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Molecular Dynamics of a Stearic Acid Monolayer

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Abstract—Dynamic properties of a stearic acid monolayer were studied. The cases of gas phase, condensed phase, and supercondensed phase were considered. A number of autocorrelation and cross-correlation functions of the dynamic degrees of freedom of the system were analyzed.

Key words: stearic acid, monolayer, molecular dynamics, condensed medium

INTRODUCTION

Although there is a considerable body of literature considering the computer dynamic experiment, only an insignificant fraction of these works have been devoted to studies of monolayers. Usually, these studies consider the monolayer structure and its changes under variable conditions. Although the approximations of continuous medium, collisional medium, etc. are commonly used in molecular calculations, they do not allow one to trace the effects of interaction between the concrete molecular structures. It should be noted that this interaction is of particular importance in strongly anisotropic molecular systems. These systems are at present widely used in microelectronics, medicine, and chemical technology. In addition to direct practical implications, fatty acid monolayers and similar structures can be regarded as models of biological membranes. Therefore, studies of these structures can provide a new insight into the mechanisms of biological processes. Recent progress in experimental studies of the atomic and submolecular structure of molecular films (e.g., using atomic-force microscopy) is also a challenge for studying molecular dynamics in such systems.

In contrast to the results described in [1–5], we carried out a comparative theoretical study of the molecular dynamics of a monolayer using a computer experiment. The computations were based on solving a set of simultaneous classical equations of atomic motion including all the actual types of interatomic interaction: potentials responsible for formation of valence bonds and angles, potential energy of rotation about valence bonds, and that of van der Waals interatomic interactions [6–8]. The equations of atomic motion were integrated numerically with a step of 0.001 ps. A collisional thermostat was used. The trajectory length varied from 30 to 100 ps. The temperature was taken to be300 K. Original program packages were used for calculating the motion trajectories at constant fixed pressure and periodic boundary conditions (PUMA) [9, 10] and for processing the motion trajectories (CORREL) [10–13]. Visual information

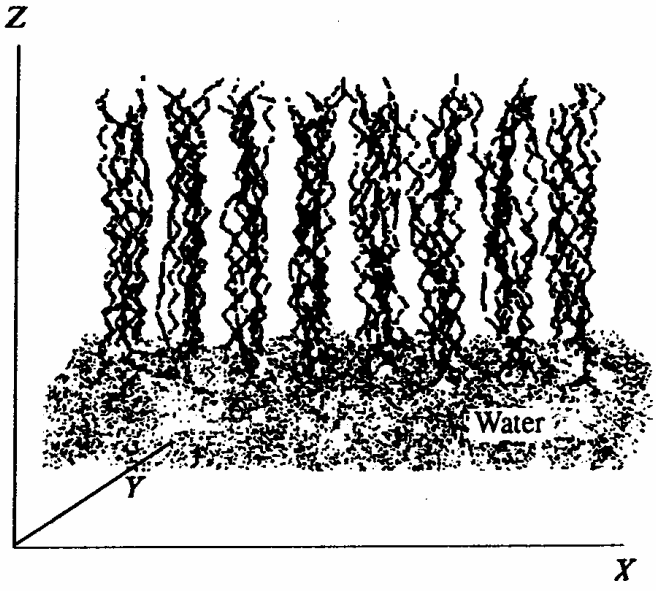

Fig. 1. Model of 64 molecules of stearic acid adsorbed on water surface. Quadratic packing with mean surface area per molecule of 20 Å^2.

