

# Molecular Dynamics Simulations of Hexane Deposited onto Graphite: An Explicit-Hydrogen Model at $\rho = 1$

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## ABSTRACT

We present the results of parallel Molecular Dynamics computer simulations of hexane ( $C_6H_{14}$ ) adlayers physisorbed onto a graphite substrate in the density range  $0.5 \leq \rho \leq 1$  in units of monolayers, with emphasis on monolayer completion ( $\rho = 1$ ). The hexane molecules are modeled to explicitly include hydrogens and the graphite is modeled as a six – layer all atom structure. In the explicit hydrogen simulations, the herringbone solid loses its orientational order at  $T_1 = 140$  °K, fairly consistent with results of UA simulations. However there is almost no nematic meso-phase or negative energy change at the loss of herringbone order. The explicit hydrogen melting temperature is  $T_2 = 160$  °K—somewhat lower than seen in experiment and in UA simulations. Generally, results for the all-atom model agree well with experiment, as the molecules remain overall flat on the substrate in the solid phase. At densities below about  $\rho = 0.875$  the system supports a connected network which stabilizes it against thermal fluctuations and yields much more reasonable sub-monolayer- melting behavior. The united atom picture, on the other hand, departs significantly from experiment at most sub-monolayer- densities and gives melting temperatures several decades below what is experimentally observed. The purpose of this work is to compare the results of UA and explicit hydrogen MD simulations of hexane on graphite mainly at  $\rho = 1$ , to discuss cursory explorations at sub-monolayer- densities and mention open questions related to the system that are worth pursuing. Various structural and thermodynamic order parameters and distributions are presented in order to outline such differences.

## I. INTRODUCTION

Extensive Molecular Dynamics (MD) studies of hexane on graphite using the United Atom (UA) approximation have provided a framework for advancing our understanding of physisorbed alkanes. In

the UA approximation, methyl ( $CH_3$ ) and methylene ( $CH_2$ ) pseudo-atoms replace the actual corresponding functional groups in a molecule. The main utility of such an approximation is a considerable savings of computational effort. Because of the highly anisotropic nature of the hexane molecule

as well as the graphite substrate, including the hydrogens on the hexane molecules can help better represent steric effects as well as molecule–substrate interactions. The program NAMD is a parallel MD simulation package and allows for the use of an existing and validated simulation method. NAMD has also been optimized for computational efficiency by the developers, allowing for the extra calculations associated with including explicit hydrogens without significant computational cost.

Because of its utility, stability and geometry, much experimental and theoretical work has been completed on systems involving graphite.<sup>1,2</sup> Hexane on graphite has been studied experimentally<sup>3-5</sup> and computationally,<sup>6-14</sup> and details of its behavior may be found in the appropriate references. Experimentally, uniaxially incommensurate (UI) or commensurate herringbone (HB) phases are seen at low temperatures (depending on coverage), which transition into a rectangular solid/liquid coexistence region, melting finally at temperatures ca. 175 °K. Computer simulations are capable of reproducing the melting temperature at completion ( $\rho = 1$ ) fairly accurately. In the most recent UA simulations<sup>13,14</sup>, at  $\rho = 1$  a solid herringbone phase persists until a transition temperature  $T_1 = 130$  °K. Then there is a transition to an orientationally ordered nematic meso-phase up until  $T_2 = 172$  °K above which there is an isotropic liquid.

## II. COMPUTATIONAL METHOD

### a. NAMD

NAMD is a freely available parallel molecular dynamics package which is widely used in computational modeling of large and organic systems.<sup>15</sup> NAMD and VMD (Visual Molecular Dynamics) were installed on the University of Northern Iowa research clusters. The program NAMD requires several types of input files in order to carry out the simulations. To begin with, the topology file defines the name, mass, charge and type of each atom as well as bond connectivity and character (single / double), dihedral and improper angles. The second file required to run NAMD is a parameter file which defines force constants

for the bond, angle, dihedral and improper energy between each atom types along with the bond lengths and angle degrees. For the simulations presented here a standard CHARMM force field formalism is utilized. The input pdb (Protein Data Bank) and psf (Protein Structure File) files define the initial conditions of the system and the main file (extensionless) contains information of the run length, cutoff distance, temperature and thermostat, boundary conditions, etc.

### b. SIMULATION DETAILS

The hexane molecule definition in our study was obtained from the Brookhaven Protein Data Bank (PDB). The molecules are consistent with the United Atom (UA) model in earlier work in that the bond lengths are kept fixed while allowing other internal degrees of freedom to vary. A constant  $N = 112$  hexane molecule system is used for each density in an initial herringbone configuration consistent with earlier UA work.

