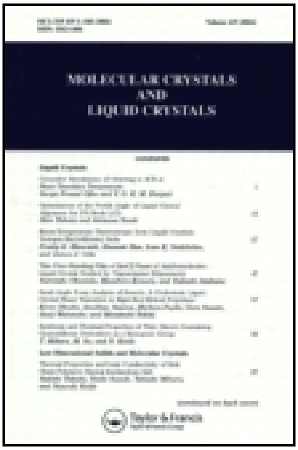

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Equation of State for Columnar Liquid Crystals

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With a consideration of the local lateral freedom of molecules, a general equation of state for columnar liquid crystals is derived, which is in agreement with the one obtained by Wensink [1] in the density limit. It is also shown that an additional negative pressure, which is not negligible, tends to be generated for thick disc-like liquid-crystalline molecules even in a high-density regime because of the cavities they create as a result of the allowed lateral motion.

Keywords: columnar liquid crystals; equation of state; lateral freedom

INTRODUCTION

Since the liquid crystals of disc-shaped molecules predicted by Landau [2], now generally referred to a as discotic liquid crystals, were first prepared and identified in 1977 [3], the study of disc-shaped molecules has attracted much interest [4–6]. A collection of disc-like molecules condense into isotropic, nematic, and columnar phases when the particle concentration is increased [7]. The most common phases exhibited by disc-like molecules are those in which the molecules stack into columns [8–12]. Because of their specific properties such as high

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anisotropy in elasticity and electric conductivity, columnar liquid crystals are widely seen as candidates for molecular electronic materials [13].

The theory of columnar liquid-crystalline phases between the liquid and crystal phases for certain compounds composed of disc-like molecules has been established [14]. Wen and Meyer argued that the entropic losses inherent in smectic ordering are more than compensated for by the concomitant reduction in the excluded volume [15], which can also be applied to the columnar phases [16]. By incorporating the rotational freedom of the discs into the framework and taking into account an effective disc thickness, Wensink obtained the equation of state (EOS) of a dense columnar liquid crystal [1]:

$$\beta PL = \frac{3\rho}{1-\rho}, \tag{1}$$

where $\beta = 1/k_B T$ is proportional to the reverse temperature and where K_B is the Boltzmann constant, P is the pressure, and $\rho = NL/\ell$ is the linear density of particles with respect to particle number N and thickness L of hard disks whose centers of mass can move freely on a line with length ℓ. Wensink's result is exactly three times the original Tonks pressure [17] and was explained as the effect due to the confinement of the disc-like molecules inside the columns. However, this is not a strict assumption so long as the columnar liquid crystals are not in their density limit, so that existing lateral freedom will allow the mass centers of disc-like molecules to move translationally to obtain a maximum entropy (minimum free energy). Yet such a motion has to be confined within the cross-section of columns so long as the columnar structure is kept. In this article we explore in detail the contribution of the translational motion to the EOS and discuss the behaviors of the columnar liquid crystals attributable to the introduced lateral freedom.

2. ANALYSIS

Consider a system consisting of disc-molecules stacked one on top of the other aperiodically to form liquid-like columns, with the different columns constituting a two-dimensional lattice. Each column is a *chain* of disc-like molecules having orientational and translational (both along and within the cross-section of the columns) freedoms, as illustrated in Fig. 1. Because of the orientational freedom of the disc-like molecules, the system will have an effective disc diameter D_{eff}, which is expressed by the polar angle θ between the particles'

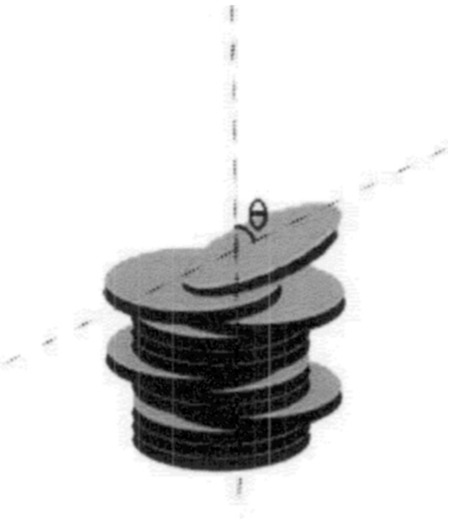


FIGURE 1 Schematic diagram of a dilute columnar liquid crystal.

