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van der Waals contribution to the surface and anchoring energies of nematic liquid crystals

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Using a continuum theory, analytical expressions are derived for the van der Waals contribution to the surface and anchoring energies of nematic liquid crystals. The results depend on an effective molecular separation parameter d, whose experimental determination is critically discussed. For liquid crystals in contact with a solid of refractive index n_s, it is found that a planar alignment is favored for small n_s and a homeotropic alignment for large n_s. Between $n_s = 1.35$ and 2.5, the van der Waals contribution $\Delta\gamma$ to the anchoring energy changes by several erg/cm^2, which is of the same order as the total anchoring energy, so that the general trend is expected to survive in the presence of other than dispersive contributions. Around $n_s = 1.5$, $\Delta\gamma$ is small, and other than dispersive contributions are likely to dominate the anchoring energy.

I. INTRODUCTION

At an interface or a surface the director in a liquid crystal usually has a well-defined angle with respect to the surface. This angle is determined by the anisotropic part $\Delta\gamma$ of the surface or interface energy. $\Delta\gamma$ is typically of the order of several erg/cm^2 which amounts to a few percent of the isotropic part. This explains the difficulty in calculating $\Delta\gamma$ from microscopic models. $\Delta\gamma$ appears as a small difference of two large numbers. At present very little is known about the microscopic mechanisms responsible for the surface anchoring energy.

Excellent reviews of the various techniques to obtain specific anchoring conditions and their relevance with regard to optical display devices and scientific experiments are due to Guyon and Urbach[1] and Haller.[2] An earlier study by Creagh and Kmetz[3] related the anchoring energy to a critical surface tension. Haller[4] was unable to confirm the simple classification scheme of Creagh and Kmetz.[3] In a more microscopic picture it is necessary to separate the different contributions to the anchoring energy. Usually the total interaction is split into steric, polar, and dispersive (van der Waals) parts. Proust and Ter Minassian-Saraga[5] have attempted to separate experimentally the polar and dispersive contribution in MBBA 4-methoxybenzylidene-4′-butylaniline in contact with an HMAB hexadecyletrimethyleammonium bromide-covered glass surface.

Of the three interactions (steric, polar, and dispersive) the one which is easiest to calculate theoretically is the dispersive energy. The dispersive energy and also its anisotropy can be obtained[6] from the dielectric functions $\epsilon(\omega)$ of the liquid crystal and the solid. Fortunately, it is not necessary to use a detailed $\epsilon(\omega)$. The van der Waals forces are controlled by the dominant uv absorption which can be approximated by a simple oscillator model.

Okano and Murakami[7] have computed the dispersive contribution $\Delta\gamma$ to the anchoring energy for p-azoxyanisole (PAA) using a detailed model dielectric function for the glass and for PAA, respectively. Their numbers result from an intricate numerical calculation. We approach the problem in a different spirit. Since in general the dispersive contribution $\Delta\gamma$ is only a fraction of the total anchoring energy, it is of limited interest to know $\Delta\gamma$ for a particular liquid-crystal–solid combination. What is more interesting is the relationship between $\Delta\gamma$ and the dielectric properties of liquid crystal and solid, respectively.

II. GENERAL FORMALISM

We investigate the van der Waals interaction between two semi-infinite planar media (1) and (3), separated by a planer slab of vacuum (2). The geometry is shown in Fig. 1. The width of the vacuum gap is denoted by d, and the dielectric tensors of the two media by $\underline{\epsilon}^{(1)}$ and $\underline{\epsilon}^{(3)}$, respectively. The form of $\underline{\epsilon}^{(1)}$ and $\underline{\epsilon}^{(3)}$ will be specified later. Media (1) and (3) can be isotropic or anisotropic, in the latter case with an arbitrary orientation with respect to the coordinate frame $(x,y,z) \equiv (1,2,3)$. We always assume to be in the nonretarded limit $2\pi c d/\omega_{k0} \ll 1$, where ω_{k0} $(k = 1,3)$ represents the characteristic absorp-

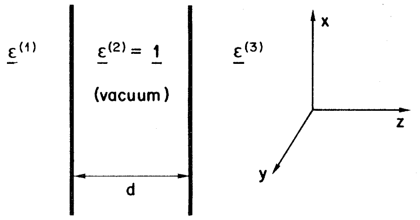

FIG. 1. Geometry for the calculation of the free energy of interaction.

tion frequency of medium (k).