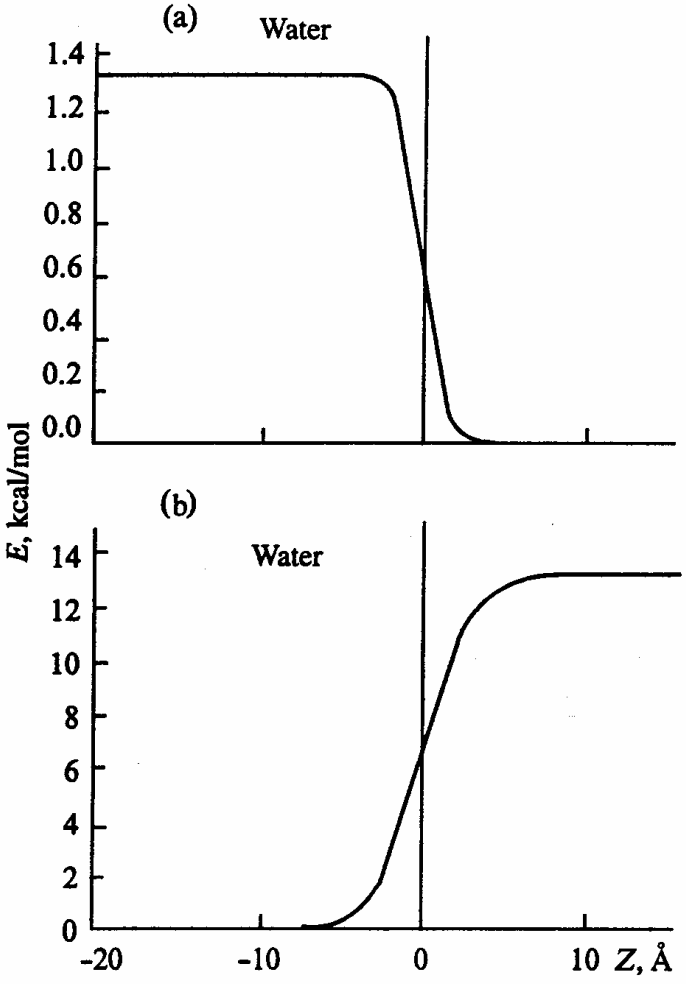

Fig. 2. Changes in the energy of CH_2 and CH_3 groups (a) and energy of COOH groups (b) induced by transfer in aqueous medium.

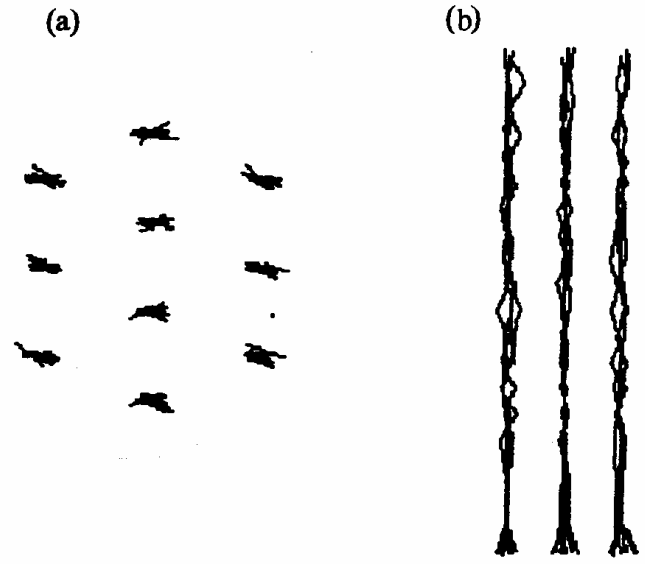

Fig. 3. Supercondensed state (surface area per molecule, 10 Å^2). At the initial moment of time, the fragment was packed at the vertices of a square: (a) top view; (b) lateral view.

on the monolayer dynamics was displayed in the molecular movie mode. Particular emphasis was placed on the spatial–temporal characteristics of the monolayer and the correlation between the molecular motion parameters in a relatively dense anisotropic medium.

The monolayer was constructed of 64 molecules of stearic acid ($C_{17}H_{35}COOH$). The carboxyl group was oriented toward the aqueous phase, whereas the aqueous phase dynamics was not considered in the model (Fig. 1). Either quadratic or hexagonal packing was taken as the initial configuration of the monolayer in numerical experiments. Lateral mobility of molecules in the monolayer was not forbidden. Interaction of methylene and carboxyl groups with water was simulated by the potential functions shown in Figs. 2a and 2b. These potential functions describe the actual spatial and energy effects that allow significant (up to about 5 Å) permeation of stearic acid molecules into the aqueous phase [1–5]. The monolayer dynamics was studied at the following values of two-dimensional density determined by the mean area occupied by one molecule: 10, 20, and 30 Å^2. In actual computer experiments, the monolayer phase states corresponding to 30, 20, and 10 Å^2 were gas, solid state, and supercondensed state, respectively. The supercondensed state is not observed in natural monolayers (model case of very high density). We also studied the effect of the packing type (quadratic or hexagonal) on the spatial–temporal characteristics of the monolayer. In the case of supercondensed state, the use of the potentials shown in Fig. 2 resulted in very strong intermolecular repulsion and rapid collapse of the monolayer. The monolayer could be stabilized under these conditions by modification of the potential function of interaction with water and a 100-fold increase of the energy barrier height (below in this work this function is called "rigid potential").

