AN ATOMISTIC TECHNIQUE FOR SIMULATING LARGE ENSEMBLES OF HIGH-MOLECULAR-WEIGHT PITCH COMPONENTS

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Introduction

Polycyclic aromatic hydrocarbons (PAH) of high molecular weight (> 400 Daltons) have a special significance in carbon science. They are the primary constituents of pitches [1], and are also formed *in situ* by cyclization, dehydrogenation, and polymerization during carbonization of diverse organic materials [2]. Polyaromatic compounds of this size are difficult to study experimentally as only a few large PAH (> 300 Daltons) have been synthesized and isolated in nearly pure form [3]. Molecular modelling can play an especially important role for investigating these molecules. There have been a number of molecular modelling and simulation studies on large disk ensembles using molecular pseudo-potentials such as the Gay-Berne potential [4]. There have been interesting studies of Gay-Berne discotic phase behaviour, but there is however no obvious way to relate detailed molecular structure (aliphatic groups, non-planar heterocylic rings, irregular polyaromatic cores) to the empirical potential parameters.

To our knowledge no studies have used atomic level information in simulations of high-MW PAH ensembles large enough to investigate phase behaviour. The goal of the current work is to demonstrate an isothermal-isobaric Monte Carlo technique for simulating large ensembles of high-molecular weight PAH using atomic pair potentials and no adjustable parameters. Such an atomistic approach could be applied to arbitrarily complex and irregular polyaromatics and provide a tool to relate molecular structural features (side chains, aliphatic groups, polyaromatic kernal shape) to pitch behaviour and carbon structure. High temperature 2D simulations have been carried out on coronene, hexabenzocoronene and a model irregular PAH. First sets of results on these molecules are presented in this paper.

Model molecular structures and interaction potentials

Figure 1a shows the model molecular structure chosen to be an appropriate challenge for this computational demonstration. It is an irregular polyaromatic hydrocarbon with 58 C and 24 H (MW 720 Daltons). It is disk-like and primarily planar but has a non-planar defect in the form of a heterocylic ring. Two of the carbons in this ring lie out of plane, but the main source of non-planarity are the four hydrogen atoms oriented normal to the molecular plane (Fig. 1b). The effect of this local non-planarity was examined directly by carrying out additional simulations on a strictly planar version produced by removal of two hydrogen atoms to produce a fully aromatic system. Assuming the molecule to be
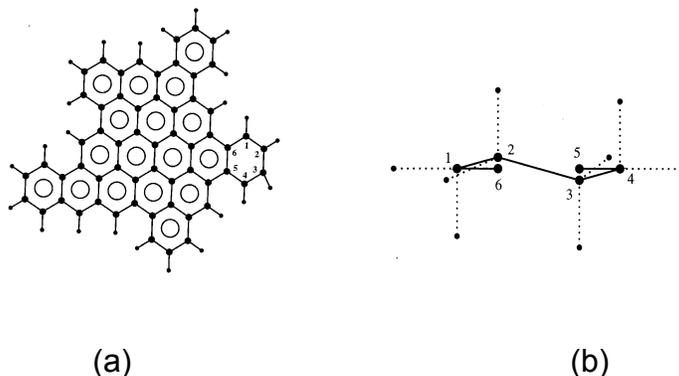
<div align="center">(a)   (b)</div>

Fig.1. (a) The structure of the model irregular PAH, MW 720, C and H atoms have been represented by big and small dots respectively. (b) Out-of-plane positions for individual atoms in the single aliphatic ring.

rigid in nature, the energetics of molecular packing into one and two dimensional aggregates can be described by nonbonded atom-atom potentials and an electrostatic contribution from the partial charges on various atoms.

$$U_{ij} = E_{ij}^{nb} + E_{ij}^{el} \qquad (1)$$

We have used the MM2 force field of Allinger [5] with the empirical parameters from MACROMODEL. The nonbonded potential for the interaction of two molecules labelled as 1 and 2 is given by

$$E_{12}^{nb} = \sum_{i,j} A_{ij} \left[2.90 x 10^5 \exp\left(\frac{-12.5 r_{ij}}{B_{ij}} \right) - 2.25 \left(\frac{B_{ij}}{r_{ij}} \right)^6 \right] \qquad (2)$$

The van der Waals interaction parameters for C and H atoms, based on MM2 semi-empirical potentials are listed in Table 1. The contributions from the electrostatic term, E^{el}, to the total packing energy of molecules, estimated to be less than 5%, is neglected for these hydrocarbons that lack dipoles.