The free energy of interaction F is determined by the quantum-electrodynamical zero-point fluctuations.[6] For the above geometry it has been calculated under different specific assumptions for $\underline{\epsilon}^{(1)}$ and $\underline{\epsilon}^{(3)}$ (Ref. 8). Using the surface-mode method,[8] we have extended these calculations and obtain the following general expression ($\hbar = 1$):

$$F = \frac{1}{(2\pi)^3} \int_0^\infty d\omega \int_0^{2\pi} d\phi \int_0^\infty d\rho\, \rho \ln[1 - \Delta^{(1)}(\omega,\phi)\Delta^{(3)}(\omega,\phi)e^{-2d\rho}], \tag{2.1}$$

where

$$\Delta^{(k)} = \frac{a_k - 1}{a_k + 1}, \tag{2.2}$$

$$\begin{aligned} a_k = [&\epsilon_{33}^{(k)} (\epsilon_{11}^{(k)} \cos^2\phi + \epsilon_{12}^{(k)} \sin 2\phi + \epsilon_{22}^{(k)} \sin^2\phi) \\ &- (\epsilon_{13}^{(k)} \cos\phi + \epsilon_{23}^{(k)} \sin\phi)^2]^{1/2} \\ &\mp i(\epsilon_{13}^{(k)} \cos\phi + \epsilon_{23}^{(k)} \sin\phi). \end{aligned} \tag{2.3}$$

In (2.1) we have replaced the sum over Matsubara frequencies by an integral (low-temperature approximation), and in (2.3) the minus sign is for $k = 1$ and the plus sign is for $k = 3$. The ω dependence of $\Delta^{(k)}$ is via the dielectric tensor,

$$\underline{\epsilon}^{(k)} \equiv \underline{\epsilon}^{(k)}(i\omega). \tag{2.4}$$

We now write $\epsilon_{ij}^{(k)}$ in the following general form:

$$\epsilon_{ij}^{(k)} = \epsilon_{\mathrm{av}}^{(k)} \delta_{ij} + \Delta\epsilon^{(k)} M_{ij}^{(k)}, \tag{2.5}$$

$$\mathrm{Tr}\underline{M}^{(k)} = 0, \tag{2.6}$$

and we assume that the anisotropy is small

$$\Delta\epsilon^{(k)} \ll \epsilon_{\mathrm{av}}^{(k)}, \tag{2.7}$$

so that the free energy can be expanded. To first order in the $\Delta\epsilon^{(k)}$ we have

$$\Delta^{(k)} = \Delta_0^{(k)} + \Delta_1^{(k)}, \tag{2.8}$$

where

$$\Delta_0^{(k)} = \frac{\epsilon_{\mathrm{av}}^{(k)} - 1}{\epsilon_{\mathrm{av}}^{(k)} + 1}, \tag{2.9}$$

$$\begin{aligned} \Delta_1^{(k)} = \frac{\Delta\epsilon^{(k)}}{(\epsilon_{\mathrm{av}}^{(k)} + 1)^2} &\times [M_{12}^{(k)} \sin 2\phi - M_{11}^{(k)} \sin^2\phi - M_{22}^{(k)} \cos^2\phi \\ &\mp 2i(M_{13}^{(k)} \cos\phi + M_{23}^{(k)} \sin\phi)], \end{aligned} \tag{2.10}$$

and

$$\ln(1 - \Delta^{(1)}\Delta^{(3)}e^{-2d\rho}) = \ln(1 - \Delta_0^{(1)}\Delta_0^{(3)}e^{-2d\rho}) - \frac{e^{-2d\rho}}{1 - \Delta_0^{(1)}\Delta_0^{(3)}e^{-2d\rho}} (\Delta_0^{(1)}\Delta_1^{(3)} + \Delta_1^{(1)}\Delta_0^{(3)}). \tag{2.11}$$

