

Critical behavior of an interphase layer and the surface properties of a liquid crystal in micropores

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The temperature dependence of Porod's invariant measured in an experiment on small-angle x-ray scattering shows that the micropores contain a liquid-crystal interphase transition layer and that the thickness of this layer is of critical importance. The corresponding critical index is 0.25.

The density of a liquid crystal in the surface layer and the temperature dependence of the thickness of the interphase transition layer are of fundamental importance. It is not clear, however, whether this dependence is critical and, if so, then what would be the value of the critical index that describes it? If the thickness of the interphase

layer at the interface between a liquid crystal and a solid is commensurate with the length of a molecule, deviations may occur from the theoretical predictions which hold for the 3D space.

To solve this problem, we used small-angle x-ray scattering method to study a pentylocyanobiphenyl system (5CB) in a microporous quartz-glass matrix. The matrix had the following characteristics: volume fractions of the solid phase and pores $\omega_1 = 0.74$ and $\omega_2 = 0.26$, mean radius of pores $R = 90 \text{ \AA}$, specific surface of pores $S/V = 1.08 \times 10^6 \text{ cm}^{-1}$, and density of the matrix framework $d_1 = 2.26 \text{ g/cm}^3$. The temperatures of the phase transitions of 5CB in the free state were $T_{CN} = 295 \text{ K}$ (crystal–liquid crystal) and $T_{NI} = 308 \text{ K}$ (liquid crystal–isotropic phase).

The x-ray measurements were carried out using a small-angle Anton Paar chamber (made in Austria) in the range of angles from $10'$ to $250'$. The signal-accumulation threshold at each point was 2.5×10^4 pulses. As samples we used 0.2-mm-thick porous-glass plates impregnated with 5CB. These plates were placed in a thermally stabilized, flat, 0.23-mm-thick cell which was filled with a liquid crystal. These measures prevented the liquid crystal from leaking out from the pores.

A structural description of such a two-phase system can be found from studies of small-angle x-ray scattering with use of Porod's¹ theory.

A quantity, called Porod's invariant, is determined experimentally. As a result of slit collimation of the beam, we can describe this invariant as

$$Q = \int_0^{\infty} I(h)h dh,$$

where I is the intensity of the scattered light, $h = (4\pi/\lambda)\sin(\theta/2)$, θ is the scattering angle, and $\lambda = 1.54 \text{ \AA}$. If I is given in absolute units, i.e., relative to the intensity of the primary beam, then Q would be related to the characteristics of the system under study by the relation

$$Q = 2\pi\lambda i_e H(\rho_1 - \rho_2)^2 \omega_1 \omega_2, \quad (1)$$

where ρ_1 and ρ_2 are the electron densities of the solid phase of the matrix and of the liquid crystal, i_e is the scattering cross section of an electron, and H is the thickness of the scattering layer. Relation (1) is valid if the electron density is constant in each phase and if it varies abruptly at the interface. The temperature dependence of Q in such a two-phase system is determined exclusively by the dependence $\rho_2(T)$, since the density of the matrix framework is nearly constant in the temperature range 0 – $100 \text{ }^\circ\text{C}$. Clearly, the density of the liquid crystal decreases with increasing T , $\Delta\rho$ increases, and hence Q should also increase. Figure 1 is a plot of the $Q(T)$ curve. We see that this curve cannot be explained in terms of the temperature dependence of the density of the liquid crystal, without appealing to the model for the interphase surface layer.

If an interphase layer with a density different from ρ_2 is formed in the liquid crystal at the interface between the phases (the inset in Fig. 1), relation (1) becomes

