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Simulations of molecular dynamics of cyanoadamantane multilayers between graphite substrates

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Constant temperature molecular dynamic (MD) simulations have been carried out to investigate structural and dynamical properties of the multilayer of cyanoadamantanes ($C_{10}H_{15}CN$) located between the graphite substrates. The velocity autocorrelation function and the second range order parameter, for several numbers of layers and temperatures ranging from 100 to 900 K have been calculated. As the number of cyanoadamantane layers increases, the chain structure of cyanoadamantanes is gradually shown up – the consequence of increasing importance of Coulomb interaction of dipolar cyanoadamantane molecules confined between graphite planes.

Key words: *cyanoadamantane; graphite walls; molecular dynamics; order parameter; simulations; velocity autocorrelation function*

1. Introduction

MD computer simulation techniques have been widely used to study the behaviour of a small quasi two-dimensional molecular system. Knowledge of the structure and dynamics of molecules near the surface is important in the context of assembly, catalysis, lubrication, molecular electronics, thin films and microfluids. Recently, much attention has been focused on the problem of adsorption of gases on planar surfaces such as graphitic material [1–4]. There are several encouraging aspects of this work. Firstly, graphitic materials provide particularly strong attraction compared to other adsorbents [5]. Secondly, corrugated surfaces provide a relatively attractive binding environment which possess the ability to model complex phases, such as plastic molecular solids, in a two-dimensional (2D) system [6]. It would be of interest to study such processes with large molecule as an adsorbate, possibly having a strong dipole moment which can reveal more clearly the process of forming such exciting phases. The molecule which possesses this feature and is currently the subject of much re-

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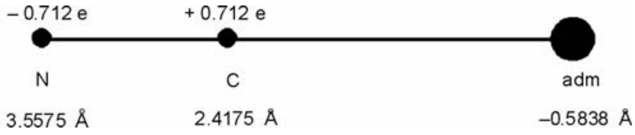
search is cyanoadamantane $C_{10}H_{15}CN$ (CNadm). The cyano group (CN) is responsible for the high dipole moment ($\mu = -3.92$ D), which causes that whole CNadm group to create interesting phases, including the plastic phase [7]. With the onset of cooling, a CNadm sample begins to evolve from the fluid phase, which is mainly characterized by translational motion, through the plastic, glassy and solid states. The plastic phase, which is also called the rotatory phase (translations frozen, rotations released), appears between the melting point at $T_m \approx 445$ K and $T_t \approx 238$ K [8,9]. This phase is characterized by the dynamic orientational disorder of molecules and translational order of molecular centres of mass (*Fm*3*m* crystalline structure).

In this work, the diffusive motions in multilayer (1–3 near each plane) cyanoadamantane, using molecular dynamics simulations, were studied and how these motions are reflected in the plots of the appropriate correlation functions was explored.

2. Simulation procedure

Modelling of real CNadm molecules is very complex, and simulation, which takes into account detailed molecular structure, is very time consuming. Therefore, the real cyanoadamantane molecule has been simplified by using a three-site model of cyanoadamantane as proposed and previously used by Cathiaux et al. [2] in their study of pure cyanoadamantane. In the diagram below we present the model of the CNadm molecule.



The cyanoadamantane molecule is represented by a rigid, three-site model, instead of the full model with 27 atoms. From the left, the first and second sites correspond to the nitrogen and carbon atoms, respectively, and the third corresponds to the whole adamantane group (supersite or pseudoatom). The interactions between the site atoms and the supersite (adm) have been modelled by Cathiaux et al. [2] in terms of the Lennard-Jones (LJ) potential shown in Equation 1.

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^m - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^n\right] \qquad (1)$$

where r_{ij} is the distance between the i-th and j-th interacting sites of different molecules, ε_{ij} and σ_{ij} are the corresponding L–J parameters. The usual values for m and n are 12 and 6, respectively, except for the interaction between the supersites which are represented by special values of exponents m and n, 16 and 10, respectively, as determined by Cathiaux et al. [2]. The values of the interaction energy parameter $\varepsilon_{\text{adm–adm}}$ and their minimum distance $\sigma_{\text{adm–adm}}$, taken from [2], are given in Table 1.

Table 1. Simulation parameters

ij	ε_{ij} [kJ/mol]	σ_{ij} [Å]
N-N	0.7099	3.25
C-C	0.3089	3.55
N-C	0.4683	3.40
N-adm	2.4290	4.70
C-adm	1.6020	4.90
adm-adm	8.3110	6.30

The interaction between the cyanoadamantane molecule and basal planes of graphite was calculated using a semi-empirical potential approach, where graphite was treated as a static surface providing the external holding potential for the molecules [1].

