

Simulating the effect of carbon nanotube curvature on adsorption of polycyclic aromatic hydrocarbons

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Abstract The results of Molecular Dynamics simulation of polycyclic aromatic hydrocarbons adsorption on single-walled (13,9) carbon nanotube are reported. We discuss the angular orientation and plausible adsorbed states of molecules. It is shown, that suggested by Gotovac et al. orientation of adsorbed molecules is correct.

Keywords Adsorption PAH · Molecular dynamics simulation · Carbon nanotubes

1 Introduction

As it was mentioned by Gotovac et al. (2007) adsorption of polycyclic aromatic hydrocarbon (PAH) molecules on carbon nanotubes can find plausible application in the surface control of isolated tubes. Moreover as it was suggested by Zhao et al. (2003) the interaction between PAH molecules and carbon material can cause changes in electronic properties of nanotubes. Therefore, the study of PAH molecules adsorption on carbon nanotubes is really interesting topic.

Recently Gotovac et al. reported experimental isotherms of PAH molecules adsorbed on single walled carbon nanotubes from toluene solution. Moreover, they studied the state of adsorbed molecules using Raman Resonance Spectroscopy and X-ray Photoelectron Spectroscopy. The chirality of tubes (13,9) was assigned from the observed Raman spectra. Authors also concluded that the most favorable adsorption states of phenantrene and tetracene molecules on

carbon nanotube (and graphite) should be so called “bridge positions”. Moreover, they also observed some structural changes i.e. expansion of the intertubular spacing after tetracene adsorption.

The major purpose of this study is to check proposed plausible adsorbed states of PAH molecules. To do this, we performed molecular dynamics simulations (MD) of PAH molecules adsorption on isolated (13,9) single-walled carbon nanotube.

2 Computational details

2.1 Molecular dynamics simulation

Molecular Dynamics simulations were carried out using GROMACS package version 4.0.3 (van der Spoel et al. 2005) and OPLSAA force field (Jorgensen et al. 1996). Single-walled carbon nanotube of chirality (13,9) was taken into consideration and modelled as infinite in axial dimension and fully flexible with bonding field parameters taken from article published by Walther et al. (2001). Adsorption of PAH series, including naphthalene, anthracene, phenanthrene, tetracene and pentacene from toluene solution was simulated. All the species were parameterized using procedure described by Seminario (1996) on the basis of quantum chemistry calculation (Gaussian 03, B3LYP/6-31G* set), where bonding force parameters were estimated from analysis of Hessian force matrix and atomic electric charges from ESP fit. So-obtained parameters were validated by reproducing experimental density values from one component simulations. Two temperature values were considered (i.e. 200 and 298 K) and preserved in a system by use of GROMACS-implemented Berendsen thermostat, as pressure of system was coupled to the value of 1 atm by also implemented

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Fig. 1 The snapshots showing equilibrium configurations of anthracene (a) phenanthrene (b) and pentacene (c) adsorbed on (13,9) single walled carbon nanotube at 298 K. Toluene (i.e. solvent) molecules are not shown for clarity

