The Behavior of Benzene Confined in Single Wall Carbon Nanotube

Yu. D. Fomin(1,2), E.N. Tsiok(1) and V.N. Ryzhov(1,2) *

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Abstract

We present the molecular dynamics study of benzene molecules confined into the single wall carbon nanotube. The local structure and orientational ordering of benzene molecules are investigated. It is found that the molecules mostly group in the middle distance from the axe of the tube to the wall. The molecules located in the vicinity of the wall demonstrate some deviation from planar shape. There is a tilted orientational ordering of the molecules which depends on the location of the molecule. It is shown that the diffusion coefficient of the benzene molecules is very small at the conditions we report here.

Keywords: Benzene, carbon nanotubes, orientational order, structure.   ■

*(1)Institute for High Pressure Physics Russian Academy of Sciences, (2) Moscow Institute of Physics and Technology (State University)

SUMMARY

It is well known that confining a liquid into a pore strongly alters the liquid behavior. Investigations of the effect of confinement are of great importance for many scientific and technological applications. Here we present a study of the behavior of benzene molecules confined in the single wall carbon nanotubes. We find that the molecules of benzene mostly group in the middle distance from the axe of the tube to the wall. The molecules located in the vicinity of the wall demonstrate some deviation from planar shape. There is no any strong ordering in the system, however, there is a tilted orientation of molecules which depends on the location of the molecule.

INTRODUCTION

It is well known that materials confined in nanoscale dimensions have properties that strongly differ from the properties of bulk systems. This is due to the reducing the dimensionality of the system and interface effects. Confining boundaries bias the spatial distribution of the constituent molecules and the ways by which those molecules can dynamically rearrange. These effects play important roles in the thermodynamics of the confined systems and influence the topology of the phase diagram[1,2]. The confinement can drastically change the thermodynamic parameters of phase transitions and even form the new phases due to interaction with the boundaries. For example, the melting temperature of confined benzene depends on the form and size of the nanopores. In most cases the melting point of the solid in the pore decreases with decreasing pore diameter[1]. In Ref.[3] the melting behavior of the confined benzene was discussed for different types of porous confinement. It was shown that no crystallization is observed in the cylindrical pores below the pore size about $4.7nm$. This value corresponds approximately to 10 molecular diameters. It was shown that benzene does crystallize in $4.7nm$ pores but vitrifies in narrower pores[4]. On the other hand, as it was shown in Refs.[5–8], experimental freezing of tetrachloromethane was observed in activated carbon fibers for the pore widths up to $0.75nm$ (less than two molecular diameters), whereas cylindrical pores of several molecular sizes are necessary to have crystallization of

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tetrachloromethane molecules.

The general motivation for the study of different nanoconfined systems follows from the fact that there are a lot of real physical and biological phenomena and processes that depend on the properties of such systems and play an important role in the different fields of modern technology. However, nanoconfinement is considerably interesting also due to the new physics observed in these systems. For example, fluids confined in carbon nanotube exhibit formation of layers, crystallization of the contact layer[9] and a superflow which depends on the confinement[10–14].

In this paper, we present a systematic molecular dynamics study of single wall carbon nanotubes (SWCN)[15,16] doped with benzene (C_6H_6) molecules. Carbon nanotubes are widely investigated first of all because of their potential applications in material science, biotechnology and medicine[17–20]. Introducing molecules into carbon nanotubes can drastically change the electronic properties of nanotubes. Benzene molecules are widely used for study the influence of doping on the properties of carbon nanotubes because of their small size which permits them to be encapsulated easily inside carbon nanotubes of different diameters. The orientation and the position of the benzene molecules inside the carbon nanotubes determine the optical, magnetic and electrical transport properties of the whole system[21–23].

In Ref.[24] a semi-analytical model for the interaction of a benzene molecule and a carbon nanotube was proposed. It was shown that the orientation of the molecule drastically depends on the radius of the nanotube. The authors found that horizontal, tilted and perpendicular equilibrium configurations are possible for the benzene molecule on the axis of the carbon nanotube when the radius of it is less than $5.580\mathring{A}$. However, when the radius of the nanotube is larger than $5.580\mathring{A}$, the equilibrium configurations occur at an offset horizontal orientation.

