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# PROPERTIES OF WALL-ADJACENT EPITROPIC LIQUID CRYSTALLINE LAYERS

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A two-component theoretical model of orientational ordering in wall-adjacent layers of a nonmesogenic liquid (consisting of monomers and dimers) with anisotropic intermolecular interaction has been developed. In the framework of the model, a number of experimental results such as the isotherms of disjoining pressure and some peculiarities in the behavior of heat capacity and dielectric permittivity of the liquid interlayers have been explained.

## 1. Introduction

Liquid layers disposed directly near solid surfaces play essential roles in the coating, lubrication, adhesion, wetting, chemical and biological processes, *etc.* A lot of experiments have suggested that the structure and properties of liquids near interfaces are different from that of the same liquid in bulk. For example, the surface force measurements of liquids between two smooth solid surfaces showed that there are oscillations in the force acting between the solid surfaces as a function of the distance between the two surfaces [1–4]. The interfacial structure of liquid layers at solid interfaces has been a subject of numerous molecular dynamics simulations [5, 6].

In a number of works [7–11], the possibility for a solid substrate to induce the orientational ordering in nonmesogenic and usually polar organic liquids was investigated. This orientational ordered state extends on a distance up to 100 molecular sizes from the solid substrate. Note that, according to [12], the orientational arrangement in polar liquids leads to the appearance of dimers. That is why this possibility should be considered in studied systems. The brightest experimental results were connected with measurements and the further processing of series of intrinsic electronic-vibrational absorption spectra [11]. These spectra were measured for ultrathin liquid interlayers in wide ranges of their thicknesses, temperatures, and concentrations [13, 14]. The statistical analysis of spectral results showed the existence of two types of absorption centers in this system. One of them is naturally connected with dimers (D) and

other one with monomers (M). The absorption spectra of monomers and dimers were connected with the spectra of the thinnest and thickest layers in the series, respectively [15]. The decomposition procedure of complicated spectra into M and D subspectra gives a possibility to establish the thickness dependence of the relative monomer concentration in a studied system. At the same time, the effect of orientational ordering of the wall-adjacent layer with the order parameter  $S \approx 0.4$  was found (here,  $S$  is a usual scalar order parameter, which is expressed by formula  $S = 0.5 \langle (3\cos^2(\theta) - 1) \rangle$ , and  $\theta$  is the angle between the molecular axis and the director). The value of  $S$  sharply decreases with the distance to the substrate to zero [9, 10] in the isotropic bulk phase.

In these layers, the peculiarities in the behavior of spectral characteristics, thermodynamic parameters, and dielectric properties were observed [9, 16–19], but the proper theoretical description of these phenomena is absent till now. The aim of this paper is to work out a theoretical model, in which these peculiarities are described adequately.

## 2. Theoretical Model

The suggested theoretical model describes different physical properties of orientationally ordered wall-adjacent liquid layers (OOWL) near the solid substrates which, in a different way, are called epitropic liquid crystals (ELC) [9]. The basic point of the model was that OOWL consist of monomers and dimers. Relatively weak van der Waals forces are responsible for the molecular bonding in dimers. That is why these associates are not stable particles, but the state of dynamic equilibrium between dimers and monomers exists in the studied system. In order to work out a proper theoretical description of these spatially confined layers, the following contributions to the excess free energy of the system were taken into account [12–14]:

– Entropy parts of the free energy for monomers and dimers;

- Dipole-dipole and disperse interaction between pairs “M-M”;
- Disperse interaction between pairs “M-M”; “M-D”, “D-D”;
- Bond energy of a dimer;
- Interaction between particles of a liquid and a solid substrate.

The minimization of the free energy expression with respect to the M- and D-densities leads to the self-consistent system of equations for the thickness dependences of the monomer order parameter ( $S_1$ ), dimer order parameter ( $S_2$ ), and relative local concentration (or local volumetric part)  $p$  of monomers in the system [13, 14]:

$$\begin{cases} S_i = \frac{1}{I_i^a} \int_{-1}^{+1} P_2(x) \exp \left\{ [pA_2^{1i}S_1 + \dots \right. \\ \left. \dots + \frac{1-p}{2}A_2^{i2}S_2 + W_1(h,T)C_2^iS_1] P_2(x) \right\} dx, \\ p = \frac{1}{1 + 2\lambda I_2/I_1 \exp(E_d/(kT))} \end{cases} \quad (1)$$

$i = 1, 2,$

where  $I_i^a$  and  $I_i$  depend, in turn, on the parameters  $S_1$ ,  $S_2$ , and  $p$ .