symmetry axis and the line unit vector, that is,

$$D_{eff} = D\langle\cos\theta\rangle = D\left(1 - \frac{\langle\theta\rangle^2}{2}\right), \tag{2}$$

where D is the diameter of molecules. The fact that the disc-like molecules are not strictly confined along the column axes in most columnar liquid crystals allows them to have a freedom to translate two dimensionally, besides the motion along the column axis, within a region in proportion to the size of discs to guarantee the stability of columns if the columnar liquid crystal is not in its density limit. This, correspondingly, gives an entropy of

$$S_{tran} \propto \ln\left[\frac{1}{4}\pi D_{eff}^2\right]^N. \tag{3}$$

In comparison with Ref. [1], now the total Helmholtz free energy density $\beta F_{fluid}/N$ has an additional part due to translational motion:

$$\begin{aligned}\frac{\beta F_{fluid}}{N} = {} & \ln[\rho\gamma] - 2\ln\ D\left[1 - \frac{1}{2}\int f(\theta)\theta^2 d\Omega\right] + \int f(\theta)\ln[4\pi f(\theta)]d\Omega \\ & - \ln\left\{1 - \rho\left[1 + \frac{D}{2L}\int f(\theta)|\theta| d\Omega\right]\right\},\end{aligned} \tag{4}$$

where γ is the thermal volume associated with the translational and orientational kinetic degrees of freedom and $f(\theta)$ is an unknown orientation distribution function restricted by the normalization condition $\int f(\Omega)d\Omega \equiv 1$ in terms of the solid angle Ω. Equation (4) is an approximation of the system with small interactions or at high T. To explore the thermodynamic properties of the system, one strict approach is to minimize the free energy Eq. (4) and obtain an integral equation about $f(\theta)$, which is obviously too difficult to solve. To simplify the problem, one alternative is to try possible approximate solutions. Taking the normalization condition into account, we make a trial of the orientation distribution function

$$f(\theta) = \frac{\alpha^3}{4\pi(\alpha + 2\mu)} e^{-\alpha|\theta|}(1 + \mu|\theta|), \tag{5}$$

for the system at thermodynamic equilibrium. Here α is given by

$$\alpha = \frac{3}{2}\frac{\rho}{1-\rho}\frac{D}{L} \tag{6}$$

the second-order contribution is neglected. μ in Eq. (5) represents the modification to the orientational distribution function $f(\theta) = \alpha^2 \exp(-\alpha|\theta|)/4\pi$ obtained by Wensink [1] due to the local lateral freedom of liquid-crystalline molecules within columns. With consideration of Eqs. (5) and (6), a functional minimization of the free energy [Eq. (4)] with respect to the orientational distribution $f(\theta)$ leads to

$$\mu = -2 \tag{7}$$

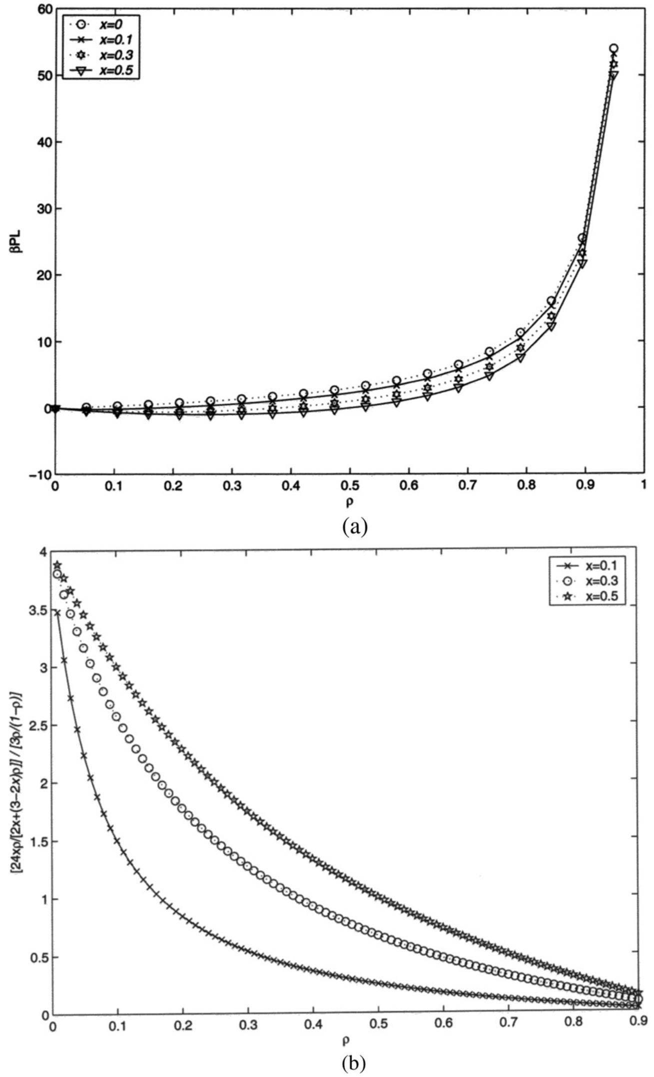
Inserting Eqs. (6) and (7) into Eq. (5) and then into Eq. (4), we acquire a free energy in terms of ρ. Taking the standard derivative with respect to the linear density ρ yields the dimensionless pressure βPL of the one-dimensional fluid:

