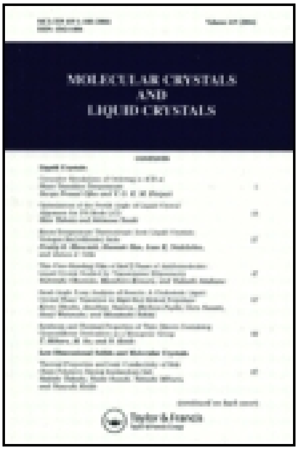

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: Hatsuo Kimura , Masahito Hosino & Huzio Nakano (1981): Molecular Statistical Theory of the Frank Elastic Constants of Liquid Crystals, Molecular Crystals and Liquid Crystals, 74:1, 55-69

To link to this article: http://dx.doi.org/10.1080/00268948108073694

Mol. Cryst. Liq. Cryst., 1981, Vol. 74, pp. 55–69
0026-8941/81/7404-0055 \$06.50/0

Printed in the United States of America

Molecular Statistical Theory of the Frank Elastic Constants of Liquid Crystals†

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(*Received September 29, 1980; in final form December 1, 1980*)

The Frank elastic constants K_1, K_2, K_3 are calculated in the mean field approximation by assuming that the intermolecular force is the sum of hard rod repulsion (length L and width D) and Maier-Saupe's type attraction. The main conclusions are as follows. (1) The inequalities $K_3 > K_1 > K_2$ necessarily hold. (2) All the K_i's are nearly proportional to the square of the orientational order parameter S. (3) In thermotropic system, K_i/S^2, $K_1/\bar{K}$ and $K_2/\bar{K}$ ($\bar{K}$: mean elastic constant) increase slowly and $K_3/\bar{K}$, K_3/K_1 and K_2/K_1 decrease slowly with temperature. At the clearing temperature T_c, K_3/K_1 increases and K_2/K_1 decreases with L/D, whereas $\bar{K}/kT_c$ is nearly constant for $L/D = 3 \sim 5$. These tendencies agree fairly well with the observations on liquid crystals with almost rigid structure. (4) In the lyotropic system in which $L/D \gg 1$, $K_1/3 = K_2 = cLk_BT/3\pi D^2$ and $K_1/K_3 = 4D/5cL$ are obtained (c: packing fraction). The estimate for PBLG solution nearly agrees with the recent experimental data.

1 INTRODUCTION

Several authors have proposed molecular statistical expressions for the Frank elastic constants K_1, K_2, K_3. As they have only assumed either of attractive and repulsive intermolecular forces, the results can not be immediately applied to discuss the observation on real liquid crystals.

Assuming an attractive intermolecular potential due to the dispersion force, Nehring and Saupe[1] got the results: $K_i \propto S^2$ and $K_1 : K_2 : K_3 = 5 : 11 : 5$ (S: the nematic order parameter). Although K_i is approximately proportional to S^2 experimentally, the orders of the magnitude of K_i's contradict with the inequalities $K_3 > K_1 > K_2$ which have been confirmed experimentally in many liquid crystals.

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† Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

On the other hand, Priest[2] and Straley[3] have discussed the elastic constants for the hard rod system according to Onsager. They derived the above inequalities between K_i's, but could not reproduce the thermotropic phase transitions in liquid crystals and therefore the temperature dependences of the elastic constants.

In the present paper, we derive the expressions for the Frank elastic constants by assuming that the intermolecular force is the sum of hard core repulsion and the Maier-Saupe type attraction.

Since Alben[4] calculated the properties of a hard rod liquid model with attractive interaction energies to discuss the nematic-isotropic phase transition, a few authors have studied a variety of model systems of the same sort.[5]

The present authors showed that this type of model can account for the characteristic propeties of the nematic-isotropic phase transition of real liquid crystals at least qualitatively.[6] The models with proper modifications were also applied to discuss the cholesteric[7] and smectic[8] phases and it was found that many properties unexplained by the pure attractive intermolecular force could be well understood.

2 EXPRESSIONS FOR THE FRANK ELASTIC CONSTANTS

We assume the intermolecular potential as

$$\phi_{ij} = \begin{cases} +\infty \text{ for the pair of } i\text{-th and } j\text{-th molecules intersecting with each other,} \\ -A(r_{ij})P_2(\cos\theta_{ij}) \text{ otherwise,} \end{cases} \tag{1}$$

where the shape of the molecule is assumed to be a rigid spherocylinder with length L and width D. The second line of (1) represents the Maier-Saupe type attraction, in which $A(r_{ij})$ is the strength of coupling, r_{ij} the distance between a pair of i-th and j-th molecules and $P_2(\cos\theta_{ij})$ is the second order Legendre polynomial as a function of the angle θ_{ij} between the largest principal axes of that pair. In the case of the director field given by

$$\left.\begin{aligned} n_x(\mathbf{r}) &= \sin(\mathbf{q}\cdot\mathbf{r}), \\ n_y(\mathbf{r}) &= 0, \\ n_z(\mathbf{r}) &= \cos(\mathbf{q}\cdot\mathbf{r}), \end{aligned}\right\} \tag{2}$$

the free energy can be expressed for small magnitude of $\mathbf{q}$, as

$$F_e = 1/2(K_1q_x^2 + K_2q_y^2 + K_3q_z^2), \tag{3}$$

where K_1, K_2 and K_3 are the Frank elastic constants for the splay, twist and bend distortions, respectively.

