

# Langmuir films

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This review deals with optical properties of Langmuir films formed by successive transfer of monomolecular layers of surface-active organic compounds from the surface of water onto a solid substrate. This gives rise to new solid-state systems consisting of stacks of weakly coupled molecular layers; the properties of molecules (optical, electrical, photochemical, etc.) are not subject to any constraints. The review deals with the properties of monolayers on the surface of water, with their transfer onto solid substrates, and with their electrical, optical, photoelectric, and electrooptic properties. The review concludes with a discussion of applications of Langmuir films in molecular electronics, which is now becoming a new technology.

## CONTENTS

1. Introduction .....	623
2. Monolayer on the surface of water .....	624
2.1. Amphiphilic molecules. 2.2. Phase transitions in a monolayer. 2.3. Properties of surface monolayers.	
3. Transfer of monolayers onto solid substrates .....	628
3.1. Langmuir–Blodgett method. 3.2. Other methods. 3.3. Structural features of films on solid substrates.	
4. Optics of monolayers and multilayers .....	631
4.1. Waveguide properties. 4.2. Dichroism and other spectral characteristics. 4.3. Molecular association. 4.4. Migration of excitation energy.	
5. Noncentrosymmetric multilayers .....	635
5.1. Comments on the structure. 5.2. Macroscopic (“spontaneous”) polarization, pyroelectric effect, and piezoelectric effect. 5.3. Photoinduced polarization. 5.4. Stark effect. 5.5. Nonlinear optical effects.	
6. Electrical, magnetic, and photoelectric properties of Langmuir–Blodgett films .....	638
6.1. Electrical and magnetic properties. 6.2. Photoelectric processes. 6.3. Photochemical transformations.	
7. Conclusions. Langmuir films and molecular electronics .....	641
References .....	641

## 1. INTRODUCTION

A feature of contemporary physics is a heightened interest in materials with a complex molecular structure. More and more often a physicist borrows materials for investigation from a chemist or a biologist. Synthetic dyes have become a unique class of materials for tunable lasers. Organic metals are being used as models in studies of superconductivity mechanisms. Liquid crystals have forced us to look anew at the problem of phase transitions in low-dimensional systems. Some organic crystals, particularly amino acids, have unique nonlinear optical properties. And now interest is growing in another unusual class of molecular systems in the form of Langmuir films.

We shall begin with a brief discussion of the terminology which is not yet fully established. Langmuir films are usually understood to be monomolecular layers of surface-active organic substances at the interface between a liquid (normally water) and a gaseous (air) medium. When such monolayers are transferred onto a solid substrate, a solid monomolecular or multimolecular (monolayer or multilayer) film is formed and it is known as a Langmuir–Blodgett film. We shall generally adopt this terminology, but we shall use the term “Langmuir film” in a wider sense meaning both original Langmuir films as well as Langmuir–Blodgett films.

The history of Langmuir films consists of three stages. From the ancient times it has been known that oil spreads on the surface of water and the effect has been employed to calm rough seas. In 1774 Benjamin Franklin even carried out the first semiquantitative experiments<sup>1</sup> and estimated the area covered by a spoonful of olive oil. The second stage began with the work of A. Pockels<sup>2</sup> and Lord Rayleigh,<sup>3</sup> at the end of the nineteenth century, who carried out detailed investigations of monolayers on the surface of water and their transfer onto solid substrates. A decisive contribution was made by Irving Langmuir, who established the monomolecular nature of surface films and proposed (together with Katharine Burr Blodgett) a method of transferring them onto a solid substrate.<sup>4,5</sup> A detailed account of the results of these investigations can be found in a monograph by G.L. Gaines.<sup>6</sup> A considerable contribution to the study of electrical properties of the interface and rheology of surface layers was at this stage made by Soviet scientists A.N. Frumkin<sup>7</sup> and A.A. Trapeznikov.<sup>8</sup> The third stage began from a series of papers by H. Kuhn and his school.<sup>9,10</sup> The basic idea of Kuhn *et al.* is the principle of molecular architecture, i.e., construction of molecular assemblies with a specified architecture from Langmuir–Blodgett films. Recent years have seen explosive growth of the number of papers on this subject. Everywhere the work on Langmuir films is being pur-

sued using the most modern physical methods.<sup>11,12</sup> This has been due to, in particular, rapidly growing interest in technical applications of such films. The technology of preparing thin and ultrathin films proposed by Langmuir and Blodgett has proved to be very promising in the construction of molecular electronic devices.

Monomolecular films at boundaries between phases and multilayer solid structures (which we shall call simply multilayers) transferred onto solid substrates have very unusual structures and a unique set of physical properties. It has become possible to study two-dimensional (or quasitwo-dimensional) solid and liquid-crystal structures and the interaction of molecules separated by rigorously controlled distances and with a rigorously set mutual orientation. Moreover, studies are being made of the processes of self-organization of matter by sensitive physical methods. Investigations of Langmuir films have provided a bridge between physics, chemistry, biology, and electronics.

Several reviews have been published of various aspects of the problem. Apart from the sources already cited,<sup>6,9-12</sup> one should mention monographs<sup>13,14</sup> dealing with physicochemical properties of monolayers on water and also reviews<sup>15-17</sup> concentrating on the applications of solid multilayers. A detailed review covering, as far as possible, the full range of physical problems has not yet been published (to the present author's knowledge). The present paper is an attempt to fill this gap. It will be largely based on papers presented at two international conferences on Langmuir-Blodgett films, the proceedings of which were published in several volumes of the journal *Thin Solid Films* (Vol. 99 in 1983 and Vols. 132-134 in 1985), which accounts for the relatively frequent citations of this highly specialized journal.

## 2. MONOLAYER ON THE SURFACE OF WATER

### 2.1. Amphiphilic molecules

It has long been known that "like dissolves in like." Let us compare, for example, the solubility of organic substances in such media as water and hydrocarbons. Water is a strongly polar solvent (with a static permittivity  $\epsilon = 81$ ) and it readily dissolves organic acids, their salts, and other substances that dissociate easily into ions. For example, some of the well-known organic dyes such as crystal violet (representing the usual violet ink) or brilliant green (used as an antiseptic) are salts. After dissociation the resultant ions readily participate in the Coulomb interaction with protons ( $H^+$ ) and hydroxyls ( $OH^-$ ) in water and this is the reason for the high solubility of these salts in water. Such compounds are hydrophilic, i.e., they love water. On the other hand, there is an extensive class of organic compounds which readily dissolve in nonpolar solvents, such as, for example,  $CCl_4$ , hexane, or other hydrocarbons. In this case the Coulomb interaction does not play any significant role and the dispersive forces are not very sensitive to details of the molecular structure, so that the dissolved substance readily replaces the solvent molecules. High solubility in fats (lipids) is the origin of the name lipophilic for this case of compounds. They are also called hydrophobic implying the "fear" of water. In truth, it is water that "fears" these compounds because their incorporation in the structure of water results in breaking of numerous hydrogen bonds without any energy compensation.

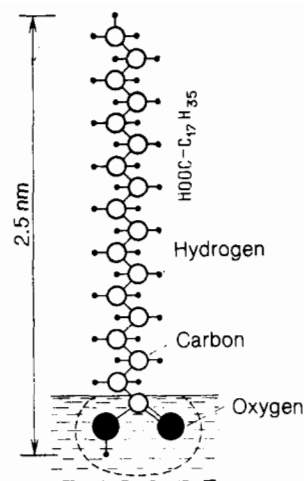


FIG. 1. Model of a stearic acid molecule and its chemical formula.

We can thus see that some organic molecules are hydrophilic and the other are hydrophobic. But that is not all. There are complex molecules which have different parts that exhibit different properties and the molecule as a whole is called amphiphilic. For example, a molecule of stearic acid (Fig. 1) has a polar head formed by the COOH group, which can give up its proton to water and become negatively charged. The head is therefore attracted to water by the Coulomb force. On the other hand, the hydrophobic hydrocarbon tail  $C_{17}H_{35}$  is pushed out of water. A compromise solution is the location of the molecule at the interface between liquid (water) and gaseous (air) phases. This is the reason why substances of this type are known also as surface-active (or surfactants).

Amphiphilic substances are not at all exotic. First of all, we meet them daily (soaps are salts of fatty acids). Moreover, they are essential to life (phospholipids) because they occur in biological membranes. Finally, chemical synthesis can be used to construct amphiphilic compounds with a great variety of molecular structures. This is a very important aspect from the point of view of our review. In fact, we can take practically any class of organic molecules with all its valuable properties and modify the molecules attaching a hydrophobic tail or sometimes a polar head. Some examples of synthetic amphiphilic compounds will be discussed later (extensive tables can be found in Refs. 9 and 11). It is important to note that many of them are polymerized and this means that they can form very strong films.

### 2.2. Phase transitions in a monolayer

What happens when a small amount of an amphiphilic substance is mixed with water? Some of the molecules in such a substance are indeed dissolved (forming a solution with a concentration of the order of, for example,  $10^{-6}$  mol/m<sup>3</sup>). Other molecules float up to the surface of water. Still others connect forming spherical aggregates (micelles) tending to hide their hydrophobic tails inside the micelles (Fig. 2). A further increase in the concentration creates cylindrical micelles and then a layered (lamellar) liquid-crystal phase. A monomolecular layer of amphiphilic molecules then appears on the surface of water. The properties of lyotropic liquid-crystal phases have been discussed on many occasions before,<sup>18,19</sup> but we shall be interested in the proper-

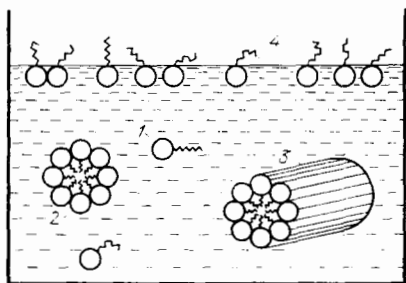


FIG. 2. Formation of micelles and of a surface monolayer by amphiphilic molecules: 1) molecule in solution; 2) spherical micelle; 3) cylindrical micelle; 4) surface monolayer.

ties of a monolayer at the boundary between two phases. It can be produced naturally by a "cleaner" method so as to avoid altering significantly the properties of the aqueous medium. This can be done by dissolving first an amphiphilic compound in a volatile solvent (for example, benzene) and then spraying the resultant solution on the surface of water. The volatile solvent evaporates and the amphiphilic compound forms a film on the surface of water. The amount of such a substance has to be calculated in advance so that for a given surface area of water the film is no thicker than one monomolecular layer.

Thermodynamics of a monolayer of surface-active (surfactant) molecules is usually investigated employing a Langmuir trough in which the main components are a floating barrier, which alters the area of the surface of water occupied by the substance being investigated, and a balance for the determination of the surface pressure. The surface pressure, i.e., the force per unit length of the barrier, is equal to the difference between the surface tensions of pure water ( $\sigma_0$ ) and water carrying a surface film,  $\pi = \sigma_0 - \sigma$  (in units of newton per meter). In addition to this Langmuir balance, use is also made of a Wilhelmy balance to measure directly the surface tensions  $\sigma_0$  and  $\sigma$ . Knowing the total number of amphiphilic molecules and noting the values of the area of a monolayer as the barrier moves, we can construct a  $\pi$ - $A$  isotherm, where  $A$  is the area per molecule or its "landing area." This isotherm carries information not only on the universal intermolecular interaction effects in a monolayer, but also on the specific behavior of a complex amphiphilic molecule when the surface pressure is varied (this behavior may include reorientation, conformal transformation, etc.). An example of the simplest  $\pi$ - $A$  isotherms is shown in Fig. 3. They were obtained for myristic acid  $C_{13}H_{27}COOH$  (Ref. 20), the molecules of which can only acquire a more elongated conformation as a result of changes in the surface pressure and can have various orientations relative to the normal to the surface of a monolayer.

The following chain of phase transitions may occur in fatty acids. At high temperatures (curve 1) or at very low surface pressures there is no interaction of amphiphilic molecules with one another (Fig. 4a). A film then behaves as a two-dimensional ideal gas obeying the equation

$$\pi A = kT; \quad (1)$$

here,  $\pi$  and  $A$  are in units of newtons per meter and in reciprocal meters squared, respectively, and only two degrees of freedom in the translational motion of molecules are allowed

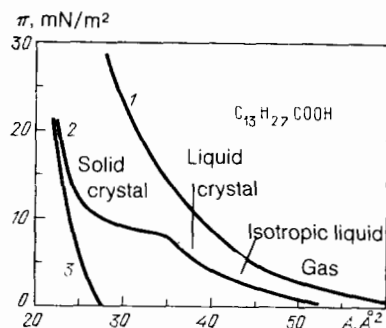


FIG. 3. Isotherms of the surface pressure  $\pi$  plotted against  $A$  per molecule of myristic acid.<sup>20</sup>  $T$ (°C): 1) 34.4; 2) 14.1; 3) 2.5.

for. An increase in the pressure because of a shift of a floating barrier naturally causes Eq. (1) to be disobeyed. As in the three-dimensional case one can use, but with caution, the two-dimensional analog of the van der Waals equation<sup>21</sup>:

$$\left(\pi + \frac{a}{A^2}\right)(A - b) = kT, \quad (2)$$

where the coefficient  $a$  allows for the correction to the pressure because of the interaction of amphiphilic molecules with one another, whereas the coefficient  $b$  corresponds to the minimum area occupied by a molecule in a continuous monolayer. The coefficient  $a$  allows for the dispersive attraction between hydrocarbon tails and the Coulomb repulsion between charged heads. In any case, the isotherm strongly depends on the degree of ionization of amphiphilic molecules which can be controlled by making water more acid (altering pH). The experimental  $\pi$ - $A$  isotherms obtained at high values of  $A$  (in the gaseous phase) lie well below those predicted by Eqs. (1) and (2). The theory can be made to agree with the experimental evidence making allowance for the association of amphiphilic molecules with one another (formation of dimers, trimers, etc.).<sup>21</sup> This reduces the number of particles forming a two-dimensional gas and, consequently, lowers the theoretical value of  $\pi$ . The same effect is produced by the formation of macroscopic islands of the solid phase at low values of  $\pi$  (Ref. 23b).