$$Q = 2\pi\lambda i_e H(\rho_1 - \rho_2)^2 (\omega_1 \omega_2 - \omega_3),$$

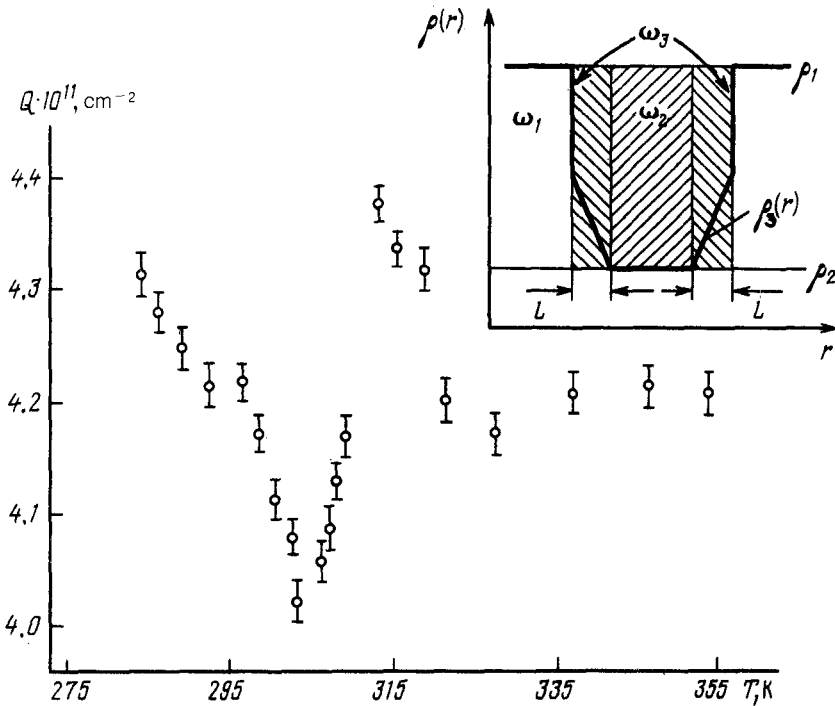


FIG. 1. Temperature dependence of Porod's invariant Q . The model of a pseudo-two-phase system is shown in the inset.

where ω_3 is the volume fraction of this layer. It is logical to assume that the layer in all pores is formed under the same conditions. We can then introduce a thickness of the transition interphase layer L (the inset in Fig. 1). Taking into account the fact that the electron and mass densities are related by the relation $\rho = N_e N_A d / M$, where N_e is the number of electrons per molecule, M is the molecular mass, N_A is Avogadro's number, and the ratio N_e / M is approximately equal to 0.5 mole/g, the following formula is valid for such a pseudo-two-phase system²:

$$Q = 2\pi\lambda_e H(N_e^2 N_A^2 / M^2)(d_1 - d_2)^2 (\omega_1 \omega_2 - LS/6V). \quad (2)$$

The dependence $L(T)$ calculated from Eq. (2) is a critical dependence (Fig. 2). A layer of thickness no less than the length of a molecule, $L_0 \approx 18 \text{ \AA}$, can be assumed to always exist, and L can be represented as a sum of L_0 and the singular part. Figure 3 is a plot of $\log(L - L_0)$ versus $\log \tau$, where $\tau = (T_c - T)/T_c$ for $T < T_c$ and $\tau = (T - T_c)/T_c$ for $T > T_c$. The straight line corresponds to $T_c = 304.5 \text{ K}$ and to the critical index 0.25 ± 0.03 . The solid lines in Fig. 2 were drawn from an equation which is based on the data in Fig. 3: $L = L_0 + A\tau^{-0.25}$, where $A = 3.2 \pm 0.2 \text{ \AA}$.

There are two ways in which $L(T)$ can be described theoretically: by using scaling and by using the theory of capillary waves. These methods give sharply differing

