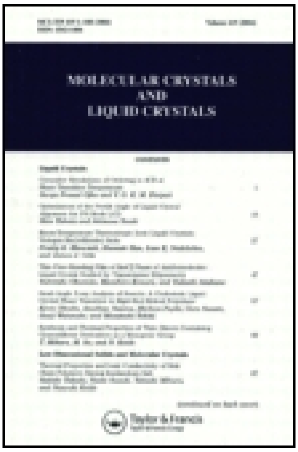
This article was downloaded by: [University of California, San Diego]
On: 20 August 2012, At: 22:02
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Elastic Constants of Binary Mixtures of Uniaxial Nematic Liquid Crystals

Andrzej Kapanowski [a] & Krzysztof Sokalski [a]
[a] Institute of Physics, Jagellonian University, ulica Reymonta 4, 30-059, Cracow, Poland

Version of record first published: 04 Oct 2006

To cite this article: Andrzej Kapanowski & Krzysztof Sokalski (1997): Elastic Constants of Binary Mixtures of Uniaxial Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 431-436

To link to this article: http://dx.doi.org/10.1080/10587259708041799

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 431–436
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

ELASTIC CONSTANTS OF BINARY MIXTURES OF UNIAXIAL NEMATIC LIQUID CRYSTALS

ANDRZEJ KAPANOWSKI and KRZYSZTOF SOKALSKI
Institute of Physics, Jagellonian University, ulica Reymonta 4,
30-059 Cracow, Poland

Abstract The statistical theory of elastic constants of binary liquid crystalline mixtures is applied to mixture of rodlike molecules of different length and to mixture of rodlike and disclike molecules. Elastic constants are calculated versus concentration at the constant temperature. Discontinous change from disclike to rodlike properties of the mixture is predicted for mixture of rodlike and disclike molecules.

Downloaded by [University of California, San Diego] at 22:02 20 August 2012

INTRODUCTION

The Frank elastic constants are the material constants of liquid crystals which appear in various contexts in numerous applications[1] and it is important to have accurate molecular expressions for them. The statistical theory of the elastic constants of one-component liquid crystals was derived by Poniewierski and Stecki (PS)[2] in 1979. The PS method require the direct correlation function $c(1,2)$ and its dependence on the mutual molecular orientations. The analysis of the adequacy of the PS theory to explain the simulation results and the experimental results on prolate and oblate results was presented by Tjipto-Margo at all[3]. We can draw a conclusion that the PS theory provide working expressions for the Frank constants of the one-component liquid crystals.

As far as technical applications are concerned, it is hard to find chemically pure substances with the desired properties. That is why mixtures are widely used and it is important to have working expressions for the Frank constants in this case.

On the base of the microscopic theory of binary mixtures of uniaxial nematic liquid crystals[4] we derived the microscopic expressions for the Frank constats of binary mixtures[5]. In the limit of one-component substance it gives the PS result provided that we replace the function $c(1,2)$ with the Mayer function f_{12}. In this limit and with the special interaction potential energy our theory also reproduces the results by Ruijgrok at all[6].

Our aim in this paper is to apply the formulae for the Frank constats to binary mixtures of prolate and oblate molecules.

MODEL

In the begining we mention the assumptions of our model.

Downloaded by [University of California, San Diego] at 22:02 20 August 2012

1. Considered mixture consists of two types of molecules (A, B) with the $D_{\infty h}$ symmetry group. Orientations are described by two angles ϕ_I and θ_I or by a unit vector $\underline{\Omega}_I$, $I = A, B$. Later we will refer to prolate and oblate molecules as rods and discs, respectively.

2. We assume small densities approximation and we take only two-body short-range order interactions into account. The potential energies Φ_{12}^{IJ} depend on a vector of the distance between molecules $\underline{u} = (u_1, u_2, u_3)$ and orientations of molecules. We do not take account of the nematic-substrate interfacial coupling which create the anchoring energy (the case of a very weak anchoring). Thus the same expression will describe the director orientation both at the interfacial surface and inside the sample.