At lower temperatures (curve 2 in Fig. 3) an increase in

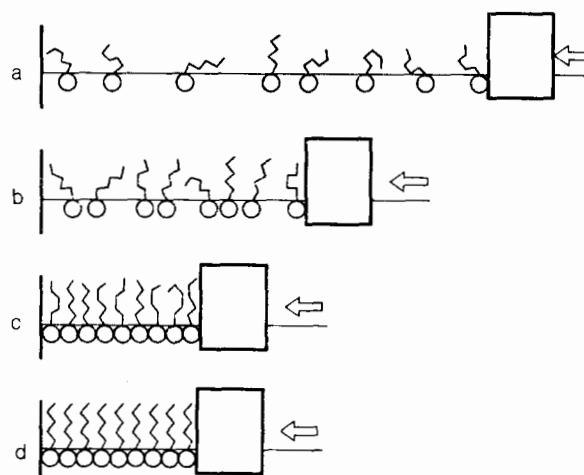


FIG. 4. Phase states of a fatty acid monolayer under different surface pressures: a) two-dimensional gas; b) liquid; c) liquid crystal; d) solid crystal.

the surface pressure results in a transition of the gaseous phase to a two-dimensional isotropic liquid phase (called earlier a "stretched" liquid). In this phase the molecules already interact strongly with one another, but there is no orientation order (Fig. 4b). The hydrocarbon tails assume a great variety of configurations, but their freedom of movement decreases on reduction in the monolayer area. The compressibility of a monolayer, given by the expression

$$\delta = -\frac{1}{A} \left( \frac{\partial A}{\partial \pi} \right)_T, \quad (3)$$

is considerably lower than in the gaseous phase.

When the barrier is moved even further to the left, a monolayer of this kind is converted into an anisotropic liquid, i.e., into a liquid-crystal phase (Fig. 4c). The hydrocarbon tails are now oriented on the average along the normal to the surface but they still remain quite flexible. Calculations<sup>22</sup> demonstrate that the parameter of the orientational order of the individual unit of a hydrocarbon chain

$$S_i = \frac{1}{2} (3 \langle \cos^2 \theta_i \rangle - 1) \quad (4)$$

(here,  $\theta_i$  is the angle of orientation of the  $i$ th -C-C bond relative to the normal to the monolayer) remains constant ( $S = 0.25$ ) for the first 5–10 components counting from the polar head and this is due to steric interactions between the chains. Further along the chain the value of  $S$  falls to zero demonstrating the randomness of the motion of the ends of the hydrocarbon tails.

Further compression of the monolayer transforms it into a two-dimensional crystalline phase (in liquid-crystal terminology this is known as the smectic  $A$ -smectic  $B$  transition<sup>23a</sup>), as shown in Fig. 4d. The hydrocarbon tails are no longer flexible and their configurations become rigidly fixed with correlated positions of atoms in the neighboring molecules. In the case of myristic acid (curve 2 in Fig. 3) this is a first-order phase transition and it is manifested by a small plateau of the isotherm. In the region of this plateau two-dimensional solid and liquid-crystal phases coexist. A further reduction of the monolayer area is accompanied by a strong increase in the pressure (curves 2 and 3 in Fig. 3), because of the low compressibility of the solid state. There may be several two-dimensional solid-crystal phases.<sup>23</sup>

A two-dimensional pressure of, for example, 50 mN/m corresponds to a three-dimensional pressure of the order of 250 atm on the end of a monolayer. Naturally, a monolayer cannot support such a load and it breaks up (monolayer collapse). In some cases a different effect is observed: at some pressure a monolayer breaks up and climbs on top of itself forming a regular multilayer structure.<sup>24</sup> Such behavior is typical of molecules tending to form three-dimensional liquid-crystal phases.<sup>25,26</sup>

The physics of phase transitions in monolayers on the surface of water has not yet been investigated sufficiently thoroughly. This is due to the fact that it is in fact impossible to obtain information on the structure of two-dimensional phases by classical x-ray structure analysis (the exception is the work cited as Ref. 213) and electron microscopy. The nature of the phase transitions can be deduced either from thermodynamic data or on the basis of theoretical models. In particular, it has been suggested that there are tricritical points on the lines representing isotropic liquid-gas<sup>27</sup> and anisotropic liquid-solid<sup>23</sup> phase transitions. A generalized

phase diagram reflecting the current point of view on the nature of phase transitions in monolayers of simple lipids on the surface of water can be found in Ref. 28.

Strictly speaking, a surface monolayer is not a two-dimensional system. The very fact of reorientation of molecules means that the "door to the third dimension" is not closed. In some cases molecules may escape from the surface into the interior of water. This is the reason for the nonhorizontal nature of the plateau in Fig. 3. Finally, there are molecules showing major changes in the conformation when the surface pressure is varied. This is true, for example, of bipolar molecules with two polar heads at the ends connected by a hydrophobic hydrocarbon chain. In this case the  $\pi$ - $A$  isotherm exhibits a wide plateau corresponding to a major change in the area per molecule.<sup>29</sup> This can be regarded phenomenologically as a first-order transition<sup>30</sup> and the microscopic picture shows that initially the molecules form an arc with the polar heads in water, and then one of the heads nevertheless leaves the surface and the molecule becomes vertically oriented. Such a reorientation can also be deduced from a change in the electric potential of the surface. The region of its rapid rise corresponds approximately to the onset of reorientation of the polar heads away from the surface.

Equally a plateau is observed also in the  $\pi$ - $A$  isotherms of fairly large molecules of amphiphilic dyes and particularly of polymer molecules.<sup>31,32</sup>

Much work has been done on the theory of phase transitions in monolayers at the water-air interface, but the problem is far from being solved quantitatively. This is due to the fact that the interactions of amphiphilic molecules with one another are fairly complex. One has to allow for the steric repulsive and dispersive attractive forces between the hydrocarbon chains and for the Coulomb and dipole-dipole forces of the interaction between the polar heads. However, this is not all. Amphiphilic molecules interact strongly with one another forming hydrogen bonds and two-dimensional hydrated crystals. Therefore, the structure of the surface layer of water is modified by the presence of amphiphilic molecules. Finally, ions dissolved in water have a strong influence on the electric potential of a double electric layer at the surface and, therefore, on the thermodynamics of phase transitions.

Approximate calculation methods have become popular and this is particularly true of the mean field<sup>23</sup> and scaling<sup>33</sup> methods, other phenomenological approaches,<sup>34</sup> Monte Carlo method,<sup>35</sup> various lattice models,<sup>27,36</sup> and other microscopic treatments.<sup>37</sup> Numerous citations of the relevant theoretical investigations can be found in Refs. 36–38.

### 2.3. Properties of surface monolayers

We shall be interested particularly in mechanical, optical, and electrical properties. Mechanical properties are closely related to the presence and nature of the translational order in a monolayer plane and, in the absence of direct x-ray structure and electron diffraction studies, they can provide valuable information on structural transformations in a monolayer. Moreover, mechanical properties determine whether a monolayer can be transferred onto a solid substrate. Optical properties can be used to judge the parameters of the orientational order of specific molecular fragments. This order is frequently retained when a monolayer is transferred onto a solid substrate, which underlies the prin-

ciple of molecular architecture. Electrical properties of a monolayer (surface potential) can be used to judge the directions of molecular dipoles, distribution of charges across a section of a monolayer, etc.

As pointed out already, structural changes in a monolayer can be deduced from the characteristics of the  $\pi$ - $A$  isotherms ( $T = \text{const}$ ). In some cases it is more convenient to consider  $T$ - $A$  isochores ( $\pi = \text{const}$ ) or to measure the compressibility of a monolayer described by Eq. (3) (Ref. 23). These methods are however insufficiently sensitive to the structure of a monolayer because it is difficult to distinguish the compressibility of, for example, a two-dimensional liquid from that of a two-dimensional liquid crystal or solid crystal. The fact that the measurements of the surface viscosity of a monolayer reveal a number of additional structural features was already established in the classical work of A. A. Trapeznikov.<sup>8</sup>

The surface viscosity  $\eta_s$  (in units of grams per second, known as surface poises) is introduced, by analogy with the bulk viscosity,<sup>6</sup> defining it as the coefficient of proportionality between a tangential force (per unit length) acting along the  $x$  axis and a gradient of the monolayer flow velocity directed along the  $y$  axis (the  $x$  and  $y$  axes lie in the monolayer plane):

$$\frac{dF}{dx} = \eta_s \frac{\partial v_x}{\partial y}. \quad (5)$$

In measurements of the surface viscosity one can use channel or torsional viscometers. In the first type of viscometer a surface pressure causes a monolayer to float onto a free surface of water via a narrow channel and the velocity of such flow is measured (this is an analog of a Poiseuille capillary); in the second variant a light disk is placed on top of a monolayer and this disk is supported by a quartz filament; damping of torsional vibrations of the disk is investigated. Measurements of the surface viscosity of monolayers of fatty acids made by both methods<sup>39</sup> demonstrated that an increase in the length of a link of an axial chain from  $n = 17$  to  $n = 23$  increases  $\eta_s$  by about two orders of magnitude and the compression Young modulus  $\delta$  of Eq. (3) also increases (approximately twofold). This does not mean that any structural changes in a monolayer take place on increase in the length of the alkyl chain, but it does reflect enhancement of the interaction between neighboring chains.

The surface shear modulus, relating the tensor of the elastic stresses to the shear strain tensor, is probably the parameter most sensitive to the structure of a monolayer. In general, this is a tensor of rank four and it is time-dependent. In the case of a two-dimensional isotropic monolayer subjected to shear deformation in its own plane the viscoelastic properties can be described by a single complex shear modulus<sup>6</sup>

$$G_s^* = G_s + j\omega\eta_s. \quad (6)$$

The appearance of a nonzero real component  $G_s$  of the shear modulus can be regarded as a criterion of a transition into a two-dimensional solid-crystal state. Detailed investigations of the dependence of  $G_s$  on the surface tension were reported in Refs. 40–42 for a number of fatty acids, their alcohols, and also phospholipids. These investigations were carried out using a torsional viscometer for the determination of the com-

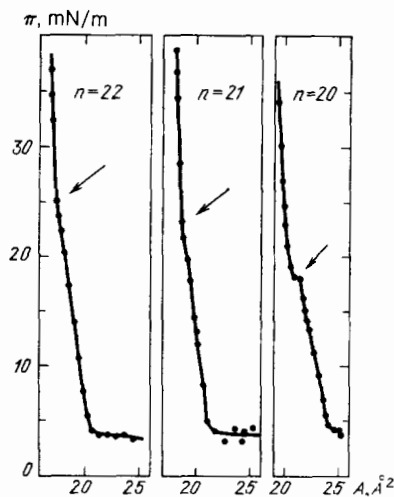


FIG. 5. Surface pressure ( $\pi$ )—area per molecule ( $A$ ) isotherms of fatty acids  $C_nH_{2n+1}OH$  with  $n = 20, 21,$  and  $22$  (Ref. 41). The kinks of the isotherms are identified by arrows.

plex shear modulus  $G_s^*$  and the technique of recording the scattering of light by surface capillary waves, which can give the surface pressure. The monolayer had a centrosymmetric shape and the pressure was varied by raising and lowering the level of liquid in a bath which was in the shape of a funnel.<sup>43</sup>

The results obtained by the group of Abraham were fairly unexpected. In the case of fatty alcohols with the general formula  $C_nH_{2n+1}OH$  they found that at pressures of the order of 20 mN/m there was a kink in the  $\pi$ - $A$  isotherm (Fig. 5). Traditionally this kink is attributed to a transition from the liquid (or liquid-crystal) phase to the solid phase on increase in the applied pressure. This interpretation is confirmed only for a homolog with  $n = 18$ . On the other hand, in the case of a homolog with  $n = 20$  the kink of the isotherm corresponds to the melting of the solid phase on increase in the applied pressure. In the case when  $n = 21$ , a reversible polymorphism is observed: on increase in  $\pi$  the solid phase melts and then solidifies again. The corresponding dependence of the shear modulus under surface tension is shown in Fig. 6. Finally, in the case of a homolog with the longest chain ( $n = 22$ ) the kink in the isotherm corresponds to a transition between two solid-crystal modifications.

