

Explicit Hydrogen Molecular Dynamics Simulations of Hexane Deposited onto Graphite at Various Coverages

M. J. Connolly,[†] M. W. Roth,^{*,†} Paul A. Gray,[‡] and Carlos Wexler[§]

University of Northern Iowa, Department of Physics, Cedar Falls, Iowa 50614, University of Northern Iowa, Department of Computer Science, Cedar Falls, Iowa 50614, and University of Missouri, Department of Physics and Astronomy, Columbia, Missouri 65211

Received October 2, 2007. In Final Form: December 21, 2007

We present results of molecular dynamics (MD) computer simulations of hexane (C₆H₁₄) adlayers physisorbed onto a graphite substrate for coverages in the range $0.5 \leq \rho \leq 1$ monolayers. The hexane molecules are simulated with explicit hydrogens, and the graphite substrate is modeled as an all-atom structure having six graphene layers. At coverages above about $\rho \cong 0.9$ the low-temperature herringbone solid loses its orientational order at $T_1 = 140 \pm 3$ K. At $\rho = 0.878$, the system presents vacancy patches and T_1 decreases to ca. 100 K. As coverage decreases further, the vacancy patches become larger and by $\rho = 0.614$ the solid is a connected network of randomly oriented islands and there is no global herringbone order–disorder transition. In all cases we observe a weak nematic mesophase. The melting temperature for our explicit-hydrogen model is $T_2 = 160 \pm 3$ K and falls to ca. 145 K by $\rho = 0.614$ (somewhat lower than seen in experiment). The dynamics seen in the fully atomistic model agree well with experiment, as the molecules remain overall flat on the substrate in the solid phase and do not show anomalous tilting behavior at any phase transition observed in earlier simulations in the unified atom (UA) approximation. Energetics and structural parameters also are more reasonable and, collectively, the results from the simulations in this work demonstrate that the explicit-hydrogen model of hexane is substantially more realistic than the UA approximation.

I. Introduction

Because of its utility, stability, and geometry, much experimental and theoretical work has been completed on systems involving graphite.^{1,2} Hexane on graphite has been studied experimentally^{3–5} and computationally.^{6–13} 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.^{3–5} At near-monolayer coverages, the melting temperature remains fairly constant, and as the coverage decreases to about $\rho = 0.5$, the melting temperature drops to about 150 K.⁴

Until recently, most computer simulations of hexane on graphite utilized molecular dynamics (MD) methods and employ the united atom (UA) approximation. In the UA approximation, methyl

(CH₃) and methylene (CH₂) *pseudoatoms* replace the respective real functional groups in a molecule. The UA approximation saves significantly on the computational effort but has significant shortfalls. The most significant are (i) the lack of in-plane space occupation due to the missing hydrogens in the UA model, (ii) the anisotropy introduced by the terminal hydrogens which is averaged out in the UA model, (iii) the effect of the interaction of the hydrogens with the graphite substrate which can be substantially different than that of the UA model, and (iv) the UA model significantly underestimates the moment of inertia of the molecule.

Such UA simulations have provided a framework for advancing our understanding of physisorbed alkanes and are capable of reproducing the melting temperature at completion ($\rho = 1$) fairly accurately. In the most recent studies,^{12,13} at $\rho = 1$ a solid herringbone phase persists until a transition temperature $T_1 \cong 130$ K. Then, there is a transition to an orientationally ordered nematic mesophase up until $T_2 \cong 172$ K above which there is an isotropic liquid. In the near-monolayer range¹³ ($0.875 \leq \rho \leq 1.05$) a uniaxially incommensurate herringbone (UI–HB) solid is present.

The simulations in the UA approximation, however, have some serious pitfalls: for example, at moderate-to-high coverages the adsorbate molecules are more prominently rolled on their side perpendicular to the surface of the substrate, which is in significant disagreement with experiment.^{4–7} Since the solid–nematic transition temperature is very sensitive to coverage, an inaccurate description of molecular rolling may result in erroneous characterization of both low- and intermediate-temperature phases.

Because of the three main limitations of the UA model mentioned earlier, we expect that including explicitly the hydrogens in the MD simulations will have a significant impact on the simulation results. First off, since the hydrogens occupy space through their collision diameters, including them stifles the molecules' ability to order and stack as seen in the UA nematic

* To whom correspondence should be addressed. E-mail: rothm@uni.edu.

[†] Department of Physics, University of Northern Iowa.

[‡] Department of Computer Science, University of Northern Iowa.

[§] University of Missouri, Columbia.

(1) Bruch, L. W.; Cole, M. W.; Zarembam, E. *Physical Adsorption: Forces and Phenomena*; Oxford University Press: Oxford, 1997.

(2) Shrimpton, N. D.; Cole, M. W.; Steele, W. A.; Chan, M. H. W. *Rare Gases on Graphite Surface Properties of Layered Structures*; Benedek, G., Ed.; Kluwer: Amsterdam, 1992.

(3) Krim, J.; Suzanne, J.; Shechter, H.; Wang, R.; Taub, H. *Surf. Sci.* **1985**, *162*, 446–451.

(4) Newton, J. C. Ph.D. dissertation, University of Missouri–Columbia, 1989.

(5) Taub, H. *NATO Advanced Study Institutes, Series C: Mathematical and Physical Sciences*; Long, G. J., Grandjean, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1988; Vol. 228, pp 467–497.

(6) Hansen, F. Y.; Taub, H. *Phys. Rev. Lett.* **1992**, *69*, 652–655.

(7) Hansen, F. Y.; Newton, J. C.; Taub, H. *J. Chem. Phys.* **1993**, *98*, 4128–4141.

(8) Velasco, E.; Peters, G. H. *J. Chem. Phys.* **1995**, *102*, 1098–1099.

(9) Peters, G. H.; Tildesley, D. J. *Langmuir* **1996**, *12*, 1557–1565.

(10) Peters, G. H. *Surf. Sci.* **1996**, *347*, 169–181.

(11) Herwig, K. W.; Wu, Z.; Dai, P.; Taub, H.; Hansen, F. Y. *J. Chem. Phys.* **1997**, *107*, 5186–5196.

(12) Roth, M. W.; Pint, C. L.; Wexler, C. *Phys. Rev. B* **2005**, *71*, 155427–155439.

(13) Pint, C. L.; Roth, M. W.; Wexler, C. *Phys. Rev. B* **2006**, *73*, 85422–85431.