Melting of Hexane Monolayers Adsorbed on Graphite: The Role of Domains and Defect Formation

C. Wexler,*,[†] L. Firlej,*,[†,‡] B. Kuchta,[†,§] and M. W. Roth*,[‖]

[†]*University of Missouri, Department of Physics and Astronomy, Columbia, Missouri 65211, [‡]LCVN, Université Montpellier 2, 34095 Montpellier, France, [§]Laboratoire Chimie Provence, Université de Provence, 13396 Marseille, France, and [‖]University of Northern Iowa, Department of Physics, Cedar Falls, Iowa 50614*

We present the first large-scale molecular dynamics simulations of hexane on graphite that completely reproduce all experimental features of the melting transition. The canonical ensemble simulations required and used the most realistic model of the system: (i) a fully atomistic representation of hexane; (ii) an explicit site-by-site interaction with carbon atoms in graphite; (iii) the CHARMM force field with carefully chosen adjustable parameters of nonbonded interaction, and (iv) numerous ≥100 ns runs, requiring a total computation time of ca. 10 CPU years. The exhaustive studies have allowed us to determine the mechanism of the transition: proliferation of small domains through molecular reorientation within lamellae and without perturbation of the overall adsorbed film structure. At temperatures greater than that of melting, the system exhibits dynamically reorienting domains whose orientations reflect the graphite substrate's symmetry and whose size decrease with increasing temperature.

I. Introduction

Hexane is the shortest alkane whose flexibility has any significant impact on its dynamics. Its behavior on a graphite substrate has been extensively studied both experimentally[1−5] and computationally.[4−13] Neutron scattering and X-ray diffraction reveal that, at near monolayer coverage, the system transits from a herringbone solid into a rectangular solid/liquid coexistence region as the temperature is raised, finally melting at temperatures of ~170 K.[1−5]

Even with a considerable body of computational work,[4−13] the detailed mechanism of the melting transition and the effect that molecular stiffness has on it have not been elucidated. There are at least three reasons why such elements of this interesting system remain poorly understood. First, the issue of simulating the formally complete monolayer at zero spreading pressure has never been investigated. Although believed to be modest in previous simulations,[6−8,10,12] any planar stress present in phase transition simulations can, and in fact does, dramatically affect the system dynamics.[11] Second, molecular flexibility was not properly accounted for in previous studies. Third, when the flexibility is properly modeled, it creates the need for surprisingly
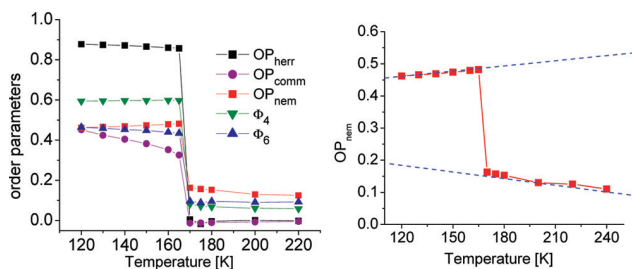
Figure 1. Various order parameters as functions of temperature (left panel) and OP_{nem} (right panel) with emphasis on the pre- and post-transition slopes.

long simulation times—equilibration plus production runs on the order of 50 to 220 ns—that have never been carried out. It is mainly the issues presented above that motivate the study reported here, which entails extensive massively parallel molecular dynamics simulations. A confluence of long equilibration times and the demand for robust statistics have resulted in the project's length of ca. 10 CPU years.

II. Computational Aspects

The all-atom description of hexane molecules used in the present study comes from the Brookhaven Protein Data Bank (PDB).[16] The initial low-temperature configuration has an important departure from the previous ones.[6−12] There are $N = 104$ hexane molecules in a herringbone arrangement atop a six-layer 68.16 Å × 68.88 Å graphite structure. Such a structure has virtually no spreading pressure. Molecular dynamics simulations were run for a total of 40 ns of stabilization followed by at least 100 ns of production runs. All other simulation parameters, including the standard CHARMM22 interaction parameters,[14] were exactly the same as those in a

*Corresponding authors.
(1) Krim, J.; Suzanne, J.; Shechter, H.; Wang, R.; Taub, H. *Surf. Sci.* **1985**, *162*, 446.
(2) Newton, J. C. Dissertation, University of Missouri-Columbia, 1989.
(3) Taub, H. In *NATO Advanced Study Institutes, Series C: Mathematical and Physical Sciences*; Long, G. J., Grandjean, F., Eds.; Kluwer: Dordrecht, 1988; Vol. *228*, p 467.
(4) Hansen, F. Y.; Taub, H. *Phys. Rev. Lett.* **1992**, *69*, 652.
(5) Hansen, F. Y.; Newton, J. C.; Taub, H. *J. Chem. Phys.* **1993**, *98*, 4128.
(6) Velasco, E.; Peters, G. H. *J. Chem. Phys.* **1995**, *102*, 1098.
(7) Peters, G. H.; Tildesley, D. J. *Langmuir* **1996**, *12*, 1557.
(8) Peters, G. H. *Surf. Sci.* **1996**, *347*, 169.
(9) Herwig, K. W.; Wu, Z.; Dai, P.; Taub, H.; Hansen, F. Y. *J. Chem. Phys.* **1997**, *107*, 5186.
(10) Roth, M. W.; Pint, C. L.; Wexler, C. *Phys. Rev. B* **2005**, *71*, 155427.
(11) Pint, C. L.; Roth, M. W.; Wexler, C. *Phys. Rev. B* **2006**, *73*, 85422.
(12) Connolly, M. J.; Roth, M. W.; Wexler, C.; Gray, P. A. *Langmuir* **2008**, *24*, 3228.
(13) Firlej, L.; Kuchta, B.; Roth, M. W.; Wexler, C. 2009, arXiv:0902.4422v1. arXiv.org e-Print archive. http://arXiv.org/abs/0902.4422.

(14) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; States, S.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187. See also http://www.charmm.org.