It therefore follows that the range of polymorphic tran-

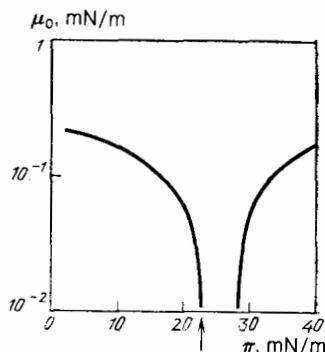


FIG. 6. Dependence of the static shear modulus of a monolayer of fatty acid  $C_{21}H_{43}OH$  on the surface pressure.<sup>41</sup> The arrow identifies the position of a kink of the isotherm on the pressure scale (see Fig. 5).

sitions of a monolayer on water is much wider than assumed before and in the immediate future all the experimental data on phase transitions in molecules should be reexamined in greater detail. It is very important to allow for the elastic stresses which appear as a result of crystallization of a monolayer.<sup>44</sup> It should also be mentioned that several optical methods have now been proposed for the determination of the dynamic elastic moduli and viscosity for different deformation geometries.<sup>28,45</sup>

Optical properties of monolayers on water are quite difficult to study because of the low optical density of these monolayers. Even in the case of amphiphilic dyes with strong absorption of light the optical density of a monolayer represents  $10^{-2}$  for a favorable orientation of an absorbing oscillator relative to the vector of polarization of light. Nevertheless, recent years have seen the development of a technique for the investigation of the absorption and reflection of light from surface monolayers<sup>46,47</sup> and of techniques based on ellipsometry,<sup>48</sup> observation of the luminescence,<sup>49,50</sup> and even the generation of the second harmonic.<sup>51</sup>

The methods of absorption or reflection spectroscopy are mainly used to determine the orientation of molecular chromophores (light-absorbing fragments) relative to the surface of water. The results of these observations are in good agreement with measurements of the specific area occupied by a molecule on the surface.<sup>47</sup> When the surface pressure is altered, the conformation of a complex amphiphilic molecule may change resulting in a phase conformation of a monolayer, which can be deduced from a change in the absorption spectrum of a monolayer.<sup>46</sup> The luminescence measurements can be used to follow the aggregate state of a monolayer molecular association processes, phase stratification, etc. This is due to the fact that the spectrum and quantum efficiency of the luminescence are very sensitive to the nature of the intermolecular interactions. In studies of the polymorphism of monolayers it is possible to combine the luminescence methods with electron-diffraction studies of monolayers transferred onto a solid substrate.<sup>48</sup>

Observations of the generation of the second optical harmonic make it possible, in principle, to determine whether a monolayer has a center of inversion and to establish a correlation between the corresponding nonlinear susceptibility  $\chi^{(2)}$  and the polar ordering parameter. However, such studies of second harmonic generation have yet to be carried out. The actual fact of doubling of the frequency of light by a monolayer of a strongly polar compound on the surface of water was first reported in Ref. 51 where the value of  $\chi^{(2)}$  was determined.

The orientation of molecular electric dipoles in a monolayer can be deduced from an abrupt change in the electrical potential in a monolayer. Usually this change is detected by the Kelvin vibrating electrode method.<sup>6,52,53</sup> In the most primitive model of a monolayer, postulating that it consists of a set of noninteracting dipole moments ( $\mu = ql$ , where  $l$  is the monolayer thickness) which are oriented identically along the normal to the surface, this abrupt change in the surface potential (in volts) can be described by:

$$\Delta U = \frac{\mu}{\epsilon \epsilon_0 A} = \frac{\mu}{\epsilon \epsilon_0} n_s \quad (7)$$

(where  $n_s$  is the number of dipoles per unit surface area).

However, it is difficult to select correctly the permittivi-

ty of a monolayer, because in fact the dipole fragments are displaced relative to the molecular framework. Moreover, at the interface with water there is a double electric layer which makes its own contribution ( $\Delta\Psi$ ) to the discontinuity of the surface potential. Finally, we have to allow for the interaction of dipoles both within the monolayer and with the surface of water. All this makes the relationship between the parameters  $\mu$  and  $\Delta U$  very far from single-valued. Nevertheless, careful experimental investigations of the dependence of  $\Delta U$  on the pH of a solution and on the length of the alkyl chain of an amphiphilic molecule can provide information on the orientation of the dipole moments (in particular, on donor-acceptor complexes and self-complexes<sup>54</sup>) and in some cases even to plot the profile of the electric potential of the monolayer.<sup>55,56</sup>

We shall end this section by mentioning the only reported measurements of the electrical conductivity of a monolayer at a gas-liquid interface.<sup>57</sup> Measurements are practically impossible on the surface of water (or mercury<sup>58</sup>), so that an investigation is made of a monolayer of amphiphilic donor-acceptor complexes on the surface of glycerin. The electrical conductivity of glycerin is low and, therefore, it is possible to observe conductivity along the plane of the monolayer and it amounts to a few tenths of a siemens per centimeter.

### 3. TRANSFER OF MONOLAYERS ONTO SOLID SUBSTRATES

#### 3.1. Langmuir-Blodgett method

Right up to the present this method has been used in the form proposed over half a century ago.<sup>4,59</sup> The idea is to form a monolayer on the surface of water in a suitable phase state and to dip across this film a solid substrate which is oriented vertically. It has been found that it is easiest to transfer films forming a two-dimensional liquid-crystal phase. The transfer may take place during the motion of the substrate in the upward or downward directions; a solid surface should be hydrophilic or hydrophobic, respectively.

The following technical procedure is followed. A solution of an amphiphilic compound in a volatile solvent (benzene, toluene,  $\text{CCl}_4$ ) is sprayed on the surface of distilled water or of a weak aqueous solution of an acid or an alkali with the required value of pH. The amount of the dissolved substance is selected so that the area of its monolayer does not exceed the area of the working surface of a Langmuir trough. Then, a floating barrier (Fig. 7) is used to set the

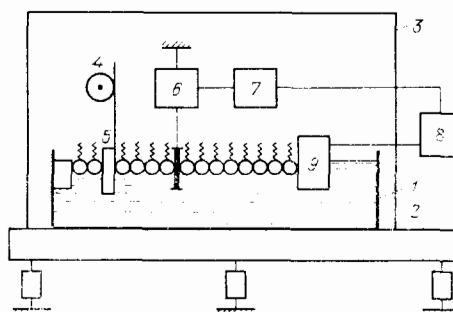


FIG. 7. Apparatus used in deposition of Langmuir-Blodgett films: 1) trough; 2) table with vibration dampers; 3) transparent protective casing; 4) mechanism for dropping and raising substrates; 5) substrate; 6) Wilhelmy electrical balance; 7) motor control circuit; 8) motor controlling mobile barrier; 9) mobile barrier.

surface pressure required to transform a monolayer to the liquid-crystal state. This pressure is recorded with a Wilhelmy balance or by some other method, such as one based on the phase velocity of capillary waves.<sup>43</sup> Next, an automatic micrometer drive is used to dip the substrate or to raise it across the monolayer at a velocity which can be varied from a few centimeters per minute to several centimeters per second.<sup>60</sup> The motion of the substrate across the liquid meniscus results in deposition of a monolayer on the solid surface and the area occupied by the part of the monolayer remaining on the water surface decreases by an amount  $\Delta S$ . In a quantitative estimate of the process we can use a transfer coefficient  $k = \Delta S/S_n$ , where  $S_n$  is the area of the substrate. Before the deposition of each subsequent monolayer the barrier is moved automatically to the left (see Fig. 7) so as to maintain the required surface pressure.

Several variants of Langmuir troughs, fully automated and computer-controlled, have been developed.<sup>61,62</sup> Some firms supply commercial Langmuir troughs: some of them have separate compartments for the formation of heterogeneous multilayers.<sup>63-65</sup> The process of deposition of monolayers on a substrate depends on many factors, the most important of which are the temperature and pH of the solution, the surface pressure, and the rate of withdrawal of the substrate. A good example showing that the skill in the preparation of Langmuir-Blodgett films can be raised to almost scientific level is provided by the report given in Ref. 66.

Depending on the direction of motion of the substrate

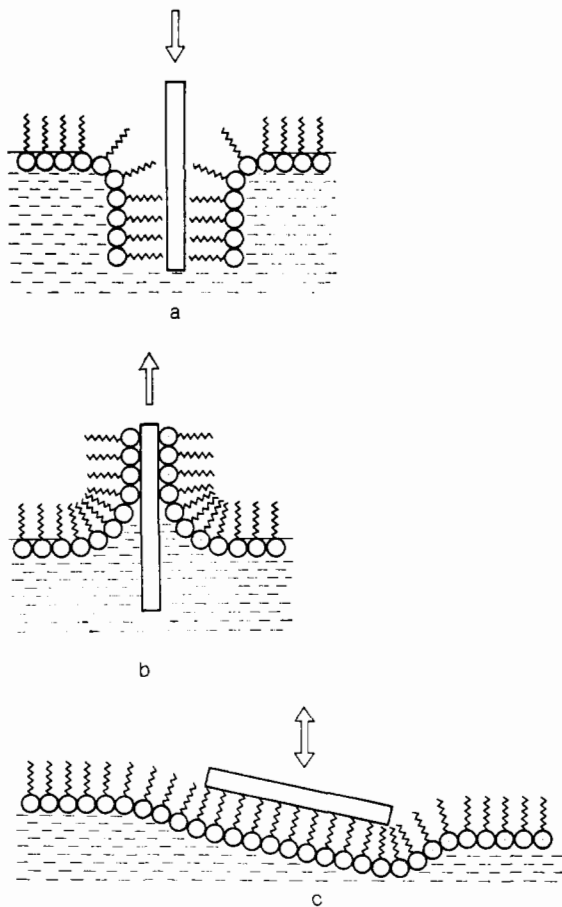


FIG. 8. Formation of X-type (a) and Z-type (b) Langmuir-Blodgett monolayers and of X-type Langmuir-Schaefer monolayers (c).

across a monolayer, it is possible to form Langmuir-Blodgett films with different molecular orientations. For example, if the substrate represents a hydrophobic solid surface, a monolayer is formed in which the hydrophobic molecular tails are oriented toward the substrate. Such a multimolecular layer (Fig. 8) is known as an X-type structure. The motion of the hydrophilic substrate across a monolayer in the upward direction produces a Z-type multilayer in which the polar heads of the molecules are directed toward the surface. Both X- and Z-type multilayers are noncentrosymmetric. Their polar axis is directed toward the normal or away from the normal to the substrate, depending on the direction of the molecular dipole moment.<sup>67</sup> Repeated passage of a substrate across a monolayer in the upward and downward directions creates a Y-type multilayer which is similar in structure to lipid bilayers in biological membranes. These multilayers are nonpolar and they have a center of inversion.

The formation of a Y-type structure automatically satisfies the condition of hydrophilic or hydrophobic nature of the substrate for each transferred monolayer, so that technologically it is easiest to prepare Y-type multilayers. In the case of X- or Z-type multilayers it is frequently found that molecules in the meniscus region are reversed, so that instead of the desired (for example, X-type) structure it is found that a Y-type structure is obtained. This mechanism has been investigated in detail<sup>68-70</sup> by determination of the contact angle of a liquid which wets (or does not wet) the solid substrate. It is particularly convenient to follow reversal of molecules using radioactive tracers introduced into an amphiphilic molecule. The position of the tracer can be deduced using the absorption of the Auger electrons emitted by the tracer by other molecular fragments.<sup>71</sup> It is now known that reversal of molecules occurs in the meniscus of a liquid at the moment of deposition of a monolayer on a solid substrate. Moreover, x-ray structure analysis has shown that the structure of the preceding monolayer already deposited on the substrate may be modified by the deposition of the next monolayer.<sup>72</sup>

In some cases the deposition of a monolayer on a preceding one<sup>60</sup> is epitaxial in nature and it reproduces the structure defects in the first monolayer throughout the whole multilayer which may be quite thick (of the order of 100 monolayers). All this evidence demonstrates that the deposition of a monolayer on a substrate does not simply involve the adhesion forces. In fact, a complex crystallization process involving formation of a monolayer at a growth step takes place in the meniscus of a liquid. It is shown in Ref. 73 that the transfer of a molecule onto a solid substrate is a thermodynamically favorable process, but it does require overcoming a potential barrier and a corresponding loss of time. This is precisely why the Langmuir-Blodgett process cannot be very fast. This is in good agreement with the experimental results reported in Refs. 60 and 74.

### 3.2. Other methods

A monolayer located on the surface of water in a two-dimensional solid phase can be transferred onto a solid phase by the Langmuir-Schaefer method.<sup>75</sup> In this case the hydrophobic tails of amphiphilic molecules become attached to a hydrophobic substrate (Fig. 8) simply because of adhesion forces. If recrystallization of monolayers does not occur, the

process of formation of an X-type multistructure can be very fast because one can bring a substrate repeatedly into contact with an undisturbed surface monolayer. The Schaefer method has been improved subsequently (it is known as the horizontal lifting method<sup>76,77</sup>) and, in principle, it can be used to form both X and Z-type structures. In the latter case the substrate is placed under a monolayer and brought into contact with it in water.<sup>78</sup> It is interesting that sometimes the Schaefer method produces not an expected X-type multilayer, but a Y-type layer.<sup>79</sup> Clearly, a structural modification may occur if a monolayer (particularly a polymer) on water is not in the solid-crystal phase.

