

Predicted properties and melting transition of krypton layers physisorbed onto Lennard-Jones spheres

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We report the results of constant-temperature, constant-density, molecular-dynamics simulations of the melting transition of Kr atoms physisorbed onto small Lennard-Jones spheres. Adlayer depletion takes place when free boundary conditions are used but utilization of a soft reflecting shell results in a broad melting transition at around $T=65$ K without any appreciable hysteresis. We introduce structural and bond-orientational parameters and utilize thermodynamic parameters to monitor the behavior of the system. The spherical geometry causes compression of the neighbor distances with respect to those for the corresponding planar case, causing enhanced interaction of the neighbor shells via interstitials/vacancies, the nature of which is further elucidated using the bond-orientational information. Quantities related to the radial degree of freedom change slowly during melting, and bond-orientational order of the Kr lattice persists well into the fluid.

I. INTRODUCTION

Many experimental, computational, and analytical studies of two-dimensional (2D) and quasi-2D phases and phase transitions have been completed.¹ By far and large, these studies employ the following: (1) theoretical particles that are modeled through their potentials with no real counterparts or (2) models of atoms/molecules that are either physisorbed onto some corrugated substrate like graphite or without structure and “floating” in a layer. In both kinds of studies a planar geometry is used. In fact, many computer simulation techniques entail the modeling of an *infinite* planar system through periodic boundary conditions of some sort with the topology of a toroid. Across the different analytical melting theories and computer simulation (or computer “experiment”) results, there is a central theme that correlations, fluctuations, and lattice topology are of central importance to melting. It is reasonable to expect that the study of systems where the relationship between neighbor spacing and neighbor index is different from those in the planar case would foster further insight into the behavior of the phases and phase transitions. Such is the situation for physisorption onto a curved substrate. The central purpose of this work is to model the phases and the melting transition of a system of atoms physisorbed onto a sphere. Specifically, we seek to tie the spherical geometry to the dynamics of the system but not to determine the transition order or whether a particular analytical melting theory is supported (see Refs. 2–5, for example, for the KTHNY theory). This paper will address our computer simulation techniques in detail, introduce order parameters and various quantities used to monitor the system’s behavior, and present the results of one representative case of melting. A companion paper planned to follow will report and discuss the results for the melting line on the phase diagram for this system.

Since the phase diagrams of certain rare gases (such as Kr) physisorbed onto graphite have been mapped out fairly well by many different methods,^{6–9} we choose to model a family of systems where various numbers of Kr atoms are

physisorbed onto a Lennard-Jones sphere. The sphere (to be discussed in detail later) may be thought of as a solid non-polarizable ball of uniform density whose differential elements interact with any Kr atom via a Lennard-Jones potential. We choose the potential parameters to be those of carbon-krypton simply because carbon is a widely used substrate in experimental work. The density of the ball is considered to be an adjustable parameter, then, and the effect of varying it is also examined. The spheres are relatively small ($R=10$ Å) for four reasons. The first is that we desire to be in a region where the curvature will be noticeable. This is the case because the sphere radius is between two and three times the nearest-neighbor spacing of the adsorbate and the first through fourth neighbors are able to fit on one hemisphere. The second reason is that we are in the proper size regime to be able to make direct comparisons and contrasts with the recent related work summarized in a paper by Pérez-Garrido and Moore.¹⁰ However it is stressed that a good understanding of this system will entail a thorough study of the scaling of the results with system size (another project in and of itself), including very large numbers of atoms (on the order of at least 10^6). The third reason is that corresponding experimental systems with comparable sizes (exohedral Fullerene complexes, for example) should be possible. The final reason is that this computing effort entailed using mini-computers for the calculations, and it was felt that examining large systems would take a prohibitively long time with the available resources.

The notion of studying finite-size scaling is especially interesting in light of the recent work of Pérez-Garrido and Moore,¹⁰ who conduct MD simulations of the melting transition of r^{-12} repulsive particles on the surface of spheres. Although their study focuses mainly on the order of the transition, it is useful to summarize it here. Their system is strictly 2D with no radial degree of freedom, and they examine various densities with 72, 122, and 272 particles. Spherical geometry requires that lattice defects be present in the solid, but such a thing could work in favor of simulations on spheres and give results closer to the thermodynamic limit for much smaller systems than in planar studies because sys-