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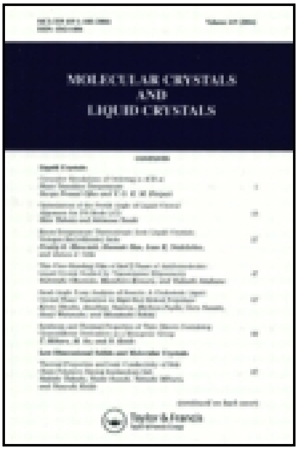

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FRANK ELASTICITY REVISITED: CONTRIBUTION OF ROTATIONAL ENTROPY

Jun-Ichi Fukuda [a] & Hiroshi Yokoyama [a b]

[a] Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba, 300-2635, JAPAN

[b] Molecular Physics Section, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305-8568, JAPAN

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Frank Elasticity Revisited: Contribution of Rotational Entropy

JUN-ICHI FUKUDA[a] and HIROSHI YOKOYAMA[ab]

[a]*Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba 300-2635, JAPAN and* [b]*Molecular Physics Section, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305-8568, JAPAN*

In previous molecular theories of nematic liquid crystals, rotational entropy, or the entropy loss due to molecular alignment, has been believed to make no contribution to Frank elasticity. We show that this is not true, using a field-theoretical method developed in polymer physics. We also give an exact expression of the contribution of rotational entropy to Frank elasticity for rod-like liquid crystals in terms of the orientational tensor order parameter.

Keywords: Frank elasticity; rotational entropy; nematic

INTRODUCTION

It is now well established that the free energy due to the inhomogeneous distortion of bulk nematic can be described by the Frank elastic energy [1,2]

$$f_d = \frac{1}{2}K_1(\nabla\cdot\boldsymbol{n})^2 + \frac{1}{2}K_2(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + \frac{1}{2}K_3(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2, \quad (1)$$

with K_1, K_2 and K_3 being the elastic constants associated with the

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splay, twist and bend distortions, respectively, and $\boldsymbol{n}$ being the director. Although the original derivation of the Frank elastic energy is based on a phenomenological argument, there have been numerous theoretical attempts [3–12] to evaluate the elastic constants on a microscopic basis and to elucidate the microscopic origin of the Frank elasticity. In nematic liquid crystals, the presence of the orientational order arises from the competition between the rotational entropy, which prefers the isotropic state, and the molecular interactions, which tend to align the liquid crystal molecules [13], and in all the previous molecular theories, Frank elasticity has been attributed to the molecular interactions. The rotational entropy, to the contrary, has never been considered to contribute to Frank elasticity.

There have also been some theoretical attempts [19,20] to calculate the free energy of main-chain liquid crystalline polymers. They used a field-theoretical method combined with a microscopic model of wormlike chains and a gradient expansion to calculate the conformational entropy of polymer chains. Their results indicate that the conformational entropy can yield the following terms corresponding to the Frank elastic energy:

$$f_d = \frac{1}{2}L_1\partial_k Q_{ij}\partial_k Q_{ij} + \frac{1}{2}L_2\partial_j Q_{ij}\partial_k Q_{ik}, \qquad (2)$$

with Q_{ij} being the orientational order parameter of second-rank tensor. This result clearly contradicts the previous molecular theories because in a system with uniform density, the conformational entropy corresponds to the rotational entropy.

In this paper, we apply the previous calculation [20] to rod-like liquid crystals and extend it to give an exact expression of the rotational entropy contribution to Frank elastic energy in terms of Q_{ij}. We also compare the contribution of rotational entropy to Frank elasticity with that of molecular interactions.