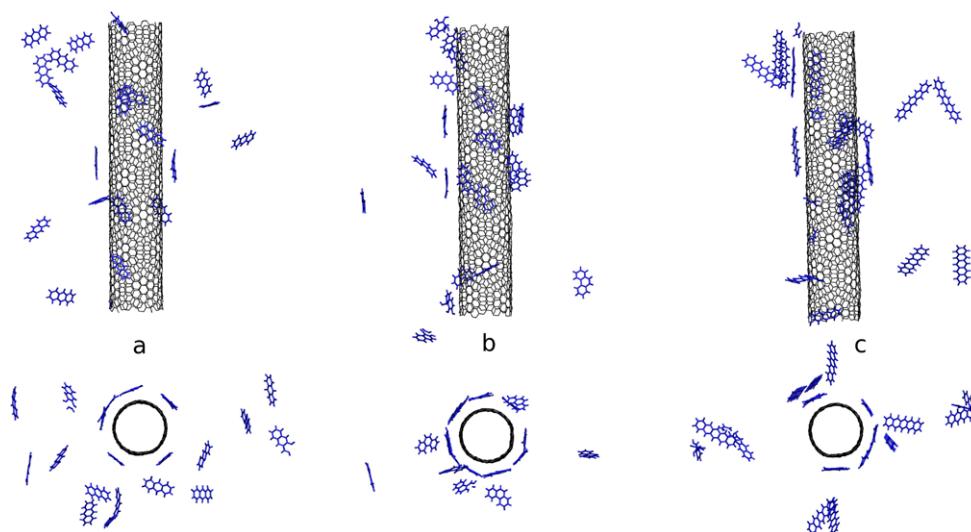
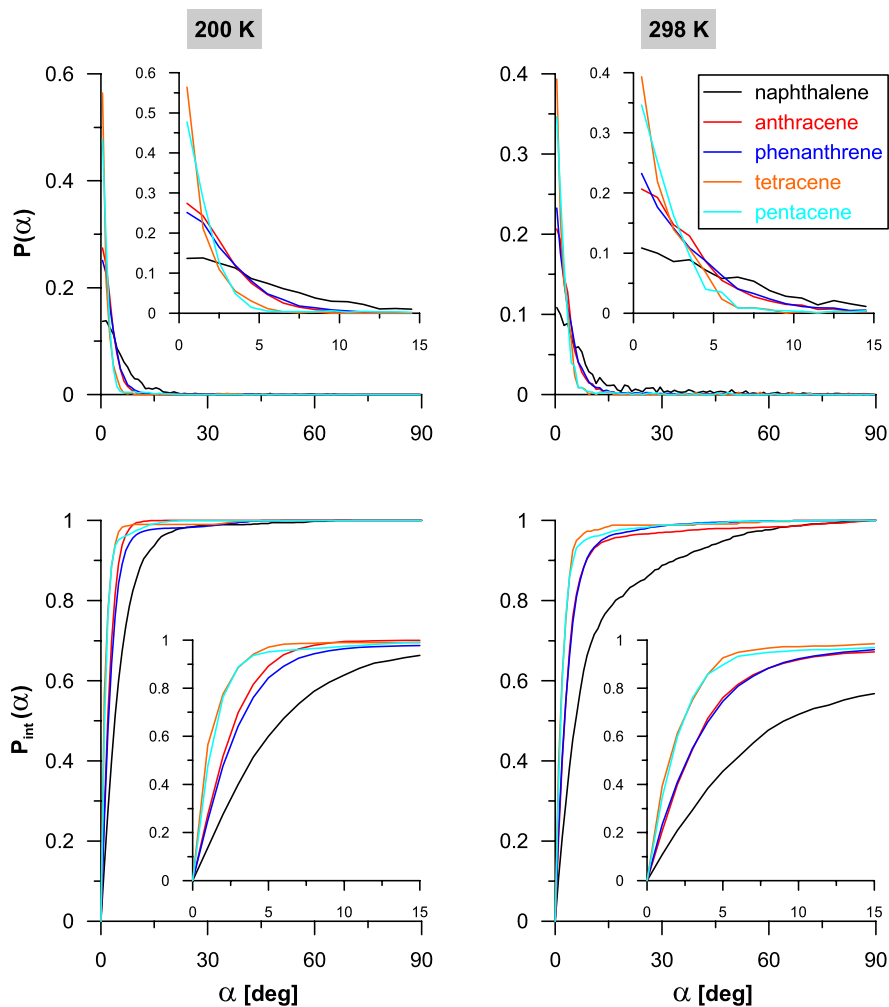


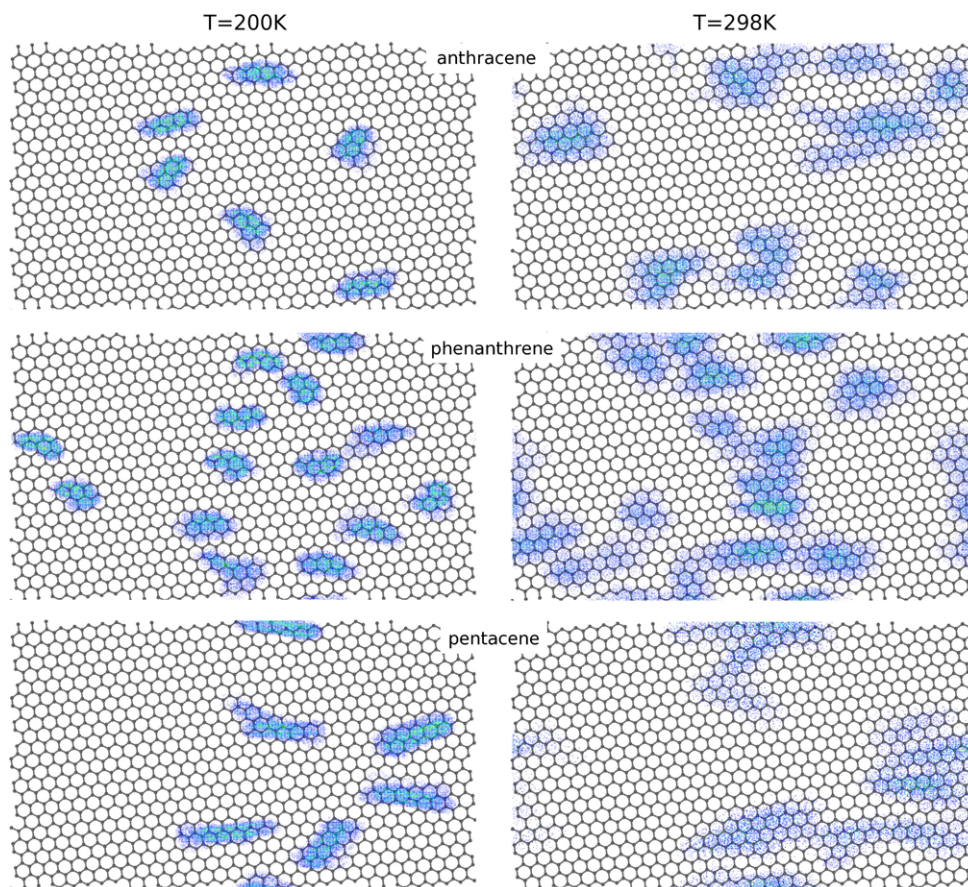
Fig. 2 Histogram of angular orientation of adsorbed PAH molecules ($P(\alpha)$) and the related integral curves ($P_{\text{int}}(\alpha) = \sum_{\beta \leq \alpha} P(\beta)$)