In addition to the methods of Blodgett and Schaefer, the book of Gaines<sup>6</sup> describes several other methods for the transfer of monolayers from the surface of water onto a solid substrate, particularly using a flow created by a surface tension gradient. Stable monomolecular layers on solid substrates can also be formed by the direct adsorption of surface-active molecules from the liquid phase.<sup>80</sup> A multilayer can form if this procedure is repeated and the preceding monolayer is chemically treated so as to make it able to accept the next monolayer.<sup>81</sup> Special techniques for the preparation of biological molecular monolayers have been developed.<sup>78</sup>

The composition of a monolayer on a solid substrate can be controlled by the process of film "skeletalization."<sup>5,82</sup> To achieve this, an initial monolayer (for example, a fatty acid layer on the surface of water) is modified by the addition of other amphiphilic molecules which after the transfer onto a solid substrate can be "washed out" from the monolayer by a special solvent. This leaves behind a monolayer "skeleton" consisting of fatty acid salts. Other amphiphilic molecules can now be grown on this skeleton. The properties of a monolayer are now different but the "memory" of the previous structure is retained. This method can be used to control some properties, such as the refractive index of a film.<sup>83</sup>

Monolayers and multilayers can be transferred from one substrate to another by the contact method.<sup>84,85</sup> The second substrate can be a flexible polymer film which is placed on a multilayer and is then detached together with the adhering top monolayer. The monolayer separated in this way can then be transferred by the same contact method to another surface.

### 3.3. Structural features of films on solid substrates<sup>1)</sup>

Some fundamental problems arise in dealing with the structure of monomolecular and multimolecular layers transferred from the surface of water onto a solid substrate.

1) Are the monolayers quasitwo-dimensional systems or is there a correlation between the distribution of molecules in the neighboring monolayers? This problem is closely related to that of two-dimensional (hexatic) and three-dimensional liquid-crystal smectics<sup>86,87</sup> and the answer to the question just posed can be provided by investigations of the correlation functions of the density in the monolayer plane.

2) To what degree does the structure of Langmuir-Blodgett films inherit the structure of the preceding monolayer on the surface of water? The understanding of the process of deposition (or growth) of a film on a solid substrate depends on the answer to this question.

3) Is the structure of Langmuir-Blodgett films in equi-

librium at all? If films are unstable, it is necessary to consider the dynamics of their structural modification and the mechanism of the loss of the structural stability.

Naturally, if x-ray or electron diffraction methods could have been used to determine the coordinates of all the atoms forming a unit cell of a Langmuir-Blodgett film and a monolayer on the surface of water, all the above questions would have been answered. However, unsurmountable difficulties of experimental (thin films, strong background of the substrate) and of fundamental (partly ordered systems) nature are preventing successful completion of this task. Therefore, the structure of monolayers and multilayers is being approached in a simplified manner approximating molecules with rods, chains, etc., and introducing various order parameters describing the ordering of molecules in respect of various translational and orientational degrees of freedom (sometimes allowing for conformational changes in a molecule).

Various types of the translational order (for example, across a multilayer or in its plane) have been studied by x-ray structure methods<sup>88-91</sup> or using electron diffraction.<sup>92-95</sup> The orientational order is being investigated by optical methods including measurements of the dichroism (in electronic<sup>96</sup> and vibrational<sup>97</sup> spectra, and in Raman spectra<sup>98</sup>) and of the linear Stark effect.<sup>99,100</sup> The structure of Langmuir-Blodgett films has been tackled recently by neutron analysis<sup>101</sup> and by the method of a standing x-ray wave,<sup>102</sup> including excitation of samples by synchrotron radiation.<sup>103</sup>

Monitoring of the distribution of the local density  $\rho(z)$  along the normal to a multilayer is particularly important in the construction of multilayer structures. The function  $\rho(z)$  can be used to determine the nature of the orientation of molecules in monolayers, to find the thickness of a single monolayer, and to determine the correlation length indicating the degree of the long-range order along the normal to a multilayer. The geometry shown as an inset in Fig. 9 is em-

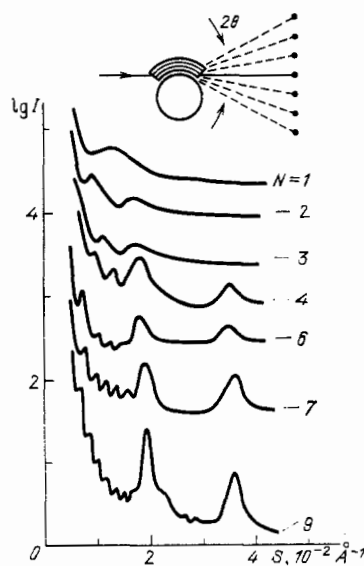


FIG. 9. Dependences of the intensity of X-ray scattering on the scattering angle for thallium behenate films consisting of various numbers  $N$  of bilayers.<sup>90,205</sup> The top part of the figure shows schematically a film on a cylindrical substrate. The parameter  $S$  is defined as  $S = 2(\sin \varphi)/\lambda$ , where  $\lambda$  is the wavelength and  $2\varphi$  is the scattering angle. Electron diffraction (in the transmission configuration) was studied using a film consisting of 21 fatty acid monolayers.<sup>74</sup>



ployed in x-ray scattering experiments.<sup>90</sup> The intensity of the scattering peaks is used to reconstruct the function  $\rho(z)$  and the width of the peaks is inversely proportional to the correlation length  $\delta_z$ . It is clear from Fig. 9 how the scattering peaks become smeared out on reduction in the number of monolayers in a film. Moreover, there is a fine scattering structure between the main peaks and this is due to the finite number of monolayers participating in the diffraction process. Such a structure has been observed before only in optical experiments on cholesteric liquid crystals.<sup>104</sup> This technique has been used<sup>89</sup> to find the function  $\rho(z)$  for amphiphilic donor-acceptor complexes doped with iodine (in particular, it has been possible to find the positions of the iodine atoms).

Unfortunately, experiments carried out in this geometry do not provide information on the presence or absence of correlations in the positions of the individual molecules belonging to different monolayers. This problem can be tackled by investigating the contours of the diffraction reflections when x rays are incident along the normal to the film. In the presence of a substrate it is necessary to employ the diffraction of a reflected x-ray beam incident at a very small angle to the film surface. An experiment of this kind has revealed very strongly smeared diffraction spots in the case of lead stearate and this is explained in Ref. 88 by assuming that a Langmuir-Blodgett film can be regarded as a pile of quasitwo-dimensional uncorrelated layers.

The electron diffraction method is more convenient for investigations of the structure in the plane of a film. Electron transmission provides clear diffraction patterns which can be used to judge the nature of the two-dimensional crystal structure.<sup>93,94</sup> Interlayer correlations can be deduced from an analysis of the distribution of the profile of the intensity of the electron scattering in a diffraction spot. Such an analysis carried out in Ref. 95 for barium stearate has shown that there is no true long-range translational order in the plane of a Langmuir-Blodgett film but only order in the orientation of the bonds or, more accurately, in the directions of one molecule relative to another.

According to Ref. 95, the long-range translational order in a multilayer plane is disturbed because of some scatter of the directions of the orientation and tilt of the hydrocarbon molecular tails. The tilt of the tails is confirmed also by optical methods (for example, in the case of stearic acid<sup>97</sup>). Optical methods can be used to determine also the distribution function  $f(\theta)$  of certain fragments of molecules in respect of their orientation relative to the normal to the film. This can be done by measuring the order parameters  $P_n$  ( $n = 1, 2, 3, 4$ ) governing the expansion of  $f(\theta)$  in terms of the Legendre polynomials. The function  $P_2$  can be deduced from changes in the dichroism,<sup>96</sup> the function  $P_4$  can be found from the Raman scattering spectra,<sup>98</sup> and the odd parameters of the polar order  $P_1$  and  $P_3$  can be deduced in principle simply by utilizing some form of a polar interaction with a film, for example, by recording the shifts of the optical absorption bands of a film in an electric field (Stark effect).<sup>99</sup> On the whole, the parameters of the orientational order parameters  $P_n$  of the investigated systems (amphiphilic azo dyes) are small. They are comparable with the corresponding (even) parameters of nematic liquid crystals probably because of the mosaic structure of Langmuir films.

## 4. OPTICS OF MONOLAYERS AND MULTILAYERS

Langmuir-Blodgett films have three features responsible for their unique optical properties. Firstly, these films consist of monolayers of precisely defined thickness (accurate to within a few angstroms). This makes it possible to vary optical properties in steps of, for example, 20 angstroms and thus construct superstructures with the required profiles of the refractive index and the extinction coefficient, and to form dielectric spacers of calibrated thickness, etc. Secondly, these films exhibit a strong optical anisotropy  $\Delta n = n_e - n_o \approx 0.01-0.3$ , depending on the molecular structure ( $n_o$  and  $n_e$  are the refractive indices for the ordinary and extraordinary waves). This is very important in studies of nonlinear interactions with a field (electrooptics, nonlinear optics). Thirdly, variation of the molecular composition within one monolayer and in the neighboring monolayers provides opportunities for investigating a great variety of intermolecular interactions, migration of energy and of quasiparticles, etc.

There is an extensive literature on the optical properties of Langmuir-Blodgett films. They have been investigated by the traditional methods of absorption and reflection spectroscopy, ellipsometry, interferometry, luminescence, etc. The results are discussed in detail in several reviews,<sup>9-12</sup> so that we shall concentrate on the latest work.

### 4.1. Waveguide properties

Waves become guided when they travel along a film with a lower refractive index than the adjoining media, so that total internal reflection by the waveguide walls takes place. A Langmuir film can be used, firstly, as a waveguiding medium<sup>105-109</sup> and, secondly, as a medium adjoining a waveguide made of glass or a polymer,<sup>110</sup> and, thirdly, as a medium coating a diffraction grating used for coupling in of radiation by an integrated optical method.<sup>111</sup>

Studies of the propagation of light waves in a film waveguide formed by the Langmuir-Blodgett technology make it possible to determine accurately the optical constants of a Langmuir-Blodgett film. For example, the thickness dependences of the effective refractive indices of various modes were found for a film of cadmium stearate on a fused quartz substrate.<sup>108</sup> Radiation from an He-Ne laser was coupled into a film by a prism and a study was made of the mode composition of the radiation when the number of monolayers in the film was altered. It is clear from Fig. 10 that an

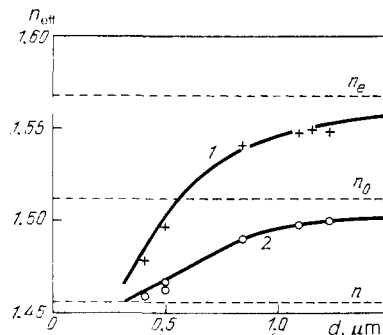


FIG. 10. Dependences of the effective refractive indices of  $TM_0$  (1) and  $TE_0$  (2) waveguide modes on the thickness of a Langmuir-Blodgett film.<sup>108</sup> Here,  $n_e$  and  $n_o$  are the principal values of the refractive index of a cadmium stearate film;  $n$  is the refractive index of the quartz substrate.

increase in the film thickness caused the effective refractive indices of the  $TM_0$  and  $TE_0$  modes to approach the values  $n_e$  and  $n_o$ . It was assumed that the film was optically uniaxial. In a different investigation<sup>112</sup> the mode composition of radiation in a waveguide was determined for films of 22-tricosanoic acid (polymerizable material) and it was established that films of this material exhibited some degree of optical biaxial behavior. The frequency dispersion of the refractive indices  $n_e$  and  $n_o$  of cadmium arachinate has also been determined.<sup>110</sup>

Unfortunately, film waveguides made by the Langmuir-Blodgett technology suffer from relatively strong attenuation. This is due to the polycrystalline structure of the films discussed above. The attenuation depends strongly on film technology.<sup>109</sup> In the case of the best samples the attenuation does not exceed 1 dB/cm (Ref. 106). However, it should be pointed out that the technology is gradually improving and new materials (particularly comb-shaped polymers<sup>113</sup>) are being prepared so there is hope of major improvements in the quality of film waveguides.

One should mention particularly the possibility of varying the profiles of the refractive index and the extinction coefficient. The refractive index of monolayers transferred from the surface of water onto a solid substrate can be varied by altering the concentration of heavy metal ions (Ba, Pb, Tl) in an aqueous solution. These ions are bound by an amphiphilic compound and this increases the refractive index of the monolayer. Another method involves utilization of the skeletalization effect in films mentioned in Sec. 3.2. Moreover, the gap between monolayers of a transparent material can be filled with light-absorbing films. This provides means for selecting those waveguide modes for which the absorbing film is located at a node of a standing wave and thus constructing spectral filters.<sup>107,114</sup>

Selection of wave modes by the anisotropy of an absorbing Langmuir film was reported in Ref. 115. A quartz waveguide modified with cesium ions was coated with a diacetylene film which absorbed light with the polarization vector directed along the molecular axes, i.e., at right-angles to the film plane. This resulted in weaker attenuation of TE waves than that of TM waves, so that the former were selected for subsequent processing. There is also special interest in waveguides with a given profile of the nonlinear susceptibility, which can be used in nonlinear optics as discussed theoretically in Ref. 116.

