Systematic studies of the anchoring transition in nematic liquid crystals

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When a nematic liquid crystal is spread on a crystalline substrate, the latter can orient the nematic molecules on top. Recently, it was shown that if water vapor is adsorbed onto the nematic-substrate interface, a discontinuous jump in the orientation can be observed. In this article we report a systematic study of the conditions under which this anchoring transition takes place. We find that, in addition to water, alcohols and diols cause a transition. Further, the nematic orientation depends only on relative humidity and not directly on temperature.

I. INTRODUCTION

Over 70 years ago, Mauguin[1] and Grandjean[2] discovered that a crystal substrate can orient a nematic liquid-crystal layer spread on top of it. This phenomenon, known as anchoring, can be explained by noting that the anisotropy of the crystal surface implies that the energy of liquid-crystal molecules at the nematic-substrate interface will depend on orientation.

Recently, we showed that the anchoring direction can change discontinuously as the amount of water vapor adsorbed onto the crystal surface is changed.[3-5] This jump between two states of the crystal-nematic interface has all the characteristics of a first-order phase transition and has been dubbed the "anchoring transition."

The original discovery of the anchoring transition was serendipitous; the experiments used a four-component liquid crystal and were limited to room temperature. One could legitimately wonder whether the particular circumstances of those experiments might not hide important features of the behavior of the transition. In this article we report on systematic studies of the anchoring transition as we vary the liquid crystal, substrate, atmosphere, and temperature. Although we do not discover the microscopic mechanism responsible for the anchoring transition, we do clarify our understanding of the conditions under which the transition takes place.

II. EXPERIMENTAL APPARATUS AND MATERIALS

The experimental apparatus, illustrated in Fig. 1, may be broadly broken down into two subunits. The first controls the humidity in the sample chamber; the second contains the optics for measuring the orientation of the liquid-crystal molecules with respect to the crystalline substrate below.

In previous work we controlled the humidity by mixing two nitrogen gas streams, one dry and one saturated, in the desired proportions. Here, we chose a different method: We enclosed the sample in a vacuum chamber and introduced a fixed amount of gas. The vapor pressure was then measured directly and the relative humidity obtained by dividing the measured pressure by the saturation pressure at the working temperature. By having

just water vapor in our sample, we could be sure that only the number of water molecules adsorbed onto the substrate-nematic interface was important. The new setup also allowed us to overcome a serious defect of the old setup, which would occur were that system used above about 50 °C. In the old setup, quantitative knowledge of the humidity depends on knowing the flow of both the dry and saturated gas streams. It is clear that all parts of the experimental apparatus in contact with the saturated gas stream must be maintained at a temperature equal to or greater than the sample temperature, in order to prevent condensation in the liquid phase. In particular, the flowmeter must be heated. Unfortunately, available precision flowmeters are designed to work at or near room temperature and were thus unsuitable. By contrast, heated pressure gauges are readily available.

The pressure-control apparatus consisted of a mechanical vacuum pump, a liquid-nitrogen cold trap, and open-shut valve (valve 1) leading to the vacuum chamber, a vacuum gauge thermostated to 100 °C,[6] and a fine-control
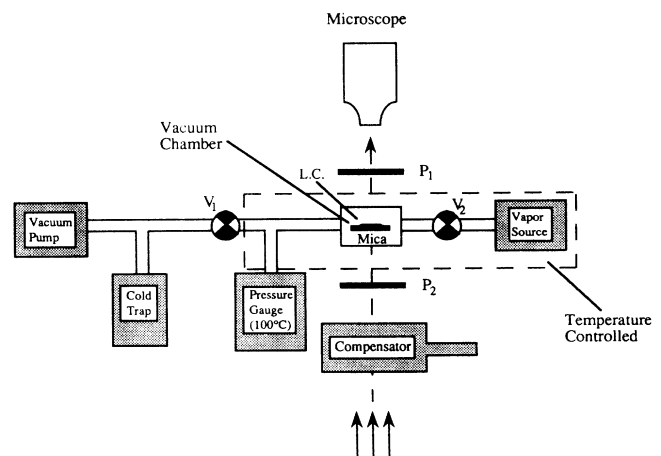

