

# Scanning tunneling microscopy and spectroscopy of low-dimension systems: Molecular films of an ion-exchange polymer

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The results of an experimental study of the electronic properties of Langmuir–Blodgett films of an ion-exchange polymer, performed by the methods of scanning tunneling microscopy and spectroscopy (STM–STS), are presented. Ordered regions with dimensions of  $\sim 1000$  Å and a  $dI/dV(V)$  curve with a conductance peak near the zero bias voltage were found. For this case the shape of the curve  $dI/dV(V)$  was found to depend on the period of the ordered structure. In the case where there was no ordering on the surface of the film, splitting of the conductance peak on the curve  $dI/dV(V)$  was observed near zero bias voltage. An additional energy gap with a width of  $\sim 40$  meV appeared. A model is proposed to explain these effects. © 1995 American Institute of Physics.

In the present paper we report the results of an experimental study, performed by the methods of scanning tunneling microscopy and spectroscopy (STM–STS), of the quantum-size effects in Langmuir–Blodgett (LB) films of an ion-exchange polymer, specifically, “anomalies” consisting of a conductance peak near zero bias voltage and the dependence of the parameters of the differential conductivity curve  $dI/dU(U)$  on the microscopic characteristics of the system. The anomalies in the spectrum  $dI/dU(U)$  have been observed in many experiments.<sup>1,2</sup> Among the possible reasons for these anomalies, we call attention to size effects, studied in Ref. 3, in disordered systems; these effects give a uniform correction to the density of states near the Fermi level.

It should be noted that such effects have been generally observed in planar contacts and at low temperatures. At present, however, phenomena of this type in many cases are not adequately understood.<sup>4</sup> In the present study we have therefore employed the STM–STS methods of local analysis of a surface in order to study at the microscopic level the formation of the electronic spectrum of low-dimension systems.

The films used by us were produced in order to obtain two-dimensional conducting

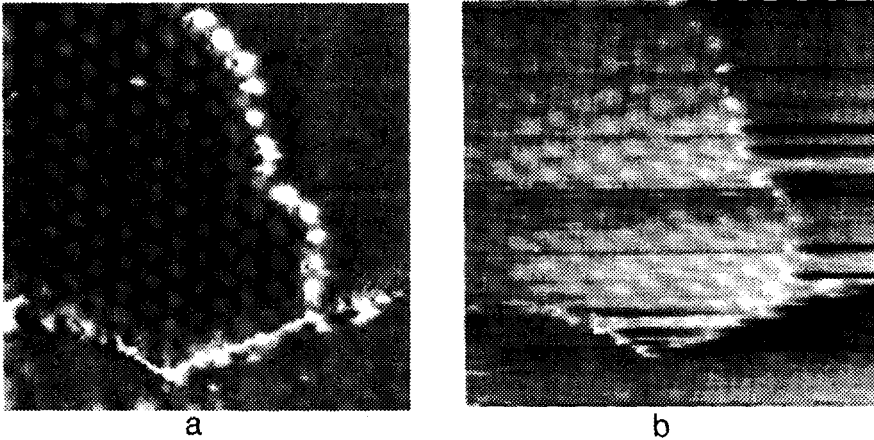


FIG. 1. a—STS image of the surface of a monolayer Langmuir–Blodgett film of an ion-exchange polymer. The frame dimensions are  $784 \text{ \AA} \times 784 \text{ \AA}$ . The gray brightness scale corresponds to relative units.  $I_t = 0.8 \text{ nA}$ ,  $U_t = -25 \text{ mV}$ ,  $U_{\text{mod}} = 15 \text{ mV}$ ; b—STM image of the surface of a monolayer Langmuir–Blodgett film of an ion-exchange polymer with  $\text{Fc}^+$  ions. The frame dimensions are  $784 \text{ \AA} \times 784 \text{ \AA}$ . The gray brightness scale corresponds to  $100 \text{ \AA}$ .  $I_t = 0.8 \text{ nA}$ ,  $U_t = -25 \text{ mV}$ .

layers separated by a nonconducting fluorinated polymer. The method used to prepare the experimental samples is described in Ref. 5. In the experiments we investigated LB films containing 1 to 25 layers with different metals: Ag, Cu, and Fc (ferrocene). The substrate consisted of a highly oriented pyrolytic graphite.