The fragments of a monolayer obtained at a packing density of 10 Å^2 per molecule (rigid potential of interaction with water) are shown in Fig. 3 (top view and lateral view). Initially, the stearic acid molecules were at the vertices of a square. It is seen that each molecule is stretched, stressed, and has low mobility. A polymorphic (phase) transition to a hexagonal lattice occurs within 10 ps. The hexagonal lattice proves to be more stable under these conditions, and it does not collapse spontaneously if it is used as the initial configuration.

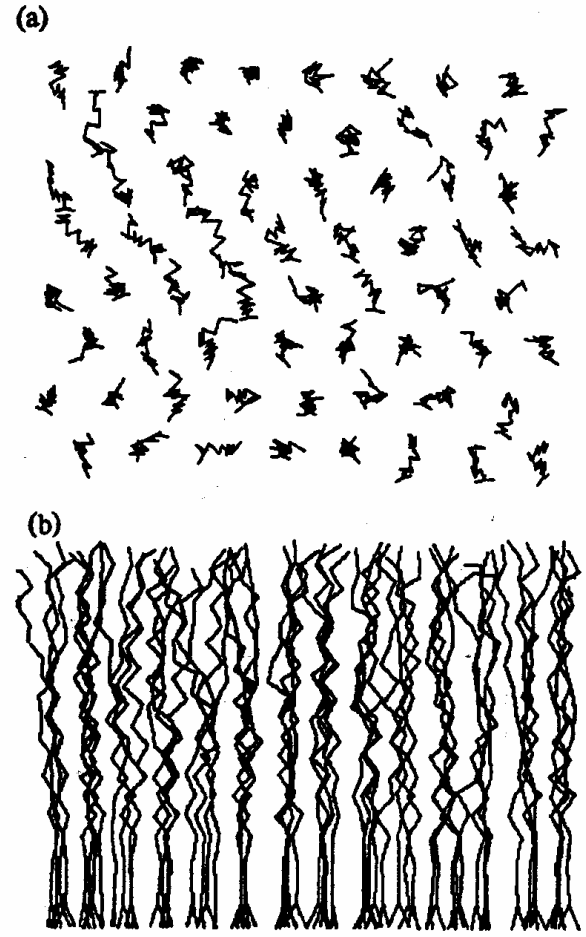

Fig. 4. Hexagonal packing at the initial point. Condensed state (mean surface area per molecule, 20 Å^2): (a) top view; (b) lateral view.