Inserting these expansions into (2.1), and performing the integration over ϕ, we then obtain

$$F \approx F_0 + F_1, \tag{2.12}$$

where

$$F_0 = \frac{1}{16\pi^2 d^2} \int_0^\infty d\omega \int_0^\infty dx\, x \ln(1 - \Delta_0^{(1)}\Delta_0^{(3)}e^{-x}). \tag{2.13}$$

$$\begin{aligned} F_1 = \frac{1}{32\pi^2 d^2} \int_0^\infty d\omega &\left(\Delta\epsilon^{(1)} \frac{\Delta_0^{(3)}}{(\epsilon_{\mathrm{av}}^{(1)} + 1)^2} (M_{11}^{(1)} + M_{22}^{(1)}) \right. \\ &\left. + \Delta\epsilon^{(3)} \frac{\Delta_0^{(1)}}{(\epsilon_{\mathrm{av}}^{(3)} + 1)^2} (M_{11}^{(3)} + M_{22}^{(3)}) \right) \\ &\times \int_0^\infty dx\, x \frac{e^{-x}}{1 - \Delta_0^{(1)}\Delta_0^{(3)}e^{-x}}. \end{aligned} \tag{2.14}$$

As the van der Waals forces are controlled by the dominant uv absorption, we now proceed by characterizing $\underline{\epsilon}^{(1)}$ and $\underline{\epsilon}^{(3)}$ through simple model dielectric functions

$$\epsilon_{\mathrm{av}}^{(k)}(i\omega) = 1 + \frac{\alpha_{\mathrm{av}}^{(k)}}{1 + (\omega/\omega_{k0})^2}, \tag{2.15}$$

$$\Delta\epsilon^{(k)}(i\omega) = \frac{\Delta\alpha^{(k)}}{1 + (\omega/\omega_{k0})^2}, \tag{2.16}$$

where ω_{k0} represents the dominant uv absorption band of medium (k). We first consider the *special case* where media (1) and (3) consist of the *same material*; i.e.,

$$\left. \begin{aligned} &\alpha_{\mathrm{av}}^{(1)} = \alpha_{\mathrm{av}}^{(3)} \equiv \alpha_{\mathrm{av}}, \\ &\Delta\alpha^{(1)} = \Delta\alpha^{(3)} \equiv \Delta\alpha, \\ &\omega_{10} = \omega_{30} \equiv \omega_0. \end{aligned} \right\} \tag{2.17}$$

For this case, F_0 and F_1 can be evaluated in full detail, and we obtain

$$F_0 = -\frac{\omega_0}{64\sqrt{2}\,\pi d^2} \frac{\alpha_{\mathrm{av}}^2}{(\alpha_{\mathrm{av}} + 2)^{3/2}} \zeta_0, \tag{2.18}$$

$$\zeta_0 = \sum_{\nu=1}^{\infty} \frac{[2(2\nu-1)]!}{2\nu^3[(2\nu-1)!]^2} \left(\frac{\alpha_{av}}{4(\alpha_{av}+2)}\right)^{2(\nu-1)}, \quad (2.19)$$

and

$$F_1 = \frac{\omega_0}{128\sqrt{2}\,\pi d^2} \frac{\Delta\alpha}{\alpha_{av}} \frac{\alpha_{av}^2}{(\alpha_{av}+2)^{5/2}} \zeta_1 \times (M_{11}^{(1)} + M_{22}^{(1)} + M_{11}^{(3)} + M_{22}^{(3)}), \quad (2.20)$$

$$\zeta_1 = \sum_{\nu=1}^{\infty} \frac{[2(2\nu-1)]!}{2\nu^2[(2\nu-1)!]^2} \left(1 + \frac{\alpha_{av}}{8\nu}\right)\left(\frac{\alpha_{av}}{4(\alpha_{av}+2)}\right)^{2(\nu-1)}. \quad (2.21)$$

We notice that the sums in (2.19) and (2.21), respectively, are accurately approximated by their first term. Even if $\alpha_{av} \to \infty$, the error is only about 11% for both ζ_0 and ζ_1.