The results of Ref.[24] were obtained for one molecule. The main goal of this article is to study the positional, orientational and dynamic behavior of the ensemble of benzene molecules in the single wall carbon nanotube.

METHODOLOGY

In the present article we study benzene molecules in carbon single wall nanotube by means of the molecular dynamics simulation. The benzene molecule consists of a ring of 6 carbon atoms. Each carbon is also bonded with a hydrogen atom out of the ring. The radius of benzene ring is about $2.8\mathring{A}$. If one takes into account the length of the hydrogen bonds then the size of benzene molecule is approximately $5\mathring{A}$. The radius of the nanotube is $6.89\mathring{A}$ and the length is equal to $250.2363\mathring{A}$. It means that the radius of the nanotube is just a bit larger then the size of the molecule. We choose this radius because it corresponds to the situation when, as proposed in Ref.[24], one can expect to find the offset horizontal orientation of the benzene molecules. The tube is oriented parallel to the z axe. The system has periodic boundary conditions in z direction while it is confined in x and y ones. Three systems were studied: $150, 200$ and 250 benzene molecules in the nanotube described above. The later system corresponds to the density $0.877 g/cm^3$ which is the density of bulk benzene at ambient conditions. All systems were simulated at three temperatures: $300K$, $400K$ and $500K$. Doing this way we could check the influence of both density and temperature on the behavior of benzene in nanotubes.

We simulate the system in canonical ensemble (constant number of particles N, volume V and temperature T). The temperature is kept constant by applying Nose-Hoover thermostat. The carbon atoms of the nanotube are held rigid in order to stabilize the system while the benzene molecules are moved in molecular dynamics runs. The timestep is $0.1 fs$. So small timestep was necessary in order to correctly take into account the motion of hydrogens in the benzene molecules.

All interactions in the system were described by AIREBO interatomic potential[26]. This potential is specially developed for simulation of the systems containing carbon and hydrogen atoms, and it allows to consider all interactions in the system in framework of the same model.

All simulations were made in lammps simulation package[27].

RESULTS AND DISCUSSIONS

The qualitative ideas on the structure of benzene inside nanotube can be obtained from the snapshots on the system. Fig. 1 (a) shows a part of the nanotube. In order to make the view of the molecules clearer we do not show the tube itself. One can see that the system does not demonstrate pronounced order. Another important conclusion from the snapshots is that if one looks at a cross section of the tube (Fig. 1 (b)) one can see that the centers of mass of the molecule do not approach both the central axe and the walls and prefer to be somewhere in the middle. In Ref.[24] a simple model of benzene in carbon nanotube was proposed. Basing on this model, the authors studied possible locations and orientations of benzene molecules inside the nanotube. It was found that for the tube radius $R < 5.580\mathring{A}$ the equilibrium position of the molecule belongs to the central axe while for higher radiuses the position moves apart. Our calculations are made at $R = 6.89\mathring{A}$ in order to compare our results with this publication.

The described features can be easily seen from the density profiles of different species. Fig. 2 shows the profiles of number density of carbon and hydrogen species and of the centers of mass of the molecules. The largest peak of the carbon density distribution corresponds to the distance $5.3\mathring{A}$ from the central axe of the tube. After that the curve rapidly vanish. So the closest approach of carbon atoms to the wall of the tube is approximately $1.5\mathring{A}$.

However, the main peak of the centers of mass of the molecules is closer to the center (Fig. 2). It corresponds to the distance $r_{cm1} = 3.73\mathring{A}$. The second peak of the centers of mass density is almost of the same height and located at $r_{cm2} = 5.04\mathring{A}$.

One can see that the closest peak to the wall is the one of hydrogen distribution. The maximum is located at $5.7\mathring{A}$, i.e. approximately $1\mathring{A}$ from the wall. So close approach of hydrogens to the nanotube can mean that some kind of effective hydrogen bonds appear in the system.

Importantly, all distributions vanish at $r = 0$ which means that at this density the particles try to avoid the central axe of the tube.

