Understanding Layer Promotion and Its Relationship to Melting in Krypton on Graphite Using Artificial Constraints

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ABSTRACT

Constant particle number, density and temperature (N, ρ, T) Molecular-Dynamics simulations are used to study second layer promotion and melting in a complete monolayer of krypton deposited onto a graphite substrate. In order to study the vertical behavior of the system and its relationship to melting, artificial horizontal constraints are introduced and their effects are systematically monitored. We find that horizontally confining each atom within an impenetrable cylinder increases the melting temperature T_m and causes melting to be less dramatic. The results also suggest that there is a limiting case of there being no transition for a sufficiently small confining cylinder. Vertical excursions of the adsorbate atoms increase at the onset of melting. The system subsequently goes through a vertical transition with increasing temperature, including second layer promotion followed by extinction of the partial second layer and the presence of a sparsely populated first layer and a large population of desorbed atoms. Horizontal confinement stifles true second layer promotion, causing the atoms to spend less time in the second layer at a given temperature and resulting in a thermal blurring of the adlayer, suggesting that in-plane fluctuations are a necessary part of the layer promotion mechanism. Horizontal confinement also raises the temperature where the vertical transition occurs but does not affect its sharpness or temperature extent.

I. INTRODUCTION

The behavior of krypton physisorbed onto a graphite substrate has been mapped out over the last twenty years [1-16], resulting in a rich and interesting landscape of commensurate phases, sub-monolayer islands, complicated domain wall structures, solid-solid and solid-liquid phase transitions and even a re-entrant fluid. In fact, the general topic of two-dimensional (2D) and quasi-2D melting is still of scientific importance. As the accessibility to an increasing variety of nanosystems grows, adsorption of species such as krypton and other gases in confined and exotic geometries becomes realizable.

There exists a vast body of work regarding the adsorption of rare gases onto pores, which illustrates that confining geometries can strongly influence the physical behavior of an adsorbed system. As a recent example, Monte Carlo computer simulations modeling adsorption of argon (Ar) at 90K in graphite pores of different shapes have been conducted [17]. There seems to be little hysteresis present in the condensation in a square-walled pore but the vertical hysteresis steps become more separated as pore width increases. The pore corners are very attractive adsorption sites and the walls are weaker; the adsorbing surface is effectively heterogeneous. The behavior of the system in the corners is very much like that of one-dimensional systems.

Although there has been significant interest and effort in understanding the behavior of systems physisorbed onto spherical substrates [18-27], systems adsorbed onto Fullerenes [28-34] and even Fullerenes and their interactions [35-46],