#### 4.2. Dichroism and other spectral characteristics

At the end of the preceding subsection we first mentioned light-absorbing molecules (diacetylene). Simple amphiphilic molecules such as stearic acid (Fig. 1) have only saturated-C-C-bonds and their electron system absorbs light only at short (ultraviolet) wavelengths. Naturally, characteristic vibrations of atoms and of the whole molecular fragments give rise to bands also in the infrared part of the spectrum. However, there is a wide class of molecules with unsaturated (double and triple) bonds. The case when unsaturated and saturated bonds alternate, forming an extended chain of conjugate bonds, is particularly important. Excess  $\pi$  electrons are delocalized along this chain; they are located in a large potential well so that the separations between their energy levels is small. Such molecules absorb

light of relatively long wavelengths (this is true of dyes, some polymers of the polydiacetylene type, etc.) and the absorbing oscillator is directed on the average along the conjugated chain.

Clearly, if a molecule absorbs light anisotropically, then a Langmuir film with a given molecular orientation will also absorb light anisotropically. One has to distinguish two types of anisotropy. In the first more typical case<sup>46,96</sup> the structure is cylindrically symmetric relative to the normal to the film. Then the normal is the only preferred direction and we can observe anisotropy by illuminating a film at a certain angle to the normal. This case is illustrated in Fig. 11 (Ref. 96), which also shows the experimental geometry and a typical dye molecule with a system of conjugate bonds. Amphiphilic rod-shaped molecules are oriented at right-angles to the plane of the film and the optical density increases proportionally to the product  $e \cdot \mu_{ij}$ , where  $e$  is the polarization vector of light and  $\mu_{ij}$  is the vector representing the dipole moment of the corresponding optical transition.

In the case of a cylindrically symmetric system of disk-shaped molecules lying in the plane of the film the light-absorbing oscillator should be in the plane of the disks when the pattern showing the dependence of the optical density on the direction of the polarization vector of light is opposite to that shown in Fig. 11. This variant is realized in practice for disk-shaped molecules of phthalocyanines and porphyrins.<sup>47,117</sup> Chlorophyll and other biologically important compounds belong to the latter category.

A second, very different, type of optical anisotropy is observed in the plane of a Langmuir-Blodgett film. This anisotropy may be created by the very process of pulling a substrate across a surface monolayer. For example, stearic acid molecules sometimes adopt a matched tilt in the direction of pulling, as demonstrated by the dichroism of infrared absorption even when light is transmitted along the normal to the film.<sup>97</sup> Another reason for the deviation of the film structure from cylindrical symmetry may be the influence of the substrate. For example, an amphiphilic dye film deposited on a cleaved surface of a gypsum crystal has been found to exhibit very strong dichroism when illuminated along the normal.<sup>118</sup> In this case the molecules are ordered along all three coordinates: the ordering is along planes, which is typical of all Langmuir-Blodgett films, and also in the plane of a film, the latter order being imposed by the epitaxial growth on an anisotropic substrate.

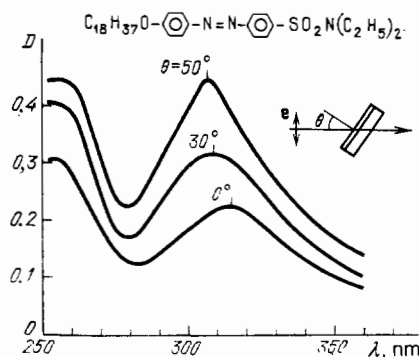


FIG. 11. Absorption spectra of an azo dye multilayer with the oscillator orientation perpendicular to the substrate, plotted for different angles  $\beta$  of the incidence of light ( $e$  is the polarization vector).<sup>96</sup>

The problem of sensitivity of various experimental methods is of major importance in studies of the structure of Langmuir films. As already mentioned, it is very difficult to study one monolayer by x-ray structure analysis or electron microscopy methods. Therefore, many recently suggested spectral methods have a sufficiently high sensitivity to study the properties of the same and sometimes even discontinuous monolayer. In all these methods use is made (in some form or another) of the effect of enhancement of the electric field of an optical wave near the surface of a metal because of excitation of local plasma oscillations or surface polaritons.<sup>119</sup>

Giant (surface-enhanced) Raman scattering has been investigated in the visible part of the spectrum.<sup>120</sup> In this case the investigated film is deposited on a diffraction grating made of a metal (for example, an Ag grating with a period of the order of hundreds of nanometers) and the intensity of the Raman-scattered light is measured for different angles of incidence of an exciting laser beam on a film. Variation of the angle of incidence results in selective enhancement of the scattering of specific molecular vibrations interacting with plasma oscillations in a metal film. A comparison of the intensities of the various peaks can be used to judge the degree of orientational order of hydrocarbon chains.<sup>121,122</sup>

The intensity of the Raman scattering is greatly enhanced if the frequency of the exciting light is close to the frequency of an electronic transition (resonance Raman scattering) and the enhancement affects only those Raman lines which correspond to vibrations that interact strongly with the  $\pi$ -electron system. This method has been used to investigate the spectral characteristics of the first monolayer which is in contact with a metal,<sup>123</sup> the differences between the vibrational frequencies in the ground and electronically excited states,<sup>124</sup> and changes in the spectra of a dye introduced in a very low concentration into a lipid monolayer.<sup>125</sup> In the last case especially high sensitivity is achieved by combination of the resonance effect with the enhancement of the Raman scattering by a metal surface.

The characteristics of the structure of the monolayer nearest to the substrate can be investigated also using infrared spectra. This can be done by Fourier spectroscopy of frustrated total reflection.<sup>126</sup> The technique of grazing reflection of infrared radiation has been used<sup>127,128</sup> to study structural modification during, respectively, heating and polymerization of Langmuir-Blodgett films. One should mention also that the structure of vibrational bands of one or several monomolecular Langmuir layers can be studied in the infrared part of the spectrum using traveling surface electromagnetic waves.<sup>129,130</sup>

The Brillouin scattering in Langmuir-Blodgett films has been investigated very recently.<sup>131,132</sup> It has been found that multilayers have an anomalously low ratio of the shear modulus to the bulk modulus, i.e., Langmuir multilayers are similar to the liquid-crystal smectic B phase.

#### 4.3. Molecular association

Organic molecules are too complex to calculate their energy spectrum or predict electronic properties with sufficient precision. This is particularly true of the molecules that interact with one another in a solution or in a solid. Information on intermolecular interactions is provided mainly by

spectroscopic investigations. In the case of electronic processes such information is usually obtained by investigating the absorption and fluorescence spectra in the visible and ultraviolet ranges. Langmuir films provide a unique opportunity for investigating intermolecular interactions between molecules with a rigorously specified orientation and definite distances between them. We shall not consider the specific properties of particular molecular systems, but discuss several typical examples of association characteristic of dye molecules.<sup>9</sup>

We shall assume that, for example, a molecule consists of a chromophore group ensuring the absorption of visible light (the  $\pi$  electrons are delocalized in the chromophore part) and two hydrocarbon tails which impart amphiphilic properties (Fig. 12a). This can be, for example, a cyanine dye with fairly wide absorption and fluorescence spectra because of the strong interaction between the electronic and vibrational subsystems of each molecule. If a monolayer of this dye is spread on the surface of water in the form of a mixture (1:1) with one of the fatty alcohols (for example, octadecanol), the optimal packing of chromophores resembles a brick wall (when the monolayer is viewed from above). The hydrocarbon tails then point upward (in the direction of the observer), as shown in Fig. 12b, and the octadecanol tails simply fill the remaining voids. This packing results in a strong interaction between the dye chromophores: their electronic oscillators combine into apparently one extended oscillator and a very strong narrow band appears in the absorption and fluorescence spectra (Fig. 12c). The brick wall packing of chromophores is known as the J aggregate.<sup>133,134</sup> Such J aggregates can be formed also by a mixture of different dyes.<sup>135</sup> It is clear that the appearance of a narrow band is due to a change in the nature of the electron-phonon coupling in a J aggregate compared with the individual molecule of a dye. This follows from a detailed analysis of the frequency dependence of the absorption band edge. The results of such an analysis give a value of the electron-phonon coupling constant typical of two-dimensional

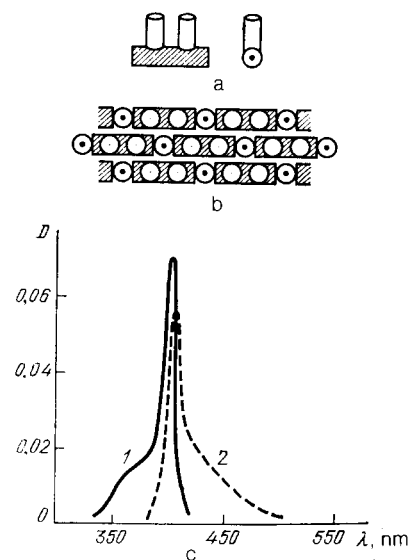


FIG. 12. Formation of J aggregates: a) schematic representation of cyanine dye (on the left) and fatty acid (on the right) molecules; b) stacking of dye and acid molecules in a J aggregate; c) absorption (1) and fluorescence (2) spectra of a J aggregate.

systems,<sup>136</sup> in agreement with the two-dimensional nature of the exciton processes in a monolayer.

In some cases the process of molecular association occurs only in electronically excited states of a dye molecule. The formation of molecular pairs in an excited state (excimers) is accompanied by a strong broadening of a fluorescence band.<sup>9</sup> The fluorescence of excimers exhibits a specific decay kinetics which can be used to determine the geometry of an associate.<sup>137</sup>

One should mention particularly the interaction of molecules in adjacent monolayers of a Langmuir–Blodgett film. The energy of this interaction depends on the geometry of the distribution of chromophores<sup>138</sup> and in the case of monotypic molecules this energy is generally low. The situation is different when donor and acceptor molecules are located in adjacent monolayers. The former have a low ionization potential and the latter have a high electron affinity. In a system of this kind an electron is transferred spontaneously from a donor to an acceptor and a charge-transfer complex is formed. The electronic spectrum of such a complex is very different from the sum of the spectra of its components. There is also a change in the infrared spectrum and the ESR spectrum exhibits a triplet structure typical of free radicals.<sup>139</sup>

#### 4.4. Migration of excitation energy

The mechanism of energy transfer in Langmuir films was discussed by the present author in Ref. 11. However, in view of the importance of this topic in demonstration of the very nature of the principle of molecular architecture of Langmuir films and in view of the aesthetic aspect of the situation related to the design of the relevant experiments,<sup>9</sup> we shall repeat briefly here the basics of the topic.

The problem of mechanisms of energy transfer from one molecule (energy donor) to another (energy acceptor) has a long history. The simplest mechanism is radiative transfer when an acceptor molecule simply absorbs light emitted as luminescence by a donor molecule. In thin Langmuir films this mechanism does not work in practice because of the weak absorption of light by one or several monolayers of a dye. Energy can also be transferred in accordance with the Förster–Galanin mechanism<sup>140,141</sup>; this mechanism operates when an acceptor molecule is separated by a short distance from a donor molecule. In the near-field zone, i.e., at distances  $R \ll \lambda$ , the electric field of a light-emitting dipole decreases proportionally to  $R^{-3}$ . An electric wave does not form in this zone, although the energy of an alternating electric field may be transferred to a neighboring oscillator. This energy transfer is assumed to be nonradiative, although the probability of this process is proportional to the degree of overlap of the luminescence band of a donor and the absorption band of an acceptor. The third (also nonradiative) mechanism of energy transfer by exciton excitations is possible only in the case of close packing of donor and acceptor molecules.

Figure 13 shows the Kuhn experimental geometry<sup>9</sup> used to determine the mechanism of energy transfer between monolayers. A monolayer of donor molecules *D* is deposited on a transparent quartz substrate (an auxiliary role is played by an isolating fatty acid monolayer). A monolayer of acceptor molecules *A* is separated from a donor layer by several

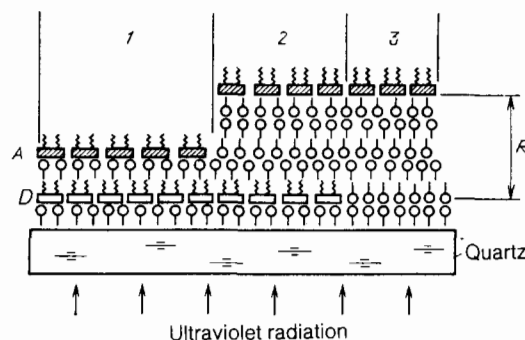


FIG. 13. Experiments of Kuhn *et al.*<sup>9</sup> demonstrating nonradiative energy transfer from excited donors (open rectangles) to acceptors (shaded rectangles).

cadmium arachinate monolayers. The number of the latter monolayers can be varied at will. Illumination of the donor across the substrate with ultraviolet radiation produces the following results. On the right-hand side (region 3) where there are no donors the field of view is dark, because acceptors do not absorb ultraviolet radiation. In region 2, where the acceptor molecules are separated by large distances from the monolayer *D* a blue fluorescence of the donor (as a result of ultraviolet absorption) is emitted. The *A* molecules absorb weakly the fluorescence of the *D* molecules so that the fluorescence spectrum is hardly affected. In region 1 the acceptor molecules emit strong fluorescence in the yellow part of the spectrum. Clearly, they receive energy from the *D* molecules by a nonradiative process. A change in the number of monolayers separating the *D* and *A* layers and measurements of the acceptor (*A*) fluorescence can be used to check the theory put forward for the Förster–Galanin mechanism. Figure 14 shows a curve (1) obtained in this way.<sup>9</sup> It is clear that this resonant nonradiative energy transfer process is effective over distances of 50–100 Å or less.