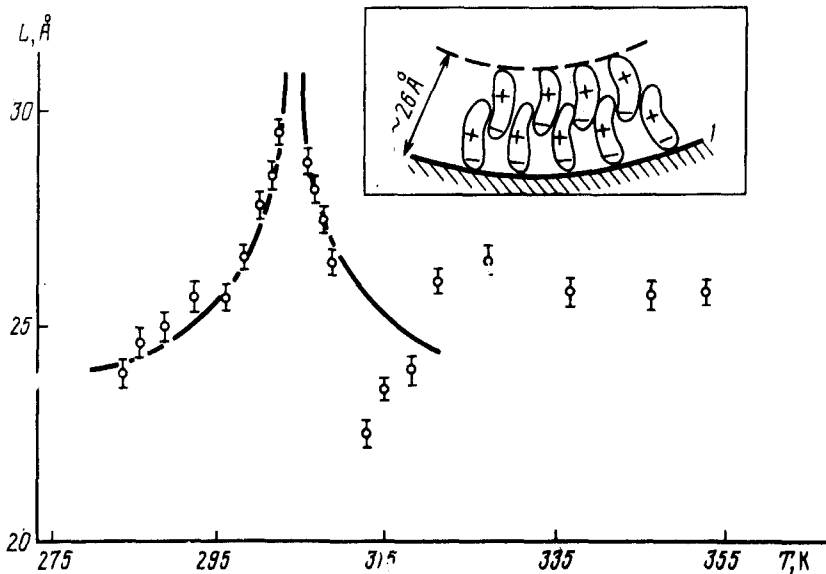


FIG. 2. Temperature dependence of the thickness of the interphase transition layer. The model of a polar bilayer is shown in the inset. 1—The liquid crystal—glass interface.

results in the case of a 2D space (see Ref. 3 and the literature cited there) and are in agreement for $D \geq 3$. According to the scaling approach, $L \sim (T_c - T)^{-\nu}$, where ν is the critical index of the correlation radius, for any dimensionality of space, and $\nu = 1$ for a 2D space,³ that

$$L \sim (T_c - T)^{-(\mu + \beta)/4}, \quad (3)$$

where μ and β are the critical indices of the surface tension and the order parameter.

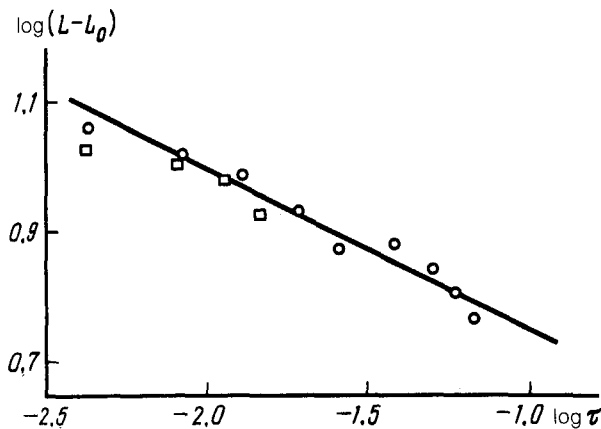


FIG. 3. Singular part of the surface layer versus the reduced temperature on the log-log scale. \circ — $T < T_c$; \square — $T > T_c$.

For a 2D space the exact values of μ and β are 1 and $1/8$ (the two-dimensional Ising model) and the critical index in (3) is $9/32$ (Ref. 3). In the system under study, the liquid crystal layer enclosed in the pore is limited, is not flat, and is not two-dimensional. At best, it may be regarded as a quasi-two-dimensional layer because of the inappreciable thickness of the transition layer. The experimental value of the critical index obtained by us is nonetheless approximately equal to the value predicted by the theory of capillary waves in a 2D space. In experimental studies of films consisting of liquid binary mixtures about 5000 \AA thick the relation between the critical temperature shift and the film thickness was described⁴ by the critical index $\beta = 1/8$, in total agreement with the 2D Ising model.

At temperatures $T > 312 \text{ K}$ the experimental points in Fig. 2 diverge sharply from the theoretical curve because of the onset of a broad (with respect to the temperature) transition to the isotropic phase, which terminates at $T \approx 332 \text{ K}$. An interphase layer of thickness $\sim 26 \text{ \AA}$, which does not depend on the temperature, forms at the wall in the same temperature region (the inset in Fig. 2). The key factors responsible for the formation of such a polar bilayer are the dipole structure of the 5CB molecules, the properties of the adsorbing surface, and the spatial restrictions imposed by the rigid substrate. The coupling responsible for the liquid-crystal order facilitates the establishment of surface order. Measurements of Q at T corresponding to the solid phase of 5CB in the pores, and hence to $L = 0$, yields a value $Q = 1.024 \times 10^{12} \text{ cm}^{-2}$, from which we find the density to be $d_2 = 1.02 \text{ g/cm}^3$. This means that the density of a liquid-crystal substance in the pores does not exceed the density of a liquid crystal in the free state and that it is approximately equal to it.

It should be noted that porous quartz glass can be used as an ideal matrix to study the influence of temperature on the surface effects that occur at the interface between the glass and the second component. Since the structural characteristics of the quartz matrix are nearly independent of the temperature, all the observable effects can be attributed to the change in the physical properties of the second component.

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