MODEL AND CALCULATION

We deal with a liquid crystal molecule as a sequence of segments like a polymer chain. We define the following two order parameters. One is the number density of liquid crystal molecules:

$$\rho(\boldsymbol{r}) = \sum_{\alpha}\int_0^l \frac{ds}{l}\delta(\boldsymbol{r} - \boldsymbol{R}^{\alpha}(s)), \qquad (3)$$

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where l is the length of the liquid crystal molecule, and $\boldsymbol{R}^\alpha(s)$ represents the configuration of the α-th molecule where s is the segment index which runs from 0 to l. The other is the orientational order per unit volume:

$$S_{ij}(\boldsymbol{r}) = \sum_\alpha \int_0^l \frac{ds}{l}\left[u_i^\alpha(s)u_j^\alpha(s) - \frac{1}{d}\delta_{ij}\right]\delta(\boldsymbol{r} - \boldsymbol{R}^\alpha(s)), \qquad (4)$$

with $\boldsymbol{u}^\alpha(s) \equiv \partial\boldsymbol{R}^\alpha(s)/\partial s$. Here $d(=3)$ is the space dimension. From the definition S_{ij} is symmetric and $S_{ij} = 0$ in the equilibrium isotropic state. We write the single-molecule Hamiltonian as $\mathcal{H}\{\boldsymbol{R}(s)\} = \mathcal{H}_0\{\boldsymbol{R}(s)\} + \mathcal{H}_1\{\boldsymbol{R}(s)\}$. Here $\mathcal{H}_0\{\boldsymbol{R}(s)\}$ is the Hamiltonian of an unperturbed molecule and we adopt the same form as that of a semiflexible wormlike chain [14–17]: $\beta\mathcal{H}_0\{\boldsymbol{R}(s)\} = \int_0^l ds\left\{\frac{d}{2\lambda}\boldsymbol{u}(s)^2 + \frac{\epsilon}{2}\dot{\boldsymbol{u}}(s)^2\right\}$, where an over-dot represents derivative with respect to s and $\beta = (k_BT)^{-1}$ is the inverse temperature. The first term and the second term in $\mathcal{H}_0$ represent the penalties for stretching and bending of the chain, respectively. We have introduced the corresponding two elastic constants λ and ϵ. In order to model a rigid molecule, we take the rigid rod limit $\epsilon \to \infty$ in the calculations below while keeping the constraint $\langle\boldsymbol{u}(s)^2\rangle_0 \equiv \int\mathcal{D}\boldsymbol{R}\boldsymbol{u}(s)^2e^{-\beta\mathcal{H}_0}/\int\mathcal{D}\boldsymbol{R}e^{-\beta\mathcal{H}_0} = 1$.

We also define the fields $h_\rho(\boldsymbol{r})$ and $h_{S_{ij}}(\boldsymbol{r})$ conjugate to the order parameters $\rho(\boldsymbol{r})$ and $S_{ij}(\boldsymbol{r})$, which is a usual technique employed in a statistical field theory. $\mathcal{H}_1$ is the Hamiltonian due to the conjugate fields,

$$\begin{aligned}\beta\mathcal{H}_1\{\boldsymbol{R}(s), h_\rho, h_{S_{ij}}\} &= \int d\boldsymbol{r}\int_0^l \frac{ds}{l}\delta(\boldsymbol{r} - \boldsymbol{R}(s)) \\ &\quad \times\left\{h_\rho(\boldsymbol{r}) + h_{S_{ij}}(\boldsymbol{r})\left[u_i(s)u_j(s) - \frac{1}{d}\delta_{ij}\right]\right\},\end{aligned} \qquad (5)$$

In Equation (5) and hereafter, summation over repeated indices are implied.

