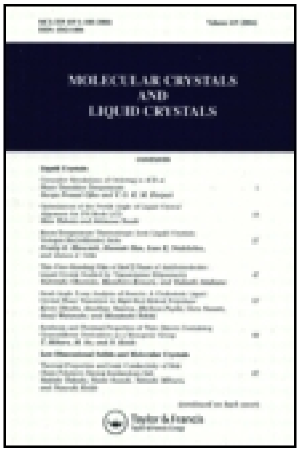

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Joachim Stelzer, Lech Longa & Hans-Rainer Trebin (1997): Rapini-Papoular Constants in a Model Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 259-263

To link to this article: http://dx.doi.org/10.1080/10587259708046969

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 259–263
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RAPINI-PAPOULAR CONSTANTS IN A MODEL NEMATIC LIQUID CRYSTAL

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Abstract The force constants for homeotropic surface anchoring of a model Gay-Berne nematic liquid crystal are derived by a local density functional method with data from molecular dynamics simulations. For the molecule–surface interaction both an anisotropic and an isotropic one-particle potential is taken. It is found that the values of the anchoring strengths are barely affected by the anisotropy of the surface potential, which indicates predominance of packing effects. Additionally, a surface-induced smectic *A* phase is being observed even though the phase is unstable in the bulk.

Surface anchoring of nematic liquid crystals is of crucial importance for applications. With the help of anchoring conditions one can taylor the director field in the bulk of a nematic liquid crystal such that the polarization plane of light is guided according to wish for display purposes. Anchoring is achieved by a suitable preparation of the cover glasses for the nematic cell, and, although empirically well-controlled, the underlying microscopic mechanisms of anchoring are not yet fully understood.

Phenomenologically, anchoring is described by a surface potential or anchoring free energy, which depends on the surface director $\hat{\mathbf{n}}$. For an anchoring configuration cylindrically symmetric about a preferred direction $\hat{\mathbf{n}}_p$, the potential most frequently used is of the Rapini and Papoular form[1]

$$\mathcal{F}_{\text{anch}} = \frac{1}{2}\, c_\theta \sin^2(\theta - \theta_p) \equiv \frac{1}{2}\, c_\theta \left[1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_p)^2\right], \tag{1}$$

where θ and θ_p are the polar angles of $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}_p$, respectively.

Alternatively one can expand the surface potential into a series of Legendre polynomials

$$\mathcal{F}_{\text{anch}} = W_2\, P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_p) + W_4\, P_4(\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_p) + \dots \tag{2}$$

The coefficients W_2, W_4 and $c_\theta = -3\,W_2 - 10\,W_4$ of the expansions (1, 2) are denoted anchoring strengths.They have been determined experimentally by Blinov *et al.*[2].

In order to study homeotropic surface on a microscopic level we perform molecular dynamics simulations at constant density (pressure). For the bulk pair interaction of the rodlike molecules the anisotropic Gay-Berne potential[3] is chosen. The phase diagram for this model has been determined by Miguel *et al.*[4]. We have used the same anisotropy parameters and have performed the simulations within the temperature and density range of the stable nematic phase.

Starting point for surface simulations has been a nematic bulk phase in equilibrium. An infinite slab was cut out by two surfaces at $z_0 = \pm z_{\rm surf}$. For simplicity, each surface was modelled on a molecular level through a one-dimensional, one-particle Lennard-Jones potential in z-direction. The depth of the potential was taken angle dependent with a maximum for orthogonal orientation. For this purpose we applied a prefactor ϵ as in the Gay-Berne potential with a reference molecule of orientation $\hat{\mathbf{k}}$ perpendicular to the surface, and the molecular separation unit vector $\hat{\mathbf{m}}$ parallel ($\hat{\mathbf{k}} \cdot \hat{\mathbf{m}} = 0$):

$$V_i^{\rm surf} = 4\,\epsilon(\hat{\mathbf{e}}_i, \hat{\mathbf{k}} \equiv \hat{\mathbf{e}}_z, \hat{\mathbf{m}}) \times \left[\left(\frac{\sigma_0}{z_i - z_0} \right)^{12} - \left(\frac{\sigma_0}{z_i - z_0} \right)^{6} \right]. \tag{3}$$