In the general case, where the two media (1) and (3) are different, we now evaluate F_0 and F_1 in an approximation which exactly corresponds to taking only the first term in ζ_0 and ζ_1, respectively. The results can be represented as follows:

$$F_0 \approx - \frac{1}{32\sqrt{2}\,\pi d^2} \frac{\alpha_{av}^{(1)}\alpha_{av}^{(3)}\omega_{10}^2\omega_{30}^2}{\xi_1\xi_3(\xi_1+\xi_3)}, \quad (2.22)$$

$$F_1 \approx -\tfrac{1}{4}F_0\left[\frac{\Delta\alpha^{(1)}}{\alpha_{av}^{(1)}}\left(1 - \frac{\alpha_{av}^{(1)}\omega_{10}^2(2\xi_1+\xi_3)}{2\xi_1^2(\xi_1+\xi_3)}\right)(M_{11}^{(1)} + M_{22}^{(1)}) + \frac{\Delta\alpha^{(3)}}{\alpha_{av}^{(3)}}\left(1 - \frac{\alpha_{av}^{(3)}\omega_{30}^2(\xi_1+2\xi_3)}{2\xi_3^2(\xi_1+\xi_3)}\right) \times (M_{11}^{(3)} + M_{22}^{(3)})\right], \quad (2.23)$$

where

$$\xi_k = \omega_{k0}(\alpha_{av}^{(k)}+2)^{1/2}, \quad k=1,3. \quad (2.24)$$

III. SURFACE AND ANCHORING ENERGIES OF LIQUID CRYSTALS

In the following we first apply our general results to calculate the van der Waals contribution to the surface energy of a liquid crystal (free surface), and then consider a liquid crystal in contact with an isotropic solid.

According to Sec. II, the solid as well as the liquid crystal are characterized by simple model dielectric functions. For the isotropic solid we write

$$\epsilon(i\omega) = 1 + \frac{\alpha_S}{1+(\omega/\omega_{S0})^2} \quad (3.1)$$

and the liquid crystal is represented by the principal-axis dielectric functions

$$\epsilon^{\parallel}(i\omega) = 1 + \frac{\alpha^{\parallel}}{1+(\omega/\omega_{L0})^2} \quad (3.2)$$

and

$$\epsilon^{\perp}(i\omega) = 1 + \frac{\alpha^{\perp}}{1+(\omega/\omega_{L0})^2}. \quad (3.3)$$

In terms of the quantities α_{av}, $\Delta\alpha$, and $\underline{M}$, the liquid crystal is then characterized by

$$\alpha_{av} = \tfrac{1}{3}(\alpha^{\parallel} + 2\alpha^{\perp}), \quad (3.4)$$

$$\Delta\alpha = \tfrac{1}{3}(\alpha^{\parallel} - \alpha^{\perp}), \quad (3.5)$$

and

$$M = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 2-3\cos^2\theta & 3\sin\theta\cos\theta \\ 0 & 3\sin\theta\cos\theta & -1+3\cos^2\theta \end{pmatrix}, \quad (3.6)$$

where θ denotes the angle between the director of the liquid crystal and the direction of the surface normal. We notice that for liquid crystals the dielectric anisotropy $\Delta\alpha/\alpha_{av}$, in general, is sufficiently small to justify our approximations of Sec. II (restriction to the terms up to linear in $\Delta\alpha/\alpha_{av}$).

A. Free surface (isotropic contribution)

The surface energy γ of a free liquid-crystal surface is given by

$$\gamma = -\tfrac{1}{2}F^{L,L}, \quad (3.7)$$

where the superscripts denote that media (1) and (3) represent the same material (liquid crystal). We first estimate γ by neglecting the anisotropy completely; i.e.,

$$\gamma \approx \gamma_0 = -\tfrac{1}{2}F_0^{L,L}. \quad (3.8)$$

From (2.18) we then obtain

$$\gamma_0 = \frac{A}{24\pi d^2}, \quad (3.9)$$

where

$$A = \frac{3}{16\sqrt{2}} \frac{\alpha_{av}^2}{(\alpha_{av}+2)^{3/2}} \omega_{L0}\zeta_0 \quad (3.10)$$

is the Hamaker constant and ζ_0 is defined in (2.19).

B. Determination of the parameter *d*

In order to evaluate (3.9) we must know the parameter d. This problem has been investigated in some detail in the case of various saturated hydrocarbons[10]. As shown in Fig. 1, d represents the distance between two continuous phases considered as continuous dielectric media. Each medium may be thought to end at a surface defined by the position of the outermost polarizable electrons. Therefore, the mean distance between the centers of two liquid-crystal molecules is no meaningful estimate for d. As suggested in Ref.