FIG. 1. Diagram of experimental apparatus. P_1 and P_2 denote polarizer and analyzer, respectively. V_1 and V_2 denote valves that permit entry and exit of gases from the experimental chamber. LC denotes the liquid-crystal layer spread on top of the crystalline substrate.

needle valve (valve 2)[7] leading to a vapor source. The vapor source was a piece of cotton dipped in the liquid whose vapor is to be introduced into the cell, the cotton serving to create a large surface area that enhances the evaporation of the liquid. The temperature of the experimental chamber was controlled by circulating water from a thermostated bath[8] around the cell. The sample temperature, as measured by a four-wire platinum resistance probe, was constant to ± 0.01 C during each run. The vacuum valves and various tubing were wrapped in heating tape.

At the start of an experiment, a thin (several micrometers) layer of liquid crystal was spread on a freshly cleaved substrate. The chamber was then pumped down to less than 0.1 mb. Valve 1 was shut and valve 2 opened until the pressure rose to the desired level. With both valves shut the pressure was constant to 0.1 mb and could be read to 0.01 mb on the vacuum gauge, which had a 1000-mb range. Depending on the sample temperature (-5 to $+70\,°C$) and the vapor used (water, ethanol, etc.), typical vapor pressures ranged from 2 to 200 mb. One limitation of the experiment was that the vapor pressure of the adsorbed chemical had to be higher than that of the liquid crystal, restricting us to relatively volatile substances.

The optical setup was the same as used in previous studies. A polarizing microscope[9] was used in conjunction with a Soleil compensator[10] that removed the optical effects of the substrate birefringence. The azimuthal orientation of the molecules could then be determined (to $\pm 1°$) by rotating crossed polarizers (P_1 and P_2 in Fig. 1) until the field was extinguished. Although the anchoring transition is between different states of a two-dimensional interface, the orientation of the liquid-crystal molecules in the bulk of the sample follows those on the substrate surface, so as to eliminate any twist deformation of the director field. The top surface of the liquid crystal is free and does not constrain the bulk.

III. EXPERIMENTAL RESULTS

A. Materials studies

The goal of this part of the experiment was to characterize the materials needed to produce the anchoring transition. We examined the effects of different substrates, liquid crystals, and adsorbed vapors. The results are summarized in Table I. With one exception, the substrates that showed an anchoring transition with a given liquid crystal on a given vapor showed a transition with all of the liquid crystals or vapors listed in the "yes" column. The exception was 4-n-hexyl-4'-cyanobiphenyl (6CB) (marked by an asterisk in Table I), which showed an anchoring transition with gypsum and calcite but not with any of the micas.

The vapors that produced an anchoring transition also sometimes caused a wetting transition (at different critical vapor pressures), which caused the nematic layer, which normally wets completely the substrate, to break up into many partially wetting droplets. This effect was observed in all vapors except water and the ethylene

glycol family. The wetting transition is not too surprising in itself since the well-known Young's criterion[11] predicts that a fluid will wet a substrate if

$$\gamma_{SV} > \gamma_{SL} + \gamma_{LV} \, , \tag{1}$$

where γ_{SV} is the surface tension between the substrate and the surrounding vapor, γ_{SL} that between the substrate and the liquid crystal, and γ_{LV} that between the liquid crystal and the vapor. When the vapor pressure changes, all three surface tensions will in general change as well, and it is easy to imagine that the inequality in Eq. (1) might be reversed.