Here,  $h$  is the distance to the solid substrate,  $C_2^i$  and  $C_0^i$  are coefficients that characterize the isotropic and anisotropic interactions of a liquid particle with the solid substrate;  $\lambda$  is the Lagrangian multiplier to be determined;  $E_d$  is the energy of a dimer bond; index  $i = 1, 2$  corresponds to M and D, respectively;  $P_2(x)$  is the Legendre polynomial of the second order; and  $A_{0,2}^{i,j}$  are the effective potentials of the dipole-dipole and disperse interactions between liquid particles.

Using the intermolecular potential in the Buckingham form, we may write the following expression, which characterizes the interaction energies between liquid particles and the solid substrate:

$$\begin{aligned} W_i(h,T) = k & \left[ - \left( \frac{T_1}{T} \right) \left( \frac{h_0}{h} \right)^3 + \dots \right. \\ & \left. \dots + \left( \frac{T_2}{T} \right) \left( 2 + \frac{h}{h_0} \right) \exp \left( - \frac{h}{h_0} \right) \right] \times \\ & \times [C_0^1 + C_2^1 S_1 P(x)], \end{aligned} \quad (2)$$

where  $k$  is equal to 1 for monomers and varies in the range (1.5, 2) in the case of dimers;  $T_1$ ,  $T_2$  are fitting

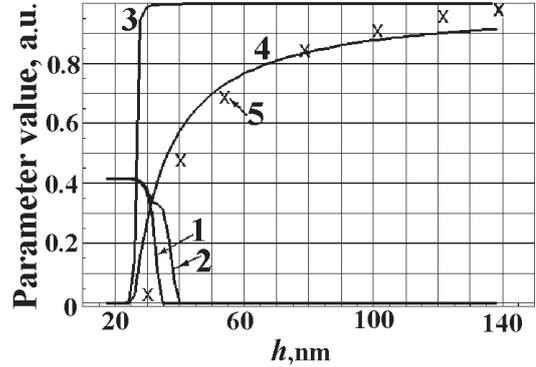


Fig. 1. Theoretically calculated thickness dependences of the order parameters of monomers  $S_1$  (1); dimers  $S_2$  (2), local volumetric part of monomers  $p = p(h)$  (3), and  $\bar{p}(h) = \frac{1}{h} \int_0^h p(x) dx$  (4) averaged over the interlayer thickness. The last one was experimentally measured for anisole OOWL near quartz substrate by spectral method (5)

parameters of the Buckingham potential, and the fitting parameter  $h_0$  determines the OOWL equilibrium thickness. The parameters of orientational interaction  $C_0^1$  and  $C_2^1$  are the coefficients of expansion of the anisotropic interaction potential of the liquid particles with the substrate in a power series in Legendre polynomials.

After calculating the integrals, the expression for free energy [13] may be written in the form [20]

$$\begin{aligned} F_0 = \frac{F}{NkT} = \frac{p^2}{2} & \left( A_{11}^0 + A_{11}^{(2)} S_1^2 \right) + \dots \\ & \dots + \frac{1}{2} \left( \frac{1-p}{2} \right)^2 \left( A_{22}^0 + A_{22}^{(2)} S_2^2 \right) + \dots \\ & \dots + \frac{p(1-p)}{2} \left( A_{12}^0 + A_{12}^{(2)} S_1 S_2 \right) - \frac{1+p}{2} + \lambda^*, \end{aligned} \quad (3)$$

where  $\lambda^*$  is some constant.

System (1) was solved numerically, and the results are shown in Fig. 1 together with our experimental results. Further, the calculated values  $S_1$ ,  $S_2$ , and  $p$  were substituted in expression (3).

Let us consider the semiinfinite layer of an anisotropic liquid, which is adjacent to a lyophilic solid substrate. Figure 2 presents different types of solutions of the system of equations (1). These types of solutions naturally depend on the values and the signs of the parameters of orientational interactions  $C_0^1$  and  $C_2^1$ .