Fig. 3 (a) and (b) demonstrate the influence of the total density N/V on the local densities distribution of carbon and centers of mass of the molecules. As one expects from general
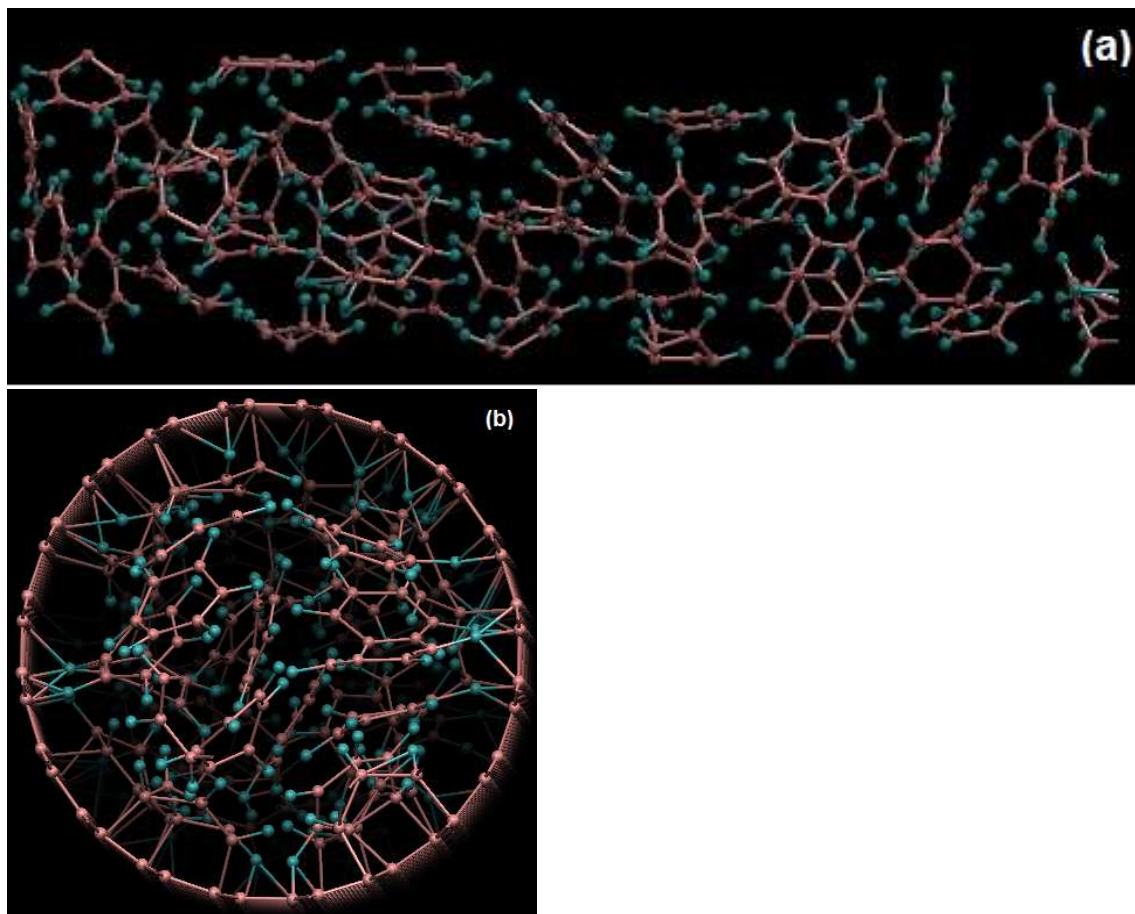
Figure 1: (a) Snapshot of benzene molecules in the SWCN. The nanotube itself is not shown. (b) Cross section of the system. $N = 250$, $T = 300K$.
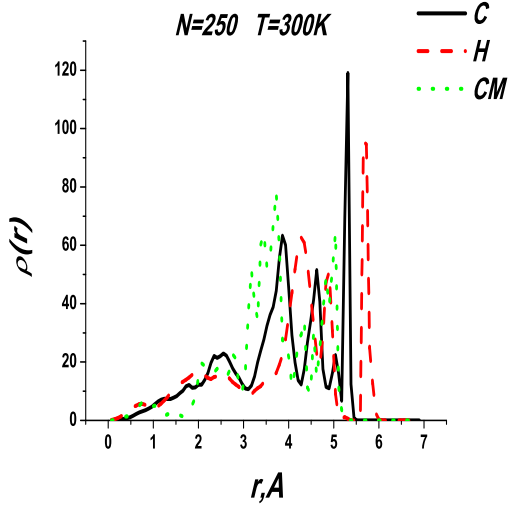
Figure 2: Radial distribution of number densities of carbon, hydrogen and centers of mass of the molecules for $N = 250$ and $T = 300K$.
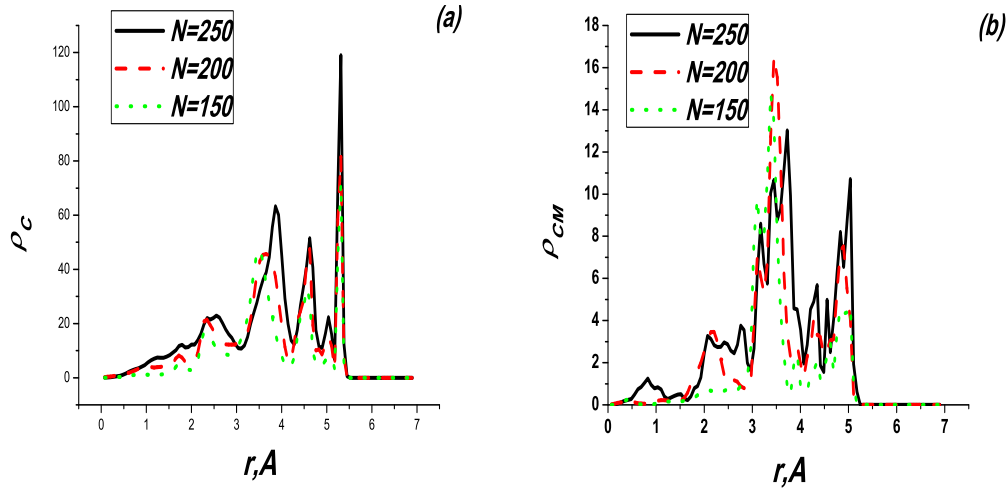