The CNadm possess a nonzero dipole moment along the cyano group axis with the value $\mu = -3.92$D. Two charges with the value 0.712*e*, negative on the nitrogen atom and positive on the carbon atom, were added. In addition, the momentum of inertia of the cyanoadamantane molecule was taken as $I_{xx} = I_{yy} = 580$ au Å^2.

The above models were used to carry out a series of constant temperature ensemble simulations with slab periodic boundary condition along the graphite wall. This means that the system was periodic in the *x* and *y* directions, but not in the *z* direction. That type of boundary condition is particularly useful for simulating surfaces.

The effects of the long-range electrostatic contribution to the intermolecular potential was taken into account using the Hautman–Klein–Ewald method [11], instead of the standard Ewald summation, because of the 2D boundary condition. A series of MD simulations with 64, 128, and 192 molecules of CNadm at several temperatures ranging from 100 to 900 K were carried out. The number of particles were 2496 (2304 graphite C + 64 three site CNadm) for the smallest system up to 2880 (2304 graphite C + 192 three site CNadm) for the largest. The 2304 carbon atoms possess two basal graphite surfaces situated parallel to the *XY* plane of the simulation box. The surface edges lengths were $x = 39.392$ Å and $y = 38.358$ Å, respectively. The CNadm molecules were placed between them, with separation distances of *z* from 30 Å to 70Å. Each plane was treated as a static surface and models the crystal structure of graphite (Fig. 1).

Two distinct planes of carbon hexagons are stacked with *P*63*/mmc* symmetry. This structure was described in an earlier work [12]. In Figure 2a one can see a single graphite plane. It is interesting to note that the nearest neighbour spacing in the carbon nanotube is essentially the same as the inter-planar spacing of the graphite (~3.4 Å).

The time step in the simulation was 1 fs, which guarantees fluctuation of the potential energy below ~0.2%. The equilibration runs were about 5×10^5 time steps. The time for evaluating correlation functions was 50 ps after the period of 20 ps required for stabilization of the chosen temperature.

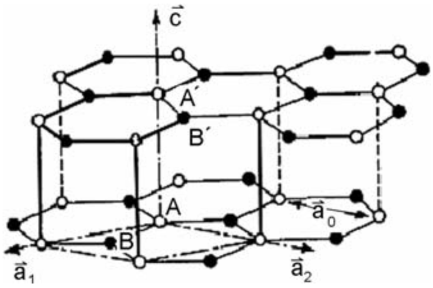


Fig. 1. Structure of graphite planes

3. Results

The cross section of three simulated systems are shown in Fig. 2.