The sign of  $C_0^1$  affects the value of M-concentrations in OOWL and in the bulk phase:  $C_0^1 > 0$  – only monomers exist in OOWL and the bulk phase (Fig. 2, b, c), if  $C_0^1 \leq 0$

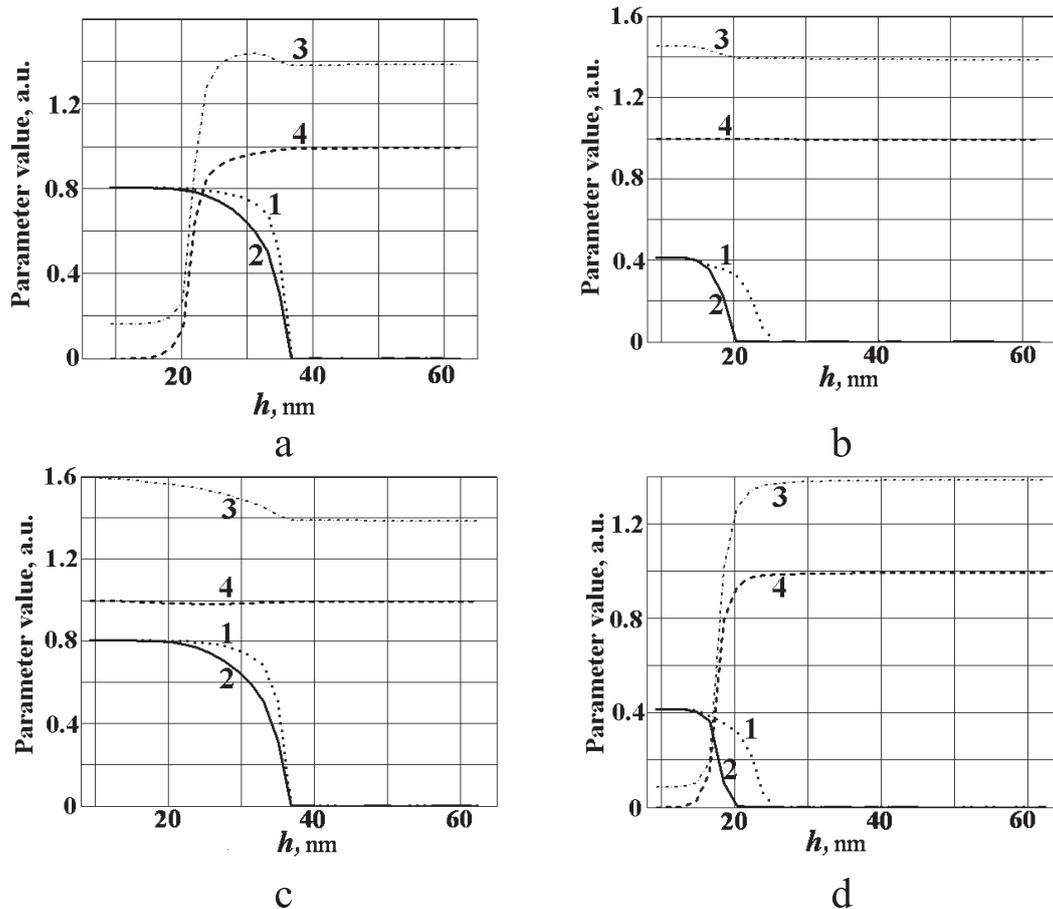


Fig. 2. Calculated thickness dependences of different OOWL characteristics: 1 – D order parameter  $S_2$ , 2 – M order parameter  $S_1$ , 3 – dimensionless value of free energy  $F_0$ , 4 – M relative density  $p$ . Cases a, b, c, d correspond to different combinations of  $C_0$  and  $C_1$  signs: a –  $C_0 = -0.4$ ,  $C_1 = +0.4$ , b –  $C_0 = +0.4$ ,  $C_1 = -0.4$ , c –  $C_0 = +0.4$ ,  $C_1 = +0.4$ , d –  $C_0 = -0.4$ ,  $C_1 = +0.4$

– the M concentration in OOWL is equal to zero, and a jump to 1 in the bulk phase takes place (Fig 2, a, d). Also the sign of  $C_0^1$  determines the behavior of the free energy  $F_0$ . In the case of  $C_0^1 > 0$ , decreasing  $h$  firstly does not change  $F_0$ . But then its value increases (Fig. 2, b, c). This means that these states are unstable and practically unrealized.

