

Simulated effects of odd-alkane impurities in a hexane monolayer on graphite

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(Received 4 February 2005; revised manuscript received 28 December 2005; published 3 March 2006)

We present the results of molecular-dynamics simulations of odd-alkane impurities present within the hexane (even alkane) monolayer. We simulate various temperatures at approximately 3%, 5%, 10%, and 15% impurities of propane (C_3H_8), pentane (C_5H_{12}), heptane (C_7H_{16}), nonane (C_9H_{20}), and undecane ($C_{11}H_{24}$), each having a low-temperature solid phase belonging to a different space group as compared to hexane, to study the effects of impurities on the various phases and phase transitions for hexane monolayers that are well characterized through previous experimental and theoretical work. Based upon preferential adsorption, we provide two emerging pictures of how impurities could affect the monolayer, for impurity chain lengths longer and shorter than that of the hexane molecules. We provide evidence that impurities in the monolayer, even in small proportion to the hexane, could induce significant changes in the phase behavior and phase transitions, and we propose that because of the size of pentane with respect to hexane, and the nature of the solid herringbone (HB) phase, pentane impurities give the best representation of the phase behavior observed for the pure hexane monolayer. We find that impurities with chain lengths longer than hexane tend to distort the sublattices of the solid HB phase, and hence lead to a phase transition into an “intermediate” phase significantly prior to that observed for a pure hexane monolayer. We discuss possible application of our results toward experiment, as we find that extremely small amounts of impurities in the monolayer often induce significant changes in phase-transition behavior.

DOI: [10.1103/PhysRevB.73.115404](https://doi.org/10.1103/PhysRevB.73.115404)

PACS number(s): 68.43.-h, 68.35.Rh, 64.70.-p, 71.15.Pd

I. INTRODUCTION

The study of molecules adsorbed onto surfaces has been a topic of considerable interest in recent years due to advances in methods of studying these systems experimentally as well as the theoretical techniques and increasing computer performance that allows simulations to be an excellent tool for investigation into these systems as well. Of particular interest in such studies has been the family of linear short-chained n -alkanes, whose unique combination of a molecule with a linear chain length (and hence significant number of degrees of freedom) and properties that are still extremely useful for industrial applications (such as lubrication, adhesion, wetting on the surface, etc.) has motivated several studies of adsorption of monolayers and multilayers of these alkanes physisorbed onto the surface.

Since the n -alkanes are abundant in nature in multicomponent mixtures (such as various petroleum products), their usefulness in industrial applications is usually limited to primarily those applications involving such mixtures, as these are much cheaper and more readily available than pure alkanes. However, pure alkane layers usually tend to be the focus of experimental studies because of the complexity that is introduced by involving combinations of alkanes on a surface. Therefore an understanding of how the dynamics and energetics of the phases and the phase transitions in mixtures differ from those in pure monolayers is of fundamental interest to both of these.

In this study, we investigate the presence of odd impurities in an even alkane (hexane) monolayer. The hexane monolayer is specifically chosen due to the significant amount of both experimental and theoretical work that has been previously completed regarding the study of the phases and phase behavior the monolayer exhibits. Previous experi-

mental work completed over hexane monolayers^{1–3} has indicated that the monolayer arranges in a solid herringbone (HB) phase at low temperatures. This phase then continues until $T=151$ K where experiment reports that commensurability is lost with the substrate and the phase behavior involves what diffraction patterns suggest to be rectangular-centered (RC) islands coexisting with a liquid phase. This persists until approximately 176 K where a melting transition takes place into an isotropic fluid. Further experimental work⁴ over hexane monolayers and multilayers, as well as several other short-chained even alkanes, reports the same type of behavior, and reports that for multilayers of short-chained n -alkanes, the solid-liquid coexistence region corresponds to what these authors refer to as a solid monolayer persisting above the bulk melting point.

Simulations conducted in recent years^{5–11} have confirmed many of these experimental observations. In particular, most recent simulations¹¹ of hexane monolayers indicate the presence of an “intermediate” phase with nematic order (or RC order) that exists between the solid HB phase and the fluid phase. However, simulations predict this transition (into the intermediate phase) occurs at approximately 138 K, and it is believed that the absence of a coexistence region in simulations is largely due to the finite size of systems available to simulations for study.

The impurities that are studied in the hexane monolayer involve chain lengths that vary in length from propane (C_3H_8) to undecane ($C_{11}H_{24}$). With the exception of propane, whose low-temperature phase behavior is not yet fully understood,¹² the odd-alkanes studied occupy a different two-dimensional (2D) space group¹³ (cm , involving a low-temperature rectangular-centered solid phase) than the even alkanes⁴ (pgg , involving a low-temperature solid HB phase).