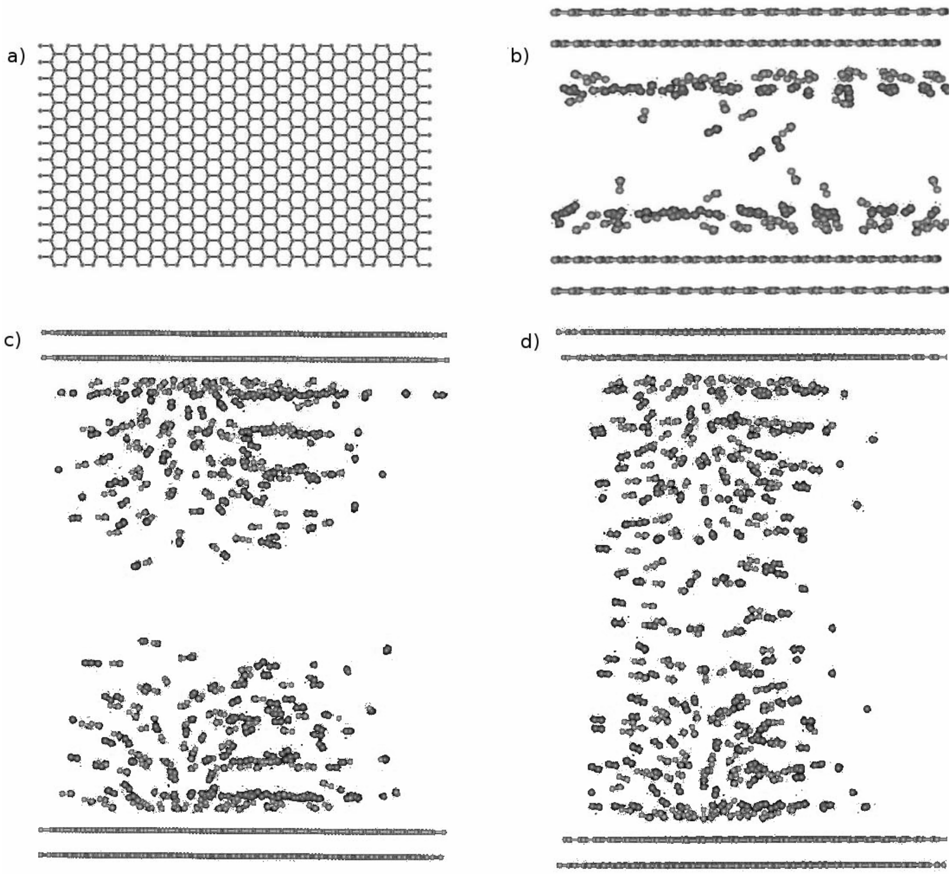


Fig. 2. Sample snapshot of the studied system: a) the structure of a single graphitic layer, b–d) the cross sections of investigated systems with 64, 128 and 192 CNAdm molecules, respectively; black balls – the centre of mass of adamantane group, gray – nitrogen, light gray (same as wall colour) – carbon

One can see in the system with 64 (b), 128 (c) and 192 (d) of CNadm molecules (from one to three layers of CNadm between graphite planes). In the case of two and more layers the formation of chains composed of CNadm molecules is clearly observed (see. Fig. 2c, d). In this situation, the second range order parameter P_2 [10] which indicates the degree of orientational order of a system could be most informative.

In Figure 3, the second-rank-order parameter P_2 calculated for (a) single- and (b) two-layer CNadm systems is presented.

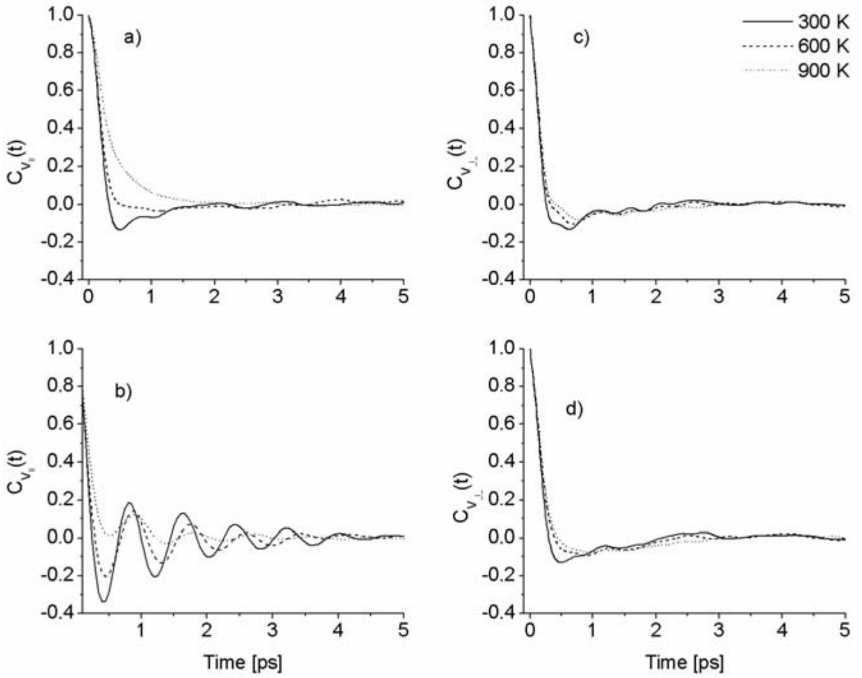


Fig. 3. The velocity autocorrelation functions $C_V(t)$ parallel (a, c) and perpendicular (b, d) to graphite planes calculated in single (b, d) and multilayer (a, b) systems

This parameter P_2 is the largest eigenvalue of the ordering matrix with the elements given by [13]

$$Q_{ij} = \frac{\left\langle 3\cos\theta_i \cos\theta_j - \delta_{ij} \right\rangle}{2} \tag{2}$$

where $i,j = x, y, z$ are indices referring to the laboratory frame. The brackets <> represent a thermal averaging (over the whole sample and simulation time), θ is the angle between the molecular long axis and the eigenvector of the order tensor Q corresponding to the maximum eigenvalue.