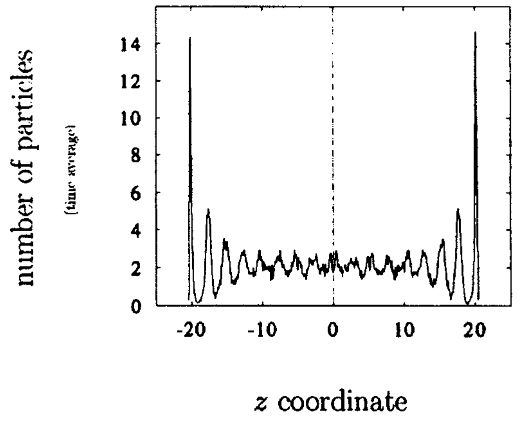

FIGURE 1 The x-y integrated density profile of nematic phase in the presence of surface anchoring. Parameters used are: temperature $T = 1.00$, pressure $P = 4.35$, volume density $\rho = 0.33$, surface density $\sigma = 0.44$.

Fig. 1 displays the x-y integrated density profile along the surface normal z. Interestingly, *the surfaces have induced a smectic A phase* penetrating into the bulk nematic. Such a phase is not present in Miguel's bulk phase diagram of Gay-Bernium[4]. The number of the layers and their coherence length decrease linearly with growing temperature. Surface-induced smectic A phases have been observed experimentally by x-ray scattering under glancing angles[5]. Coherence lengths of about 100 Å have been measured, corresponding to about three to six smectic layers as in our simulations.

During the molecular dynamics runs, temperature, pressure and nematic director were monitored. For the calculation of the anchoring strengths the order parameters, *i.e.* averaged values of the Legendre polynomials P_n: $< P_n > = < \frac{1}{N} \sum_i P_n(\cos(\hat{\mathbf{e}}_i \cdot \hat{\mathbf{n}})) >$, and the angle dependent pair distribution function $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ were evaluated. The latter was processed as an expansion into spherical harmonics.

In order to evaluate the surface anchoring strengths we have developed a local density functional theory. The free energy density is expanded into the one-particle distribution function ρ up to pair correlations:

$$\begin{aligned} \beta\mathcal{F} &= \frac{1}{2} \int \mathrm{d}^3\mathbf{r}_i \, \mathrm{d}\Omega_i \, \mathrm{d}^3\mathbf{r}_j \, \mathrm{d}\Omega_j \, c(\mathbf{r}_{ij}, \Omega_i, \Omega_j) \\ &\quad \times \rho_1(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_i) \, \rho_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_j) \end{aligned} \tag{4}$$

Here $c(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ denotes the direct pair correlation function (DCF). It is related to the numerically determined total pair distribution function $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ (PDF) via the Ornstein-Zernicke equation. For the conversion of the molecular dynamics data for the PDF into the desired DCF we extended an iterative solution of the Ornstein-Zernicke equation, based on a Wiener-Hopf factorization, to orientational degrees of freedom. The detailed numerical procedure and the approximations used are discussed in Ref.[6]. Finally we obtain the DCF in terms of its spherical harmonics expansion coefficients.

The surface energy $\mathcal{F}_{\mathrm{surf}}$ arises due to an interrelation between the bulk orientational distribution function ρ_1 (further denoted ρ) and the surface confined function ρ_2 (fixed to the surface via a *delta*-function: $\rho_2 \equiv \sigma\delta(z_i)$. This interrelation occurs in a thin layer close to the surface, mediated by the short-range DCF.

$$\begin{aligned} \beta\mathcal{F}_{\mathrm{surf}} &= \frac{1}{2} \int \mathrm{d}^3\mathbf{r}_i \, \mathrm{d}\Omega_i \, \mathrm{d}^3\mathbf{r}_j \, \mathrm{d}\Omega_j \, c(\mathbf{r}_{ij}, \Omega_i, \Omega_j) \\ &\quad \times \rho(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_i) \, \sigma(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_j) \, \delta(z_i) \qquad (5) \\ &= -\frac{1}{2} \int \mathrm{d}^3\mathbf{r}_{ij} \, \mathrm{d}\Omega_i \, \mathrm{d}\Omega_j \, c(\mathbf{r}_{ij}, \Omega_i, \Omega_j) \\ &\quad \times \rho(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_i) \, \sigma(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_j). \qquad (6) \end{aligned}$$

The anchoring energy $\mathcal{F}_{\mathrm{anch}}$ is then defined as the change in the surface energy, when the director on the surface is turning away from the preferred orientation.