On the basis of the observations reported in Table I, we can advance a scenario for the anchoring transition that is plausible and consistent with our data: When vapor is introduced into the system, it diffuses through the thin liquid-crystal layer and adsorbs onto the nematic-substrate interface. For the substrate-vapor combinations that show anchoring transitions, the adsorption energy is dominated by hydrogen bonding. Because hydrogen-bond energies are greater than the van der Waals interactions that attract the liquid-crystal molecules to the surface,[12] the latter are displaced from the surface by the vapor molecules. The surface, whose interactions determine the nematic orientation, is thus modified. One can frame the argument in terms of a Landau equation for the grand thermodynamic potential Ω:[13]

$$\Omega = \Omega_0 + \sum_{m=1}^{\infty} a_m \cos(m\theta + \delta_m) \, , \tag{2}$$

where θ is the angle between the nematic director $\hat{n}$ and a fixed direction in the cleavage plane and Ω_0 is the isotropic part of the potential. Since nematics are invariant under $\hat{n} \to -\hat{n}$, only even values of m are allowed. The symmetry of the crystal surface can also impose constraints on the allowed terms. Our discussion above is then tantamount to saying that one can have discontinuous anchoring transitions as the coefficients a_m vary continuously as a function of the pressure of the gas atmosphere. This statement is easily verified by examining Ω and its derivatives for various values of a_m. To take a trivial example, if Ω is dominated by the first term (and if we define $\theta = 0$ such that $\delta_2 = 0$), then $\Omega = a_2 \cos 2\theta$. The system will choose $\theta = 0$ for $a_2 < 0$ and $\theta = \pi/2$ for $a_2 > 0$.

One specific prediction that this scenario implies is that, in the absence of a liquid-crystal layer, the density of adsorbed molecules on the substrate does not jump as one crosses the vapor pressure at which the transition occurs. In other words, we suppose that there is no singularity in Ω_0 and that the transition is provoked by smooth variations in the a_m coefficients. We are currently testing this idea via ellipsometry.[14] It might also be possible to check the idea using the infrared-visible light sum-frequency technique.[15]

B. Temperature studies

The second part of our study concerned the effect of temperature on the anchoring transition. For this work we used water as the adsorbed chemical, gypsum and

mica as the substrates, and 6CB, 5OCB, and E9 as the liquid crystals.[16] The main results are summarized in Figs. 2 and 3. Figure 2(a) shows the azimuthal orientation of 6CB on gypsum as a function of absolute water vapor pressure for temperatures ranging from 10 to 25 °C. Figure 2(b) shows that when the absolute vapor pressure is scaled by the saturation vapor pressure at that temperature, as determined experimentally or through tables, the data may be plotted on one curve. Similar curves are obtained using E9 and 5OCB as liquid crystals. In other words, the transition depends only on relative humidity. In Fig. 3 we show that the transitions observed on muscovite and phlogopite mica occur at the same relative humidity for a variety of temperatures, for two different liquid crystals. Note that many of these observations were conducted at temperatures at which the nematic was supercooled by as much as 25 °C.

In the Landau expansion discussed above, these observations imply that the coefficients a_m in Eq. (1) are functions only of the relative humidity, i.e., that $a_m = a_m(P/(T)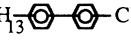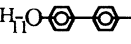/P_{sat}(T))$. At first glance, the relative humidity scaling of the angles is difficult to understand. At constant temperature, the surface coverage by the adsorbed molecules can be expressed in terms of the relative humidity. One would then be tempted to conclude that a transition occurs for a given surface coverage, i.e., that $a_m = a_m(x)$, where x is the number of molecules per unit area of water adsorbed onto the mica.

A difficulty with this scenario is that because water forms a hydrogen bond with the surface, we expect chemisorption to dominate. This implies that molecules require an activation energy Q to escape from the surface. Normally, Q is larger than kT, implying strong temperature effects. However, when expressing the surface coverage in terms of _relative_ humidity, the temperature dependence is dominated by[17]

$$e^{(Q-Q_v)/kT} , \qquad (3)$$

where Q_v is the vaporization energy of the liquid phase of the adsorbed molecule. Since the interactions of the water molecules with each other and with the substrate are

TABLE I. List of materials for which the anchoring transition takes place. Except for 6CB (denoted with an asterisk), the anchoring transition occurs for all combinations of substrates, vapors, and liquid crystals if it works for one particular combination.