10, a better estimate can be obtained from the mean distance between the centers of individual atoms. If the volume is thought to be occupied by a close-packed assembly of spheres, their diameter $\hat{d}$ can be obtained from the relation

$$\frac{4\pi}{3}\hat{d}^{\,3}=\frac{\pi\sqrt{2}}{3}\,\frac{1}{nN}\,, \qquad (3.11)$$

where n is the density of molecules, and N the number of atoms per molecule. If the interfacial separation is taken as the distance between adjacent close-packed planes, we obtain

$$\bar{d}=0.916(nN)^{-1/3}\,. \qquad (3.12)$$

In the case of saturated hydrocarbons[10], $\bar{d}$ is in reasonably good agreement with the value of d obtained, via Eq. (3.9), from the measured surface energy. For n-dodecane, e.g., where $N=38$ one has[10] $\bar{d}=1.85$ Å and $d=1.97$ Å.

The situation is quite different, however, if we turn to liquid crystals. As an example we consider PAA (p-azoxyanisole), for which[7,9] $\alpha_{\mathrm{av}}\approx 1.7$ and $\omega_{L0}=6.28\times10^{15}\ \mathrm{sec}^{-1}$. This leads to $A\approx 3.6\times10^{-13}$ erg, and with the experimental value[9] of $\gamma_0\approx 38$ erg/cm^2 we then obtain $d\approx 1.13$ Å. On the other hand, Eq. (3.12) applied to PAA leads to $\bar{d}=2.04$ Å. The disagreement between d and $\bar{d}$ is thus substantial and needs to be explained. There is the problem of what fraction of the measured surface energy is due to the dispersive forces. In the case of PAA, and other liquid crystals, there may exist a dipolar contribution to the surface energy which is not present in saturated hydrocarbons. The magnitude of such a contribution is difficult to estimate because there is no reliable information about the electric field at a free surface. For MBBA the dipolar contribution γ_p has been deduced experimentally,[5] $\gamma_p\sim 10$ erg/cm^2; i.e., γ_p is about 25% of the total surface energy. As $\gamma\sim 1/d^2$, this is not sufficient to explain the difference between d and $\bar{d}$, which is almost a factor of 2.

The main difference between saturated hydrocarbons and PAA (or liquid crystals in general) comes from the fact that in PAA the polarizable electrons are on aromatic orbitals. As these orbitals are much more extended than those in the hydrocarbons, the analysis which leads to Eq. (3.12) is obviously less convincing for liquid crystals.

A different way to obtain information about d is to relate it to the heat of transition ΔU and to the change of volume ΔV at the nematic to isotropic phase transition. Within our model the two quantities are related through

$$\Delta U=F\Delta\gamma \qquad (3.13)$$

and

$$\Delta V=\tfrac{1}{2}F\Delta d\,. \qquad (3.14)$$

Here F is the total surface of the molecules, and

$$\Delta\gamma=-2\gamma_0\,\Delta d/d \qquad (3.15)$$

is the change in the surface energy. For PAA the experimental values are[11] $\Delta U\approx 0.574$ kJ/mole, $\Delta V/V=0.36\times10^{-2}$, and $V=221$ cm^3. This results in

$$d=\left(\frac{A}{6\pi}\,\frac{\Delta V}{V}\,\frac{V}{\Delta U}\right)^{1/3}\approx 1.38\ \text{Å}\,. \qquad (3.16)$$

This value for d leads to a dispersive contribution [Eq. (3.9)] to the surface energy of PAA of about 25 erg/cm^2, implying a dipolar contribution of 13 erg/cm^2. Compared to the experimental results obtained for MBBA,[5] these values seem very reasonable.

C. Anisotropy of the surface energy

We now proceed with the calculation of the angular dependence of the surface energy. The θ dependence of γ can have two different origins. One contribution is due to the anisotropy of the dielectric function and vanishes if $\Delta\alpha=0$. Within our approximation, this contribution is contained in

$$\gamma(\theta)=-\tfrac{1}{2}F_1^{L,L}=\frac{\Delta\alpha}{\alpha_{\mathrm{av}}}\,\frac{2\gamma_0}{(\alpha_{\mathrm{av}}+2)}\,\frac{\zeta_1}{\zeta_0}\,P_2(\cos\theta)\,, \qquad (3.17)$$