In practical calculations the free energy is expanded into spherical harmonics. This allows to perform analytically integrations over all solid angles reducing the anchoring energy to a simple series

$$\beta\mathcal{F}_{\mathrm{anch}} = \sum_{n}^{\mathrm{even}} \left(\sqrt{\frac{2n+1}{4\pi}} \, \rho_0 \, \sigma_0 \, J_{n,n,0} \, \overline{P_n}^2\right) P_n(\cos(\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_p)). \tag{7}$$

Here the abbreviation

$$J_{n,n,0} = \int \mathrm{d}r_{ij}\, r_{ij}^2\, c_{n,n,0}(r_{ij}) \tag{8}$$

is used for the remaining integrations of the expansion coefficients of the DCF over the intermolecular separations. These were performed numerically by use of Simpson's rule. ρ_0 denotes the volume particle density, σ_0 stands for the lateral particle density in the molecular layer closest to the surface.

A comparison of series (7) with the definition of the macroscopic anchoring energy (2) yields the microscopic expressions for the surface anchoring strengths W_2 and W_4. The simplicity of (7) is due to the neglection of the z-dependence of the nematic order parameters and of the direct correlation function. This approximation is legitimate for the homeotropic anchoring.

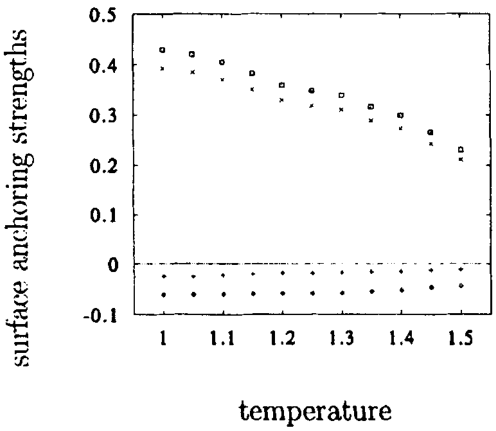

FIGURE 2 The temperature dependence of anchoring strengths. Parameters and symbols used are: pressure $P = 4.35 - 4.8$, volume density $\rho = 0.33$, surface density $\sigma = 0.44 - 0.40$; rhombi: W_2, crosses: W_4, squares: c_θ (anisotropic), ×-symbols: c_θ (isotropic surface)

We have studied, how the anisotropy of the molecule–surface interaction influences the anchoring strengths by performing two independent molecular dynamics series. The first one is based on the "anisotropic" surface potential (3), where surface and bulk Gay-Berne parameters were taken equal. In the second series we took an "isotropic" surface potential, with the ground state energy ϵ independent of the molecular orientations. For both types of surfaces the Rapini-Papoular constant differed by less than 10% (Fig. 2). In both cases we observed surface-induced smectic A layering and found that the numerical values of W_2 are mainly dependent on the number of surface induced smectic layers, that is on the smectic coherence length. We conclude that *the homeotropic surface anchoring in the nematic studied is to a large extent an "excluded volume" effect*, related in the first place to the geometry of the surface.

The detailed temperature variation of the surface anchoring strengths is displayed in Fig. 2. We found that *the absolute values of the constant W_4 are half an order of magnitude smaller than those of W_2.* Thus our calculations reveal a rapid convergence of the expansion for the anchoring energy (2). Due to the negative values of W_2 and W_4 the Rapini-Papoular constant c_θ is positive. Hence the homeotropic anchoring yields a stable configuration for the Gay-Berne nematic, *i.e.* the anchoring energy (2) has its absolute minimum at the preferred orientation $\theta_p = 0$.

The ratios of the Rapini-Papoular constant to the bulk elastic constants have been measured by Blinov *et al.*[2]. The experiments are based on the dependence of the Fréedericksz threshold voltage on the thickness of the LC cell or, alternatively, on the flexoelectric effect surface-stabilized by a magnetic field. The experimental results are within a range between 10^{-5}N/m and 10^{-6}N/m. Considering typical values for the bulk elastic constants $K = 10^{-12}$ N and the thickness of the LC cell 10^{-6} m, the results of our simulations for the ratio c_θ/K are at the lower edge of the experimental data.

ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under grant No. Tr 154/7-2, by the CNPQ Committee in Brasil and by the European Community under Grant No. ERBCIPDCT940607.

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