The sign of  $C_2^1$  determines the order parameter  $S$ : if  $C_2^1 > 0$ , the value of  $S$  in OOWL is about 0.4 (this value is usually characteristic of the nematic phase) and jumps to zero in the bulk (Fig. 2, a, c). If  $C_2^1 < 0$  (Fig. 2, b, d), then the  $S$  value is about 0.8.

The most stable states correspond to cases a and d, because the transition “bulk phase – OOWL” causes the jump of the free energy to zero. The state of type b may be characterized as a nematic-like state (which exists near the dielectric surface – ELC), and the state of type d may be characterized as a smectic-like state

(it exists near conductive substrates, for example, near quartz substrates covered with a thin metallic film [15]). Note that states presented in Fig. 2, c, d are unrealized, because, in these cases, the value of free energy near the solid substrate exceeds its bulk value.

### 3. Results and Discussion

#### 3.1. Disjoining pressure

One of the important functions that characterize the state of orientational ordering in OOWL is the disjoining pressure  $\pi$ , which was firstly introduced by B.V. Derjaguin [16] as the first derivative of the excess free energy with respect to the layer thickness  $\pi = -(\partial F / \partial h)_T$ . Early, it was precisely measured experimentally [8] in orientationally ordered nitrobenzene wetting films.

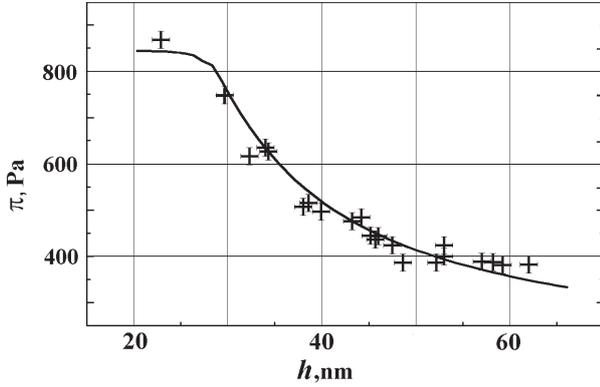


Fig. 3. Disjoining pressure isotherms experimentally measured [17] and theoretically (solid line) calculated according to (4). Case of nitrobenzene near the quartz substrate

Taking Eq. (2) for the interaction energy between liquid particles and the solid substrate into account and making simple transformations of Eq. (3), we can calculate the thickness dependence of the disjoining pressure at a fixed temperature (disjoining pressure isotherm). In our model, it can be expressed by the relation

$$\pi = -\left(\frac{z_0}{h}\right)^4 + a(1 + h/h_0)\exp(-h/h_0). \quad (4)$$

The first and second terms are related, respectively, to the molecular part of the free energy and to its structural part. The parameters  $z_0$ ,  $a$ , and  $h_0$  ( $z_0 = 59.73$  nm,  $a = 10^3$ ,  $h_0 = 25.49$  nm) were varied for the best fitting with experimental results. Figure 3 presents the reasonable agreement between experimentally measured and theoretically calculated isotherms.

### 3.2. Heat Capacity

The thickness dependence of the heat capacity of ultrathin liquid interlayers and wetting films was directly measured in calorimetrical experiments [[9]] of a liquid disposed in a disperse system (quartz powder or aerosil). In the framework of our two-component model using the well-known thermodynamic equations, we obtained the expression for the specific heat capacity at a fixed temperature in the following form (neglecting the small second derivative  $(\partial^2 F/\partial T^2)_p$ ):

$$C_p = 2\frac{F_0}{T_0} + 4\frac{T}{T_0}\left(\frac{\partial F_0}{\partial T}\right)_p + \frac{\lambda^*}{T_0}. \quad (5)$$

This formula contains two arbitrary parameters  $T_0$  and  $\lambda^*/T_0$ , which are chosen by the least square method in order to obtain the best agreement with the experiment.

