

Molecular simulations of intermediate and long alkanes adsorbed on graphite: Tuning of non-bond interactions

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Abstract The interplay between the torsional potential energy and the scaling of the 1–4 van der Waals and Coulomb interactions determines the stiffness of flexible molecules. In this paper we demonstrate for the first time that the precise value of the nonbond scaling factor (SF)—often a value assumed without justification—has a significant effect on the critical properties and mechanisms of systems undergoing a phase transition, and that, for accurate simulations, this scaling factor is highly dependent on the system under consideration. In particular, by analyzing the melting of n-alkanes (hexane C₆, dodecane C₁₂, tetracosane C₂₄) on graphite, we show that the SF is not constant over varying alkane chain lengths when the structural correlated transformations are concerned. Instead, monotonic decrease of SF with the molecular length drives a cross-over between two distinct mechanisms for melting in such systems. In a broad sense we show that the choice for SF in any simulation containing adsorbed or correlated long molecules needs to be carefully considered.

Keywords Alkanes on graphite · Long molecules on graphite · Molecular dynamics · Scaling of CHARMM parameters · Surface phase transitions

Introduction

During the last half century computational physics has grown in scope and importance to a point where it became a third part added to the traditional divisions of experimental and theoretical physics. Computer simulations have brought remarkable insight into the behavior exhibited by complex systems with large numbers of degrees of freedom. Recent advances in computer power and algorithms have facilitated detailed simulations of systems comprised of thousands to millions of atoms, for periods of ns to μ s, permitting detailed pictures of diverse phenomena, ranging from simple atomic processes to complex behavior of biological macromolecules.

The integrity of the results of computer simulations of any real system depends, however, on the quality of the force fields in the theoretical model. This becomes critically important when modeling large systems of flexible molecules, such as biomolecules (especially proteins or lipids) or polymers, for which alkanes are prototypes. In such systems, correlations between internal and external degrees of freedom determine the local conformational stability of molecules (*i.e.*, folding). Conversely, the same correlations affect intermolecular correlated processes (*e.g.*, phase transitions). Being able to correctly account for the energy and ordering of conformations is essential if force field methods are to be considered as predictive.

Recently, a number of auto-assemblies for alkanes on graphite have been studied by molecular dynamics (MD) methods [1–8]. Two important conclusions emerged from

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