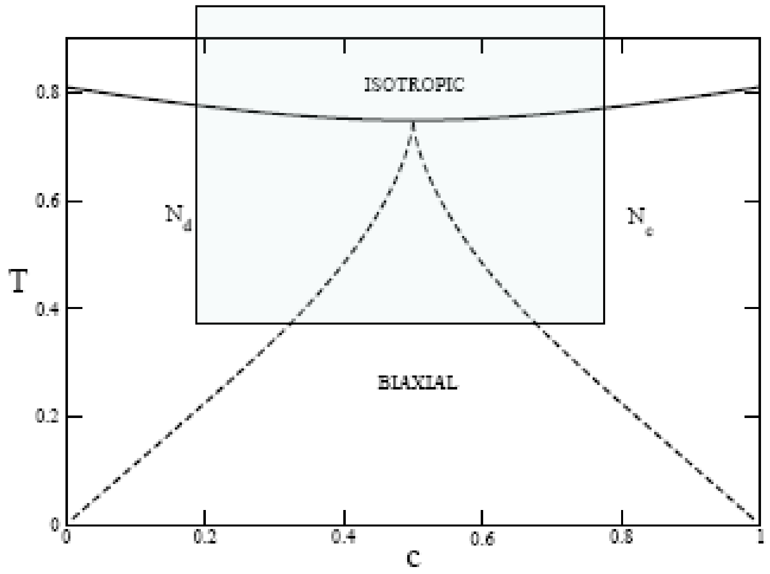


FIG. 1. Phase diagram of the potassium laurate (KL)–1-decanol–D_2O system.



Statistical models of mixtures with a biaxial nematic phase

E. do Carmo, D. B. Liarte, SRS – PRE 2010

nossos trabalhos

1. Statistical models of mixtures with a biaxial nematic phase, E. do Carmo, D. B. Liarte, SRS
PRE 81, 062701 (2010)
- competição entre variáveis lentas (quenched) e rápidas ou termalizadas (annealed) – introdução de dois reservatórios …

2. Phase diagram of a model for a binary mixture of nematic molecules on a Bethe Lattice, E. do Carmo, A. P. Vieira, SRS
PRE 83, 011701 (2011)
- cálculos para o sistema "annealed"

3. Elastic Maier-Saupe-Zwanzig model and some properties of nematic elastomers, D. B. Liarte, SRS, C. S. O. Yokoi
PRE 84, 011124 (2011)
- novos materiais: polímeros nemáticos + borracha não lienar …

Em andamento: modelos com variáveis contínuas; modelo MSZ intrinsecamente biaxial; polimorfismo "annealed" …

PHYSICAL REVIEW E **81**, 062701 (2010)

Statistical models of mixtures with a biaxial nematic phase

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(Received 20 October 2009; revised manuscript received 14 January 2010; published 4 June 2010)

We consider a simple Maier-Saupe statistical model with the inclusion of disorder degrees of freedom to mimic the phase diagram of a mixture of rodlike and disklike molecules. A quenched distribution of shapes leads to a phase diagram with two uniaxial and a biaxial nematic structure. A thermalized distribution, however, which is more adequate to liquid mixtures, precludes the stability of this biaxial phase. We then use a two-temperature formalism, and assume a separation of relaxation times, to show that a partial degree of annealing is already sufficient to stabilize a biaxial nematic structure.

PHYSICAL REVIEW E **83**, 011701 (2011)

Phase diagram of a model for a binary mixture of nematic molecules on a Bethe lattice

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(Received 2 September 2010; published 11 January 2011)

We investigate the phase diagram of a discrete version of the Maier-Saupe model with the inclusion of additional degrees of freedom to mimic a distribution of rodlike and disklike molecules. Solutions of this problem on a Bethe lattice come from the analysis of the fixed points of a set of nonlinear recursion relations. Besides the fixed points associated with isotropic and uniaxial nematic structures, there is also a fixed point associated with a biaxial nematic structure. Due to the existence of large overlaps of the stability regions, we resorted to a scheme to calculate the free energy of these structures deep in the interior of a large Cayley tree. Both thermodynamic and dynamic-stability analyses rule out the presence of a biaxial phase, in qualitative agreement with previous mean-field results.

PHYSICAL REVIEW E **84**, 011124 (2011)

Elastic Maier-Saupe-Zwanzig model and some properties of nematic elastomers

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(Received 20 April 2011; published 18 July 2011)

We introduce a simple mean-field lattice model to describe the behavior of nematic elastomers. This model combines the Maier-Saupe-Zwanzig approach to liquid crystals and an extension to lattice systems of the Warner-Terentjev theory of elasticity, with the addition of quenched random fields. We use standard techniques of statistical mechanics to obtain analytic solutions for the full range of parameters. Among other results, we show the existence of a stress-strain coexistence curve below a freezing temperature, analogous to the P-V diagram of a simple fluid, with the disorder strength playing the role of temperature. Below a critical value of disorder, the tie lines in this diagram resemble the experimental stress-strain plateau and may be interpreted as signatures of the characteristic polydomain-monodomain transition. Also, in the monodomain case, we show that random fields may soften the first-order transition between nematic and isotropic phases, provided the samples are formed in the nematic state.