By making use of the method of symmetry breaking potential[9] in the lowest order or mean field approximation, the expressions for the Frank constants are obtained as

$$\left.\begin{aligned} K_1 &= \frac{1}{2}\left\{\frac{\tilde{A}}{k_BT} + 3\gamma_e n\left(1 - \frac{<P_4>}{S}\right)\right\}R^2S^2nk_BT, \\ K_2 &= \frac{1}{2}\left\{\frac{\tilde{A}}{k_BT} + \gamma_e n\left(1 - \frac{<P_4>}{S}\right)\right\}R^2S^2nk_BT, \\ K_3 &= \frac{1}{2}\left\{\frac{\tilde{A}}{k_BT} + 3\gamma_e n\left(1 + \frac{4<P_4>}{3S}\right)\right\}R^2S^2nk_BT, \end{aligned}\right\} \tag{4}$$

with

$$\tilde{A} \equiv n\int A(r_{ij})d\mathbf{r}_{ij}, \tag{5}$$

$$\gamma_e \equiv 5\pi DL^4/224R^2, \tag{6}$$

where n denotes the number density of molecules, R the mean distance between the pair of nearest neighbor molecules, and S and $<P_4>$ are the orientational order parameters defined below. The first and second terms in the respective expressions are the contributions from the attractive and repulsive interactions, respectively. On the basis of the present model, it has previously been shown[6] that the nematic phase is stable in the case

$$\Gamma \equiv \frac{\tilde{A}}{k_BT} + \gamma n > \Gamma_c = 4.54, \tag{7}$$

where the quantity

$$\gamma \equiv (5\pi DL^2/16)(1 - D/L)^2 \tag{8}$$

represents the excluded volume effect due to the hard core repulsion. The order parameter S has been determined from the self-consistent equation

$$\eta_0 = \Gamma I_1(\eta_0)/I_0(\eta_0) \equiv \Gamma S, \tag{9}$$

in the case of no distortion in the nematic phase,[6] where

$$I_n(\eta) \equiv \int_0^1 \{P_2(\cos\theta)\}^n \exp\{\eta P_2(\cos\theta)\}d(\cos\theta), \tag{10}$$

$$(n = 0, 1, \ldots)$$

Similarly, we have for $<P_4>$

$$<P_4> = \int_0^1 P_4(\cos\theta)\exp\{\eta_0 P_2(\cos\theta)\}d(\cos\theta)/I_0(\eta_0). \tag{11}$$

The calculated values of S, $<P_4>$ and $<P_4>/S$ are shown in Figure 1 as functions of Γ. By substituting these results into (4), we can obtain the Frank constants as functions of the temperature, the shape of molecule, and the interaction coupling.

It is easily seen that the expression (4) leads to the inequalities

$$K_3 > K_1 > K_2, \tag{12}$$

which have been confirmed experimentally in many liquid crystals: e.g. PAA and MBBA,[10] MBBA, MBCA, APAPA and MBAPB,[11] OHMBBA, APAPA-n($n = 2 - 5$),[12] PCH-n($n = 3, 5, 7$),[13] n-CB($n = 5 - 7$),[14] p,p'-di-n-alkylazoxybenzenes and p,p'-di-n-alkoxyazoxybenzenes.[15]

The mean elastic constant is obtained from (4) as

$$\bar{K} \equiv \frac{1}{3}(K_1 + K_2 + K_3) = \frac{1}{2}\left(\frac{\tilde{A}}{k_BT} + \frac{7}{3}\gamma_e n\right)R^2S^2nk_BT, \tag{13}$$