The P_2 parameter was calculated for two cases, namely, parallel and perpendicular to the graphite surfaces. Figure 3 shows that the parallel order parameters are not influenced by increasing temperature, for both one and two layers. However, the distinction between the P_2 value calculated in the parallel and perpendicular direction is clearly seen. In the case of one layer $P_{2(\|)}$ has a large value of ~0.7, whereas, in the two-layer system these values are reduced to ~0.25. This was interpreted that in the one-layer system, CNadm molecules are strongly constrained by the appearance of the graphite plane. Moreover, when the second layer was added, molecules which belong to this layer are not strongly influenced by the graphite planes and this causes a reduction of the order parameter in the plane direction. It is interesting that this reduction of the P_2 parameter is not observed in the perpendicular direction. In both cases the values are similar and equal to ~0.5 for all temperatures studied. The explanation is obvious when one remembers the snapshot (see Figs. 2c, d) with the chains composed of CNadm molecules. As a result of the corrugated graphite surface, the interaction potential possesses holes and the cyanoadamantane molecules aggregate around them. After that, in the neighbourhood of CNadm trapped by a hole (in the case of two and more layers), the chain structure of cyanoadamantanes develops because of the strong dipole–dipole interaction of CNadm molecules

Information about the microscopic dynamic is usually provided in MD simulations by means of the velocity autocorrelation function (VAF) $C(t)$ which is calculated from the following expression:

$$C_v(t) = \frac{\langle v(t)\, v(0)\rangle}{\langle v^2(0)\rangle} \tag{3}$$

where v(t) is the velocity of the centre of mass of the molecule. Depending on the component of the velocity chosen correlations for the parallel, or perpendicular direction ($\|$ or $\perp$) could be obtained. As an example, in Fig. 4 the adamantane VAFs calculated for *xy* and z components of velocity ($\|$ and $\perp$) at three temperatures T = 300, 600, 900 K are shown.

In Figure 4a, b, the previously mentioned function obtained from simulations with one CNadm layer is given. The distinction between two parallel and perpendicular motions is clear. Planar motions (see Fig. 4a) are similar to fluid at low temperature T = 300 K and gaseous at T = 900 K. Perpendicular movements, however, are strongly constrained by the graphite planes. As a result of the caging effect, the correlation function falls to a negative value and exhibits dumped oscillations descending to zero value after a long time. Moreover this process is reduced by higher temperatures. When comparing these pictures, with those obtained from two CNadm layers adsorbed on graphite planes, the difference is clearly seen in VAFs for perpendicular velocity component. These functions (see Fig. 4 c, d) are similar to AVFs obtained from fluid like systems as the CNadm molecules can diffuse, not only in the *xy* plane, but also between the layers in the *z* direction.

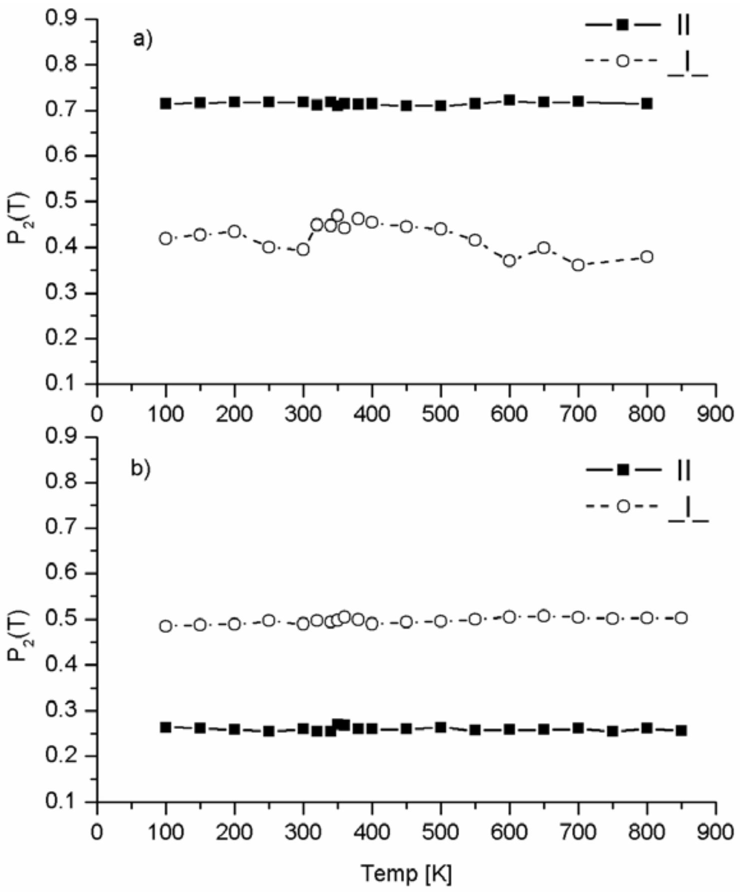


Fig. 4. The temperature dependence of the second-order parameters P_2 for single (a) and multilayer (b) cyanoadamantane systems

4. Conclusion

These computer experiments may contribute to the future “real life” experimental studies of confined nanoscale layers.

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