

Molecular dynamics simulations of submonolayer hexane and pentane films on graphite

M.W. Roth^{a*}, M. Kaspar^a, Carlos Wexler^b, L. Firlej^c and B. Kuchta^d

^aDepartment of Physics, University of Northern Iowa, Cedar Falls, IA 50614, USA; ^bDepartment of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA; ^cLCVN, Université Montpellier 2, 34095 Montpellier, France; ^dLaboratoire Chimie Provence, Université de Provence, 13396 Marseille, France

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We present results of molecular dynamics computer simulations of hexane (C₆H₁₄ or C6) and pentane (C₅H₁₂ or C5) adlayers physisorbed onto a graphite substrate, for various submonolayer coverages. The hexane and pentane molecules incorporate explicit hydrogens and the graphite is modelled as a six-layer all-atom structure. Even though C6 and C5 have different structures at monolayer completion, both systems generally behave similarly in the submonolayer regime and results are in reasonable agreement with experiment for both systems. Specifically, there are four distinct topological regimes involving empty space: at densities closest to full coverage, there are large domains with individual vacancies, then with decreasing density, large vacancy patches appear first, followed by the formation of connected networks of smaller domains with multiple orientations that ultimately separate into individual patches. The energetics and melting behaviour of all systems are readily understood within the framework of the topology presented at various densities.

Keywords: simulations; hexane; pentane; submonolayer; graphite

1. Introduction

Understanding the behaviour of carbon compounds – the compounds of life and fossil fuels among other things – is part and parcel to our ability to better control, care for and utilise our environment. Hydrocarbons are molecules that contain only hydrogen and carbon, and of them alkanes (with the general chemical formula C_nH_{2n+2}) are probably the most widely used – in heating, lighting, transportation, machinery, detergents, lubrication, refining, adhesives and many others. It is this ubiquitous usefulness that motivates us to choose them to study. As a chemical family, they are a nice compromise of simplicity (as far as organic molecules go) and complexity (their internal degrees of freedom can affect the overall system behaviour). In their conventional bulk (three-dimensional) regime, many physical properties of alkanes can be fairly precisely related to their molecular structures. However, they behave in interesting and counter-intuitive ways while physisorbed onto surfaces. It is because of the modification of system interactions through a strong substrate–adatom interaction that the molecules interact more strongly with each other than they do in the bulk. As a result, such quasi-two-dimensional systems exhibit a rich landscape of behaviour not realised in the system's corresponding bulk state.

Short alkanes ($n < 12$) adsorbed onto a graphite substrate behave markedly different when n is odd and even. At monolayer coverage, odd alkanes form a low-temperature solid rectangular-centred (RC) phase that is commensurate for $n = 7$ and 9 but not for $n = 5$ [1–6].

X-ray and neutron diffraction studies of pentane and heptane on graphite at a coverage of 1.01 monolayers concluded that combinations of rotated RC and herringbone phases are present [2].

For pentane near monolayer completion, a sharp melting transition has been found at $c.99–105$ K [3–6]. Furthermore, it appears that the solid monolayer does not coexist with a bulk fluid phase, but melts very near to the bulk melting temperature of pentane [3]. The issue of solid–fluid coexistence is important and in fact can help validate the thermodynamic accuracy of molecular simulations. With that in mind, the most recent study on pentane concluded that melting for 1.01 monolayers takes place from an RC solid at $T_m = 99$ K and presents a coexistence of dense clusters with the fluid through a temperature range of about 30 K above melting [6]. A similar effect has been observed for C6 on graphite but over a shorter temperature range after melting [7–12].

Hexane on graphite was first studied by Krim et al. [7] using both the low-energy electron diffraction and the neutron diffraction. For submonolayer coverage ($\rho \sim 0.93$) and low temperature, a uniaxial incommensurate (UI) herringbone phase was observed, melting at about $T = 151$ K in a first-order transition; however, a determination of the molecular orientations was not possible. As the coverage is increased, the UI phase evolves continuously into a $2 \times 4\sqrt{3}$ commensurate structure at completion. More recently, Taub and co-workers [7–12] completed extensive neutron and X-ray diffraction studies of hexane

*Corresponding author. Email: rothm@uni.edu