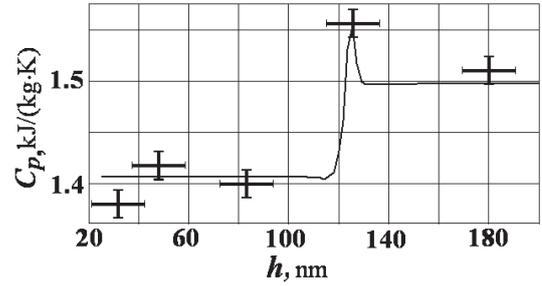


Fig. 4. Thickness dependence of the specific heat capacity experimentally measured [9] and theoretically (solid line) calculated according to (5). Case of nitrobenzene near a quartz substrate

In the case of nitrobenzene near the lyophilized quartz or glass substrate ( $T = 291$  K), we found  $T_0 = 200$  K and  $\lambda^*/T_0 = 1.4$ .

Figure 4 illustrates a good agreement of the temperature dependence of the heat capacity  $C_p(T)$  measured experimentally and calculated theoretically according to (4).

### 3.3. Dielectric Permittivity

Dielectric properties of thin wall-adjacent liquid layers were investigated earlier in [18], where the difference between the value of their dielectric permittivity and the permittivity of the bulk liquid was pointed out. It was found that the thinning of the interlayer results in decreasing its dielectric permittivity. Further, the precise measurement of dielectric properties of nitrobenzene interlayers bounded by metal substrates was carried out [19, 20].

In order to explain the observed decrease of the dielectric permittivity near a solid substrate, we propose a physical model which is based on the De Jeu–Bordewijk theory for such orientationally ordered systems as nematic liquid crystals [22]. In this model, the mean value of dielectric permittivity can be expressed as follows:

$$\bar{\varepsilon} = 1 + \frac{1}{3} \left[ \frac{\alpha_{\parallel} (1 + \kappa S)}{1 - \alpha_{\parallel} [A \cdot B + E \cdot F]} + \frac{2\alpha_{\perp} (1 - \kappa S)}{1 - \alpha_{\perp} [C \cdot D - G \cdot F]} \right], \quad (6)$$

$$A = \left(\frac{1}{3} - 2w\right); \quad B = (1 + 2\kappa S);$$

$$C = \left(\frac{1}{3} + w\right); \quad D = (1 - \kappa S);$$

$$E = 2w(1 - \kappa); \quad F = (1 - S);$$

$$G = w(1 + 2\kappa).$$

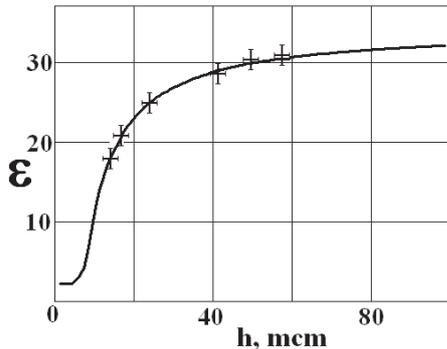


Fig. 5. Thickness dependence of the dielectric permittivity experimentally measured [19] and theoretically (solid line) calculated according to (6), (7) in nitrobenzene interlayers bounded by metallic substrates ( $T = 291$  K)

Here,  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$  are the components of the molecular polarizability tensor; as usual,  $\kappa \approx 0.3$  [22]; parameter  $w$  is related to the asymmetry of a molecular shape  $w = \frac{2}{45} \ln [m(m+1)/2]$ ,  $m = L/D$  ( $L$  is the length of a molecular cylinder, and  $D$  is its diameter); and  $S$  is the order parameter.