3. The mixture has symmetry of the $D_{\infty h}$ group. Therefore we use only one director of the mean field $\underline{n}(\underline{r})$ in phenomenological equations for both types of molecules.

4. We assume that a deformation of a sample is small and the mean field is close the homogeneous distribution $\underline{n}^{(0)} = (0, 0, 1)$.

Elastic Constants

We have derived the following general expressions for the Frank constants[5] ($s = 1, 2, 3$)

$$\beta K_s = \frac{1}{2} \int d\underline{\Omega}_1 \, d\underline{\Omega}_2 \, d\underline{u} \, u_s^2 \, \Omega_{1x} \, \Omega_{2x} \, W_{12}, \tag{1}$$

where

$$W_{12} = \sum_{I,J=A,B} f_{12}^{IJ} \, G'_{0I}(\underline{n}^{(0)} \cdot \underline{\Omega}_1) \, G'_{0J}(\underline{n}^{(0)} \cdot \underline{\Omega}_2), \tag{2}$$

$G_{0I}(\cos\theta_I) = f_I(\cos\theta_I) \, N_I/(4\pi V)$ for $I = A, B$ are the one particle distribution functions for homogeneous phases; they have the normalization $\int_0^1 dx \, f_I(x) = 1$, N_I denotes a number of molecules I in volume V, f_{12}^{IJ} are the Mayer functions $f_{12}^{IJ} = \exp(-\beta\Phi_{12}^{IJ}) - 1$, $\beta = 1/(k_B T)$. Let us define also concentrations $x_I = N_I/(N_A + N_B)$ which measure the portion ot the molecules I in the mixture. The variable $x_A \equiv x$ is assumed to be independent.

For the sake of simplicity we consider the Square-Well Potential Energy of the form $\Phi_{12}^{IJ}(r/\sigma^{IJ})$ with

$$\sigma^{IJ} = \sigma_0^{IJ} + \sigma_{11}^{IJ}(\underline{\Delta} \cdot \underline{\Omega}_1)^2 + \sigma_{12}^{IJ}(\underline{\Delta} \cdot \underline{\Omega}_2)^2 + \sigma_2^{IJ}(\underline{\Omega}_1 \cdot \underline{\Omega}_2)^2, \tag{3}$$

where $\underline{u} = |\underline{u}| \, \underline{\Delta}$ and

$$\Phi_{12}^{IJ}(r/\sigma^{IJ}) = \begin{cases} +\infty \; for \; (r/\sigma^{IJ}) < 1; \\ -\epsilon_{SW} \; for \; 1 < (r/\sigma^{IJ}) < R_{SW}; \\ 0 \; for \; (r/\sigma^{IJ}) > R_{SW}; \end{cases} . \tag{4}$$

Note that the parameter ϵ_{SW} determines the energy scale whereas the σ^{IJ} determines the scale of length and its unit has been chosen $1 \mathring{A} = 10^{-10} m$. The elastic

Downloaded by [University of California, San Diego] at 22:02 20 August 2012

constants will be given in $\epsilon_{SW}/(1\mathring{A})$. The distribution function f_I can be expanded in an infinite series with respect to Legendre polynomians

$$f_I(x) = \sum_{j-even} (2j+1) \langle P_j \rangle_I \, P_j(x) \tag{5}$$

where the order parameters are defined as

$$\langle P_j \rangle_I = \int_0^1 dx \, P_j(x) \, f_I(x). \tag{6}$$

We insert the expansion (5) into the general expressions for the elastic constants (1) and get ($s = 1, 2, 3$)

$$\beta K_s = \sum_{I,J=A,B} \sum_{j,k-even} \eta^{IJ} \, F^{IJ}_{s,jk} \, \langle P_j \rangle_I \, \langle P_k \rangle_J, \tag{7}$$

$$\eta^{IJ} = (\sigma_0^{IJ})^5 \, B_4^*(T^*) \, (\pi^3/2) \, N_I N_J/(4\pi V)^2. \tag{8}$$