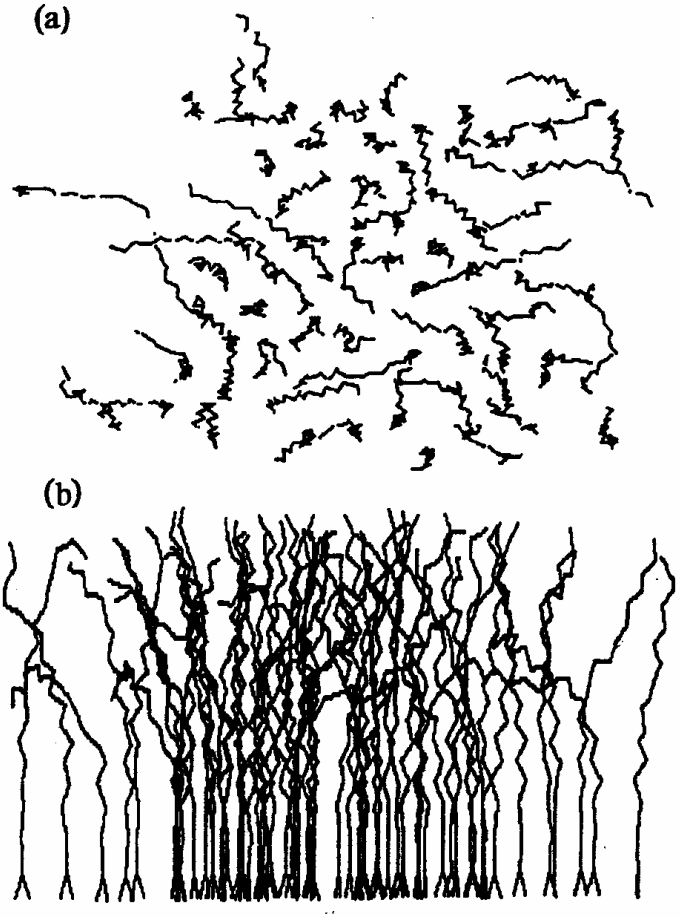

Fig. 5. Low-density state (mean surface area per molecule, 30 Å^2): (a) top view; (b) lateral view.

The case of hexagonal packing at the mean area of 20 Å^2 per molecule is shown in Fig. 4 (top and lateral views; square lattice packing is shown in Fig. 1). This case corresponds to the solid body phase close to collapse. It is seen that the molecular mobility in this case is higher than in the case of supercondensed packing, because the free space volume is enough for the microconformational mobility associated with rotation around molecular bonds. This causes partial disorder of monolayer, particularly near the end groups. The mean intermolecular distance in the hexagonal lattice is slightly larger than in the quadratic lattice, and this decreases the internal stress of the structure and increases the molecular mobility.

The "gaseous" phase state of the monolayer is illustrated by Fig. 5. The packing density in this case is 30 Å^2 per molecule. Molecular mobility is very high and even includes reorientation of sufficiently long terminal segments of fatty acid chains. It is also seen that a random cluster with enhanced packing density is formed at the center of the cell.

The distributions of the probability of atom location along Z axis were calculated from model trajectories (Fig. 1). The solid body phase (20 Å^2 per molecule) distributions over the Z axis are shown in Fig. 6. The distribution shown in Fig. 6a corresponds to the potential function for interaction with water molecules having physically sensible parameters. It is seen that marked restriction of the carboxyl group mobility along the direction perpendicular to the monolayer plane imposes substantial constraints on the mobility of the chain as a whole.

Consider the dynamic organization of the monolayer by calculating various correlation functions of interaction between different degrees of freedom within one molecule; correlation between the same degrees of freedom in neighboring molecules, in those separated by molecule, by two, by three, etc.; and correlation between molecular lengths and distances between the tails of stearic acid molecules. The cross-correlation functions calculated as described in [11–13] for the torsion angles located at the end, middle, and