Figure 3: Radial distributions of number densities of (a) carbon and (b) centers of mass of the molecules for different densities of benzene at $T = 300K$.
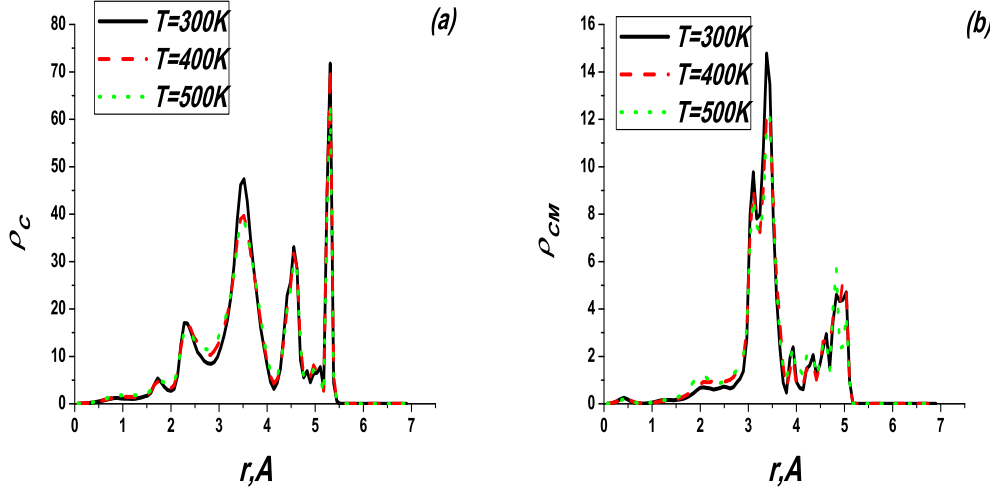
Figure 4: Radial distributions of number densities of (a) carbon and (b) centers of mass of the molecules for different temperatures. The number of benzene molecules inside the tube is $N = 150$.

point of view, as the density increases the peaks become more pronounced. In the case of the local density of carbon one can see that at the lower number of molecules ($N = 150$ and 200) the peaks are almost of the same height. However, as the number of particles increase the peaks next to the wall rapidly increase while the increase of the second peak is rather modest.

In the case of the distribution of the centers of mass the situation is more complex. At the smallest number of molecules ($N = 150$) the main peak is located at $3.38\mathring{A}$. As the number of molecules increases to $N = 200$ this peak rises up. However, further densification of the system leads to placing the molecules closer to the wall and the second peak ($\approx 5\mathring{A}$) starts to increase while the first one even decreases with respect to the previous values.