Anchoring Transition

	YES	NO
SUBSTRATES	gypsum mica ⟨muscovite / phlogopite⟩ calcite	quartz silicon (<100>, <110>, <111>)
LIQUID CRYSTALS	E9 15% 3OCB, 38% 5OCB 38% 7OCB, 9% 5CT 6CB* C_6H_{13}—◯—◯—CN 5OCB C_5H_{11}O—◯—◯—CN	——
VAPORS	water ethanol methanol ethylene glycol diethylene glycol triethylene glycol	acetic acid carbon tetrachloride

both dominated by hydrogen bonds, it is at least plausible that the difference between Q and Q_v is small compared to kT, even when each quantity is itself larger than kT. An explicit test would be to show that adsorption isotherms of water on mica, when expressed in terms of layer coverage versus relative humidity, do not depend noticeably on temperature for $\Delta T/T \cong 30/300 = 0.1$. Such isotherm behavior has been observed in other systems — for example, in the adsorption of water in hexyl alcohol by silica gel.[18]

We can extract a few more conclusions from the data in Figs. 2 and 3. First, we note that we observe a continuous dependence of θ on P for gypsum, whereas for mica, the angle is constant until the transition point is reached. Also the jump in mica is 90°, whereas in gypsum, it varies from 40° to 80°, depending on the temperature, time after cleavage, and liquid crystal used. These observations are consistent with the Landau theory given above. We have discussed the structure of both gypsum and muscovite mica elsewhere; here, we note only that the surface of gypsum has a C_2 symmetry (180° rotation), whereas mica has a (slightly broken) C_s symmetry (mirror plane). For gypsum, Ω will thus be of the form
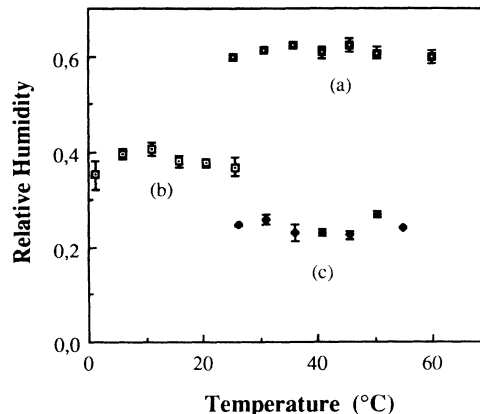
FIG. 3. Values of relative humidity at which the anchoring transition is observed as a function of temperature. (a) E9 on phlogopite mica, (b) E9 on muscovite mica, and (c) 50CB on muscovite mica.

$$\Omega = a_2\cos(2\theta + \delta_2) + a_4\cos(4\theta + \delta_4) + \cdots , \qquad (4)$$

whereas for muscovite mica, it will have the form

$$\Omega = a_2\cos(2\theta) + a_4\cos(4\theta) + \cdots . \qquad (5)$$

Inspection of Eq. (4) shows that nonzero phases δ_3 and δ_4 imply that the angles θ^* at which the potential has a minimum ($\partial\Omega/\partial\theta = 0$) depend on the coefficients a_2 and a_4, i.e., that $\theta^* = \theta^*$ ($a_2, a_4, \ldots$). More physically, each term in the expansion tries to align the molecules along a different axis. Since there is no mirror symmetry in the plane for gypsum, there is no reason that the axis of the $\cos2\theta$ term should have any special relation with the axis of the $\cos4\theta$ term. The actual alignment then depends on the relative strengths of each term. By contrast, in Eq. (5), $\theta^* = 0°$ and $\theta^* = 90°$ are extrema for all $a_2, a_4, \ldots$ (note that there are also other orientations θ^* that do depend on $a_2, a_4, \ldots$.)