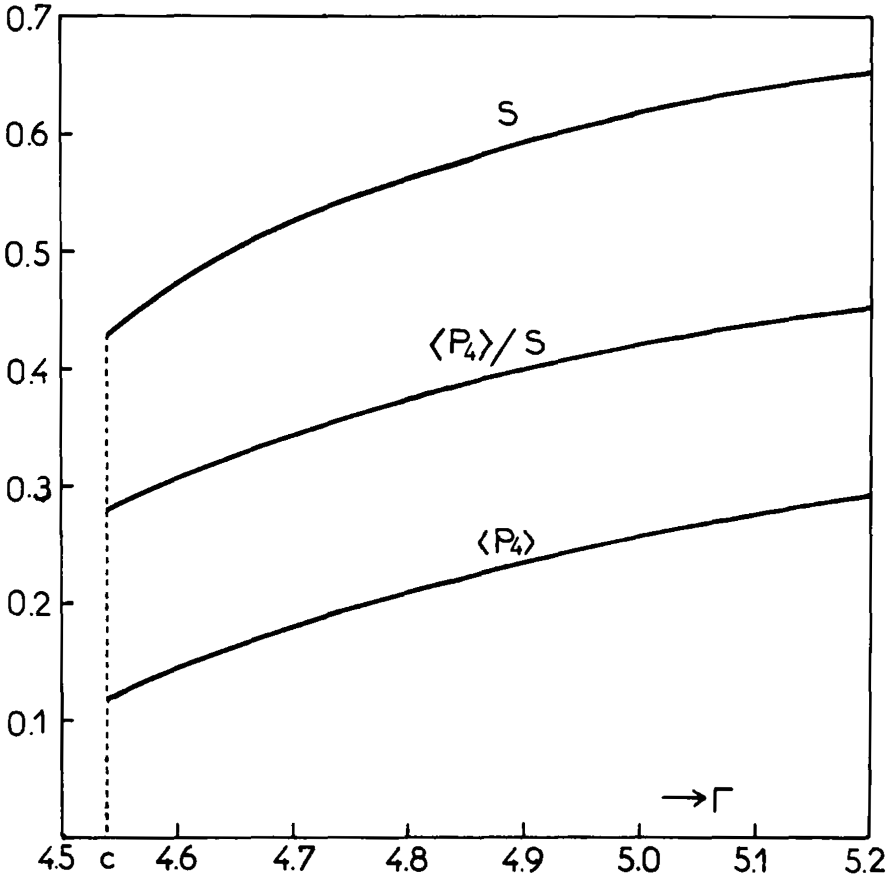

FIGURE 1 Calculated values of S, $<P_4>$, and $<P_4>/S$ as functions of Γ.

which is proportional to S^2. This agrees qualitatively with the observations in thermotropic liquid crystals.

On the basis of the inequality (7), the present model is regarded to represent a thermotropic system with the clearing temperature

$$T_c = (\tilde{A}/k_B)/(\Gamma_c - \gamma n), \tag{14}$$

so far as $\gamma n < \Gamma_c$. On the other hand, in case $\gamma n > \Gamma_c$, the nematic order appears at all temperatures and the model corresponds to a lyotropic system.

3 ELASTIC PROPERTIES OF THERMOTROPIC SYSTEM

We assume the parameters as follows: $L = 20\text{Å}$, $D = 5\text{Å}$, $T_c = 409\text{K}$ and $n = 2.68 \times 10^{21}\text{cm}^{-3}$, which are likely adequate for para-azoxyanisole (PAA).[6] Thus, we get

$$\left.\begin{aligned} \gamma n &= 2.96, & \gamma_e n &= 1.89, \\ R &= 8.9\text{Å}, & \tilde{A}/k_B T_c &= 1.58, \end{aligned}\right\} \tag{15}$$

where the relation $R = (6/n\pi)^{1/3}$ is assumed. The numerical results are shown in comparison with experimental data by de Jeu *et al.*[10] in Figure 2. The magnitudes and the trend of temperature variation of the calculated value are consistent with the observations fairy well. In fact, the character as shown in Figure 2 is widely recognized in various liquid crystals.

Several typical features of the result will be given in the following.

(1) Temperature dependences of $K_i/\bar{K}$

The temperature dependences of both K_i and $\bar{K}$ are mainly due to the factor S^2. The ratios $K_i/\bar{K}$ are expected to change, even if slightly, with temperature from (4) and (13). On the other hand, if only the intermolecular attraction is relevant to the elastic constants, the temperature dependence of the ratios $K_i/\bar{K}$ should disappear at all. Therefore, the effect of repulsion can be estimated from the temperature dependence of $K_i/\bar{K}$. The temperature dependences of $K_i/\bar{K}$ calculated from (4) and (13) with the use of the same parameters as before are shown in Figure 3, with the experimental values. Here, we note that the quantity $\langle P_4 \rangle / S$ is a decreasing function of temperature and reaches 0.28 at $T = T_c$. The theoretical and experimental values agree well with each other. The ratios $K_1/\bar{K}$ and $K_2/\bar{K}$ increase slowly with temperature in contrast with $K_3/\bar{K}$ which decreases slowly. Such a trend is recognized generally through several substances.[11]

(2) Temperature dependences of K_2/K_1 and K_3/K_1

The calculated values are compared with experimental data on PAA[10] in Figure 4. If the repulsive force is irrelevant, both of K_2/K_1 and K_3/K_1 should be independent of temperature.

