Finite computational cell-size effects and the nature of the melting transition of Kr adlayers deposited on graphite

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The recently developed histogram Monte Carlo (MC) method is employed in conjunction with a (N,ρ,T) MC ensemble with periodic boundary conditions to study monolayer and submonolayer melting transitions of a krypton adlayer physisorbed on a graphite substrate. The simulation results are found to depend on the size of the model system. The number of atoms in the MC cell are 900, 400, 324, 289, and 100. The calculated coverage-temperature (ρ,T) phase diagram exhibits three distinct regions: an upper section $(0.7 \lesssim \rho \leq 1)$ in which the melting temperature T_m is very sensitive to ρ, a steep intermediate region $(0.25 \lesssim \rho \lesssim 0.7)$ where $T_m \approx 85$ K and is relatively insensitive to ρ, and a lower part $(0 < \rho \lesssim 0.25)$ in which sensitivity to the density resumes. The $N = 400$ solid-fluid boundary agrees well with the experimental phase diagram, and investigations at $N = 900$ confirm that the $N \gtrsim = 400$ results are closely approaching those of the thermodynamic limit; the $N = 400$ simulation is taken to be a reasonable model of the krypton-graphite system in the $\rho \leq 1$ regime. Departures from such large-N behavior with decreasing N are understood by applying artificial stabilization arguments in the upper and intermediate regimes of the solid-liquid phase boundary and using finite-patch size-effect arguments in the lower regime. An examination of a series of atomic configurations shows that the three separate parts of the phase boundary correspond to different types of melting: vacancy-mediated melting in the upper wing, the melting of a connected atomic network in the intermediate section, and individual patch melting on the lower portion where sensitivity of T_m with ρ resumes.

I. INTRODUCTION

For many years, phase transitions exhibited by two-dimensional (2D) systems have remained topics of curiosity and controversy.[1–8] General theoretical studies include Monte Carlo (MC) and molecular dynamics (MD) computer simulations of idealized systems,[9–18] as well as analytical treatments of the 2D melting transition and various phases incorporated therein[19–21] and other 2D order-disorder transitions.[22,23] Attention has also been paid to the roughening transition[24,25] and the freezing of some model systems and rare-gas monolayers,[26–28] as well as the empirical Lindemann law of melting as related to thermal fluctuations.[29] Of particular interest are krypton adlayers physisorbed on a graphite substrate (Kr-gr). The latter phase diagram has been thoroughly studied.[30]

A recent series of high-resolution x-ray diffraction measurements of Kr-gr (Ref. 31) provides a relatively complete characterization of the phase diagram and various phase structures exhibited by this system. The melting transition was previously studied using calorimetry[32] and x-ray diffuse scattering.[33] A strongly first-order melting transition was found at submonolayer coverages. This transition becomes more second-order-like as the coverage ρ is increased towards completion (in units of 0.0636 atoms/Å^2). The solid-solid commensurate-incommensurate (CI) transition has been studied in detail using He scattering,[34] low-energy electron diffraction (LEED),[35] extended x-ray-absorption fine structure,[36] and x-ray diffuse scattering.[37,38] This transition, which occurs for $\rho > 1$, involves a relatively complicated domain wall structure as well as a reentrant,[31] or domain wall,[30] fluid and is more continuous[33] than the submonolayer transitions. Studies of the fluid-registered solid transition include vapor pressure isotherm work. From these investigations, the transition is determined to be first order up to 115 K.[39] Interesting adsorption isotherm investigations have also been done on Kr-BN (Ref. 40) and the wetting of graphite by Kr and Xe.[41] LEED and reflection high-energy electron diffraction work and H-atom scattering have been conducted on multilayer Kr-gr.[42,43] Attention has also been given to the tricritical point[44] of the Kr-gr system and also to a model incorporating an incipient triple point.[45]

The Kr-gr system has been the subject of considerable theoretical work. The reentrant melting of Kr-gr is rather complicated;[46] a renormalization-group treatment has been put forth[47] using vacancy and domain wall network arguments to explain the melting mechanism. Phonon-dispersion curves have been calculated for incommensurate phases near registry[48] and it is postulated that striped and hexagonal phases may be exhibited by the system.[49] However, Koch, Rudge, and Abraham conclude that a honeycomb network is stabilized with respect to the striped phase by virtue of its ability to breathe.[50] Surface melting as opposed to that of the bulk has been studied[51] and the CI phase transition has been addressed[52,53] and was determined to be continuous.[53] The dynamics and fluctuations of the $(\sqrt{3}\times\sqrt{3})R30°$ solid phase of Kr-gr have also been considered.[54,55] Computer simulations[56] support the observation that the incommensurate melting transition is continuous and a melting mecha-