The situation is quite different when an acceptor molecule with a structure similar to that of a donor molecule is introduced into a continuous monolayer formed by donor molecules.<sup>142</sup> As mentioned earlier, close-packed chromophores (in this case the donor molecules) form ordered J aggregates which absorb and emit light collectively in narrow spectral intervals. The acceptor molecules introduced into this monolayer accept effectively the energy from the J aggregates and convert it into their own luminescence. Figure 15 shows the luminescence spectrum of a mixed monolayer in which there is only just one acceptor molecule for every 250 sensitizer molecules. In spite of the very large difference between the donor and acceptor concentrations, the intensity of the long-wavelength (acceptor) fluorescence

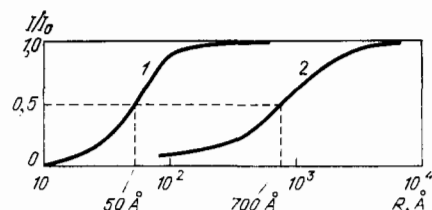


FIG. 14. Dependences of the intensity of the fluorescence emitted by molecular energy acceptors on the distance between acceptor and donor monolayers in Fig. 22 (1) and between acceptor molecules incorporated in a donor monolayer (Fig. 24) (2).

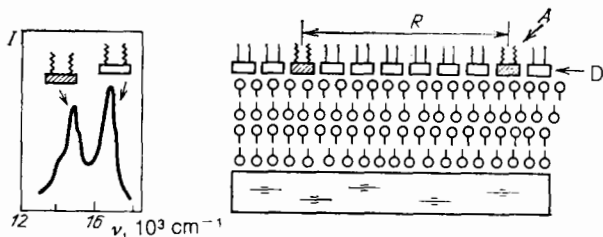


FIG. 15. Fluorescence spectrum of energy acceptors and donors located in the same monolayer.<sup>142</sup> The open rectangles are donors and the shaded rectangles are acceptors.

band is practically the same (and at nitrogen temperatures even higher) as that of the short-wavelength band due to the donor. This demonstrates that the energy of light absorbed by a large number of donor molecules is concentrated in one acceptor molecule, i.e., the "photon funnel" effect occurs.

This "photon funnel" principle plays a key role in the mechanism of photosynthesis when one trap molecule collects the energy from about 300 chlorophyll molecules, and also in the mechanisms responsible for the photosensitization of various materials.<sup>143</sup>

## 5. NONCENTROSYMMETRIC MULTILAYERS

### 5.1. Comments on the structure

The first successful attempt to construct a polar multilayer Langmuir-Blodgett film exhibiting electric polarization and all the associated properties (pyroelectric and piezoelectric effects, linear electrooptic effect, etc.) was reported by the present author and his colleagues in Ref. 67. We were tackling a problem of practical importance which is the provision of suitable materials for sensors of thermal and mechanical effects, nonlinear-optical converters of light, etc. The number of papers dealing with polar structures and their applications has in fact been rapidly increasing in the last few years.

In Sec. 3 in the course of discussion of structure problems we pointed out that the thermodynamic equilibrium of the structure of Langmuir-Blodgett films (including polar) is not yet understood, although they can be stable for years. Therefore, one can speak of the presence of a "spontaneously" polarized state in the films only with caution, although the growth of a multilayer substrate is fundamentally similar to the growth of a polar crystal from, for example, a solution. The first studies of the polar properties have been concerned with noncentrosymmetric multilayers of the X and Z type (Fig. 8), although they are quite difficult to prepare. Another variant of a noncentrosymmetric structure is shown in Fig. 16. This multilayer consists of alternate monolayers of different molecules combining to form bilayers: such a structure can be called conveniently an X-Z (or Z-X) structure, depending on the orientation of the monolayer deposited first on the substrate. In the technology of such systems the hydrophobic or hydrophilic nature of the substrate, necessary for the deposition of the next monolayer, is ensured automatically so that X-Z (Z-X) structures are more stable than X- or Z-type multilayers (in this sense they are close to Y-type multilayers). Moreover, in the case of X-Z structures one can use donor and acceptor molecules, thus transferring charge between monolayers and controlling the electrical

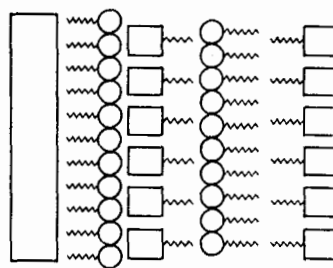


FIG. 16. Multilayer of the X-Z type consisting of two different amphiphilic molecules.

properties of a multilayer. Preparation of such structures is described in Refs. 63 and 65.

### 5.2. Macroscopic ("spontaneous") polarization, pyroelectric effect, and piezoelectric effect

In the interpretation of a discontinuity of the surface potential across a monolayer lying on the surface of water the use of Eq. (7) provides an approximation which is too rough for the description of the real situation. This is a consequence of the influence of an aqueous medium. However, in the case of a monolayer transferred onto a solid substrate we can relate directly the surface charge density  $\sigma$  (or the dipole moment  $p$  per unit volume) to the static molecular dipole moment  $\mu_0$ :

$$\sigma \equiv p \equiv \frac{1}{V_m} (\mu_0 \mathbf{m}), \quad (8)$$

where  $\mathbf{m}$  is the vector of the normal to the surface and  $V_m$  is the molecular volume.

If  $M$  is the molecular weight and  $N_A$  is the Avogadro number, the macroscopic polarization can be expressed in terms of the density  $\rho$  of a monolayer,

$$p = \frac{N_A}{M} \rho \mu_0 \langle \cos \psi \rangle, \quad (9)$$

where  $\psi$  is the angle between the molecular dipole and the normal to the film.

In the case of a multilayer the values of  $p$  for individual monolayers are algebraically additive, so that the resultant macroscopic polarization

$$P = \frac{1}{N} \sum_i p \quad (10)$$

is either maintained (in the case of X- or Z-type films) or it alternates (in the case of Y-type films) on increase in the number of monolayers  $N$ . In structures of the X-Z type (superlattices) the macroscopic polarization is again finite,<sup>144</sup> the pyroelectric coefficient is independent of the number of bilayers,<sup>145</sup> and its value is two orders of magnitude higher for a superlattice than for Y-type layers prepared separately from its components.<sup>146</sup>

The alternation of the polarization can be observed by measuring the pyroelectric coefficient  $\gamma$  of multilayers with different values of  $N$ . In fact, we have

$$\begin{aligned} \gamma &= \frac{dP}{dT} \\ &= \frac{N_A}{M} \left( \mu_0 \langle \cos \psi \rangle \frac{\partial \rho}{\partial T} + \rho \langle \cos \psi \rangle \frac{\partial \mu_0}{\partial T} + \rho \mu_0 \frac{\partial \langle \cos \psi \rangle}{\partial T} \right). \end{aligned} \quad (11)$$

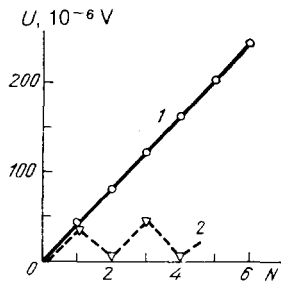


FIG. 17. Dependence of the amplitude of a pyroelectric signal on a number of monolayers in X-type (1) and Y-type (2) multilayers.<sup>147</sup>

In the case of an X-type structure the sign of  $\langle \cos \psi \rangle$  does not change from layer to layer, whereas for a Y-type structure it does change and the corresponding pyroelectric signal alternates in the latter case (Fig. 17).<sup>100,147</sup> The maximum value of the pyroelectric coefficient of a monolayer is  $10^{-6}$ – $10^{-5}$   $C \cdot m^{-2} \cdot K^{-1}$ .

It follows from Eq. (11) that the pyroelectric effect may be associated with the thermal expansion of a film ( $\partial \rho / \partial T$ , giving rise to what is known as the secondary effect), disordering of dipoles ( $\partial \langle \cos \psi \rangle / \partial T$ ), or temperature dependence of the dipole moment ( $\partial \mu_0 / \partial T$ ). The last quantity can be controlled by varying the molecular structure.

The sensitivity of the pyroelectric method is sufficiently high to observe a response from a single monomolecular layer.<sup>148</sup> This in fact means that an electric emf is measured for an individual molecule, because molecular heads or tails are on two equipotential surfaces. To the best of our knowledge, such a situation occurs only in Langmuir films.

The piezoelectric effect in polar multilayers has been investigated and reports are given in Refs. 67 and 149. In the first of these investigations the effect was excited by a pulse of hypersound generated in a substrate which absorbed a laser radiation pulse. In the second case a film was deformed mechanically either by bending or by pressure along the normal to the film and estimates of the corresponding piezoelectric moduli were obtained.

### 5.3. Photoinduced polarization

The macroscopic polarization  $P$  of polar X- or Z-type multilayers can be altered not only by heating a film (pyroelectric effect), but also by a direct photoelectric process. For this the molecule is selected specially. Illumination of it should result in a quantum transition accompanied by an intramolecular spatial transfer of an electron from the donor to the acceptor end. This changes the dipole moment of the molecule by an amount  $\Delta \mu = \mu_b - \mu_0$ , where  $\mu_b$  and  $\mu_0$  are the static dipole moments of the excited and ground states. In the case of continuous illumination with light from the spectral range where such a quantum transition takes place the macroscopic polarization changes by an amount

$$\Delta P = n_{ph} \tau \Delta \mu, \quad (12)$$

where  $n_{ph}$  and  $\tau$  are the concentration and lifetime of molecules in the photoexcited state. If a multilayer of, for example, X-type is between electrodes, it forms a capacitor (Fig. 18) and the following voltage appears on the capacitor electrodes:

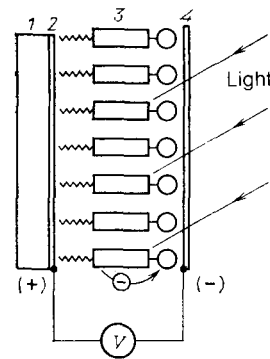


FIG. 18. Photoinduced polarization in a dye monolayer with intramolecular charge transfer: 1) substrate; 2) aluminum electrode; 3) amphiphilic dye monolayer; 4) semitransparent aluminum electrode.

$$\Delta U = \frac{q}{C} = \frac{\Delta P \cdot S}{C} = \frac{\Delta P l}{\epsilon \epsilon_0}, \quad (13)$$

where  $C$  is the capacitance of such a structure, and  $l$  and  $S$  are the thickness and area of the multilayer. Naturally, under steady-state conditions a change in the polarization is compensated by leakage due to the electrical conductivity of the medium, but the photoinduced polarization can be observed under transient conditions<sup>150</sup> and the sign of the signal is (as expected) opposite for X- and Z-type multilayers.

This experiment is interesting because purely electrical measurements have been used for the first time to detect an intramolecular photoprocess. This has been done earlier only by studies of luminescence kinetics.

### 5.4. Stark effect

It is clear from the above discussion that the nature of the molecular orientation in a multilayer is the key to the molecular architecture concept. Naturally, electrical measurements can provide information on the orientation of molecular dipoles in the individual monolayers, but they are still affected by the influence of other (stray) electrical processes, such as the electrical conductivity, photo-emf, thermo-emf, etc. Therefore, it is very important to have some optical methods for investigating polar structures. In principle, these should be methods sensitive to the presence or absence of a center of inversion of the medium. There are two such methods. One of them is generation of the second optical harmonic (discussed in the next subsection) and the other is the Stark effect or electrochromism effect.<sup>151,152</sup> In both methods use is made of a nonlinear interaction of the field with the medium, but only in one case (Stark effect) is the field quasistatic, whereas in the other use is made of the field of an electromagnetic wave.

We shall now consider the principle of investigation of the nature of the orientation of dipoles in a multilayer by the Stark effect method. We shall assume that a molecule is oriented rigidly relative to the direction of the field. In general, the absorption of a photon is accompanied by a change in the static dipole moment of a molecule from  $\mu_0$  to  $\mu_e$ . In an external field the energies of the corresponding ground and excited states change as shown in Fig. 19 and the frequency of the optical transition shifts linearly with the field:

$$h \Delta \nu_{l,m} = (\Delta \mu E), \quad (14)$$

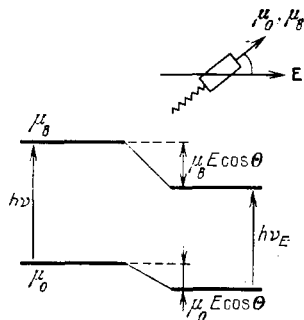


FIG. 19. Linear shift of the energies of the ground and excited states of a dipole molecule induced by an external electric field. The shift of the transition frequency is proportional to  $\cos \Theta$ .

where  $\Delta\mu = \mu_e - \mu_0$  is the change in the dipole moment due to this transition. In addition to the linear—in respect of the field—shift of the optical band described by Eq. (14), there is also a quadratic shift proportional to the difference between the polarizabilities of the investigated molecule in the ground and excited states  $\Delta\alpha = \alpha_e - \alpha_0$ :

$$h\Delta\nu_{\text{Quadr}} = \frac{1}{2} \Delta\alpha E^2. \quad (15)$$

We shall not discuss the quadratic effect to maintain the simplicity of the treatment.