In distinction with the classical model, we consider the dependence of the order parameters and the dimer concentration on the distance to the surface substrate calculated in the framework of the two-component model. In the studied ELC layers, there exist both monomers and dimers. That is why the parameters  $\alpha_{\parallel}$ ,  $\alpha_{\perp}$ , and  $S$  are chosen to be equal to their mean values:

$$\alpha_{\parallel} = pa_1 + (1-p)a_2; \quad (7)$$

$$\alpha_{\perp} = pa_3 + (1-p)a_4; \quad S = pS_1 + (1-p)S_2.$$

Parameters  $w$ ,  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$  were obtained by least square method:

$$w = 0.0195, \quad a_1 = 2.8293;$$

$$a_2 = 0.0016, \quad a_3 = 2.9246, \quad a_4 = 0.0109.$$

Near the substrate surface ( $h$  is small), dimers prevail, and the dielectric permittivity is small and relatively constant ( $\varepsilon = 2.5$ ). This confirms the conclusion that, in ELC, the sandwich type dimers (antiparallel molecular orientation) have almost zero dipole moment. The monomer concentration increases with the distance to the surface. That is why the dielectric permittivity asymptotically approaches the table value [23] for the bulk nitrobenzene  $\varepsilon = 32.5$  (Fig. 5).

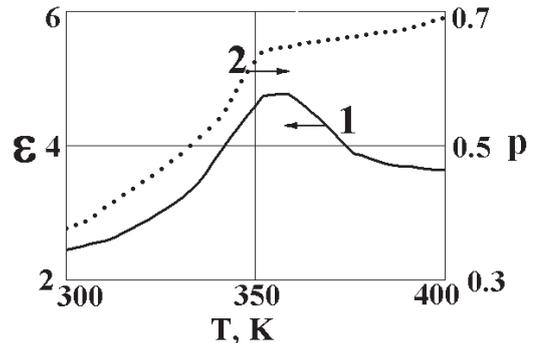


Fig. 6. Temperature dependence of the dielectric permittivity  $\varepsilon$  calculated according to (1), (6), and (7) and the monomer concentration  $p$  in nitrobenzene interlayer ( $h = 2.7$   $\mu\text{m}$ ) bounded by metallic substrates

The temperature dependence  $\varepsilon(T)$  is connected with the temperature dependences of the order parameters, relative M concentration, and effective potentials of the dipole-dipole and disperse interactions.

The calculated temperature dependences  $\varepsilon(T)$  and  $p(T)$  for a relatively thin interlayer ( $h = 2.7$   $\mu\text{m}$ ) are presented in Fig. 6. One can see the nonmonotonous behavior of  $\varepsilon(T)$ . Firstly at low temperatures,  $\varepsilon$  increases with the monomer part  $p$ . Further at  $T > 350$  K, the growth of monomers becomes slower, and the universal decrease of the permittivity for polar liquids with temperature plays the important role. For large thicknesses of the interlayer ( $h$  100  $\mu\text{m}$ ), the presence of dimers can be neglected ( $p \sim 1$ , nearly all liquid interlayer is in the isotropic bulk phase). That is why the usual temperature dependence for isotropic bulk liquids takes place.

#### 4. Conclusions

1. A theoretical model of orientational ordering (induced by a solid substrate) in ultrathin wall-adjacent liquid layers (ELC) was worked out.
2. This model involves the evidence of monomers and dimers in the interlayers and the interaction between them and a solid substrate and satisfactorily explains the peculiarities of the behavior of main thermodynamical characteristics of ELC layers. The orientationally ordered liquid crystalline phase is near the solid substrate and is separated from the isotropic bulk phase by the relatively sharp boundary. D and M dominate in OOWL and in the bulk phase, respectively.
3. The analysis of the thickness dependence of the free energy determines the existence of two most stable solutions among the set of possible solutions of our model.

One of them corresponds to the nematic-like and the other one – to the smectic-like type of a phase state.

4. The proposed model also gives a reasonable explanation of the peculiarities in the thickness and temperature dependences of the dielectric susceptibility in wall-adjacent ELC layers.

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#### ВЛАСТИВОСТІ ПРИСТІННИХ ЕПІТРОПНИХ РІДКОКРИСТАЛІЧНИХ ШАРІВ

О.Ю. Поповський, В.І. Михайленко

#### Резюме

Запропоновано двохкомпонентну теоретичну модель орієнтаційного впорядкування у пристінних шарах немезогенних рідин, які складаються з мономерів та димерів з анізотропною міжмолекулярною взаємодією. У межах цієї моделі пояснюється низка раніше одержаних експериментальних результатів, таких як поведінка ізотерми розклинюючого тиску, товщинних залежностей теплоємності та діелектричної проникності.