where P_2 is the Legendre polynomial

$$P_2(\cos\theta)=\tfrac{1}{2}(3\cos^2\theta-1)\,. \qquad (3.18)$$

A second contribution to the θ dependence of $\gamma(\theta)$ is due to a possible anisotropy of $d(\theta)$. We define

$$\Delta d=d(0)-d(\tfrac{1}{2}\pi)\,, \qquad (3.19)$$

and put $d(\frac{1}{2}\pi)\equiv d$. To first order in $\Delta\alpha/\alpha_{\mathrm{av}}$ and $\Delta d/d$ we then obtain the following expression for $\gamma_\perp-\gamma_\parallel\equiv\gamma(0)-\gamma(\frac{1}{2}\pi)$:

$$\gamma_\perp-\gamma_\parallel\approx\frac{3\gamma_0}{(\alpha_{\mathrm{av}}+2)}\,\frac{\zeta_1}{\zeta_0}\,\frac{\Delta\alpha}{\alpha_{\mathrm{av}}}-2\gamma_0\,\frac{\Delta d}{d}\,, \qquad (3.20)$$

where γ_0 is defined in (3.9) and (3.10). With $\alpha_{\mathrm{av}}=1.7$ and $\Delta\alpha=0.3$, which are the appropriate values for PAA at 125 °C,[7,9] we obtain

$$(\gamma_\perp-\gamma_\parallel)/\gamma_0=0.18\,, \qquad (3.21)$$

if we put $\Delta d=0$. This is in good agreement with the result obtained by Okano and Murakami.[7] Our expansion with respect to $\Delta\alpha/\alpha_{\mathrm{av}}$ and the approximation of $\epsilon(\omega)$ by its dominant uv resonance seem therefore accurately justified.

It should be noted that $\Delta\alpha$ depends on the nematic order parameter S, whose value near the surface may be different from that in the bulk.[12] The possibility of such a spatial variation of S is not included in our present treatment. The influence of a $\Delta d \neq 0$ on $\gamma_\perp - \gamma_\parallel$ is illustrated by the two model examples of the following section.

D. Anchoring energy

We now consider a liquid crystal (L) in contact with an isotropic solid (S). The interface energy γ' of the liquid crystal is then given by

$$\gamma'(\theta) = -\tfrac{1}{2}F^{L,L}(\theta) + F^{L,S}(\theta)\,, \tag{3.22}$$

so that the anchoring energy becomes

$$\gamma'_\perp - \gamma'_\parallel = \gamma_\perp - \gamma_\parallel + F^{L,S}(0) - F^{L,S}(\tfrac{1}{2}\pi)\,. \tag{3.23}$$

The superscripts L and S again refer to media (1) and (3) in our general expressions for F, and after quite some algebra we finally obtain

$$\frac{\gamma'_\perp - \gamma'_\parallel}{\gamma_0} = A\,\frac{\Delta\alpha}{\alpha_{\text{av}}} + B\,\frac{\Delta d}{d}\,, \tag{3.24}$$

where

$$A = \tfrac{3}{2}\left(1 - \frac{3\alpha_{\text{av}}\omega_{L0}^2}{4\xi_L^2} - \frac{4\alpha_S\omega_{S0}^2}{\alpha_{\text{av}}\xi_S(\xi_S+\xi_L)} - \frac{\alpha_S\omega_{S0}^2}{(\xi_S+\xi_L)^2}\right), \tag{3.25}$$

$$B = 2\left(\frac{4\alpha_S\omega_{S0}^2\,\xi_L^2}{\alpha_{\text{av}}\omega_{L0}^2\xi_S(\xi_S+\xi_L)} - 1\right), \tag{3.26}$$

$$\xi_S = \omega_{S0}\sqrt{\alpha_S + 2}\;, \tag{3.27}$$

$$\xi_L = \omega_{L0}\sqrt{\alpha_{\text{av}} + 2}\,, \tag{3.28}$$

and γ_0 is as defined by (3.9) and (3.10). For a model glass with $\alpha_S = 1.25$ and $\omega_{S0} = 10^{16}\ \text{sec}^{-1}$, and with the previous data for PAA, we obtain

$$(\gamma'_\perp - \gamma'_\parallel)/\gamma_0 \approx -6.5\times10^{-3}\,, \tag{3.29}$$

which is again in good agreement with the result of Okano and Murakami.[7]

We finally present two model calculations which illustrate the dependence of the anchoring energy $\Delta\gamma \equiv \gamma'_\perp - \gamma'_\parallel$ on the dielectric anisotropy Δn of the liquid crystal, on the refractive index n_S of the solid, and on $\Delta d/d$. As our formulas are expressed in terms of polarizabilities α, rather than in terms of refractive indices n, we notice that the two are related by $\alpha = n^2 - 1$. The results for the two examples are presesented in Figs. 2 and 3, respectively, and the choice of the model parameters is explained in the corresponding figure captions.