Table 1: van der Waals parameters from MM2 force fields [5] for saturated and unsaturated hydrocarbons

Interaction	Saturated hydrocarbon		Unsaturated hydrocarbon	
	A (kcal/mol)	B (Å)	A (kcal/mol)	B (Å)
C-C	3.80	0.0440	3.88	0.0440
C-H	3.34	0.0460	3.44	0.0455
H-H	3.00	0.0470	3.00	0.0470
H offset	0.915		0.915	

Simulation Technique

The simulations were carried out in two steps. In the first step, a 2D ground state crystal structure was generated for the model PAH molecule based on the principles of organic molecular crystallography [6]. Scaringe and Perez [7] have shown that only four types of 1D aggregates occur in 92% of all organic crystals, and Scaringe [8] has further shown that these can combine to form only seven types of layers. A lowest energy 1D aggregate structure was generated using a Monte Carlo cooling technique [9]. A 2D monolayer was then determined, consistent with the lowest energy and closest packing. This simulation technique was also used to generate 2D structures for both coronene and hexabenzocoronene. An excellent agreement was observed between the simulated and experimentally observed structures for these molecules.

Phase behaviour at high temperatures was investigated in the second step in an isothermal-isobaric ensemble, with the molecules occupying a 16 x 16 lattice in their ground state configuration. The outer ring of molecules in the simulation lattice was used as fixed walls, giving the cell a fixed volume. While the molecules in the outer ring were kept fixed and did not undergo any change in orientation or position during a simulation run, they participated in the energy computations of inner cell molecules. The application of pressure after a number of constant volume runs, allowed for the volume and shape changes to the simulation cell permitting the structure to attain its natural state. A molecule was chosen at random from the inner 14 x 14 simulation lattice. Keeping the molecule rigid, it was allowed one of the five possible moves: three changes to molecular orientation and two positional movements. The energy of the system was computed before and after the molecular movement using MM2 force field parameters. The energy change ΔE due to the molecular move was calculated. The molecular movement was accepted for $\Delta E \leq 0$. For $\Delta E > 0$, the move could be accepted with a transition probability depending on the system temperature [10]. A dimensionless, reduced temperature parameter, T ($= k_B T^* / A_{c-c}$), was used to represent the simulation cell temperature. A_{c-c} (= 3.8 kcal/mol) represents the nonbonding C-C interaction paramerter A from MM2 force fields (Table 1).

Simulations were carried out for a range of temperatures and pressures. Temperature and pressure were kept constant during a given run. Typically 100 000 to 500 000 Monte Carlo cycles were found sufficient ensuring the system had reached equilibrium. Each cycle consisted on ~2000 molecule trial moves at constant volume followed by a trial shape change, in which the dimensions of the simulation cell were randomly altered. The final equilibrium configuration was analysed in terms of system energy, centre of mass/atomic positions and molecular orientations, and the orientational order parameter.

Simulation results and discussion

Phase diagram simulations were carried out on both the planar and the nonplanar molecules with temperature T ranging from 0.05 to 1.5 and pressure P ranging from 1 to 20. A number of phase transformations were observed in both systems. These transitions were however not very well defined for constant volume simulations. This is to be expected as some of these transitions are accompanied by a volume change and could be suppressed to an extent in a fixed volume simulation. The energy of the model molecules as a function of temperature, in the final equilibrium configurations is shown in

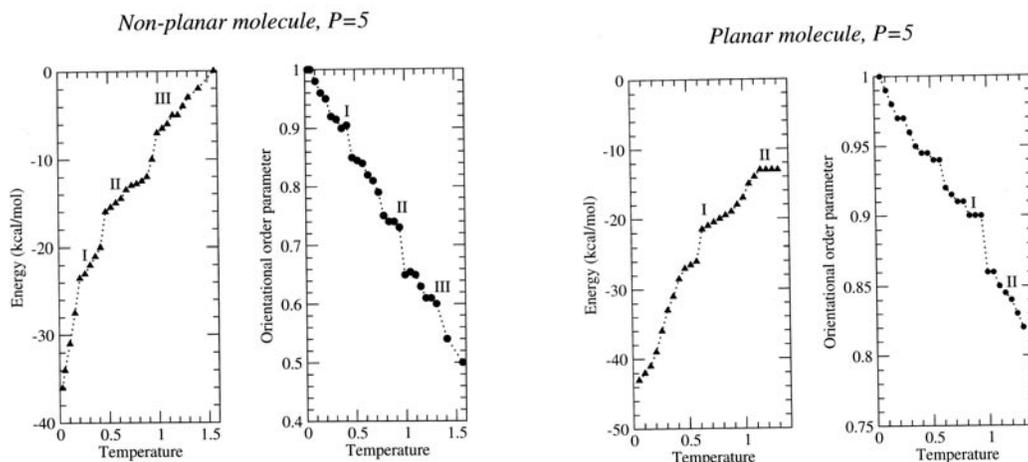*Non-planar molecule, P=5*   *Planar molecule, P=5*

Fig. 2: Equilibrium configuration energy and orientational order parameter for the non-planar and the planar molecule as a function of temperatures.