We calculated the coefficients $F^{IJ}_{s,jk}$ ($j, k = 2, 4, 6, 8, 10$) and the order parameters according to the Hammerstein-Onsager equation[5]. Note that only a finite number of them is necessary. The function $B_4^*(T^*)$ belongs to the set of functions defined as

$$B_s^*(T^*) = \int_0^\infty dx \, x^s \, f_{12}(x) = \int_0^\infty dx \, x^s \left[\exp(-\beta \Phi_{12}^{IJ}(x)) - 1\right], \tag{9}$$

where $T^* = 1/(\beta \epsilon_{SW})$ is a dimensionless temperature. For the case of the Square-Well Potential Energy we have

$$B_s^*(T^*) = \frac{1}{s+1} \left[(\exp(1/T^*) - 1)(R_{SW}^{s+1} - 1) - 1 \right]. \tag{10}$$

RESULTS

We considered two mixtures with a constant density equal 1/5 of the close-packed density and $R_{SW} = 2$. There is a close relation between dimesions of the molecules and the parameters σ_i^{IJ}. We have chosen the following set of this parameters

	σ_0^{AA}	σ_1^{AA}	σ_2^{AA}	σ_0^{BB}	σ_1^{BB}	σ_2^{BB}
Mixture 1	4	3	0	3	9/2	0
Mixture 2	4	3	0	10	-4	0

The remaining parameters satisfy the relations[4]

$$\sigma_{11}^{II} = \sigma_{12}^{II} \equiv \sigma_1^{II}, \tag{11}$$

$$\sigma_0^{IJ} = (\sigma_0^{II} + \sigma_0^{JJ})/2, \tag{12}$$

$$\sigma_{11}^{IJ} = (2\sigma_1^{II} + \sigma_2^{II} - \sigma_2^{JJ})/2, \tag{13}$$

$$\sigma_{12}^{IJ} = (2\sigma_1^{JJ} + \sigma_2^{JJ} - \sigma_2^{II})/2, \tag{14}$$

$$\sigma_2^{IJ} = (\sigma_2^{II} + \sigma_2^{JJ})/2. \tag{15}$$

Downloaded by [University of California, San Diego] at 22:02 20 August 2012

The shape of a molecule is represented by an equipotential surface of the potential energy Φ_{12}^{II} [4,6].

Mixture of Rodlike Molecules of Different Length

The mixture 1 consists of short rods (A) and long rods (B). The transition temperatures of unary systems from isotropic to nematic phase are $T_A^* = 0.555$ and $T_B^* = 0.852$. We considered the mixture at the temperature $T^* = 0.54$. On changing the composition of the mixture we were looking for the order parameters. It appeared that there were three solutions for any x_A between 0 and 1:

1. The stable nematic solution with $\langle P_2 \rangle_A > 0$ and $\langle P_2 \rangle_B > 0$.
2. The nonstable isotropic solution with $\langle P_2 \rangle_I = 0$.
3. The stable nematic solution with $\langle P_2 \rangle_A < 0$ and $\langle P_2 \rangle_B < 0$.

We considered the stability of all solutions against perturbations of nematic symmetry. The lowest energy stable solution was the solution (1) for all x_A. The elastic constants K_i are presented in Figure 1.

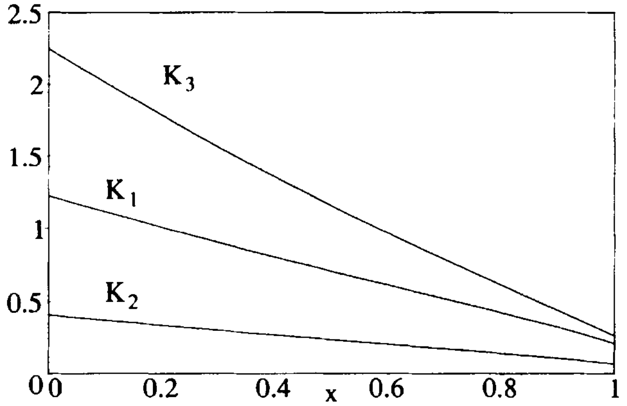


FIGURE 1 Elastic constants of the mixture 1 at $T^* = 0.54$.