To determine the characteristic features of the electronic spectrum of the LB film of ion-exchange polymer, the film was investigated in both the ordinary topographic  $Z(x,y)$  mode of STM and in the regime of measurement of the spatial distribution of the first derivative of the tunneling current with respect to the bias voltage  $dI/dU(x,y)$ . We also measured in the experiments the tunneling current  $I(V)$  as a function of the voltage and the first derivative of the current  $dI/dU(U)$  at fixed points of the surface, and also the tunneling current  $I(z)$  as a function of the distance between the tip and the sample. The measurement method for all regimes is described in Refs. 5 and 6. The investigations were performed in air.

## EXPERIMENTAL RESULTS

In the analysis of the surface structure of the LB monolayer we observed islands with a pronounced periodic structure (Fig. 1) and disordered regions, separated from one another by a sharp boundary. The typical size of the islands with the ordered structure is about  $100 \text{ nm}$ , and the characteristic period of the observed structure was  $1\text{--}6 \text{ nm}$ . On the average, one such island was observed in an area of  $1.5 \times 1.5 \text{ \mu m}$ . Disordered sections of the surface of the film were observed in the form of a collection of clusters  $1\text{--}6 \text{ nm}$  in size. This diversity of sizes in the observed structure of the surface of the LB film can apparently be explained by the volume properties of films of this polymer: The film has an amorphous-crystalline structure (crystalline islands in an amorphous matrix) with

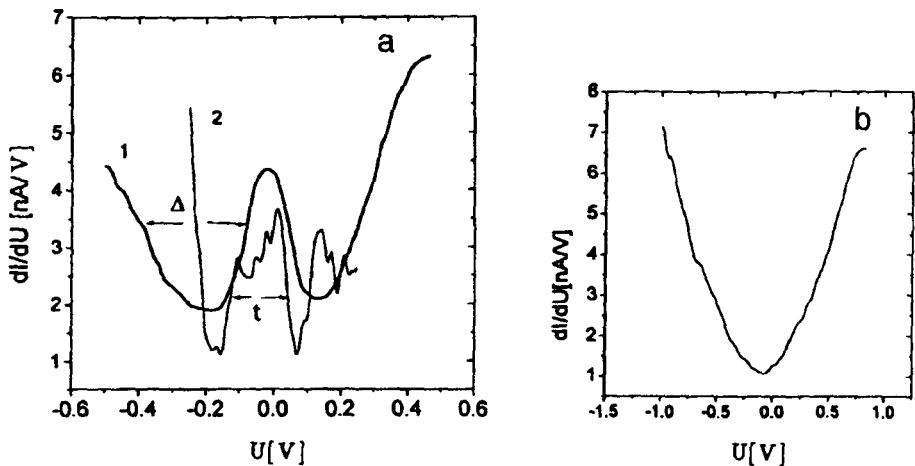


FIG. 2. a—Conductivity  $dI/dU$  versus the bias voltage. The curves were obtained for a Langmuir–Blodgett film consisting of three layers with  $\text{Ag}^+$  ions. Curve 1 was obtained for a section of the film surface with a lattice period of  $11.5 \text{ \AA} \times 11.5 \text{ \AA}$ .  $I_t = 0.8 \text{ nA}$ ,  $U_t = -30 \text{ mV}$ ,  $U_{\text{mod}} = 20 \text{ mV}$ . Curve 2 was obtained for a section of the film surface with the lattice period  $65 \text{ \AA} \times 40 \text{ \AA}$ .  $I_t = 0.8 \text{ nA}$ ,  $U_t = -30 \text{ mV}$ ,  $U_{\text{mod}} = 20 \text{ mV}$ ; b—conductivity  $dI/dU$  versus the bias voltage; the curves were obtained for a section of the surface with no Langmuir–Blodgett film.  $I_t = 0.8 \text{ nA}$ ,  $U_t = -30 \text{ mV}$ ,  $U_{\text{mod}} = 20 \text{ mV}$ .

