Calculated phase boundary including corrugation effects for krypton layers physisorbed onto spherical substrates

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A molecular-dynamics technique is utilized to calculate the melting curve of submonolayer and complete layers of krypton atoms physisorbed onto a spherical substrate. Two models of the substrate are used. In the first model the substrate is treated as a spherical continuum whose differential elements interact with krypton atoms via Lennard-Jones (LJ) potential. Hysteresis is present in the melting transition for low coverages, which disappears as the melting becomes more gradual near complete coverage. The melting temperature at completion is very sensitive to second-layer promotion, which in turn depends strongly on the radial boundary conditions. In the second model the melting transition is also examined for 100 Kr atoms adsorbed onto spheres that exhibit corrugation in their potential interactions with the asdorbate. Addition of corrugation in the form of a C_{60} lattice effectively serves to merely raise the average LJ substrate sphere density slightly and leave the melting transition unaffected, but replacing the LJ sphere with a cubic carbon lattice raises the melting temperature by about 3 K (4.6%) while dramatically affecting the desorption behavior of the adlayer and lowering its spatial order. Various bond-orientational distributions and snapshot configurations are employed in understanding the completion process.

I. INTRODUCTION

In a previous article[1] we reported in detail the computational approach and parameters calculated in the study of the properties and melting transition of krypton atoms physisorbed onto a spherical Lennard-Jones (LJ) substrate treated as a continuum (referred to as an LJ sphere). We have extended our earlier work on Kr physisorption by examining the melting transition for layers of various adsorbate coverages on 10-Å spheres and also the effects of corrugation of the spherical substrate. We calculate the melting curve of the submonolayer and complete monolayer phase diagram for krypton layers absorbed onto LJ spheres, use various bond-angle distributions to link the phase diagram to the system's dynamics, better understand the process of monolayer completion, make comparisons of the results for spherically absorbed systems in this study with those for planar systems, and explore the effects of corrugation of the spherical substrate on the melting behavior of the system. Our study anticipates the results of experimental investigations of inert-gas physisorption on physical substrates with curvature, e.g., C_{60} and other carbon cages.

II. COMPUTATIONAL APPROACH

The computational method utilized for this work has been discussed previously[1] and will be summarized here. We utilize an LJ pair potential to model the krypton-krypton interactions and an integrated LJ potential[1] to describe the krypton-sphere–substrate interactions. In the first model of the substrate-krypton interaction we employ an integrated LJ potential,[1] treating the substrate as a spherical continuum. We use an $(N, \rho=N/4\pi R^2, T)$ molecular-dynamics (MD) scheme. Here N is the total number of Kr atoms in the simulation adsorbed onto a Lennard-Jones substrate sphere of radius R and T is the temperature in degrees Kelvin. It should be noted that the "projected density" ρ is not the same as the monolayer density. The latter is given by the total number of asdorbate atoms on the substrate sphere divided by the surface area of the sphere that the adsorbate occupies on the average. We use shrinking-sphere initial conditions when needed, where the Kr atoms are initially placed randomly on the surface of a "starting substrate sphere" of radius $R_0 > R$. This is to ensure that the Kr atoms are not placed unphysically closely on the smaller substrate sphere of radius R. As equilibration proceeds the larger substrate sphere shrinks linearly in simulation time to the desired radius R (which is the radius of the substrate we intend to study). When soft reflecting shell boundary conditions are employed during equilibration as well as in production runs, the shell is placed at $R_b = R + ah$. h is a radial altitude above the surface of the substrate sphere where the reflecting wall is placed, and a is a dimensionless multiplier. $a=2$ is most widely used, but $a=1.1$ is employed to calculate the melting temperature at completion for reasons that will be discussed later. We utilize $h=2.7$ Å and a range of R_0 between 10 Å (where no shrinking is needed) and 14.5 Å and anywhere from 2×10^5 to 10^6 equilibration steps. The temperature is held constant by velocity rescaling and a standard velocity Verlet method with a time step $\Delta t = 0.004$ ps is utilized to integrate the equations of motion. Production times range from 0.08 to 4 ns.

In the second model of the spherical substrate we introduce two different forms of corrugation of the substrate potential. The general form of the potential for both corrugations of the substrate is as follows. M carbon atoms are placed on or interior to the LJ continuum sphere surface and