As one could expect we obtained a continous change of properties of the mixture.

Mixture of Rodlike and Disclike Molecules

The mixture 2 consists of short rods (A) and discs (B). The transition temperatures of unary systems from isotropic to nematic phase are $T_A^* = 0.555$ and $T_B^* = 0.734$. We considered the mixture at the temperature $T^* = 0.52$. We were changing the composition of the mixture and we looked for the order parameters. It appeared that there were three solutions for any x_A between 0 and 1:

1. The nonstable isotropic solution with $\langle P_2 \rangle_I = 0$.

2. The stable nematic solution with $\langle P_2 \rangle_A > 0$ and $\langle P_2 \rangle_B < 0$.
3. The stable nematic solution with $\langle P_2 \rangle_A < 0$ and $\langle P_2 \rangle_B > 0$.

We considered the stability of all solutions against perturbations of nematic symmetry. The lowest energy stable solution was the solution (3) or (2) for $0 < x_A < 0.65$ or $0.65 < x_A < 1$, recpectively. This solution was used to calculate the elastic constants of the mixture. The results are presented in Figure 2.

Downloaded by [University of California, San Diego] at 22:02 20 August 2012

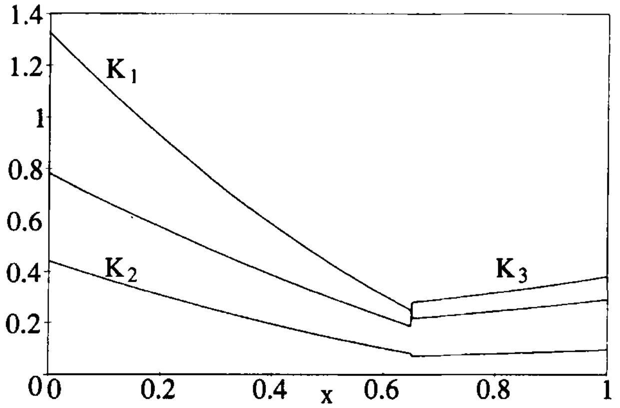


FIGURE 2 The elastic constants of the mixture 2 at $T^* = 0.52$.

We observe a discontinous change from disclike to rodlike properties of the mixture at $x_A = 0.65$ on increasing a portion of rods in the mixture.

CONCLUSIONS

We presented applications of the statistical theory of elastic constants[5] to two model binary mixtures. For the mixture of prolate molecules of different length a continous change of rodlike properties on changing concentration was obtained. The most interesting result was obtained for the mixture of prolate and oblate molecules. We predicted a discontinous change from disclike to rodlike properties at a certain concentration when a portion of prolate molecules in the mixture was increasing.

We conclude that despite of its limitations the considered theory of elastic constant can be very helpful for studying binary mixtures of uniaxial nematic liquid crystals. An extension of this theory to biaxial systems is in progress.

REFERENCES

1. P. G. de Gennes, J. Prost, The Physics of Liquid Crystals (Carendon Press, Oxford, 1993).

2. A. Poniewierski, J. Stecki, Mol. Phys., 38, 1931 (1979).

3. B. Tjipto-Margo, G. T. Evans, M. P. Allen, D. Frenkel, J. Phys. Chem., 96, 3942 (1992).

4. A. Chrzanowska, K. Sokalski, Phys. Rev. E, 51, 2295 (1995).

5. A. Kapanowski, K. Sokalski, submitted to Physica A.

6. K. Sokalski, Th. W. Ruijgrok, Physica A, 113, 126 (1982).

Downloaded by [University of California, San Diego] at 22:02 20 August 2012