Fig. 2. The corresponding changes in the orientational order parameter S have also been plotted. For the non-planar molecule, three distinct discontinuities, suggesting possible phase transitions can be seen. The discontinuities in the energy plot also correspond to breaks in the orientational order parameter. The planar molecule shows only two structural transformations for the range of temperatures and pressures investigated. Regime I appears to be quite similar to the regime I observed for the nonplanar molecule. But the transition temperature (~0.6) in this case is much higher than the corresponding temperature (~ 0.27) for the nonplanar molecule. Similarly the transition to regime II has also shifted to a much higher temperature (~0.95) as compared to the ~ 0.55 for the nonplanar molecule. In Fig. 3, we have plotted the positions of centres of mass, directors and atomic positions at T=1.15 for both molecules. These results point towards the important role played by the molecular structure wherein minor changes in structure can result in significant changes in stacking behaviour and structural transition points.

Monte Carlo simulations were also carried out on two regular PAH molecules: coronene and hexabenzocoronene. These molecules are however much smaller in size as compared to the model irregular PAH molecule investigated in this work. These molecules show a tendency to pass directly from crystalline order to isotropic phases, as observed experimentally. In the case of the model high-MW irregular PAH molecules, the molecules showed a predominant preference towards translational rather than rotational motion, especially in the lower temperature simulations. For the regular molecules on the other hand, rotational movement was the preferred choice at all temperatures, and this may be responsible for the loss of orientational order concurrently with loss of positional order (simple melting).
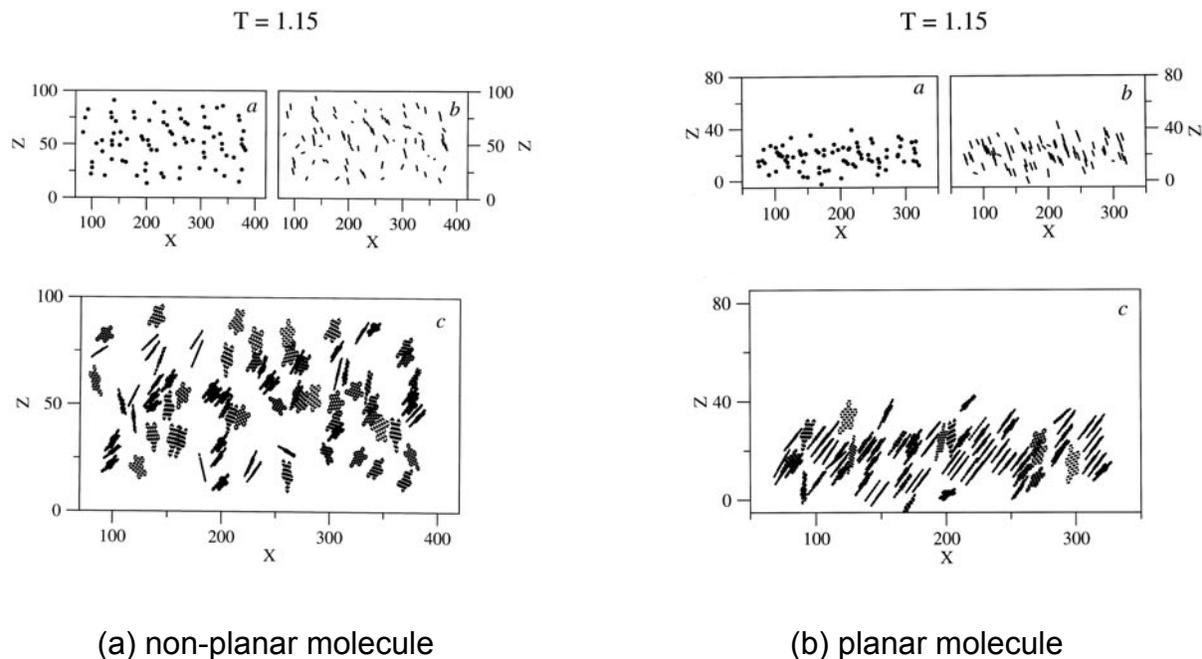
T = 1.15

T = 1.15

(a) non-planar molecule   (b) planar molecule

Fig.3: Molecular configurations at T=1.15 for (a) non-planar and (b) planar molecules. Plots *a*, *b* and *c* respectively represent centre of mass positions, molecular directors and atomic positions for the molecules. The X and Z axes in these 2D plots are in the ratio 1:1. The plots for atomic positions have been magnified four times to bring out the atomic detail.

Conclusions

Large ensemble simulations (196 molecules) based on atomic pair potentials are shown to be feasible for irregular, high-MW PAH (720 Daltons) representative of those in pitch. The simulations show columnar phases at low temperatures and the gradual loss of long-range columnar order with heating. The power of the atomistic approach is its ability to investigate the effects of specific molecular structural features such as side chains or aliphatic rings with no empirical parameters. The results obtained here show that the supramolecular structures in these ensembles and their transition temperatures are quite sensitive to the addition of even one aliphatic ring, which causes a local non-planar defect in the large polyaromatic mesogen.

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