# The Nature of the Melting Transition for a Mixed Monolayer System Physisorbed onto Graphite: Argon and Krypton Patch Impurities

M. W. Roth

*Department of Natural Sciences, Texas A&M International University, 5201 University Boulevard, Laredo, Texas 78041*

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A constant density ($\rho = 1$) constant temperature molecular dynamics method with periodic boundary conditions is utilized to examine the melting transition for argon impurity patches embedded in krypton monolayer matrixes (as well as for the complement system) deposited onto graphite for various values of argon impurity fraction $X$. The character and temperature $T_m$ of melting are found to be dependent on the impurity fraction as well as adsorbate topology vis-à-vis which species is the patch impurity and which is the matrix. No phase separation is observed, as the melting temperature of the matrix is coincident with that of the patch in all cases examined. Much of the behavior exhibited by the system in this study can be understood by vacancy formation arguments.

## I. Introduction

For many years the nature of quasi-two-dimensional (2D) melting has been of scientific interest. Although many significant milestones have been made with respect to the understanding of 2D melting[1−16] and in particular that on a graphite substrate,[17−19] there still remain some points of curiosity and debate. As outlined in many well-known works, one prominent theory is the KTHNY theory of melting which ascertains that the transition takes place in two second-order steps, placing an orientationally ordered hexatic phase between the solid and isotropic fluid.[3−6] Other theories predict that the dislocation/disclination KTHNY transitions should be pre-empted by first-order processes such as in the Chui theory for grain-boundary induced melting.[2] In addition some relatively recent computational models of physisorbed atomic systems[20] suggest that lattice defects and vacancies play a central role in determining the nature of melting. Although it is very difficult to determine the order of the melting transition in computer simulations and even in some experiments, the previous observations suggest that there is much that could be learned about melting by examining physisorbed mixtures whose components exhibit different types of melting signatures when pure.

The purpose of this work is to better understand the difference in melting between two such systems, to better understand the dynamics of 2D melting in physisorbed systems, and to further delineate the role of adsorbate topology and boundary conditions in their melting transition. The two systems chosen are argon on graphite (Ar/gr) and krypton on graphite (Kr/gr) not only because they exhibit markedly different melting properties but also because the potentials describing necessary interactions are of the same analytical form and are well-known and the systems are accompanied by a wealth of experimental data.

The phase diagrams of Kr/gr and Ar/gr have been thoroughly studied and mapped out.[19] Briefly put, Kr/gr is commensurate and exhibits a strongly first-order melting transition in the submonolayer regime ($\rho < 1$) which becomes more continuous[21−24] as monolayer completion is approached at $\rho = 1$. The Ar/gr system, on the other hand, is incommensurate and exhibits more continuous melting[25−32] in the submonolayer coverage region up to completion at $\rho = 1.26$.[32] Some of the more recent work makes the interpretation that Ar/gr might melt in a two-stage process.[31]

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