THE MODEL OF A TOTAL DIPOLE MOMENT TIME CHANGE OF LANGMUIR FILM FLOATING ON THE WATER SURFACE SUBJECTED TO MECHANICAL COMPRESSION BASED ON AN APPROXIMATION OF WEAK INTERACTING POLAR MOLECULES

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ABSTRACT

In this paper it is proposed and analysed a model explaining the dielectric dynamic response measurements of total electric dipole moment change of organic monolayer floated on water surface during mechanical lateral compression. We relatively successful explained experimental data by analysis of model, based on analogy with non-ideal gas. In presented paper, besides own theoretical model, we are also comparing this analysis with measured data.

1 INTRODUCTION

Monolayers formed of molecules of organic amphiphilic materials at the air/water interface provide a 2-dimensional system with interesting physical properties and various applications. For investigating Langmuir films optical methods are commonly used [1]. In [2] a new approach was described for the first time, the study of dielectric dynamic response of the total electric dipole in the organic monolayer floating on the water surface, which is subjected to mechanical lateral compression. Experimentally it is recorded as an electric current through a short-circuited capacitor being formed by two parallel plates, one in air above the monolayer detached at a certain spacing, another immersed in water below the monolayer. During the compression of the monolayer, the external mechanical force, which drives a movable barrier, results in the change of surface concetration of the molecules as well as in the orientational change of the direction of the molecular electric dipoles [3]. The theoretical explanation of the behaviour of a similar system can be found in [4] and is based on the theory of the rotational Debye-Brown motion.

The measurement analysed in my work was executed on Dept. of Physics FEI STU an monolayer formed of stearic acid molecules. More details about the experimental device are described in [5]. Measurements were carried out at various speeds of compression.

2 CALCULATIONS

The model is based on the assumption that each molecule behaves as a weak dipole moment with the negative pole bound to the water surface. In [6] it is shown that for a linear hydrocarbon chain the description of electric properties using the dipole approximation is sufficient. The influence of the polar water molecules on a final measured signal was neglected. A basic assumption of the model is that the individual dipole moments have random directions within some solid angle. The molecules execute a random precessional motion with a maximal possible dipole moment tilt θ_A from the vertical axis and is defined by the relation $\cos\theta_A = \sqrt{1-A/A_c}$, where A is the area per molecule and the A_c is the critical area for the molecule lying on the water surface [4]. Generally, we consider the molecule as a rod-like rigid body.

The statistic mean value of $\cos\theta$, where θ is the angle between the vector dipole moment and the vertical axis, is defined by relation

$$\langle\cos\theta\rangle = 2(2\pi)^{-3}\int \cos\theta \exp\left(-U/kT\right) \mathrm{d}\Omega_n \mathrm{d}\Omega' \mathrm{d}\Omega'' \tag{1}$$

where $\mathrm{d}\Omega_n$, $\mathrm{d}\Omega'$, $\mathrm{d}\Omega''$ are the solid angles, in which the dipole moments μ', μ'' lie with the base direction vectors $\vec{\nu}'$, $\vec{\nu}''$ and the vector $\vec{n}$ connects the polar heads of a chosen pair of molecules.

The mutual interaction between molecules consists of two-body dipole-dipole interaction similar to one in the non-ideal gas theory. Repulsive and dispersive potential energy components of the system are expressed by well-known Buckingham's modified potential.

$$U = C\exp\left(-\frac{r}{r_0}\right) - \frac{B}{r^6} + \frac{\mu'\mu''}{4\pi\varepsilon_0}\left[\vec{\nu}'\cdot\vec{\nu}'' - 3(\vec{\nu}'\cdot\vec{n})(\vec{n}\cdot\vec{\nu}'')\right] \tag{2}$$

where r is the center-to-center separation of the particles and C, B, r_0 are constants. For the empirical and semiempirical two-body potentials the manybody effect implicitly will be included by justification of parameters with experimental obtained data [7]. If we assume $|U| \ll kT$, the integral has an analytic solution and we can expand the exponent in a series where we take only the first two elements into consideration.

If we imagine the organic film as a system of electric dipole moments then induced charge on the upper electrode is

$$Q_i = \langle\mu_z\rangle NG = \mu\langle\cos\theta\rangle NG \tag{3}$$

where G is the geometrical factor (constant in our case) for the experimental setup and N is the number of molecules under the electrode.

The current flowing between the electrodes can be obtained as a time change of the induced charge

$$I = \frac{\partial Q_i}{\partial t} = G\mu N\frac{\partial\langle\cos\theta\rangle}{\partial t} + G\mu\frac{\partial N}{\partial t}\langle\cos\theta\rangle \tag{4}$$

The obtained results are shown in Fig.1.

The calculation predicts the position stability of the measured maximum in the dependence I versus area per molecule A various rates of compression β and a ratio

$$I_1/\beta_1 = I_2/\beta_2 = \cdots \tag{5}$$

is conserved. This theoretical prediction was fully confirmed by the experiment (Fig.2).

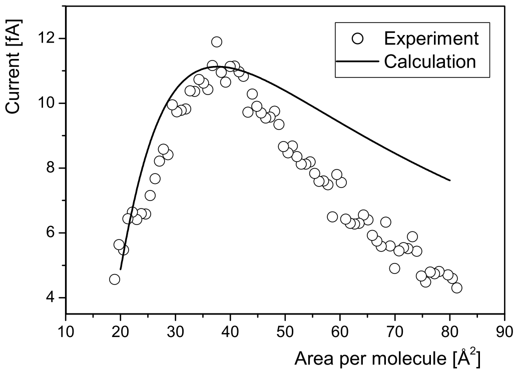

Figure 1: Comparison of typical experimental results with theoretical calculations for our model.

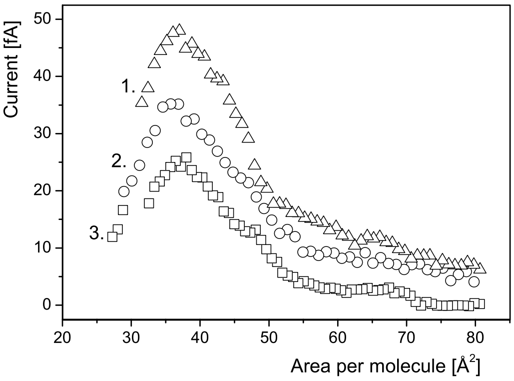

Figure 2: Comparison of three different rates of compression: (1) 100cm^2/min, (2) 75cm^2/min, (3) 50cm^2/min.

3 CONCLUSION

We rather successfully explained the experiment by analysing the model, based on the analogy with a non-ideal gas. This approximation can be justified for the ensemble with weak intermolecular forces even though the concentration is higher that in a real gas.

The generated concentration gradient is not included here, therefore is not possible to calculate relaxation effects after stopping the compression. The difference between the model and the experiment can be caused by an omission of the monolayer-subphase interaction and the contribution of the subphase to the dipole moment. The formula used for potential (2) is not correct when the tilt angle of any dipole deviates from zero.

In future, we intend to utilise a method based on the cluster interaction potential. In the end I like to thank to J. Cirák, P. Tomčík and D. Barančok to giving me the experimental data for analysis. They were already open to discussion and ready to explain background.

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