$$\beta PL = \frac{3\rho}{1-\rho} - \frac{24x\rho}{2x + (3-2x)\rho}, \tag{8}$$

where $x = L/D$. This equation consists of two parts: the first term acquired by Wensink and the second term due to the lateral freedom within the columns.

3. DISCUSSION

Equation (8) indicates that the dimensionless pressure βPL obtained here is less than the pressure obtained by Wensink [1] because of the negative second term. Figure 2a shows the dependence of dimensionless pressures βPL on density ρ in a columnar liquid crystal with a



(a)

(b)

FIGURE 2 (a) Pressure versus density. (b) Ratio between the pressure contributed by lateral freedom and the result obtained by Wensink.

consideration of lateral freedom of disc-like liquid-crystalline molecules. It reveals that the effect of lateral freedom, which contributes negatively to the pressure, becomes negligible in density limit $\rho \rightarrow 1$ or for ideal disc-like liquid-crystalline molecules. To illustrate the effect of lateral motion, the comparison between the second term and the first term of Eq. (8), expressed by a ratio, is plotted in Fig. 2b against ρ at different disk dimensions. It is clear from Fig. 2b that if x increases, the second term cannot be neglected even in a high-density region like 0.8 (which falls into the columnar phase as estimated by Ref. [1]), compared with the first term of Eq. (8) proposed by Wensink. Columnar liquid crystals consisting of extremely thin disc-like molecules ($x = 0$) have the same equation of state as the one derived by Wensink. This is reasonable as molecules with $x = 0$ can be treated as ones with extremely large radii, which make the lateral motion negligible compared with longitudinal motion. It is not surprising that Wensink's paper demonstrated excellent agreement with the EOS from computer simulations, for small L/D of 0.1 and 0.05. The lateral freedom contributes negatively to the total pressure, because if the lateral motion of the disc-like molecules are allowed, they will create cavities, which in equilibrium have to be balanced by a force exerted by the liquid crystalor otherwise the columnar state will collapse. This gives a negative pressure that is, under positive stress, in addition to the overall one. From Eq. (8), it seems that there will be a surprising result $P < 0$ at low ρ when $x \geq \rho/[2(1-\rho)]$. However, this corresponds to a limit where the columnar phase is not thermodynamically stable, and hence an overall negative pressure is not likely to occur. Even at the columnar phase limit close to, nematic phase, with the smallest volume fraction normalized to its close-packing value $\phi^* = 2\sqrt{3}\phi/\pi = 0.48$, corresponding to $\rho = 0.63$ [1], a minimum value of $x = 0.85$ is needed for a negative overall pressure to occur. In this case the molecules are not disc-like anymore. Thus $\rho = 0.63$ is the validity limit of the present article.

4. CONCLUSION

In summary, a general EOS is derived by considering the lateral freedom in a columnar liquid crystal. An additional negative contribution to the overall pressure is obtained due to the cavities created, which cannot be neglected even in the high-density regime when x is not so small. Nevertheless, an overall negative pressure will not occur because the thick disc-like molecules and the small densities make the overall pressure in Eq. (8) negatively fall into a regime where the columnar phase is not thermodynamically stable, and hence a negative overall pressure is not likely to occur.

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