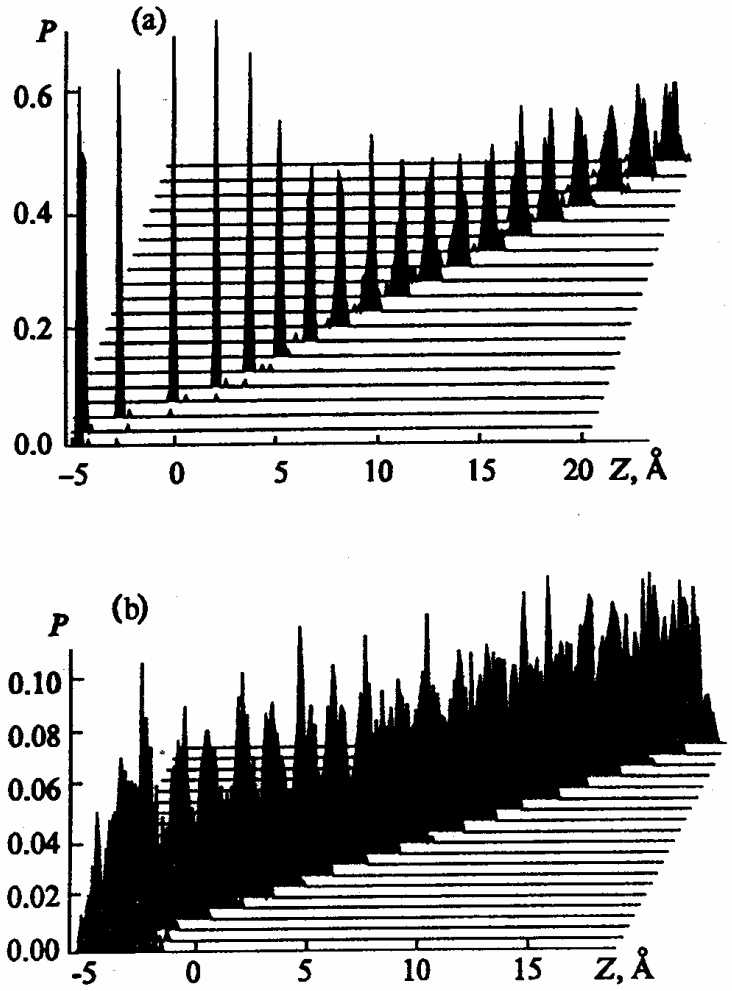

Fig. 6. Probability density along the Z coordinates of heavy atoms (carbon, oxygen). The Z axis is perpendicular to the membrane plane. Each line corresponds to one heavy atom. Atomic numbers are from the carboxyl group to the tail of the stearic acid molecule. The mean surface area per molecule is 20 Å^2: (a) rigid interaction with water; (b) potential function for interaction with water molecules having physically sensible parameters (Fig. 2).

head parts of the stearic acid molecule are shown in Figs. 7–9.

The results of calculation of a hexagonal lattice at a packing density of 20 Å^2 per molecule (potential function for interaction with water molecules having physically sensible parameters) are shown in Fig. 7. A dynamic pattern of the correlation function of the tail torsion angle of the molecule is shown in Fig. 7a. Short-term minor correlations are seen. Damped oscillations demonstrate the effect of "effacing" the torsion angle value in the neighboring molecule.

Short-term minor correlations were also observed in the torsion angle values in the middle part of the stearic acid chain. At the head of the molecule, there was a statistically significant correlation caused by a closely located support. However, the initial correlation is rapidly effaced during molecular motion.

The cross-correlation functions of the torsion angles in the tails of neighboring molecules, those spaced by one molecule, and and those spaced by two are shown in Fig. 8. This case corresponds to a hexagonal lattice with the packing density of 20 Å^2 per molecule and potential function for interaction with water molecules shown in Fig. 2. The dynamic correlation of the torsion angles in this case is associated with the molecular adjustment during motion. This dynamic correlation represents concerted behavior of moving molecules. The characteristic time of correlation is about 0.1 ps. The autocorrelation functions of molecular lengths and distances between molecular tails are shown in Fig. 9. The autocorrelation function of deviation of the molecular length from its mean value is shown in Fig. 9a. In this case, dynamic correlation decays within the time interval of about 0.5 ps. At longer time intervals, the head and tail of the molecule move independently. The amplitude of the molecular length fluctuations is about 0.25 Å^2. The autocorrelation functions of deviation of the tail-to-tail distances of neighboring molecules from the corresponding mean value is shown in Fig. 9b. It is seen that there is a dynamic correlation within the time interval of no less than 1.5 ps. This correlation is due to molecular adjustment during motion in a dense medium. The amplitude of fluctuations in the distances between the end atoms of the molecules is about 0.16 Å^2.

Thus, in this work we considered a molecular dynamic model of a monolayer composed of 64 molecules of stearic acid adsorbed on water surface. The role of structure and free volume of the system in its dynamic behavior was clearly demonstrated. The dynamic behavior of the system manifested itself as the extent of the phase state stress and existence of dynamic correlation. There are also correlations between neighboring torsion angles with characteristic times of about 0.1 ps. The extent of correlation depends on the two-dimensional density of the system. It should also be noted that hexagonal packing of stearic acid monolayer is more favorable than quadratic packing. Even if the initial conditions correspond to quadratic lattice, the system within 10–30 ps undergoes a polymorphic transition to the hexagonal packing. This conclusion is supported by experimental data. The mean length of stearic acid molecule in monolayer