IV. DISCUSSION

From Fig. 2 we find that $\Delta\gamma$ depends only weakly on the dielectric anisotropy Δn of the liquid crystal. For $\Delta d/d = 0$, $\Delta\gamma$ is very small for all reasonable values of Δn, but a small anisotropy in the separation parameter leads to an appreciable contribution.

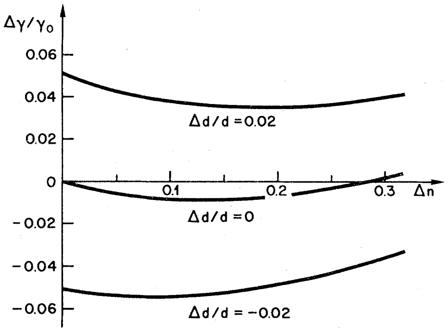

FIG. 2. van der Waals contribution $\Delta\gamma$ to the anchoring energy vs Δn, the dielectric anisotropy of the liquid crystal. The model liquid crystal is otherwise characterized by $n_\perp = 1.5$ and $\omega_{L0} = 7.54\times10^{15}\ \text{sec}^{-1}$, the solid by $n_S = 1.5$ and $\omega_{S0} = 10^{16}\ \text{sec}^{-1}$. The three curves correspond to $\Delta d/d = 0$ and ±0.02, respectively.

The calculations presented in Fig. 3 demonstrate that the dispersion contribution to the total anchoring energy follows a simple trend. Large-refractive-index solids favor homeotropic alignment and small-refractive-index solids favor planar alignment. The total amplitude in the shift of $\Delta\gamma$ when going from $n_S = 1.3$ to 2.5 is of the same order as the total anchoring energy, i.e., several erg/cm^2. Superimposed to this trend are shifts resulting either from the angular dependence of the separation parameter d or from other than dispersive contributions. These contributions are likely to dominate the anchoring energy in the vicinity of $n_S = 1.5$ where $\Delta\gamma$ is very small for $\Delta d/d = 0$. The sign of other than dis-

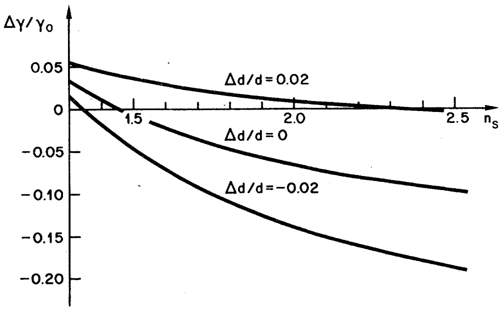

FIG. 3. van der Waals contribution $\Delta\gamma$ to the anchoring energy vs the refractive index n_S of the isotropic solid. The model parameters for the liquid crystal are chosen as follows: $n_\parallel = 1.7$, $n_\perp = 1.5$, and $\omega_{L0} = 7.54\times10^{15}$ sec^{-1}, whereas the solid is characterized by $(n_S^2 - 1)\omega_{S0}^2 = \text{const}$ ($\omega_{S0} = 10^{16}\ \text{sec}^{-1}$ at $n_S = 1.5$). As in Fig. 2, the three curves correspond to $\Delta d/d = 0$ and ±0.02, respectively.

persive contributions usually can be guessed. For steric contributions the sign is evident from the form and orientation of surfactant molecules, and dipole forces align the effective dipole of the liquid-crystal molecule along the field. We note, however, that if the liquid-crystal molecule lacks an inversion symmetry the angular dependence of d introduces a polar part into the dispersive interaction: In the homeotropic orientation the dispersive energy γ depends on which end of the molecule faces the surface.

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