Figs. 4 (a) and (b) demonstrate the influence of temperature on the density profiles of carbon and centers of mass of the molecules. As one can expect, the peaks become higher as the temperature decreases.

In our previous work we studied benzene in graphite and amorphous carbon slit pores[25]. It was shown that in the case of graphite walls and relatively small pore sizes (the distance between the walls below approximately $14.5\mathring{A}$) benzene molecules form graphite-like

sheets. This phenomenon was related to the close match of the carbon-carbon bond length in graphite and in benzene ring. Basing on this observation one can ask a question whether benzene molecules located in the vicinity of the nanotube mimic the shape of the wall. If so, the molecules loose theirs planar shape and become scrolled.

In order to estimate the degree of deviation from planar shape of the benzene ring we employ the following procedure. Denote all carbon atoms in a ring by numbers from 1 to 6 and define the vectors connecting them: $1-2$, $2-3$, ..., $6-1$. Now we take three neighboring atoms, say, $1, 2, 3$. Since they do not belong to the same straight line there is a unique plane containing these points. The normal vector of this plane can be identified as a vector product of the vectors $1-2$ and $1-3$. If we repeat this procedure for all six carbons of the ring we obtain 6 vectors perpendicular to the ring. If the molecule is ideally planar then all these vectors should be parallel. One can check if these vectors are parallel by taking theirs scalar product. One can construct 15 different pairs. We compute all 15 scalar products and sum up the absolute values of the resulting products. In the case of ideal plane the result should be equal to 15, so we divide the final result over 15. We denote the final quantity as P. It measures the "planarity" of the ring. By definition the planarity can be less or equal to unity. The deviation of P from unity can characterize the deviation of benzene molecule from planar shape.

In order to check the validity of the P parameter we calculate its value for pure bulk benzene at ambient conditions. We find it to be $P = 0.97$ which corresponds to the case of almost planar rings. In our previous publication we described the structure of benzene in graphite slit pore[25]. For the case of the pore size $12.462 \mathring{A}$ we find $P = 0.95$ which is very close to the pure benzene result. Fig. 5 shows the P parameter for the case of $N = 200$ at three different temperatures. One can see that up to the distance $r = 4\mathring{A}$ the value of P is 0.87 which is lower then in the bulk case. Closer to the walls of the tube the planes become even more distorted. The minimum value of P is reached at $r = 4.8\mathring{A}$ which corresponds to one of the peaks of the center of mass density distribution. The magnitude of P at this distance is $P_{min} = 0.53$. One can conclude that close to the walls of the tube the rings bend from planar shape but the effect is rather weak. The temperature effect on this planarity parameter is negligible and mostly appears in low r limit. The curves at different densities
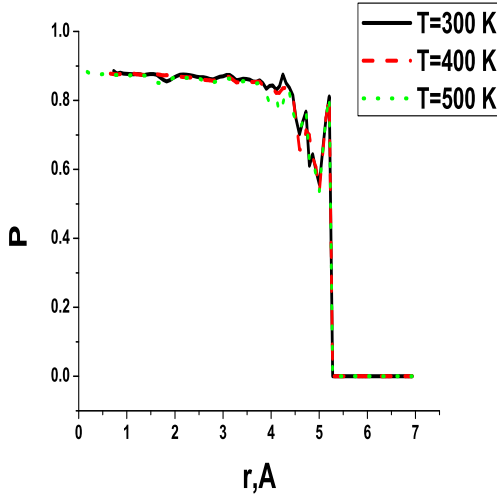
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Figure 5: P parameter which characterizes the deviation of the benzene ring from planar shape for $N = 200$ and different temperatures.

also look qualitatively very similar. For this reason we do not show these curves for other numbers of particles studied in our work.

Although the deviation of the rings from planar shape can be quite large one can define the orientational order parameter via second order Legender polynomial $P_2(cos(\theta)) = 1.5cos^2(\theta) - 0.5$ where θ is the angle between the normal vector to the plane of a ring and z direction. If the benzene ring is perpendicular to the axe of the tube, $P_2 = 1$ while if the molecule is parallel to the axe of the tube $P_2 = -0.5$. The normal vector to the benzene ring was defined as an arithmetic average of six vectors described above for planarity calculations.