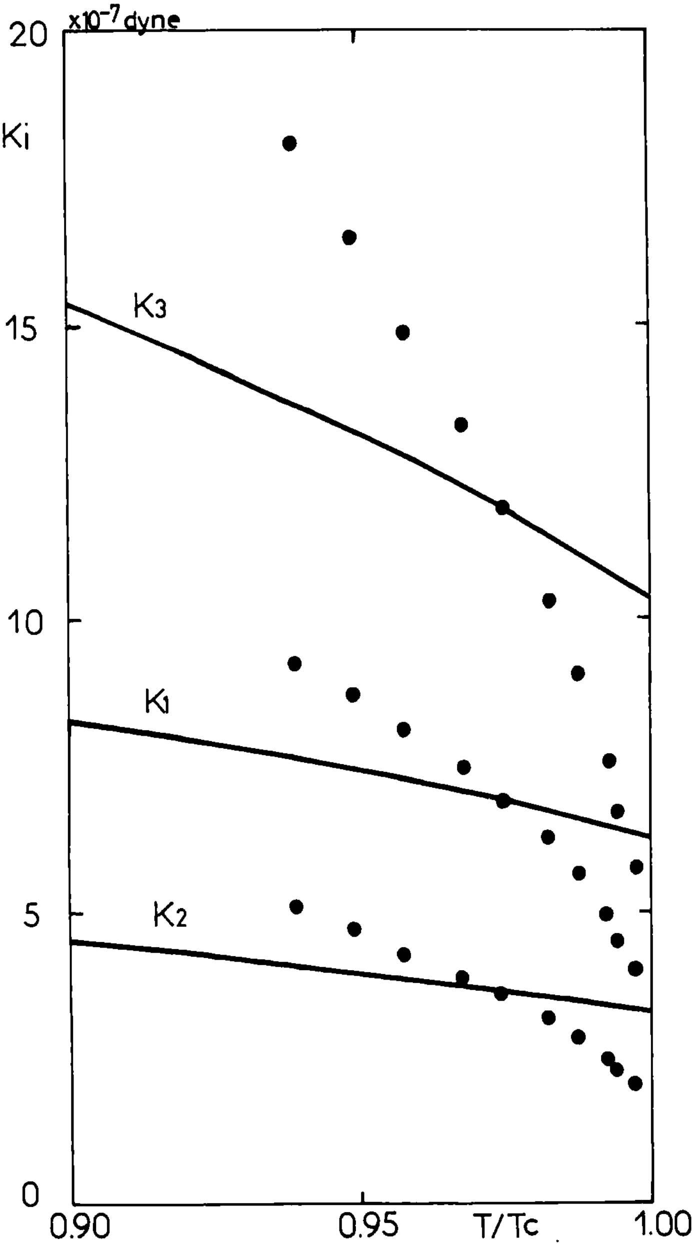

FIGURE 2 Temperature dependences of the Frank elastic constants K_1, K_2, and K_3 calculated from Eq. (4) with the parameters given in (15); the experimental data for PAA by de Jeu *et al.*[8] are shown by dots.

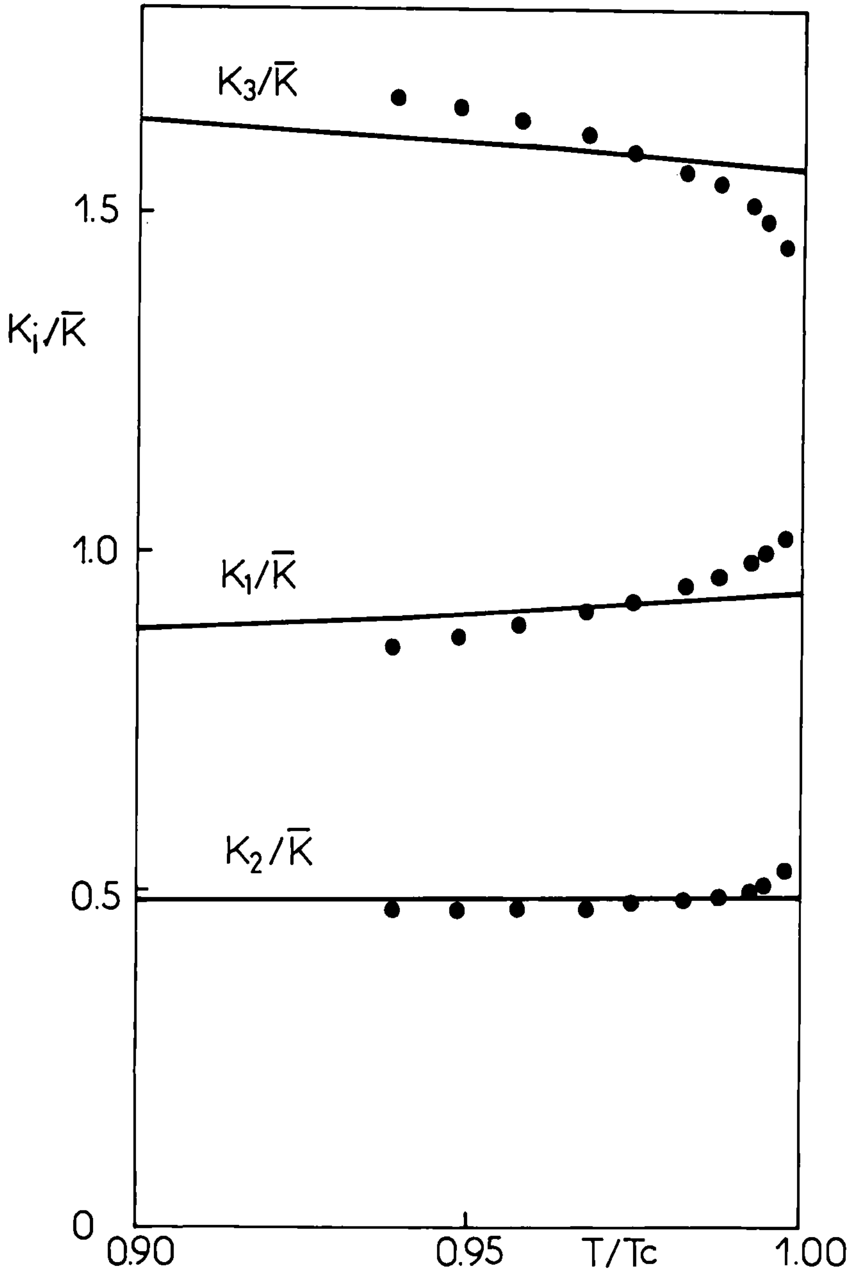

FIGURE 3 Temperature dependences of the ratios $K_i/\bar{K}$ calculated with the parameters given in (15); the experimental data for PAA are shown by dots.[10]