$\sim 10\%$  crystalline regions, ionogenic groups together with counterions have a tendency to form large clusters (up to 5 nm) which can form a periodic structure. The size of these clusters depends on many conditions; in particular, it depends strongly on the humidity.<sup>7</sup>

Investigations of the films revealed that the shape of the curve  $dI/dU(U)$  depends on the presence of ordering and on a characteristic period of the surface structure. Above the regions of the film surface where ordering exists, the function  $dI/dU(U)$  has a smooth, characteristic maximum near zero bias voltage and two minima whose width increases as the dimensions of the surface structure decrease (Fig. 2a, curves 1 and 2). The width of this minimum was measured at the level 0.7 times the amplitude of the peak. The measurements of  $dI/dU(U)$ , which we are comparing, were performed above the sections of the lattice with maximum conductivity (open spots in Fig. 1). It should be noted that for regions in which there is no film the curve  $dI/dU(U)$  has the shape indicated in Fig. 2b.

In the case where there is no ordering of the image in the STM, splitting of the conductance peak in the curve  $dI/dU(U)$  near zero bias voltage is sometimes observed, and an additional energy gap with a width of about 40 meV appears. The split maxima have a characteristic width of the order of 20 meV (Fig. 3).

## DISCUSSION

The experimental results which we obtained can be interpreted as follows. The structure observed in the STM can be regarded as a collection of metallic clusters (open spots in Fig. 1). Quantum-size levels exist for electrons inside each cluster:

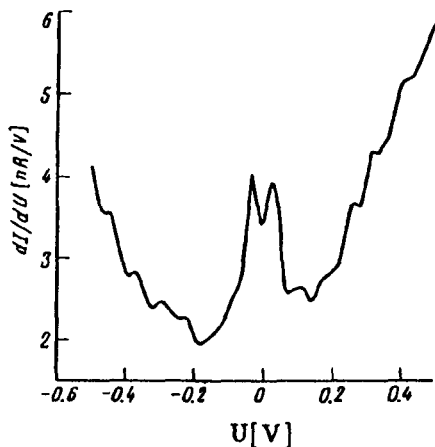


FIG. 3. Conductivity  $dI/dU$  versus the bias voltage. The curve was obtained for a disordered surface of a monolayer Langmuir-Blodgett film with  $\text{Fc}^+$ .  $I_f = 0.8$  nA,  $U_f = -30$  mV,  $U_{\text{mod}} = 20$  mV.

$$E_n \sim 2\hbar^2 n^2 / d^2 m_{\text{eff}},$$

(this is a rather crude estimate for this system), where  $d$  is the size of the cluster, and  $m_{\text{eff}}$  is the effective mass of the electrons. The periodic structure of such clusters can be characterized in the strong-coupling approximation by a collection of energy bands associated with the quantum-well energy level  $E_n^i$  of a cluster (the index  $i$  enumerates clusters). The electronic transitions between different clusters smear the separate quantum-well levels into a band of delocalized states. The width of this band is determined by the amplitude of the transition of an electron between clusters,  $t(d, L)$ , where  $L$  is the period of the structure. If

$$t < \delta E \sim \hbar^2 / d^2 m_{\text{eff}},$$

then the electronic spectrum of the system consists of a collection of allowed energy bands separated by gaps (Fig. 4a). The gap width is  $\Delta \sim \delta E$ , so that the magnitude of the gap decreases with increasing size of the clusters, consistent with the experimental results (Fig. 2a, curves 1 and 2). It should not be expected, however, that for a real system the gap width will have the dependence  $\sim 1/d^2$ , since the shape and the depth of the effective potential well for the electrons, which corresponds to a cluster with size  $d$ , is unknown. Moreover, the expression  $\delta E \sim \hbar^2 / d^2 m_{\text{eff}}$  is valid only for the low-lying quantum-size levels (small  $n$ ). For the higher-lying levels the dependence can have the form  $1/d$ .