At very low pressures (less than 0.1 mb), the gypsum samples became homeotropic, or perpendicular to the gypsum substrate. (Since at the air-6CB interface, the molecules are also homeotropic, the sample was homeotropic throughout its bulk and was thus optically isotropic when viewed in the microscope, from above.) It thus seems likely that the rapid variation of θ with vapor pressure observed at low P is associated with the molecule's lifting out of the plane. (When the molecules are nearly aligned along the line of view, a slight change of orientation will change θ greatly.)

Finally, we attempted to observe the behavior of the anchoring transition near the nematic-isotropic (NI) transition temperature T_{NI}, where one expects that the energy barrier separating different minima for Ω tend to zero. Unfortunately, such observations were not possible because T_{NI} varied 2–3 °C as the vapor pressure was increased from 0 to P_{trans}. Two (related) causes are immediately apparent: T_{NI} could be directly a function of
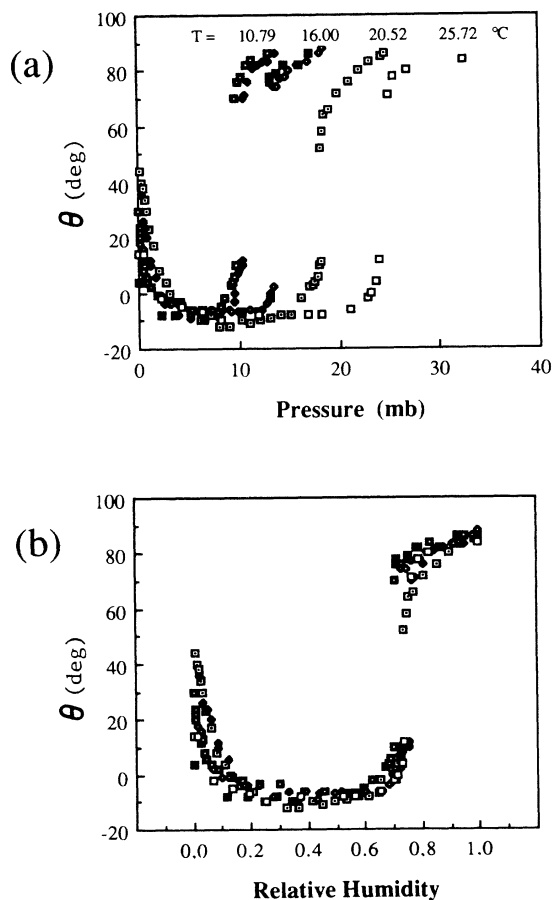

FIG. 2. (a) Azimuthal orientation of liquid-crystal molecules, as a function of absolute water vapor pressure, for 6CB on gypsum. (b) Azimuthal orientation as a function of relative humidity for the same system.

P, via the Clausius-Clapeyron law;[19] alternatively, T_{NI} could depend on the amount of water molecules absorbed in the bulk liquid crystal. These would act as an impurity and lower the equilibrium T_{NI} via the van t' Hoff law.[20] By comparing $T_{NI}(P)$ for water vapor and air, we determined that the latter effect dominates.

IV. CONCLUSIONS

We have conducted systematic studies of the anchoring transition as we vary the substrate, liquid crystal, and vapor involved. We conclude that the vapor must adsorb onto the substrate in preference to the liquid crystal in order for the transition to occur. We also suggest further experiments that could check this scenario at a more microscopic level.