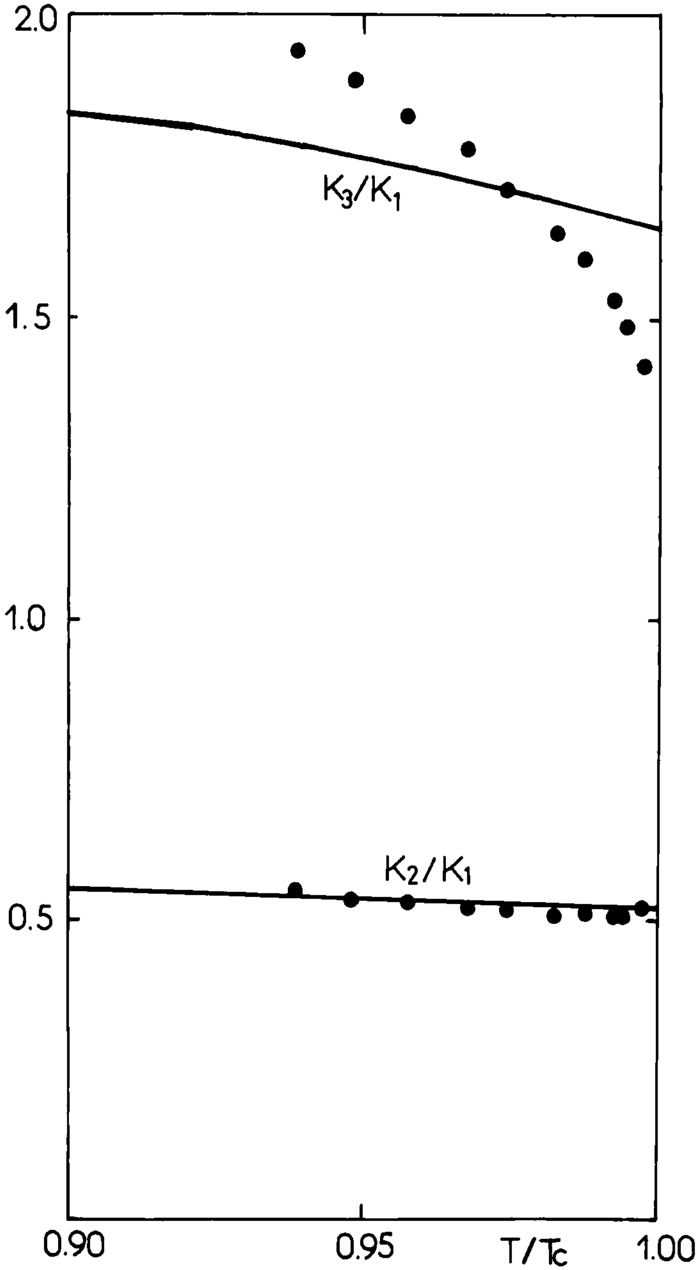

FIGURE 4 Temperature dependences of the ratios K_3/K_1 and K_2/K_1 with the parameters given in (15); the experimental data for PAA are shown by dots.[10]

The theoretical values are in good agreement with the observed ones. The decrease of K_3/K_1 with temperature has been observed in various substances such as APAPA, MBCA, MBBA, APAPA4 and OHMBBA,[12] PCH-n(n = 3, 5, 7).[13]

(3) Temperature dependences of the reduced elastic constants

Several authors have investigated the reduced elastic constants $C_i = K_i n^{-7/3}/S^2$, according to Saupe.[16] The values of C_i from the present calculations are shown in Figure 5. Experimentally, the slight increases of C_1 and C_2 with temperature have been observed in PAA[17] and also in MBBA and some other compounds,[14] whereas the data of C_3 seem to scatter in various substances.

(4) Effect of the shape on the elastic constants

We can rewrite (4) as

$$\left.\begin{aligned}
K_1 &= \frac{1}{2}\left\{1 + \frac{3\gamma_e n}{\Gamma_c - \gamma n}\left(1 - \frac{<P_4>}{S}\right)\frac{T}{T_c}\right\}(\Gamma_c - \gamma n)R^2 S^2 n k_B T_c,\\
K_2 &= \frac{1}{2}\left\{1 + \frac{\gamma_e n}{\Gamma_c - \gamma n}\left(1 - \frac{<P_4>}{S}\right)\frac{T}{T_c}\right\}(\Gamma_c - \gamma n)R^2 S^2 n k_B T_c,\\
K_3 &= \frac{1}{2}\left\{1 + \frac{3\gamma_e n}{\Gamma_c - \gamma n}\left(1 + \frac{4<P_4>}{3S}\right)\frac{T}{T_c}\right\}(\Gamma_c - \gamma n)R^2 S^2 n k_B T_c.
\end{aligned}\right\} \tag{16}$$

By assuming the theoretical values $S = S_c = 0.43$ and $<P_4> = 0.12$ at the clearing temperature T_c we have

$$\overline{K} = \tfrac{1}{2} k_B T_c S_c^2 R^2 n(\Gamma_c - \gamma n + \tfrac{7}{3}\gamma_e n) \tag{17}$$

and

$$\left.\begin{aligned}
K_2/K_1 &= \left(1 + \frac{0.72\gamma_e n}{\Gamma_c - \gamma n}\right)\Big/\left(1 + \frac{2.16\gamma_e n}{\Gamma_c - \gamma n}\right),\\
K_3/K_1 &= \left(1 + \frac{4.12\gamma_e n}{\Gamma_c - \gamma n}\right)\Big/\left(1 + \frac{2.16\gamma_e n}{\Gamma_c - \gamma n}\right).
\end{aligned}\right\} \tag{18}$$