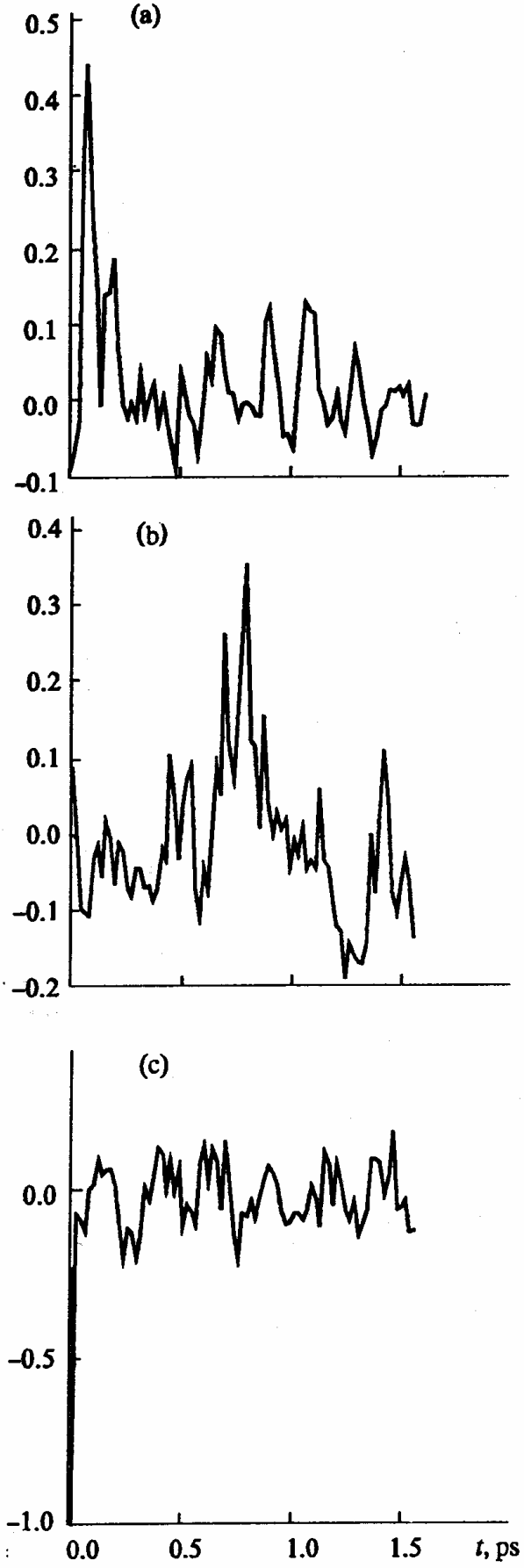

Fig. 7. Dynamic cross-correlation functions for torsion angles in stearic acid molecule. Hexagonal packing (mean surface area per molecule, 20 Å^2): (a) cross-correlation functions for torsion angles of rotation about C–C bonds 2 and 3 as numbered from the tail of the molecule; (b) same for bonds 9 and 10; (c) same for bonds 16 and 17.

