

**Behavior of hexane on graphite at near-monolayer densities: Molecular dynamics study**

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We present the results of molecular-dynamics studies of hexane physisorbed onto graphite for eight coverages in the range  $0.875 \leq \rho \leq 1.05$  (in units of monolayers). At low temperatures, the adsorbate molecules form a uniaxially incommensurate herringbone solid. At high coverages, the solid consists of adsorbate molecules that are primarily rolled on their side perpendicular to the surface of the substrate. As the coverage is decreased, the amount of molecular rolling diminishes until  $\rho=0.933$ , where it disappears (molecules become primarily parallel to the surface). If the density is decreased enough, vacancies appear. As the temperature is increased, we observe a three-phase regime for  $\rho > 0.933$  (with an orientationally ordered *nematic* mesophase); for lower coverages, the system melts directly to the disordered (and isotropic) liquid phase. The solid-nematic transition temperature is very sensitive to coverage, whereas the melting temperature is quite insensitive to it, except for at low coverages where increased in-plane space and, ultimately, vacancies soften the solid phase and lower the melting temperature. Our results signal the importance of molecular rolling and tilting (which result from the competition between molecule-molecule and molecule-substrate interactions) for the formation of the intermediate phase, while the insensitivity of the system's melting temperature to changing density is understood in terms of in-plane space occupation through rolling. Comparisons to experimental results are discussed.

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**I. INTRODUCTION**

The study of quasi-two-dimensional (2D) systems (such as atoms and molecules adsorbed onto a surface) has become the focus of much activity over the past few decades. In particular, the adsorption of alkanes has been of interest because of the many applications that these simple hydrocarbons have to commercial lubricants and adhesives. Specifically, hexane ( $C_6H_{14}$ , or  $CH_3-(CH_2)_4-CH_3$ ) is a member of the family of straight-chained *n*-alkanes whose members differ only in their length ( $C_nH_{2n+2}$ , or  $CH_3-(CH_2)_{n-2}-CH_3$ ). This family is simple in structure compared to other organic molecules, yet they still exhibit many internal degrees of freedom, thus, representing an interesting challenge to study.

When modeling adsorption of molecules, such as alkanes, there are a large variety of possible surfaces that could be used to study the phases and dynamics of the adsorbed system. Arguably, graphite is one of the best candidates to implement in such an endeavor as a substrate because it exhibits good mechanical stability, is very readily available, and has a high degree of symmetry. As a result of its properties, there has been a wealth of experimental and theoretical work that has been completed on systems involving graphite.<sup>1,2</sup> Hexane on graphite has been studied experimentally<sup>3-6</sup> and computationally,<sup>6-12</sup> and details of its behavior may be found in the appropriate references. In essence, 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 fairly accurately. However, recent molecular-dynamics (MD) simulations<sup>12</sup> of monolayer hexane on graphite found an extended orientationally ordered, "nematic," phase with a transition from a commensurate herringbone solid to an orientationally ordered liquid crystal at about  $T=138$  K. This phase persists until about  $T=176$  K, where the system then melts into an isotropic fluid. Moreover, the results of simulations<sup>12</sup> suggest that in-plane room has a very strong influence on molecular rolling and tilting, in turn, affecting various phase transitions exhibited by the system.

Although simulations lend much insight into the physics taking place in the real system, they clearly have shortcomings that require extensive study in order to facilitate their understanding and, ultimately, their improvement. Therefore, it is of considerable interest to study this system at coverages somewhat different from the previous extensive studies performed at completion.

Specifically, the purpose of this work is to: (i) study the continuous evolution of some of the interesting properties of monolayer hexane on graphite as the density is varied from completion; (ii) gain an understanding of the phase transitions and phases of near-monolayer hexane on graphite; (iii) study the effects that added or reduced in-plane room has; (iv) further the study of the properties of the nematic (liquid-crystal) phase that was observed at monolayers,<sup>12</sup> and understand the driving mechanism for the solid-to-nematic phase transition; (v) compare the near-monolayer results to hexane at full-monolayer coverages,<sup>12</sup> thereby placing the complete monolayer results in a broader context; and (vi) better understand the limitations of the models used for these simulations in view of the partial disagreement with experiments.