The results of calculation of K_2/K_1 and K_3/K_1 are shown in Figure 6. We have assumed the packing fraction $c = nv_m$ to be 0.6, where the molecular volume v_m is given by

$$v_m = D^2 L(1 - D/3L)/4. \tag{19}$$

The experimental values from the data by Leenhouts *et al.*[11] for some rigid

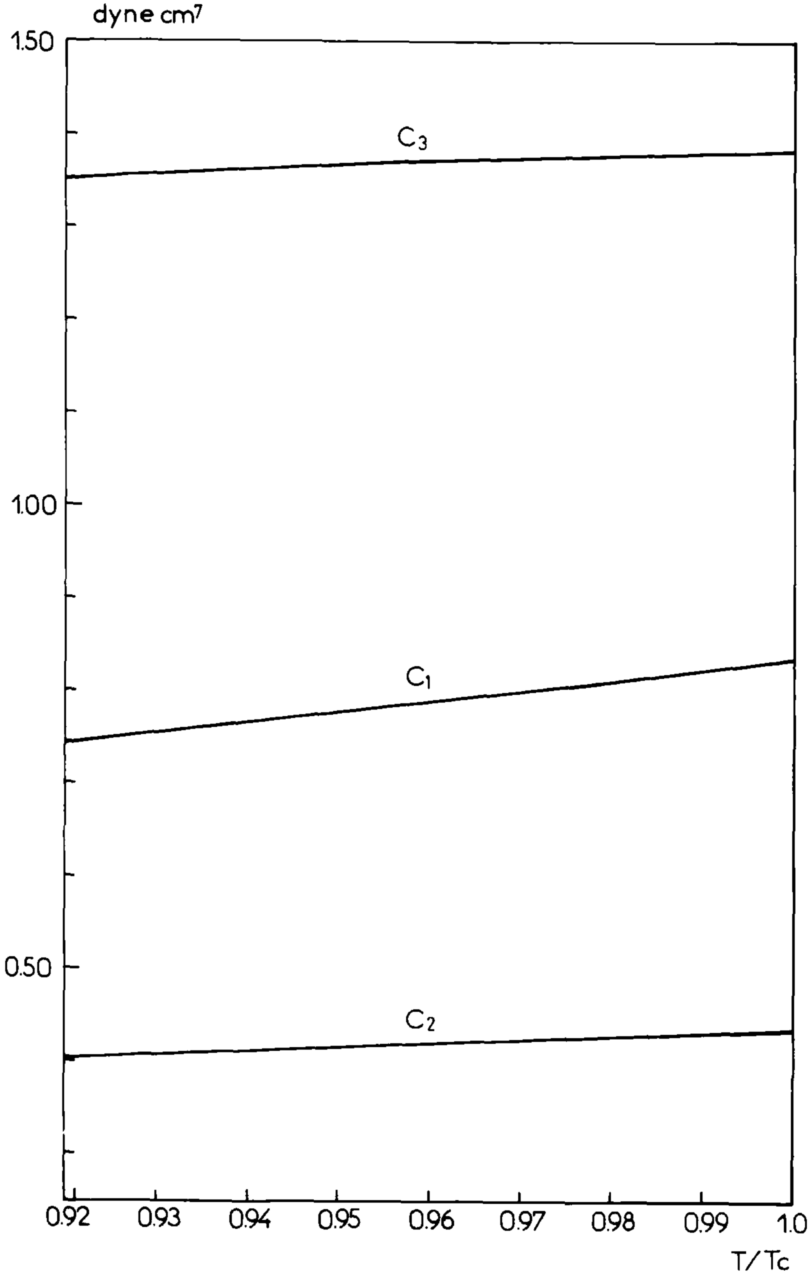

FIGURE 5 Temperature dependences of the reduced elastic constants calculated with the parameters given in (15).

