

Phase transitions in hexane monolayers physisorbed onto graphite

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We report the results of molecular dynamics simulations of a complete monolayer of hexane physisorbed onto the basal plane of graphite. At low temperatures the system forms a herringbone solid. With increasing temperature, a solid-to-nematic liquid-crystal transition takes place at $T_1=138\pm 2$ K followed by another transition at $T_2=176\pm 3$ K into an isotropic fluid. We characterize the different phases by calculating various order parameters, coordinate distributions, energetics, spreading pressure, and correlation functions, most of which are in reasonable agreement with available experimental evidence. In addition, we perform simulations where the Lennard-Jones interaction strength, corrugation potential strength, and dihedral rigidity are varied in order to better characterize the nature of the two transitions. We find that both phase transitions are facilitated by a “footprint reduction” of the molecules via tilting and to a lesser degree via creation of gauche defects in the molecules.

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I. INTRODUCTION

The physical adsorption (physisorption) of atoms and molecules onto a substrate to form a quasi-two-dimensional (2D) film has resulted in the observation of a rich variety of behavior not realized in the system’s corresponding three-dimensional (3D) or “bulk” state.

Among the species used as adsorbates, alkanes are of considerable interest because of their technological importance (e.g., as lubricants), and because they are among the simplest families of molecules of compounds whose members differ mainly in their lengths. In fact, straight-chained n alkanes represent a fine balance between complexity (i.e., many internal degrees of freedom, which also affect the interaction *between* molecules) and the simplicity of their structure (as compared to other organic molecules). In fact, over the past decades there has been a constant and renewed effort to better understand the adsorption of alkanes over a variety of substrates. Among the substrates used for physisorption studies, graphite, with its excellent mechanical stability, availability, and symmetry, has proven to be one of the best choices. A considerable amount of experimental, theoretical, and computational work has, thus, been devoted to these studies.

Hexane on graphite was first studied by Krim *et al.*¹ using low-energy electron diffraction (LEED) as well as neutron diffraction. For submonolayer coverage a uniaxial-incommensurate (UI) herringbone phase is observed below approximately $T=151$ K, where a first-order melting transition is found (but note that a determination of the molecular orientations was not possible). At low temperatures, as the coverage is increased, the UI phase evolves continuously into a $2\times 4\sqrt{3}$ commensurate structure at completion. More recently, Taub³ completed extensive neutron^{2,3} and x-ray² diffraction studies of hexane on graphite for submonolayer,² monolayer,²⁻⁶ and multilayer² coverages. Their findings indicate that at low temperatures a complete monolayer forms a

commensurate herringbone structure which evolves with increasing temperature into a rectangular centered solid/liquid coexistence region by approximately 150 K and melts at around 175 K.²⁻⁶ For submonolayer coverages, these authors proposed a structure corresponding to a UI phase comprised of commensurate regions separated by low-density fluid filled domain walls.²

In the 1990s, Hansen and co-workers reported studies combining molecular dynamics (MD) computer simulations with neutron and x-ray diffraction studies of butane and hexane on graphite at monolayer completion.^{4,5} Experimentally, butane melts abruptly at around $T=116$ K, directly from a solid, commensurate, rectangular-centered herringbone (HB) phase into a liquid. Orientational ordering about the surface normal is lost through rotation about the center of mass, which is simultaneous with melting. Hexane, on the other hand, undergoes a loss of translational order at about 150 K into a phase with short-range order that is thought to involve mobile rectangular-centered (RC) islands within a fluid. Then, at around $T=175$ K the system melts into a fluid.

The computer simulations of Hansen and co-workers^{4,5} showed that, for hexane, the internal formation of gauche defects coupled with out-of-plane tilting is concurrent with melting. The necessary creation of in-plane room by either gauche defects or tilting at the onset of melting is referred to as a “footprint reduction” mechanism. These simulations showed, furthermore, that the nature and temperature of the transition is very sensitive to the presence of gauche defects, as the melting temperature rises drastically when gauche-defect formation is suppressed. However, the resulting melting temperature of a hexane monolayer was found to be 222 K, significantly different from the experimental value of 175 K. This discrepancy was addressed in a series of MD simulations of hexane on graphite by Velasco and Peters⁷ who found a better agreement with experimental values of the melting temperature when a considerably lower adsorbate-interaction strength was used, and under those