In the mean-field approximation, the contribution of the rotational entropy to the free energy and that of the molecular interaction can be considered separately and here we will concentrate on the contribution of the rotational entropy. For this purpose, we take the density functional approach originally developed by Tang and Freed [18] for flexible Gaussian chains and later extended to semiflexible chains by Liu and Fredrickson [19] and Fukuda [20]. Here we

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do not present the details of the calculation, the part of which has already been given in the previous article [20], and show here only the final result for the second order contribution in the gradients:

$$\begin{aligned}\beta f_{en}^{(2)}\{\rho, Q_{ij}\} \quad = \quad & \frac{C_0}{2\rho}(1+d\mathrm{Q})_{ij}\partial_i\rho\partial_j\rho \\ & - L_0\left((1+d\mathrm{Q})_{ij}\partial_i\partial_j\rho + d\partial_i\rho\partial_j Q_{ij} + d\rho\partial_i\partial_j Q_{ij}\right) \\ & + \frac{1}{2}L_1\rho(1+d\mathrm{Q})_{ij}(1+d\mathrm{Q})^{-1}_{k\mu}(1+d\mathrm{Q})^{-1}_{l\nu}\partial_i Q_{kl}\partial_j Q_{\mu} \\ & + \frac{1}{2}L_2\rho(1+d\mathrm{Q})^{-1}_{ij}\cdot\frac{1}{2}(\partial_k Q_{ik}\partial_l Q_{jl} + \partial_k Q_{il}\partial_l Q_{jk}),\end{aligned} \tag{6}$$

with $C_0 = L_0 = l^2/12d, L_1 = l^2d/24$, and $L_2 = l^2d/6$. Here $Q_{ij} \equiv S_{ij}/\rho$ stands for the orientational order per molecule, $\mathbf{1}$ is a $d \times d$ unit matrix and $(\mathbf{1}+d\mathrm{Q})^{-1}$ is the inverse matrix of $(\mathbf{1}+d\mathrm{Q})$. The first line is the contribution of surface tension, which is anisotropic in the presence of orientational order. The second line is the additional coupling between the fluctuation of the density and the orientational order. The last two lines correspond to the Frank elastic energy. We note that this result is exact up to infinite order in Q_{ij}. The detail of the calculation not presented in Reference [20] will be given elsewhere.

DISCUSSION

As noted in the Introduction, the contribution of rotational entropy to Frank elasticity has never been discussed in contrast to that of molecular interactions, to which numerous theoretical studies have been devoted. It should be therefore worthwhile to compare these two contributions. As the molecular interaction, we consider here only the excluded volume repulsion, because the contribution of the energetic interaction should be sensitive to the detail of the interaction. From the result presented in the preceding section, the Frank elastic constants due to the rotational entropy satisfy $\beta K_{en} \sim \rho l^2$. The contribution of the excluded volume repulsion through the translational entropy, on the other hand, is roughly written as [4–6] $\beta K_{ex} \sim \rho^2 a l^4$, where a is the diameter of the molecule. When the molecular aspect ratio l/a is sufficiently large, the nematic-isotropic transition occurs at a density $\rho a^2 l (\sim$ the volume fraction of liquid crystals$) \sim a/l$ [13]. Therefore we find that near the nematic-

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isotropic transition point,

$$\frac{K_{en}}{K_{ex}} \sim \mathcal{O}(1). \tag{7}$$

This implies that the rotational entropy can make a non-negligible contribution to Frank elasticity. Moreover, the contribution of rotational entropy can be dominant in the low-density limit because it is proportional to ρ, while the contribution of excluded-volume interaction is proportional to ρ^2. Although the system is isotropic in the low-density limit, it can possess orientational order and Frank elasticity under some external field. Therefore the measurement of the Frank elastic constants of low-density liquid crystals under an external field will be able to give a clue to understand how the rotational entropy contributes to Frank elasticity.

CONCLUSION

In this paper we have revisited the molecular origin of Frank elasticity. It has been believed in previous molecular theories that the rotational entropy cannot make any contribution to Frank elasticity. We have shown, however, that the rotational entropy *does* yield Frank elasticity, using a field-theoretical treatment developed in polymer physics. We have also derived an exact expression of the rotational entropy contribution to the Frank elastic energy for rod-like liquid crystals in terms of the tensorial orientational order parameter. Since the contribution of rotational entropy is non-negligible according to our result, the previous attempts to compare the Frank elastic constants calculated theoretically with the values obtained by experiments or molecular simulations might need a critical reexamination.

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