The gap width (at the level 0.7 times the amplitude of the peak) versus the size of the observed structure is shown in Fig. 4b for a different number of layers and different counter ions. However, the width  $t$  of the band is virtually independent of the period of the structure. This apparently stems from the fact that a change in the period of the structure, on the one hand, results in an increase of  $t(d, L)$ , since the width of the effective potential barrier between the clusters decreases and, on the other, it results in stronger Coulomb repulsion of the electrons localized on the quantum-size levels, i.e., an

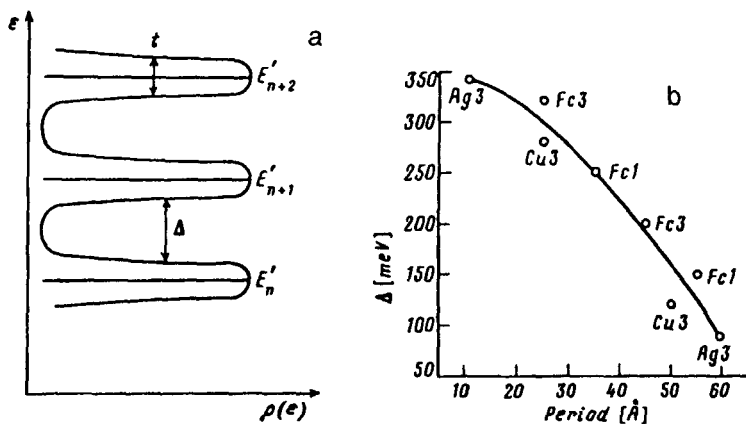


FIG. 4. a—Schematic representation of the energy bands associated with the quantum-size level; b—gap width  $\Delta$  versus the period of the observed structure for different number of layers and different counter ions. Ag3—three layers with silver ions, Cu3—three layers with copper ions, Fc1—one layer with ferrocene ions, Fc3—three layers with ferrocene ions,  $I_t=0.8$  nA,  $U_t=-30$  mV,  $U_{\text{mod}}=20$  mV.

increase in the height of the potential barrier between the clusters. The competition between these two effects weakens the dependence of the width of the band on the period of the structure.

As noted above, for a disordered region with separate close-lying electronic clusters, the distance between whose boundaries is of the order of several angstroms, a gap of the order of 40 meV appears on the curve  $dI/dU(U)$  in the range of voltages where a band of delocalized electronic states was observed in the case of a periodic structure. It should be noted that this splitting exists only in the case where the STM tip is located directly above a given pair of clusters. Separate broadened quantum-size levels are observed above an isolated cluster. As the STM tip is moved away from the clusters, both the separate quantum-size levels and their splitting disappear, in contrast with the size effects studied in Ref. 3, which give a correction, which is uniform over the sample, to the density of states. An interaction apparently occurs between the quantum-size levels of close-lying clusters, which leads to splitting of the levels into two sublevels:<sup>8</sup>

$$E_{1,2}^n \sim E^n \pm \epsilon_0 e^{-\kappa r},$$

where  $\kappa^{-1}$  is the localization length of the electronic wave function of a state with energy  $E^n$ ,  $r$  is the distance between neighboring clusters, and  $\epsilon_0$  is the matrix element of the interaction. The observed additional gap corresponds to the splitting between these split pairs of energy levels, and the peaks in the density of states correspond to the energies of these levels, which can undergo both thermal and inhomogeneous broadening. The width of the observed peaks, which is of the order of 20 meV, most likely corresponds to thermal broadening.

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