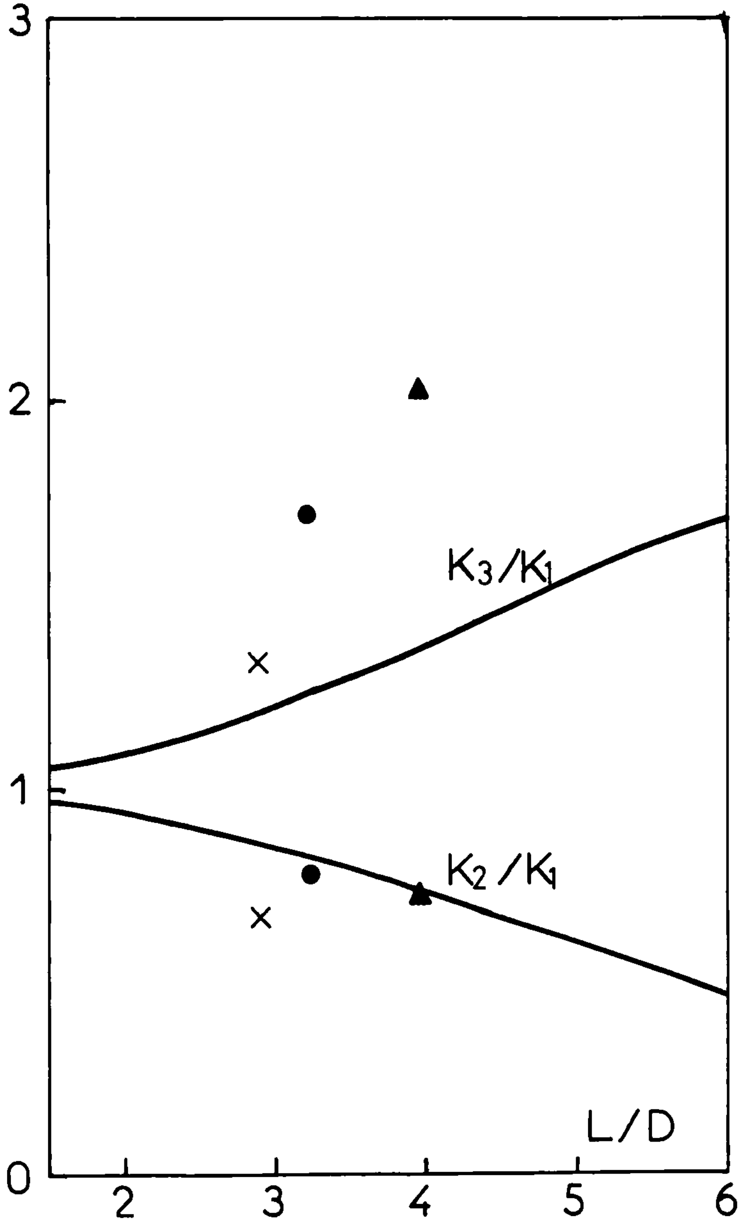

FIGURE 6 Dependences of K_3/K_1 and K_2/K_1 on the molecular shape factor L/D calculated from Eq. (18) at the clearing temperature T_c. Experimental points are due to Leenhouts *et al.*:[11] × : MBCA, ●: APAPA, ▲: MBAPB.

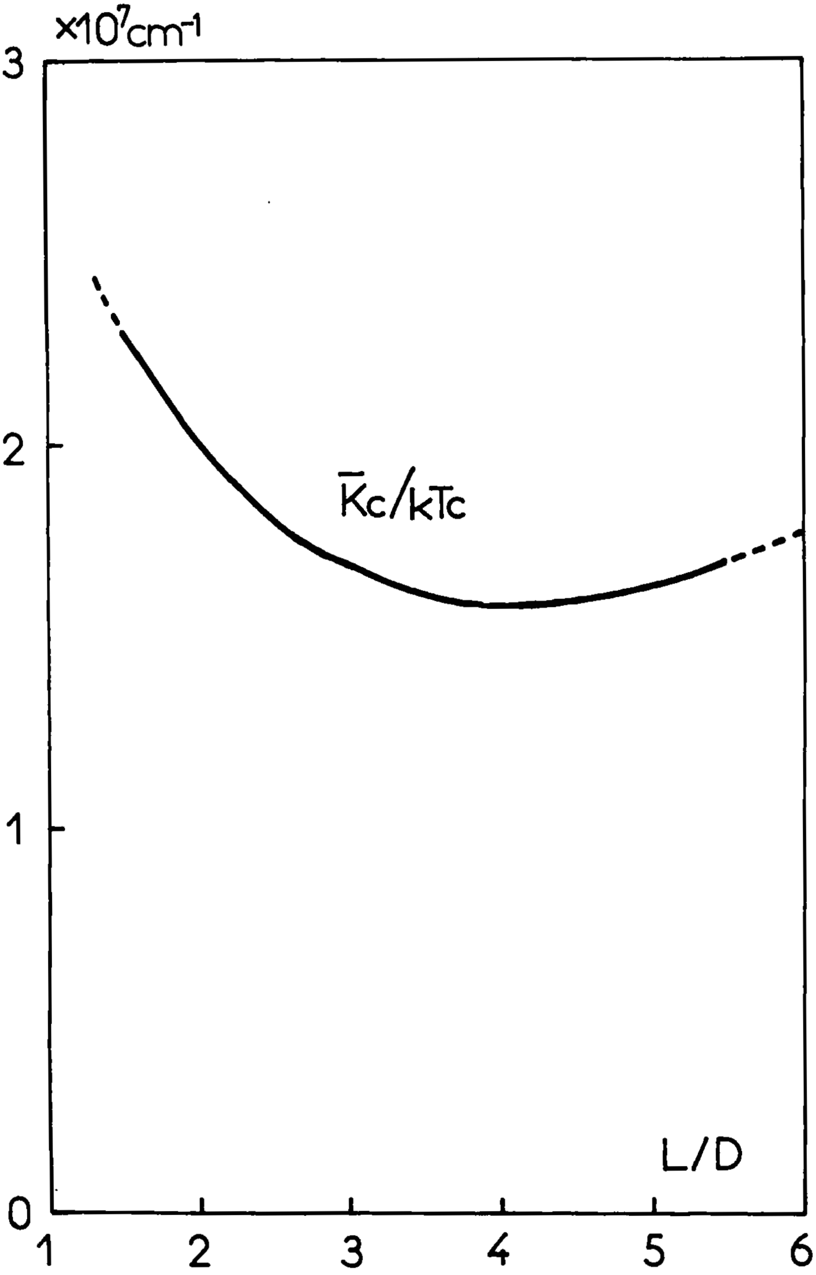

FIGURE 7 Dependence of $\overline{K}/kT$ at $T = T_c$ on L/D calculated with the packing fraction $c = 0.6$.

molecules are shown for comparison. The tendency of theoretical results seems to be consistent with the experiments.