The hexane molecules are physisorbed onto six identical stacked graphite sheets, which are also obtained from the Brookhaven PDB and staggered in the known (-A-B-A-B-) stacking form. The dimensions of the graphite sheets are varied for each density studied, as are shown in Table 1. Only results for density  $\rho = 1$  will be discussed in detail in this paper.

Density $\rho$ (monolayer)	X (Å)	Y (Å)
$\rho = 1.00$	68.16	68.88
$\rho = 0.966$	67.45	71.34
$\rho = 0.878$	71.71	73.80
$\rho = 0.614$	84.89	86.10
$\rho = 0.509$	93.72	98.40

**Table 1.** Dimensions (X, Y) of the graphite substrate for the various densities under investigation. For each density, the number of hexane molecules is kept constant ( $N = 112$ ).

All simulations in this study are constant molecule number, density and temperature ( $N = 112$ ,  $\rho$  and  $T$  respectively). Simulations of each density from Table 1 are performed for temperatures from 100 to 200°K at intervals of approximately 10 °K. To maintain a constant temperature the velocities are rescaled within NAMD. In addition, periodic boundary conditions are applied in the  $x$  and  $y$  directions for the system.

The time step for all simulations is 1 fs [femto-seconds or  $10^{-15}$  seconds], and each simulation ran for 500,000 - 750,000 time steps. Periodic snapshots of the system are converted from raw binary DCD format to a series of recognizable PDB files for each snap shot using NAMD's sister program Visual Molecular Dynamics (VMD). The atom positions from the PDB files are then reduced to several system behavior characterizing order parameters and thermodynamic measurements of interaction energies, which are explained in the results section.

### III. RESULTS AND DISCUSSION

As temperature is changed for the system, various indicators of its structure and energetics must be monitored in order to facilitate understanding of the phase transition. The molecular order parameters used to quantify the behavior of the system used in the UA approximation<sup>13,14</sup> are also utilized in the NAMD model. The herringbone order parameter  $OP_{Herr}$  gives a measure of the orientational order of the molecular axis with respect to the graphite substrate. Here the "molecular axis" is along a molecule's smallest principal moment of inertia.  $OP_{Herr}$  is defined by

$$OP_{Herr} \equiv \frac{1}{N_m} \left\langle \sum_{i=1}^{N_m} (-1)^j \sin(2\phi_i) \right\rangle. \quad (1)$$

The integer  $j$  is assigned values which account for the orientational differences exhibited by adjacent vertical herringbone sublattices.  $OP_{Herr}$  is equal to unity if all molecular axes are oriented at 45° and 135° and drops as a result of thermal fluctuations to a value of zero for random in-plane rotation. Since the static herringbone lattice for the systems studied here has angles at

about 30° and 150°,  $OP_{Herr}$  has a zero-temperature limiting value of about 0.866 and drops from there.

The nematic order parameter is necessary to provide information on the nematic-to-isotropic-liquid transition. The nematic order parameter gives a measure of the long-range orientational order (and thereby the nematic character) of the system. It is given by

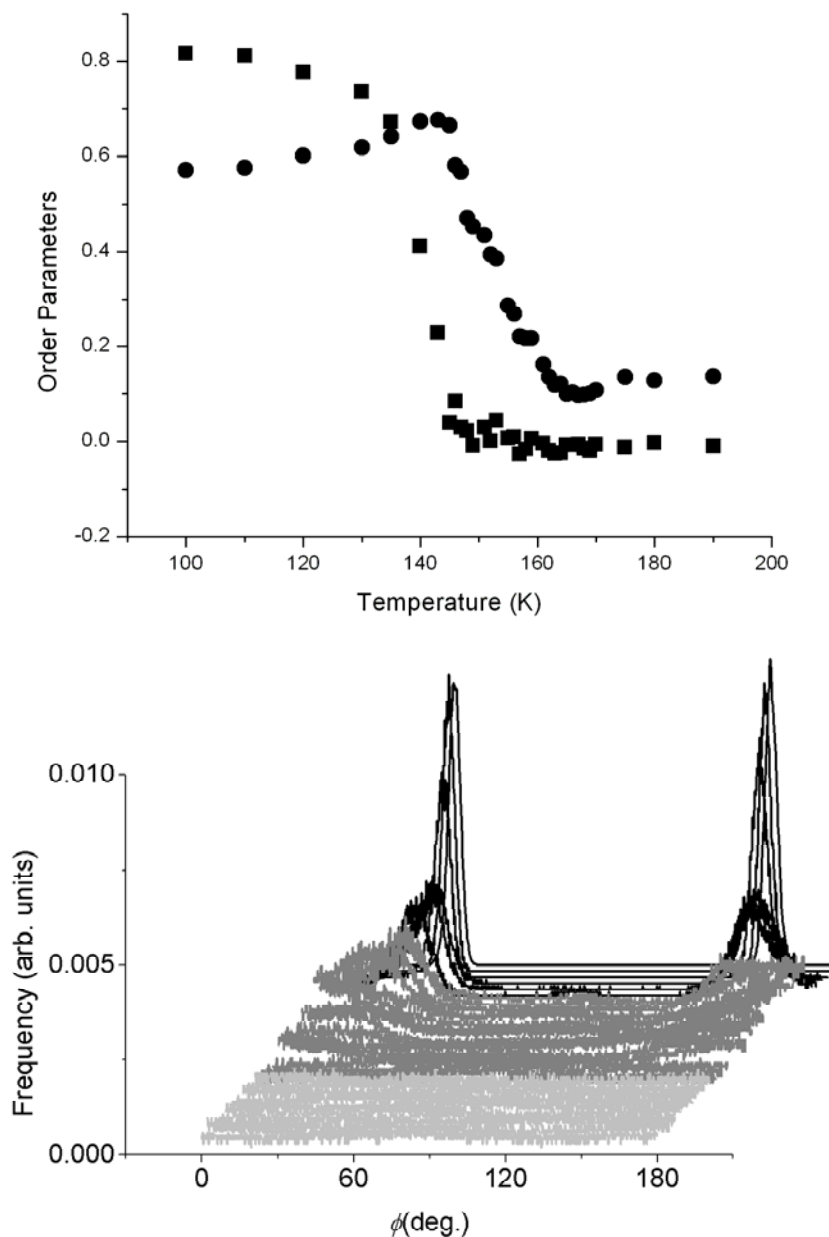
$$OP_{Nem} \equiv \frac{1}{N_m} \left\langle \sum_{i=1}^{N_m} \cos 2(\phi_i - \phi_{dir}) \right\rangle, \quad (2)$$