Fig. 6 shows the radial distribution of P_2 for $N = 250$ and $T = 300K$, i.e. the highest density and the lowest temperature studied. One can see that although there is a small peak at origin the distribution does not demonstrate strong ordering. It means that unlike the case of graphite slit pores benzene does not have strong orientational order being confined in cylindrical geometry. In Ref.[24] it was obtained that for the nanotube radius above $5.580\mathring{A}$ the equilibrium position of a benzene molecule is the one parallel to the tube axe apart from the central line. In our simulation we do not find strong orientational order, however, there is a tilted orientation which depends on the location of the molecule. Comparison of Fig. 6 with Fig. 2 shows that inside the layers where the local density is higher, the benzene
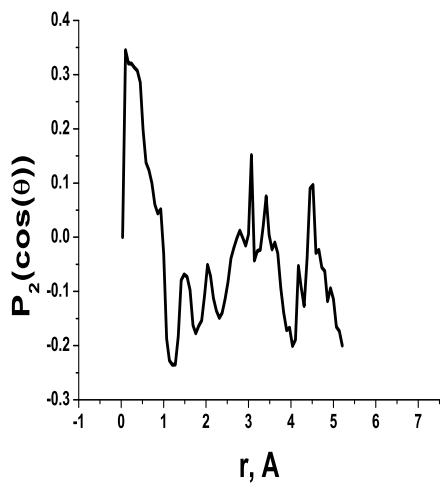
Figure 6: Legender polynomial $P_2(cos(\theta))$ for $N = 250$ and $T = 300K$.

molecules are oriented more perpendicular than between the layers. Mean field calculations in Ref. [24] do not take into account the heterogenous structure of the system and present only qualitative tendency in orientations of the benzene molecules.

Finally we discuss the dynamic properties of benzene in carbon nanotube. Correct calculation of diffusion coefficient requires simulation in microcanonical ensemble. Our calculations are done in canonical one. Although such calculations do not give completely correct numerical value of diffusion coefficient they allow to get the correct qualitative picture.

The radius of the nanotube we simulate is $6.9\mathring{A}$ which is just above the size of benzene molecule. It means that the molecules are confined in a very narrow channel. In such a narrow channel the system can be roughly considered as one dimensional. In the case of $1D$ system one does not expect large diffusion. The particles are strongly caged by theirs nearest neighbors. This is what we observe in our simulation. Fig. 7 shows the mean square displacement in the radial directions and in the direction of the axe of the tube at the lowest density ($N = 150$) and highest temperature $T = 500K$ studied. One can see that the mean square displacement in both directions grows very slowly which means strong confinement of the molecules. The diffusion coefficient in both directions is very small in the limits of the errors of calculations.
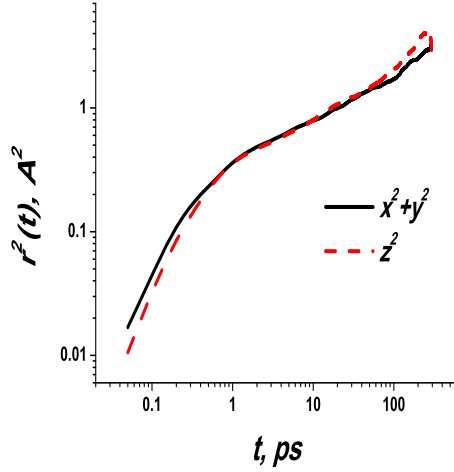
Figure 7: Mean square displacement of centers of mass of the molecules in radial direction and in the direction of the axe of the tube.$N = 150$, $T = 500K$

Conclusions

This paper reports simulation study of benzene molecules confined into the single wall carbon nanotube. We study the structure and dynamics of benzene for three densities and three temperatures. We find that the molecules of benzene mostly group in the middle distance from the axe of the tube to the wall. The molecules located in the vicinity of the wall demonstrate some deviation from planar shape. There is no strong ordering in the system in contrast to the semianalytical model, proposed in Ref.[24], however, there is a tilted orientation of the molecules which depends on the location of the molecule. Comparison of Fig. 6 with Fig. 2 shows that inside the layers where the local density is higher, the benzene molecules are oriented more perpendicular than between the layers. Last, we find that benzene molecules are almost immobile at the conditions we report here.

ACKNOWLEDGMENTS

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