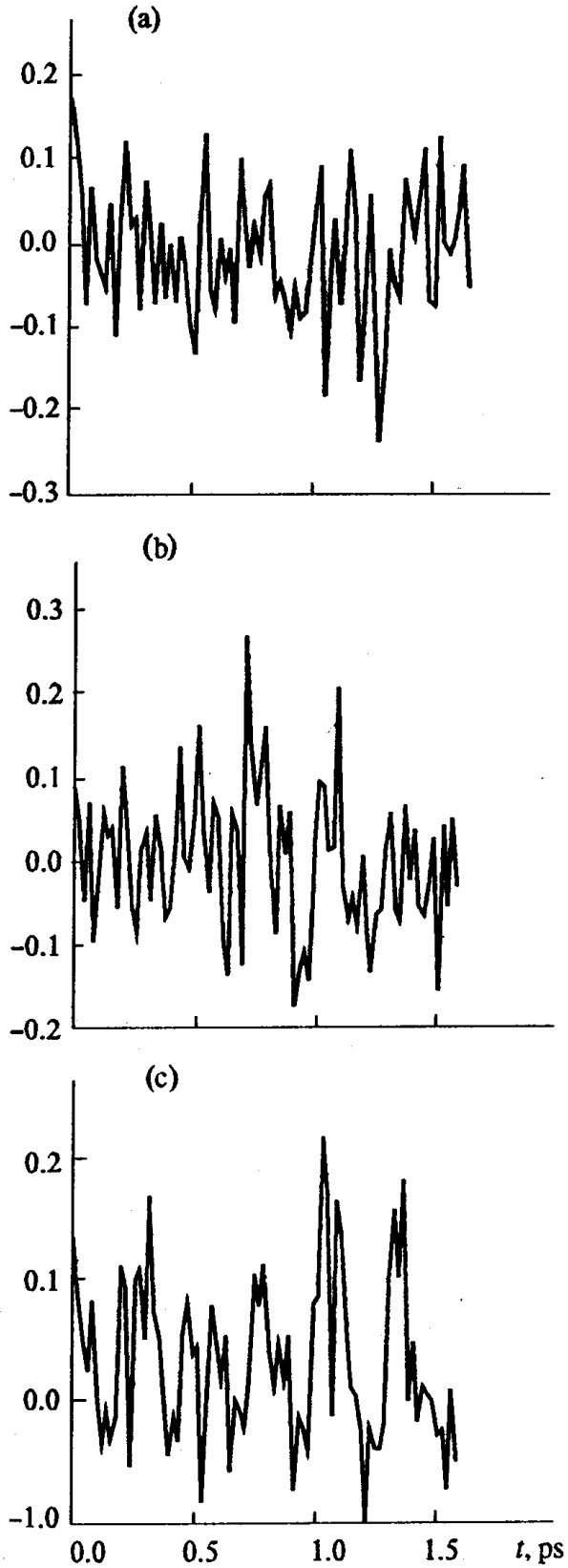

Fig. 8. Dynamic cross-correlation functions for rotation about the torsion angles of the end atoms of stearic acid chain: (a) neighboring molecules; (b) molecules separated by one molecule; (c) molecules separated by two molecules of stearic acid. Hexagonal packing (mean surface area per molecule, 20 Å^2).

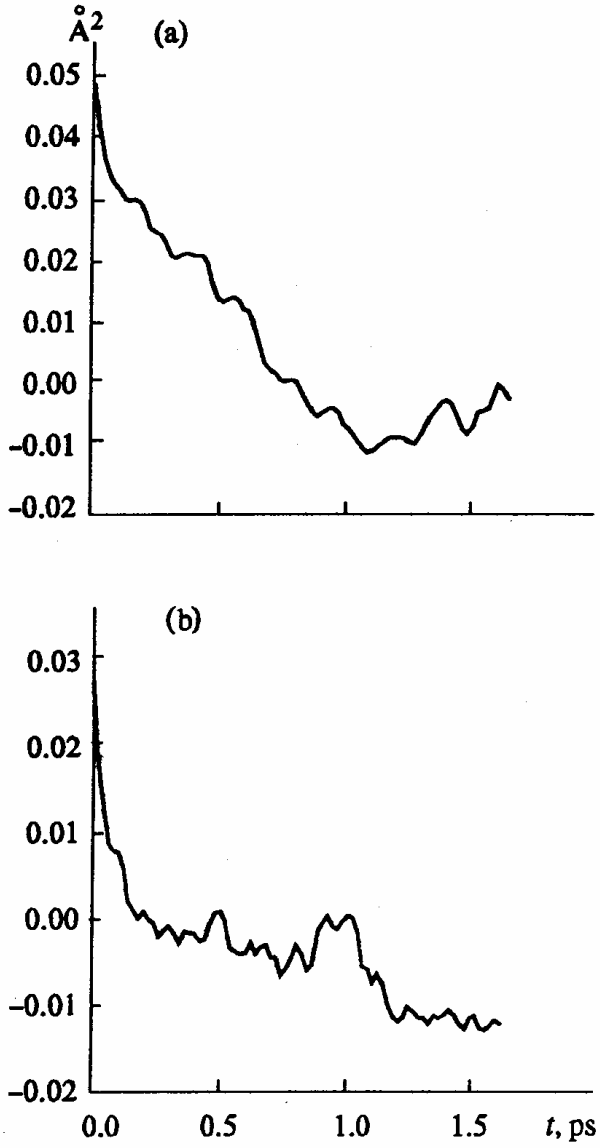

Fig. 9. Autocorrelation function (Å^2) of molecular length (a) and distance between the end atoms of neighboring molecules (b) of stearic acid. Hexagonal packing (mean surface area per molecule, 20 Å^2).

and monolayer thickness significantly depend on the density of the system. At the packing density of 20 Å^2 per molecule, the mean length of the molecule is 22 Å^2, which is consistent with the experimentally observed value.

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