where  $\phi_i$  is the angle that the axis of molecule ( $i$ ) makes with the  $x$  - axis and  $\phi_{dir}$  is a director which is essentially the average orientation of the system. Plots of  $OP_{Herr}$  and  $OP_{Nem}$  as functions of temperature are shown in Figure 1.

The herringbone order parameter shows the system to be in a solid herringbone phase at low temperature, and other information (not shown) confirms that the overlayer is commensurate with the graphite substrate. A solid herringbone order-disorder transition is seen at about  $T = 140$  °K, and the nematic order parameter shows that the system retains orientational order for  $140$  °K  $\leq T \leq 162$  °K, after which point it also drops to zero, signaling the presence of an isotropic liquid. The peaks azimuthal angle probability distributions in Figure 1 confirm that the herringbone phase at low temperature is lost most rapidly as  $OP_{Herr}$  drops fastest.

In the explicit hydrogen hexane/graphite systems the herringbone phase persists up until about  $T = 145$  °K and then changes to a much stronger nematic, which in turn persists until about  $T = 170$  °K when the system melts into the isotropic liquid. The absence of the strong nematic phase in this work can be seen not only by the absence of a sharp increase in  $OP_{Nem}$  after herringbone order is lost but also in the absence of high peaks in the azimuthal angle probability distributions in the region between herringbone order loss and nematic order loss. It can be seen in this work that there is some very weak nematic ordering after  $OP_{Herr}$  drops to zero that diminishes when  $OP_{Nem}$  drops.

In order to gain a broader perspective of the transitions involved in this

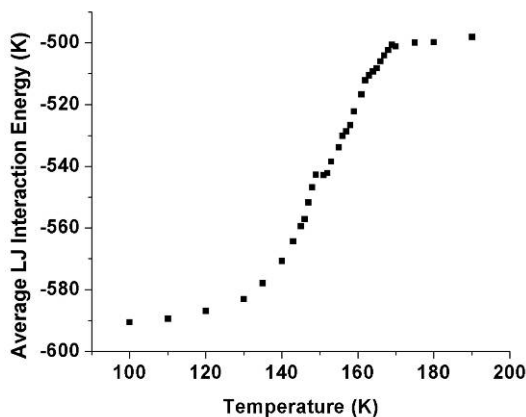


**Figure 1.** Herringbone order parameter  $OP_{Herr}$  (top panel; squares)  $OP_{Nem}$  (top panel; circles) as functions of temperature for  $\rho = 1$ . The lower panel shows the probability distributions of the azimuthal angle  $\phi$  for the solid (black), through herringbone order loss (medium gray) and after  $OP_{Herr}$  has dropped to zero (light gray).

study, we also examine the average adatom–adatom Lennard–Jones interaction as a function of temperature,

$$U = \left\langle \sum_{i=1}^N \sum_{j>i} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\rangle \quad (3)$$

which are shown in Figure 2. The herringbone to nematic transition is accompanied by a sharp drop in the molecule – molecule interaction energy in the United Atom picture, which is not seen in the explicit hydrogen model. The marked suppression of the nematic phase brought



**Figure 2.** Average Lennard–Jones adatom–adatom interaction energy as a function of temperature for  $\rho = 1$ .

about by including the hydrogens has to do with not only the hydrogen atoms' occupying more space but also their anisotropic interaction with the substrate, which is averaged out in the UA model. Both the explicit hydrogen and the UA model agree with experiment in the high temperature realm. UA was able to predict accurately the melting temperature (nematic to isotropic phase transition) to be around  $T = 170$  °K. However, although the UA model accurately predicted a loss of long range orientational ordering, an artificial jump in Lennard–Jones potential energy is shown due to a reduction of space by excluding the hydrogen atoms.

