Bond-orientational structure and melting signature in krypton physisorbed onto graphite at complete coverage

M. W. Roth
Department of Natural Sciences, Texas A&M International University, 5201 University Boulevard, Laredo, Texas 78041
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A constant-temperature, constant-density molecular-dynamics method is utilized to study the bond-orientational structure and behavior in Kr-gr for the solid, fluid, and melting transition regimes at monolayer completion ($\rho=1$). Several bond-orientational order parameters are introduced to help monitor the system's symmetry behavior, both with respect to the substrate as well as intrinsic. The first- and fourth-neighbor shells exhibit random thermal fluctuations in the absence of significant interaction with other neighbor shells in the solid. The fluctuations magnify as temperature increases, promoting the decay of structural order through melting and into the fluid. The second and third shells exhibit not only thermal fluctuations but also interaction via local shared-lattice defects (vacancy/interstitial pairs) that begin in the low-temperature solid. Multiple-consecutive vacancies or interstitials are found to be far rarer in occurrence than single ones. The monolayer loses all bond-orientational order with respect to the graphite substrate upon melting, while floating (intrinsic) bond-orientational order in the lattice itself is maintained through the high-temperature fluid ($T\approx 250$ K). The intrinsic bond-orientational order of the fluid after melting is insensitive to change in temperature, and therefore local vacancy production does not increase with increasing temperature until the generation of vacancies created by the onset of desorption at $T\approx 200$ K. Finite-size scaling results show that the algebraic exponent for the order parameter OB6 reaches the critical value of $\eta_6=\frac{1}{4}$ simultaneously with the onset of melting around $T=100$ K illustrating that neither a hexatic phase nor an intermediate region is supported in the system in this study. [S0163-1829(98)07319-6]

I. INTRODUCTION

Quasi-two-dimensional (2D) melting continues to be an area of scientific interest. As theoretical and experimental resources have been continuously improving over the past decade, many research efforts in the field are products of renewed interest and revisitation of unresolved issues oftentimes accompanied with conflicting results. Such issues are, among others, the mechanism and order of the 2D melting transition.

Many analytical theories with a diverse variety of results describing possible melting mechanisms have been developed.[1–8] Some theories predict a first-order transition, while others describe second-order or higher transitions. One particular theory credited to Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY) requires a two-stage melting scheme where the solid melts into a hexatic sixfold-symmetric bond-orientationally ordered fluid through dislocation pair unbinding and subsequently makes a transition at a higher temperature to an isotropic fluid via disclination pair unbinding.[4–6] The solid possesses long-range bond-orientational order and quasi-long-range translational order; the hexatic fluid has a short-range translational order but has quasi-long-range bond-orientational order and the isotropic fluid possesses short-range bond-orientational and translational order. In addition to KTHNY theory, Strandburg[2] outlines Chui's theory where grain-boundary related translational-order loss drives the melting mechanism for a single first-order transition. It is mainly from the fact that KTHNY theory is at odds with many experimental and computational results that so much interest has lately been focused on the order of the melting transition and the role of bond-orientational order loss in melting.

Currently, the order of melting and the nature of the melting transitions in real physisorbed systems as well as idealized 2D systems[9,10] are controversial issues. In fact, recent computer simulations and experiments do observe a hexatic phase and two-stage melting in a system of interacting dipoles.[11] Chen, Kaplan, and Mostoller have completed an interesting molecular dynamics (MD) computer simulation of a Lennard-Jones system using as many as 102 400 atoms and observed a metastable hexatic phase existing between solid and fluid.[12] In addition, a smaller system in the solid phase melted when the system was made larger, which is an indication of the influence of long-range correlations being important for second-order phase transitions.[12] On the other hand, new studies of melting in 2D quantum systems report a first-order-type transition.[13] Naidoo and Schnitker conducted a MD study of r^{-12} repulsive particles and concluded that some aspects of first-order melting were present (two-phase coexistence) as well as a hexaticlike phase.[14] This work also examined the sensitivity of results on initial conditions and adequate phase-space sampling. Zollweg[15] and McTague, Frenkel, and Allen[16] studied the bond-orientational behavior of 2D hard disk and r^{-6} repulsive systems, respectively, and presented results for the oriented and isotropic fluids in general agreement with KTHNY theory. Weber and Marx[17] present a study involving scaling of the bond-orientational order parameters and behavior of Binder's cumulant for the hard-disk melting transition that favors a first-order melting transition. Aoiki and Yonezawa[18] report an MD study of sixfold bond-orientational order in a system of repelling spherocylinders. The system went from a solid to a smectic