We have also shown that the anchoring transition is much more sensitive to the relative humidity of the ad-sorbent molecule than it is directly to temperature. The dependence on relative humidity suggests that anchoring transitions occur for a given surface coverage by ad-sorbed molecules. In terms of a Landau theory for Ω, the phenomenological coefficients depend on the coverage x but not (greatly) on T. One might speculate that it is possible to vary the a_m independently by co-adsorbing two or more chemicals onto the substrates [i.e., $a_m = a_m(x_1, x_2, \ldots)$]. This would give ternary and higher-order phase diagrams having second-order lines and critical points, in addition to the first-order transitions already observed. Indeed, in unpublished work we show that these hopes are well founded.[21]

V. ACKNOWLEDGMENTS

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[1]C. Mauguin, Bull. Soc. Fr. Cryst. **34**, 71 (1911).

[2]F. Grandjean, Bull. Soc. Fr. Cryst. **39**, 164 (1916).

[3]P. Pieranski and B. Jérôme, Phys. Rev. A **40**, 317 (1989).

[4]P. Pieranski, B. Jérôme, and M. Gabay, Mol. Cryst. Liq. Cryst. (to be published).

[5]P. Pieranski and B. Jérôme, in Proceedings of the NATO ASI on Phase Transitions in Soft Condensed Matter, Geilo, 1989, edited by T. Riste (unpublished).

[6]MKS Barotron, Model 128A.

[7]Edwards High Vacuum International, Model E2M2.

[8]Messgeräte-Werk Lauda, Model RCS 20.

[9]Olympus Optical Co., Model BH-2.

[10]Melles-Griot.

[11]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1959), pp. 471–473.

[12]G. C. Pimental and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1959).

[13]Ω is here a surface quantity and is the appropriate thermodynamic potential because the vapor molecules in the bulk act as a quasi-infinite reservoir of atoms that may be adsorbed onto or off the interface.

[14]F. Heslot and J. Bechhoefer (unpublished).

[15]Y. R. Shen, Nature **337**, 519 (1989).

[16]All purchased from British Drug House Chemicals, Ltd. "6CB" is 4-n-hexyl-4'-cyanobiphenyl, "50CB" is 4-n-pentyloxy-4'-cyanobiphenyl, and "E9" is a mixture consisting of 15% 30CB, 38% 50CB, 38% 70CB, and 9% 5CT.

[17]Arthur A. Adamson, *Physical Chemistry of Surfaces,* 2nd ed. (Interscience, New York, 1967), Chap. XIII.

[18]Arthur A. Adamson, Ref. 17, p. 408.

[19]L. D. Landau and E. M. Lifshitz, Ref. 11, pp. 257–259.

[20]L. D. Landau and E. M. Lifshitz, Ref. 11, pp. 275–277.

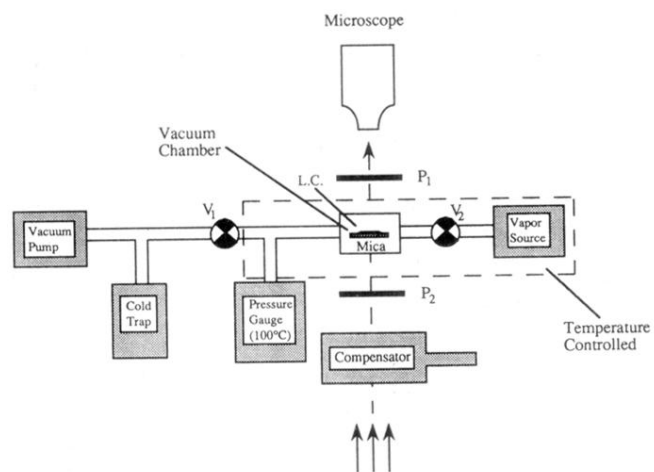[21]J. Bechhoefer, J-L. Duvail, F. Masson, B. Jérôme, R. M. Hornreich, and P. Pieranski (unpublished).

FIG. 1. Diagram of experimental apparatus. P_1 and P_2 denote polarizer and analyzer, respectively. V_1 and V_2 denote valves that permit entry and exit of gases from the experimental chamber. LC denotes the liquid-crystal layer spread on top of the crystalline substrate.