We shall consider an X- or Z-type multilayer in which all the dipoles are oriented in one direction (Fig. 8) and, consequently, the vectors  $\Delta\mu$  also have the same orientation. It then follows from Eq. (14) that the direction of the spectral shift of an absorption band of all the molecules can be described by  $\cos \Theta$ , where  $\Theta$  is the angle between  $\mathbf{E}$  and  $\Delta\mu$  (Fig. 20a). For a given direction of  $\Delta\mu$  relative to the molecular skeleton the sign of  $\cos \Theta$  is the same for X- and Z-type multilayers and it can be distinguished in accordance with the direction of the spectral shift of the band. It is usual to determine experimentally the depth of modulation of light by an alternating field,<sup>153</sup> so that the measured "field correc-

tion" to the spectrum (Fig. 20b) is proportional to the derivative  $dD/d\nu$ , where  $D$  is the optical density in the investigated absorption band.

In the case of the Y-type multilayer some of the dipoles are oriented along the field and the others against the field. Consequently, the spectral shifts will be of opposite signs for different multilayers and the result is simply broadening of the combined absorption band (Fig. 20c). The spectrum of the field correction is now proportional to the second derivative  $d^2D/d\nu^2$ .

It follows that a study of the Stark effect can be used to determine the nature of the dipole orientation in monolayers and multilayers. Moreover, the method can be used to obtain quantitative estimates of the disordering of dipoles, i.e., to determine the value of  $\langle \cos \Theta \rangle$ , as shown in Ref. 154, and a more rigorous analysis of the spectrum can also yield the value of  $\langle \cos^3 \Theta \rangle$  (Ref. 155). The sensitivity of the Stark effect method is sufficient for measurements on one monomolecular layer.<sup>156</sup>

We shall now go back to X- and Z-type superlattices (Fig. 16). Different molecules have different absorption bands, but the spectral positions of these bands are independent (at least in the first approximation) of the orientation of molecules in the "sublattice." The application of an electric field lifts such degeneracy and some bands begin to move toward longer wavelengths and others toward shorter wavelengths, so that an analysis of the spectrum of the Stark effect can be used to monitor the orientation of molecules in a superlattice. This procedure was used in an experimental study reported in Ref. 157.

Recently the interest in the Stark effect has increased considerably<sup>158-160</sup> because it is possible to control the positions of narrow spectral lines of organic molecules at low temperatures by the application of an electric field. This is particularly important in experiments involving burning of spectral dips or holes<sup>161,162</sup> with the purpose of storing information by a frequency selection method. In the nearest future these methods will be extended also to Langmuir films.<sup>163</sup>

### 5.5. Nonlinear optical effects

Investigations of nonlinear optical properties of Langmuir films are proceeding along two main directions. The generation of the third optical harmonic is being studied in centrosymmetric multilayers.<sup>164,165</sup> This is due to the fact that organic molecules with a highly developed system of conjugate bonds can have very high nonlinear susceptibilities. On the other hand, a strong optical anisotropy of Langmuir multilayers makes it possible to achieve readily phase-matched harmonic generation. Finally, it is possible to generate optical harmonics in an integrated optical variant. Investigations have been made in the case of polydiacetylene films.<sup>164,165</sup> The cubic nonlinear susceptibility of this compound is a record for organic compounds ( $\chi^3 > 10^{-10}$  cgsu). This is two orders of magnitude higher than, for example, for a  $\text{CaCO}_3$  crystal.

The application of an external electric field of centrosymmetric multilayers of polydiacetylene suppresses the inversion center and, therefore, allows generation of the second optical harmonic.<sup>166</sup>

In polar multilayers the second optical harmonic can be

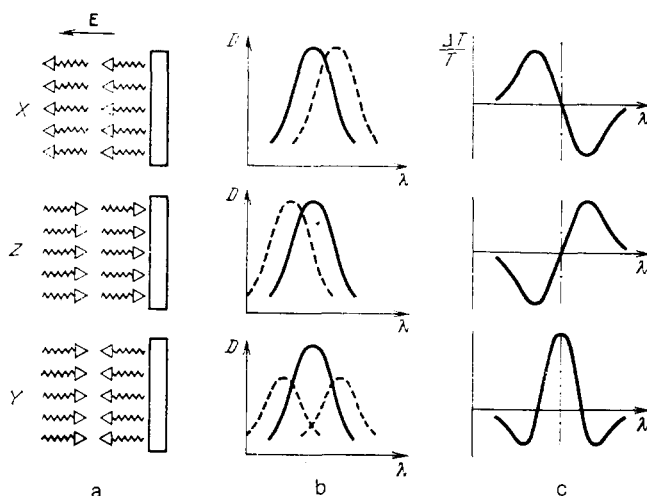


FIG. 20. Spectral shift of the optical absorption bands of multilayers of the Z-, X-, and Y-types. The curves on the extreme right are the differential spectra recorded by modulation of the optical transmission  $T$  with an electric field.

excited also in the absence of an external field. This was first demonstrated in Ref. 167 for a single multilayer of an azo dye. The second harmonic was observed on reflection from a monolayer, as in the case of generation of the second harmonic in a monolayer on the surface of water reported in Ref. 51. An increase in the number of monolayers resulted in a linear increase of the intensity of the second harmonic,<sup>168</sup> which was in qualitative agreement with the pyroelectric effect experiments (Fig. 17). The quadratic nonlinear susceptibility ( $\chi^{(2)} \approx 4 \times 10^{-8}$  cgsu) was comparable with the corresponding value for lithium niobate, which is one of the best optical frequency doublers.

Second harmonic generation has been observed also for a single monolayer of a merocyanine dye<sup>169</sup> in X-Z superlattices composed either of a lasing dye and intermediate layers of one of the fatty acids<sup>170</sup> or of two lasing dyes of the donor and acceptor types.<sup>171</sup> As expected, in the latter case the value of  $\chi^{(2)}$  was almost double compared with the simple sum of the susceptibilities of the individual components.

A review of the work on applications of nonlinear organic materials in integrated optics can be found in Ref. 172.

## 6. ELECTRICAL, MAGNETIC, AND PHOTOELECTRIC PROPERTIES OF LANGMUIR-BLODGETT FILMS

### 6.1. Electrical and magnetic properties

The relatively long hydrocarbon tail is an unavoidable attribute of an amphiphilic molecule and it can be used to form and transfer monolayers. Since all or nearly all chemical bonds in such a tail are saturated, the conditions are unfavorable for the generation of carriers in this region. Therefore, the part of the monolayer occupied by the alkyl tails is a good insulator. This is confirmed by dielectric measurements on film sandwich structures to which an external field is applied along the normal to the film. If short circuits can be avoided, it is found that the electrical capacitance is inversely proportional to the number of monolayers in a multilayer.<sup>173</sup> The absolute values of the permittivity of almost all amphiphilic compounds are practically the same ( $\epsilon \approx 2.5-3.5$ ).<sup>174</sup>

Langmuir-Blodgett films have an exceptionally high electric strength (breakdown fields are of the order of  $10^8$  V/m). It is interesting to note that individual monolayers can withstand fields up to  $10^9$  V/m or higher. This is due to the fact that the voltage across a monolayer does not exceed 1-3 V so that the energy of carriers acquired from the applied field cannot exceed 1-3 eV and this is insufficient for creating a structure defect in the film and causing breakdown. The high field intensity by itself can only cause significant spectral shifts (Stark effect) or induce some polarization effects which are not dangerous to the continuity of the film.

In discussing the electrical conductivity of films it is desirable to distinguish right from the beginning two cases of electron transport across a multilayer and in the plane of a multilayer. This is due to the fact that the heights of the potential barriers are very different in these two cases. In the case of motion across a multilayer a carrier should overcome "dielectric or insulating spacers" made of hydrocarbon chains. However, in the plane of a multilayer the molecular packing may be such as to facilitate maximally the transport of electrons (close contact of chromophore groups of dyes,

alternate packing of donor and acceptor components, etc.).

We shall begin by summarizing our knowledge of the transverse conductivity of Langmuir-Blodgett films. If we are dealing with just one monolayer, the current across it is usually due to the tunnel mechanism<sup>175-178</sup> and the formally introduced conductivity under an infinitesimally small voltage is an exponential function of the thickness  $l(n)$  of a hydrocarbon chain consisting of  $n$  links:

$$\sigma = \sigma_0 \exp \left[ -\frac{2}{\hbar} (2m\Psi)^{1/2} l(n) \right], \quad (16)$$

where  $m$  is the mass of an electron and  $\Psi$  is the barrier height. The tunnel mechanism of the flow of an electric current across one monolayer is supported by direct determinations of the tunnel spectra<sup>179,180</sup> and of the Josephson effect.<sup>181</sup>

If we now increase the film thickness not by increasing the monolayer thickness, but by adding further monolayers, the exponential dependence on  $l$  changes immediately to linear.<sup>173,182</sup> This can be explained by the presence of a wide energy spectrum of surface states of monolayers in a multilayer: a carrier can now tunnel across each monolayer in turn and the total electrical resistance of the whole structure consists of series-connected resistances of the tunnel junctions (for details see Refs. 11 and 78).

The presence of a chain of conjugate (alternately double and single) bonds oriented along the normal to a monolayer facilitates electron transport across a monolayer (by reducing the width of the barrier for tunneling). This is known as the "molecular wire" effect and is described in Ref. 183.

We shall now consider the possibility of constructing two-dimensional molecular layers which conduct in the monolayer plane. Conducting multimolecular structures of this type have been prepared recently from donor-acceptor complexes.<sup>184,185</sup> This is done as follows. A monolayer of a charge-transfer complex is deposited on the surface of water: this monolayer consists of an amphiphilic donor fragment in the form of pyridine (Fig. 21) and a nonamphiphilic acceptor in the form of tetracyanoquinodimethane. The stability of a monolayer on water is ensured by the amphiphilic nature of the donor, whereas the acceptor is attracted to the donor by the Coulomb forces. Systems of this kind can be called semiamphiphilic.<sup>54</sup> The monolayers of such complexes are transferred from the surface of water onto a solid substrate. The electrons in each monolayer are transferred from donors to acceptors and therefore, an excess electron is localized at the acceptor molecules and this electron can form a conduction band. However, in view of the Peierls instability this band has an energy gap<sup>186</sup> so that metallic conduction requires that the system be doped with an additional impurity. Iodine vapor has been used in reported studies.<sup>184,185</sup> Iodine is incorporated in the multilayer structure (Fig. 21)<sup>89</sup> and this creates conducting molecular layers of just 4 Å thickness. The conductivity of these layers amounts to  $10 \Omega^{-1} \cdot \text{m}^{-1}$ , but contrary to expectations it is of semiconducting nature although the activation energy is low (of the order of 0.15 eV). These investigations are interesting also from the fundamental point of view because they provide the first insight into electrical properties of quasitwo-dimensional layers of molecular thickness.

The Langmuir-Blodgett technology can be used in



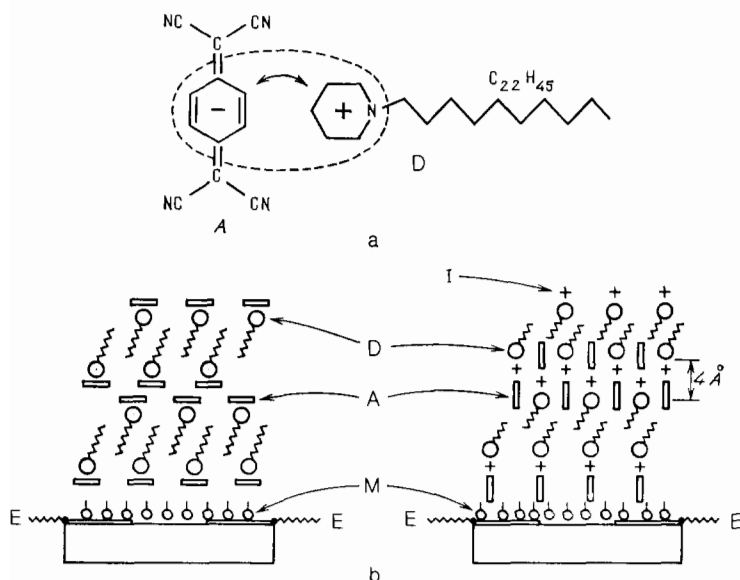


FIG. 21. Molecular structure of a semi-amphiphilic donor-acceptor complex (a) and structure of conducting multilayers based on this complex (b) before and after doping with iodine.<sup>89</sup> Here D is a donor, A is an acceptor, and I is iodine; E are the electrodes on the substrate and M is a fatty acid monolayer.

principle to form a two-dimensional ordered lattice of magnetic atoms. The atoms of Fe, Ni, and Mn should be incorporated in certain fragments of amphiphilic molecules and then transferred onto solid substrates in the form of monolayers or multilayers. This raises the interesting problem of the possibility of ferromagnetic ordering of a two-dimensional system. It is known that one-dimensional magnetism is impossible, whereas in the two-dimensional case it is found that different models give different results. The first experiments on manganese stearate Langmuir films revealed ferromagnetic ordering at low temperatures (near 1 K).<sup>187,188</sup> Later experiments carried out employing a sensitive SQUID magnetometer<sup>189</sup> demonstrated that at low temperatures one monolayer exhibits weak ferromagnetism which changes to antiferromagnetic ordering at higher temperatures. On the whole, the question of two-dimensional magnetism is not yet finally solved.