The explicit hydrogen picture also shows promise in resolving important issues regarding simulation of alkane / gr systems. The UA model has difficulty accurately simulating sub-monolayer densities, while recent work with the explicit hydrogen model has shown considerable promise at these low densities, as shown in figure 3. Moreover, in the UA simulations molecules are able to roll on their sides readily while in the explicit hydrogen model rolling is not so energetically favorable. The fact that the explicit hydrogen molecules lay flatter on the substrate is shown in Figure 3 and is consistent with experiment.

Examining systems four times the size of  $N = 112$  system shows that, at a density  $\rho = 1$ , there is considerable stress in the lattice. As density is decreased, even slightly, the monolayer registers and the stress manifested as bent columns and molecules on their sides seems to

disappear. This suggests that the smaller systems are artificially stabilized through finite size effects and we may even need to re–think our definition of monolayer completion for this system.

#### IV. REMARKS

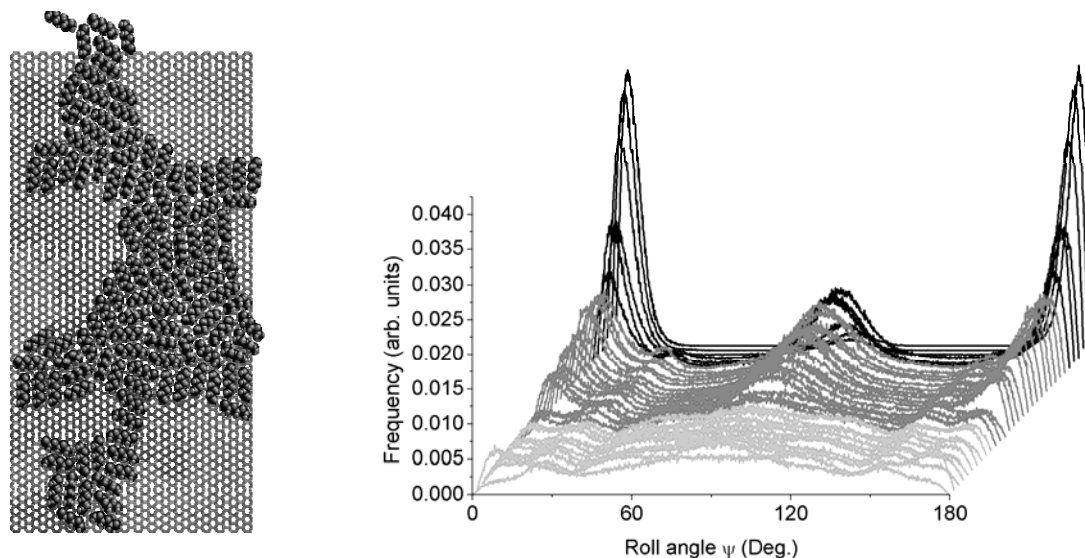
Our studies have shown the differences between the explicit hydrogen model using NAMD and the UA model. We can see that at higher temperatures (around the melting point) the UA model presents a reasonably accurate description of the system. However at low temperatures and densities for the system the explicit hydrogen model picks up where the UA model fails as the hydrogen–substrate interactions and steric effects are more important and accurate in the model. The improved accuracy in describing the molecule–molecule and molecule–substrate interactions result in connected networks as well as patches for various sub-monolayer densities as well as molecules which lie flatter on the substrate than in the UA model. Hence in one sense it provides a much better model for the system but it remains to be understood why the melting temperature is somewhat less than what is seen in other simulations as well as experiment. The new simulations we are using will help decipher more of the complicated experimental results seen at sub-monolayer densities and since experimental work does not exist for densities lower than near 0.5, the simulation can serve in a predictive capacity as well.

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**Figure 3.** Aspects of the hexane/graphite system model the explicit hydrogen model helps resolve. A connected all-atom hexane network at  $\rho = 0.5$  and  $T = 110$  K (left). Such structures are not supported in similar united atom simulations of the same size. Molecular roll angle distribution (right) illustrating that the explicit hydrogen molecules lay on their sides much more readily than in the UA model.

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