Predicted Effects of Confinement on the Melting Transition in Krypton-Argon Adlayers

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ABSTRACT

We report the results of (N,ρ,T) Molecular-Dynamics computer simulations of krypton-argon mixtures physisorbed between two graphite sheets. Three novel aspects of the system's behavior emerge from this study. To begin with, new high-temperature commensurate solid phases for both argon and krypton as a result of confinement are predicted, as well as a family of confinement-induced solid-liquid phase transitions. In addition, we observe that the melting temperature of the system can be adjusted within a given range by the graphite sheet spacing. Finally, in the case of argon-krypton mixtures, certain temperatures and sheet spacings result in almost complete impurity extraction.

I. INTRODUCTION

For decades now researchers have studied the behavior of atomic and molecular species physisorbed onto graphite. For rare gas adsorbates such as krypton and argon the phase diagrams have been mapped out rather thoroughly on both experimental and computational fronts. Although the discovery of fullerenes and nanotubes has spurred scientific interest into adsorption of rare gasses onto new geometries, comparatively little has been done to study the phase transitions of physisorbed systems in confined geometries [1-4].

Both the nature and temperature of melting for commensurate monolayers on graphite (including krypton) are highly sensitive to density fluctuations at completion (an area density of 0.0636 atom/Å^2 for a monolayer) and density fluctuations in this regime are in turn strongly coupled to the vertical (out-of-plane, or $\hat{z}$) excursions of the adsorbed species. It follows, then, that the vertical boundary conditions for the system play an important role in melting. The purpose of this study is to simulate the effects of altering the $\hat{z}$ boundary conditions on physisorbed rare gas layers by modeling adsorption of the krypton-argon mixtures between two graphite sheets. The species are chosen as such because both krypton [5-20] and argon [21-33] have been studied as single layers on graphite extensively and they exhibit markedly different adsorption behavior, thus having a high potential to show the effects of selectivity imposed by the presence of the second sheet. New high-temperature commensurate solids and new confinement-induced solid-liquid phase transitions for both krypton and argon emerge from this study. As will be discussed later, this is a result of the adlayer's being forced into a region where atoms' lateral interaction with the graphite surface is very strong. Secondly, and not entirely surprisingly, we find that the melting transition in both nature and temperature can be fine-tuned purely by the spacing of the graphite sheets. Moreover we are able to explain the dependence of the melting transition on sheet spacing simply as an outcome of competition between confinement and attraction with the upper graphite sheet. Lastly, we present the results for a 50% argon-krypton mixed adlayer and observe that for certain graphite spacings and temperatures, the upper sheet adsorbs almost pure argon, suggesting that with some experimental refinement, impurity extraction can be attained.