

Structural and Phase Properties of Tetracosane (C₂₄H₅₀) Monolayers Adsorbed on Graphite: An Explicit Hydrogen Molecular Dynamics Study

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We discuss molecular dynamics (MD) computer simulations of a tetracosane (C₂₄H₅₀) monolayer physisorbed onto the basal plane of graphite. The adlayer molecules are simulated with explicit hydrogens, and the graphite substrate is represented as an all-atom structure having six graphene layers. The tetracosane dynamics modeled in the fully atomistic manner agree well with experiment. The low-temperature ordered solid organizes into a rectangularly centered structure that is not commensurate with underlying graphite. Above $T = 200$ K, as the molecules start to lose their translational and orientational order via gauche defect formation a weak smectic mesophase (observed experimentally but never reproduced in united atom (UA) simulations) appears. The phase behavior of the adsorbed layer is critically sensitive to the way the electrostatic interactions are included in the model. If the electrostatic charges are set to zero (as for a UA force field), then the melting temperature increases by ~ 70 K with respect to the experimental value. When the nonbonded 1–4 interaction is not scaled, the melting temperature decreases by ~ 90 K. If the scaling factor is set to 0.5, then melting occurs at $T = 350$ K, in very good agreement with experimental data.

Introduction

Computer studies of thermodynamic properties of intermediate-length alkanes physisorbed on solid substrates have for many reasons become a very active field of research. From a practical point of view, interfacial properties of n-alkanes are relevant to many widespread applications and problems (e.g., lubrication, adhesion, catalysis, etc.). Alkanes can also be considered to be simplified model materials that help us to understand similar but larger systems such as polymers, lipids, and proteins. In fact, on the one hand they possess a degree of complexity and are large enough to exhibit features relevant to linear molecules. On the other hand, they are still sufficiently small to be tractable in computer simulations such as molecular dynamics or Monte Carlo methods.

Nearly all extensive computer simulations of adsorbed alkane layers employ the united atom (UA) approximation. In this approach, methyl (CH₃) and methylene (CH₂) are represented as spherical pseudoatoms that replace the respective groups in the molecule. Of course, such an approximation saves a considerable amount of computational time and has led in the past to valuable progress in our understanding of the structure and dynamics of the adsorbed alkane layers (at the microscopic level). In particular, UA-based MD simulations have provided important information on the mechanism of melting of intermediate-length n-alkanes on graphite. They have shown evidence that the rotation of molecules out of the adsorption plane during monolayer melting (the “footprint” reduction) leads to a simultaneous loss of both intramolecular and translational order in the system. Such a cooperative process is related to an abrupt increase in the number

of gauche defects within the central region of the alkane chain.¹ Such an observation seems to be a key feature of melting. It suggests that melting occurs because of a strong correlation between deformations of the alkane (so-called chain melting) and the translational disorder (lattice melting).² As a consequence, the melting temperature must strongly depend on the molecular stiffness,^{1,2} which also plays a central role in this work and is discussed later in this article.

However, the UA approximation has several important shortfalls. Some of them directly result from the neglect of the exact hydrogen location along the molecular chain, and they have been enumerated in the recent paper by Connolly et al.³ In particular, the authors have shown that the lack of explicit hydrogen atoms leads to an unrealistic rolling of molecules out of the adsorption plane. Such behavior may result in an erroneous analysis of both the structural and phase behavior of the system.³

In addition, in many situations when the UA model has been used, electrostatic terms in energy calculations have been totally neglected.^{4,5} Such a simplification seems to be justified according to the recent paper by Song et al.⁶ that showed that electrostatic interactions have a negligible impact on most properties of alkanes. However, ab initio calculations indicate significant charge separation in C–H bonds (0.3–0.6 D). According to that result, the OPLS-AA models include partial charges on both carbon and hydrogen in the molecules. Although these non-negligible bond dipoles noticeably affect the interaction energies for a given configuration of two molecules, orientational averaging tends to reduce their importance. In larger alkanes, when symmetry is

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