### 6.2. Photoelectric processes

In this subsection we shall discuss briefly the tunnel phototransport of electrons, photoconductivity, and photoemf. One should stress that photoprocesses occurring within an individual monolayer at the molecular level of organization are particularly interesting in Langmuir-Blodgett films. This is not possible in the case of organic semiconductors in the form of crystals or vacuum-evaporated films because in such cases the processes of generation and transport of carriers occur at the macroscopic level. Relevant investigations have already been made on Langmuir films. For example, several monolayers consisting of donor molecules can be deposited and this can be followed by several layers of acceptor molecules and the system can be regarded as a p-n junction between two organic semiconductors,<sup>190</sup> but this loses the opportunity for investigating the dark and photoelectric processes on the molecular scale.

Studies have been made of systems in which the position of a photosensitive monolayer has been fixed exactly in space. For example, measurements of the photoconductivity of a multilayer consisting of a stack of photoelectrically inactive fatty acid monolayers and a built-in single photoactive

dye monolayer were reported in Ref. 191. Illumination released carriers (for example, electrons) from the dye and they migrated toward the anode. The photocurrent depended on the distance between the dye monolayer and the anode, as required by the theory of photoconductivity.

The tunneling of electrons from a photoexcited state of one molecule to one of the energy levels of another molecule is particularly interesting.<sup>142,192</sup> This process is known as vectorial electron transport and it is particularly important in biology (photosynthesis, mechanism of vision, etc.). However, this problem had been discussed in detail by the present author,<sup>11</sup> so that only the physical principle of vectorial transport will be demonstrated here. Figure 22 shows a structure of three monolayers consisting of amphiphilic molecules with different ionization potentials and different chemical affinity to electrons. We shall assume that light is absorbed by the central monolayer. An electron may tunnel from an excited state across a potential barrier formed by a dielectric spacer which is the region occupied by the hydrocarbon tails. After tunneling the electron is captured by a molecule with a large electron affinity acting as an acceptor. In place of an electron lost from the central monolayer we can expect a new electron from the left due to a tunnel transition from the ground state of a donor molecule. The reverse transition of a photoelectron that has escaped from the upper state is not possible. During continuous illumination of the central layer we can expect electrons to be transferred

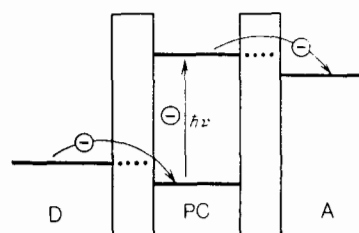


FIG. 22. Schematic diagram of an "electron pump." Here, D is an electron donor, PC is a photocatalyst of the transfer process, and A is an electron acceptor.

from lower energy levels of the electron donor to the higher levels of the acceptor and the whole system should act as a photoelectron pump. High-energy electrons are then used in some biochemical reaction. This tunnel electron transport mechanism is supported by the exponential dependence of the degree of quenching of the donor luminescence on the thickness of the dielectric spacer (i.e., on the length of the hydrocarbon tail) between the donor and acceptor.<sup>142</sup>

A photo-emf can be observed if a Langmuir multilayer as a whole, including the electrodes, exhibits a polar asymmetry. In the case of symmetric electrodes and symmetric photoexcitation, when the whole structure is illuminated uniformly, there should be no photo-emf. In this case we can observe only the transient photoinduced polarization<sup>150</sup> described earlier. If the electrodes of a cell shown in Fig. 18 are made of different metals, illumination of a multilayer with ultraviolet radiation gives rise to a photo-emf with a spectrum independent of the molecular structure of the film. This emf appears because of the photoemission of electrons from the metal into the film.<sup>193</sup> An increase in the multilayer thickness changes the photo-emf mechanism. Carriers are now generated as a result of absorption in the multilayer and then distributed to the electrodes by an internal field which is generated by the asymmetry of the potential barriers at the electrodes.<sup>194</sup>

### 6.3. Photochemical transformations

The literature on photochemical processes in Langmuir films is now quite extensive and deserves a separate discussion elsewhere. We shall briefly outline some of the ideas that are directly relevant to the physical properties and discuss some practical applications of Langmuir-Blodgett films.

We shall begin with polymerization. If a hydrocarbon tail or some other fragment of an amphiphilic molecule has an unsaturated (double or triple) chemical bond, this bond can be broken by ultraviolet radiation, electron-beam bombardment, or by a chemical reaction. If there are no external

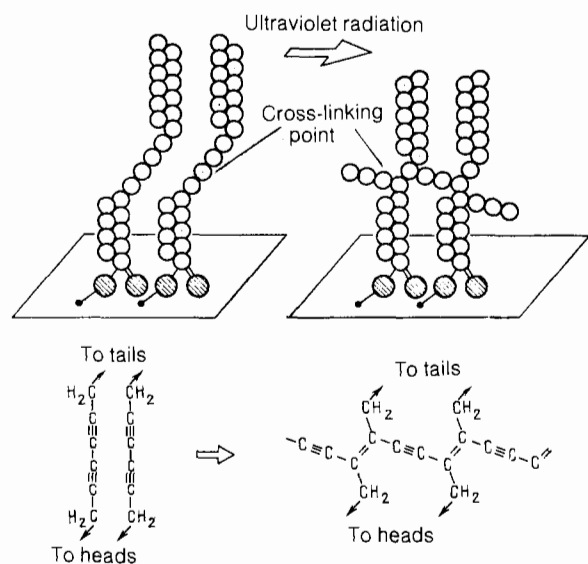


FIG. 23. Polymerization of a monolayer of amphiphilic diacetylene with ultraviolet radiation. The lower part of the figure shows the structural formulas of the photochemically active fragments.

agencies, new bonds should form but they are no longer intramolecular but intermolecular (Fig. 23), so that a monomolecular layer (and sometimes a multilayer) is effectively converted into a continuous polymer molecule. Such polymerization may take place also in a monolayer lying on the surface of water<sup>195</sup> and the converted monolayer can be transferred onto a solid substrate; conversely, one can polymerize already transferred monolayers one at a time or all simultaneously.<sup>196</sup> This makes the structural organization of a monolayer dependent on the method of its formation. In the case of layer-by-layer polymerization there is practically no correlation between the distributions of molecules in neighboring monolayers, whereas the crystal structure is fixed immediately in the course of polymerization of the whole multilayer. In any case, a polymerized layer has a high mechanical and chemical stability, which is important in practical applications,<sup>197</sup> and, moreover, such a monolayer can be separated from the substrate.

The molecules of some amphiphilic dyes form dimers, i.e., molecular pairs, under the influence of electron bombardment. Optical properties of dimers differ from the properties of the individual molecules so that an electron beam can be used to store data in a Langmuir-Blodgett film and such data can then be retrieved by an optical method. Physicochemical properties of dimers also differ from the properties of individual molecules and this makes it possible to replicate the stored data, i.e., to transfer a copy of the pattern drawn by an electron beam to the next monolayer (Fig. 24).<sup>198</sup> In the transfer of a monolayer of a dye from the surface of water onto a substrate covered by a monolayer of the same dye, which may be in the form of individual molecules or dimers, the process of growth of a new monolayer proceeds in such a manner that new dimers join the existing ones and individual molecules are joined by identical molecules. Consequently, the pattern of data in which the role of a logic unity is played by a dimer and the role of logic zero is played by an individual molecule can be reproduced in the upper monolayer. Moreover, this upper monolayer can be separated from the lower one so that a molecular copy is obtained. This process is fully analogous to the replication of long-chain ribonucleic acid (RNA) molecules on a desoxyribonucleic acid (DNA) matrix in a cell chromosome, but in this case a copy is made not of a one-dimensional but of a two-dimensional data pattern.

Some amphiphilic organic molecules, particularly those belonging to the class of spiropyranes, undergo a reversible structural modification under the influence of ultraviolet and visible radiation. This changes greatly the absorption spectrum of a molecule. The effect is known as photochromism. The photochromic effect is observed also in monolayers on the surface of water<sup>199</sup> and in Langmuir-Blodgett films.<sup>200</sup> In the latter case it is found that ultraviolet illumination of a colorless form of a dye generates J aggregates of the type shown in Fig. 12, which exhibit a strong absorption band in the red part of the spectrum and have a long lifetime. Consequently, an optical memory device can be built.

Such a device can also be based on the orientational photodichroism effect.<sup>201</sup> In this case there is no change in the chemical structure of the dye molecules, but their orientation changes in space under the influence of polarized light. The microscopic nature of this effect is not yet clear, but it is obvious that its manifestations are associated with

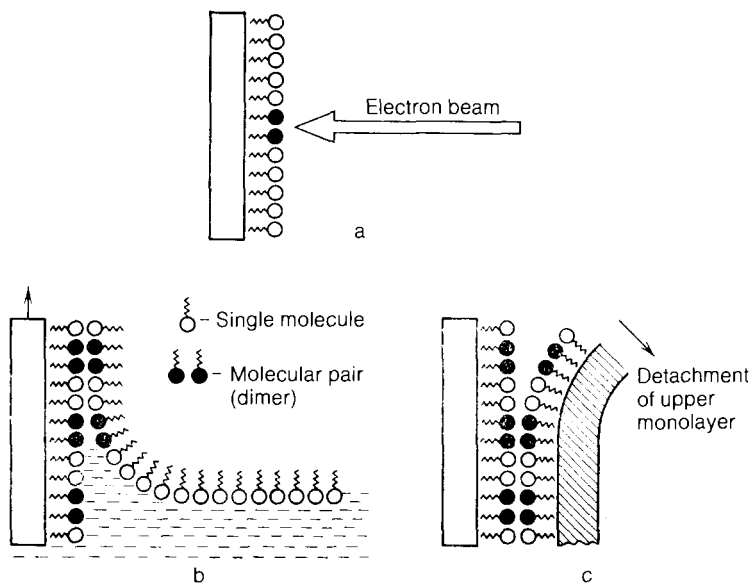


FIG. 24. Process of replication of a two-dimensional data array recorded using an electron beam in a Langmuir-Blodgett monolayer<sup>198</sup>: a) data storage; b) replica formation; c) detachment of copy.

the characteristic features of the crystal structure of Langmuir-Blodgett films.<sup>202</sup> The destruction of J aggregates by illumination can also be used to store data in Langmuir films.<sup>203,204</sup>

## 7. CONCLUSIONS. LANGMUIR FILMS AND MOLECULAR ELECTRONICS

It is obviously impossible to describe here all the practical applications of Langmuir films. This is dealt with in special reviews<sup>15,16</sup> and partly also elsewhere.<sup>11,17,205</sup> However, general comments can still be made.

In the case of fundamental investigations, the most important is the ability to study a very great variety of intermolecular interactions under conditions when the distances between molecules and their mutual orientations are rigorously fixed. These conditions are satisfied in Langmuir films. It is possible to study the spectral manifestations of the interactions of molecules within one monolayer and in neighboring monolayers. Moreover, investigations are already being made of directional chemical reactions (in particular, of polymerization) in Langmuir multilayers.

The anisotropy of the processes of generation and transport of various elementary excitations typical of organic solids can be studied in Langmuir-Blodgett films and these films can be used to construct superlattices with a known potential relief affecting carrier motion. Monolayers on the surface of water or stacks of solid monolayers interacting weakly with one another are excellent models for the investigation of phase transitions in low-dimensional systems. As mentioned already, Langmuir films can be used to model also various biological phenomena, such as photosynthetic processes, replication of data, operation of receptors, etc.

Mastering of the technology of Langmuir films leads to the problem of fabrication of materials for electronics. A new subject is growing: it is known as molecular electronics<sup>206</sup> and one of its tasks is the construction of components or devices with molecular dimensions. This should make it possible to overcome the serious physical problems which impose constraints on semiconductor integrated circuits.<sup>207,208</sup>

Polymerizable Langmuir-Blodgett films are already being used in ultrahigh-resolution electron-beam lithography and also as insulators in metal-insulator-metal structures. In the latter case a Langmuir film can perform not only the function of a high-strength (in the mechanical, chemical, and electrical senses) insulator, but can also be used as an active element sensitive to external agencies of thermal (pyroelectric), mechanical (piezoelectric), or chemical nature (the last one can be used in construction of chemical sensors). Moreover, the use of Langmuir-Blodgett films as optical waveguides is very attractive, particularly in the case when the film material also has nonlinear optical properties.

In much further future (possibly even in the science fiction realm) lies the task of construction of electronic components from biological materials.<sup>209,210</sup> The fundamental feature of biological structures is their ability to operate using logic principles differing from the simple on-off switching, in contrast to the logic elements used in today's programmable computers. Biological systems such as enzymes may exhibit continuous changes of their structure under the influence of incoming signals, exhibiting the learning process.<sup>211</sup> Moreover, in the near future there will be a demand from medicine for microprocessors which can survive inside the human body and which perform the functions of the damaged parts of the brain. One would expect the devices based on principles of bioelectronics to be much better for this purpose than the traditional circuits and fabrication of Langmuir films may provide the basic technology for the construction of such devices. This technology could also utilize the principle of self-organization of biological structures.<sup>212</sup>

<sup>1)</sup> This topic is discussed in detail in the very recent thorough review of Yu. M. L'vov and L. A. Feigin.<sup>205</sup>

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