The values of $\bar{K}$ calculated from Eq. (18) with $c = 0.6$ are shown as a function of L/D in Figure 7. It is noted that $\bar{K}/k_BT_c$ is nearly constant for $L/D = 3 - 5$, from the point of view that the members having higher clearing temperature in a certain group of nematogen have larger value of $\bar{K}$.[12]

4 LYOTROPIC SYSTEMS

For such a long molecule as $L/D \gg 1$, the orientational order appears even with no attractive intermolecular forces. In this case, the quantities γn and $\gamma_e n$ can be expressed approximately as

$$\left.\begin{aligned} &\gamma n \sim 5Lc/4D, \\ &\gamma_e n \sim 5/224(256/9)^{1/3}(L/D)^{7/3}c^{5/3}, \end{aligned}\right\} \tag{20}$$

which are fairly large: for example, $\gamma n = 12.5$ and $\gamma_e n = 68.1$ for $L/D = 100$ and $c = 0.1$. The solution of Eq. (9) is expanded as

$$S = 1 - \frac{1}{\Gamma} - \frac{4}{3\Gamma^2} - \cdots, \tag{21}$$

with which Eq. (11) gives

$$<P_4> = 1 - \frac{10}{3\Gamma} - \frac{25}{9\Gamma^2} - \cdots. \tag{22}$$

By neglecting the terms due to the attractive force, the expressions (4) reduce to

$$\left.\begin{aligned} K_1 &= \frac{7\gamma_e}{2\gamma} R^2 nk_BT = \frac{c}{\pi}\frac{L}{D^2} k_BT, \\ K_2 &= \frac{7\gamma_e}{6\gamma} R^2 nk_BT = \frac{c}{3\pi}\frac{L}{D^2} k_BT, \\ K_3 &= \frac{7\gamma_e n}{2} R^2 nk_BT = \frac{5c^2}{4\pi}\frac{L^2}{D^3} k_BT, \end{aligned}\right\} \tag{23}$$

which gives the Frank constants for the hard rod system.

On the basis of these expressions we can discuss the elastic properties of the solutions of rod-like molecules long enough such as PBLG(poly-benzil-L-glutamate). For the 20% (wt/vol) chloroform solution of molecular weight 310,000, Duke and DuPré[18] obtained the results: $K_2 = 2.1 \times 10^{-7}$ dyne and

$K_1/K_3 \sim 10^{-5}$. For this solution assuming the values $L = 2123\text{Å}, D = 15\text{Å}$ and $c = 0.15$, we obtain the following values from (23) at 300°K:

$$\left.\begin{aligned} K_2 &\cong 6.2 \times 10^{-7}\ \text{dyne}, \\ K_1/K_3 &\cong 0.04. \end{aligned}\right\} \tag{24}$$

The estimation of K_2 is near to the experimental value and the extremely small ratio K_1/K_3 also agrees qualitatively with the observation, although the experimental ratio is further smaller.

5 DISCUSSION

The present method of calculation has two advantages. The first is that it takes into account both the effects of attractive and repulsive interactions simultaneously. The second is that the orientational order parameters can be calculated at the same time. Thus we can obtain the elastic constants K_i for any liquid crystal at any temperature by making use of the values of T_c, D, L and n for that substance. Further, we can analyze the elastic properties on the basis of the attractive and repulsive intermolecular forces in relation to the nematic ordering.

For the thermotropic liquid crystals, the calculated elastic constants are consistent with the experimental data. The results show the important role of repulsive as well as attractive intermolecular forces.

The present theory can also account for the elastic properties of the lyotropic system of molecules having large ratio L/D. It has been attained by explicitly taking into consideration the dependences of the orientational order parameter on L, D and c for the system.

We have used the second virial approximation to estimate the free energy. Although the approximation is rather crude for the hard-core repulsion especially in the case of short rods, the present conclusions are regarded to be qualitatively correct. The contributions of the attractive and repulsive intermolecular forces are essentially different: say in the temperature dependence. This is regarded not as the consequence of the approximation. The attractive interaction mainly contributes to the internal energy, whereas the repulsive force to the entropy (of packing).

For the sufficiently long rods, the present approximation is quite satisfactory. Straley estimated[19] the third virial term in the free energy of the hard rods and concluded that the second virial approximation for $L/D \gtrsim 100$ commits an error smaller than 10%. In this respect we can expect the present results about the lyotropic system to be fairly reliable.

Recently, de Jeu and Classen[15] have found in certain nematic homologues series, such as the *p,p'*-di-*n*-alkyl-azoxybenzenes and the *p,p'*-di-*n*-alkoxyazoxybenzenes, that the ratio K_3/K_1 decreases with the alkyl chain length and that $K_3/K_1 < 1$ for longer chains. For these molecules, the ratio K_3/K_1 has been found to increase with temperature in contradiction with the present result. The present theory is not adequate for molecules with long flexible chains, owing to the nature of the model. For flexible molecules, we need take into consideration the effect of molecular deformation in the calculation of the elastic free energy. This is a subject for future study.

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