Berendsen routine. The box $8 \times 8 \times 8.159$ nm (periodic boundary conditions in all three dimensions) contained 1800 toluene molecules and 20 PAH molecules. Simple Coulomb-type electrostatic potential was employed with radius cut-off

1.0 nm. Simulations were maintained with a time step of 0.5 fs for 2000 ps, from which last 500 ps trajectories were taken for hydrocarbon projection on nanotube surface and mobile behavior analysis.

Fig. 3 Orientation of PAH molecules adsorbed on (13,9) tube surface



2.2 Angular orientation of adsorbed molecules

To determine the angular orientation of adsorbed PAH molecules it was assumed that the position of a molecule is determined by a vector connecting the centres of the edge benzene rings. A measure of this angular orientation is an angle formed between this vector and a plane perpendicular to the lengthening of tube radius passing the center of the vector. Thus an angle equal to 0° means the parallel orientation of a molecule and 90° is the perpendicular orientation (i.e. the vector converging the lengthening of tube radius). The analysis was performed only for those molecules being at the vicinity of the tube (i.e. the distance between at least one atom of a molecule to the nearest tube atom should be smaller than 0.5 nm).

2.3 Orientation of PAH molecules adsorbed on tube surface

To determine the orientation of PAH molecules with respect to the tube the coordinates of carbon atoms forming adsorbed molecules were projected on a tube plane (having a radius equal to 0.7495 nm). To do this, for each carbon atom a line connecting this atom with tube axis (and perpendicular to this axis) was constructed. The intersection point of

this line with a tube surface determines the position of an atom projection. Projection was performed for all adsorbed molecules and it was assumed that the distance between all carbon atoms to the nearest carbon atoms forming a tube should be smaller than 0.8 nm.

3 Results and discussion

Figure 1 shows selected snapshots of adsorbed molecules (298 K, toluene is not shown for clarity). One can observe that with the rise in the number of benzene rings in PAH molecule the number of molecules having parallel orientation increases. In fact-this is confirmed by the results shown in Fig. 2. At the both studied temperatures the rise in the size of PAH molecule leads to preferring of more flat orientation (there are practically no differences between tetracene and pentacene). Similar situation was observed previously for the results of simulation of benzene, phenol and paracetamol on carbon nanotubes, where paracetamol preferred the most flat orientation due to minimization of the solid – fluid interaction energy (Terzyk et al. 2009). As one can observe from the results shown in Fig. 2, the decrease in temperature leads to more flat orientation of adsorbed molecules. Therefore it is plausible, that at higher coverages and at larger

temperature larger number of molecules will adopt slant or even vertical orientation, as it was observed during simulation of benzene adsorption on carbon black (Vernov and Steele 1991; Do and Do 2006).

Figure 3 shows next interesting feature, namely it can be concluded that around room temperature the adsorption is mobile therefore molecules can easily translate on surface. The situation at 200 K is drastically different and we observe in fact exactly the same orientation of adsorbed molecules as it was proposed by Gotovac et al. (2007). Therefore there is apparent contradiction between the results of this paper and those published by Gotovac and co-workers. It is seen that the authors proposed the orientation of molecules consistent with simulation data but obtained for 200 K. Therefore, there is the difference in mobility of adsorbed molecules and this can be easily explained. One can remember that our simulations are performed for adsorption on a single nanotube. If one assumes that tubes form bundles the overlapping of the potential energy of interaction between adjacent tubes and adsorbed molecule occurs, therefore the potential energy of solid-fluid interactions is larger than this calculated for interaction with single nanotube (as modelled in our simulation). This is confirmed by mentioned above (and observed experimentally) structural changes i.e. expansion of the intertubular spacing after tetracene adsorption. Therefore our simulations confirm, that the plausible orientation of adsorbed molecules proposed in Gotovac et al. (2007).

4 Conclusions

Using molecular dynamics we show, that adsorbed on tube (13,9) PAH molecules are mobile at room temperature. The decrease in temperature leads to localization of adsorbed molecules and the same orientation as proposed by Gotovac et al. is observed. Adsorbed PAH molecules prefer flat orientation and this is more pronounced at smaller temperatures.

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