Calculated Melting Behavior of Partial and Complete N_2 Monolayers Deposited on Graphite

R. D. Etters, M. W. Roth, and B. Kuchta

Department of Physics, Colorado State University, Fort Collins, Colorado 80523

(Received 14 March 1990)

The melting transition of N_2 on graphite is examined using a Monte Carlo procedure with several different boundary conditions. On the basis of a simple interpretation of the experimental environment, we are able to explain and accurately reproduce the large change in melting temperature between partial and monolayer coverages.

The melting behavior of two-dimensional (2D) systems has and continues to attract attention,[1-14] partially because of intrinsic interest and because it may provide insight into analogous behavior in 3D. The primary purpose of this work is to examine the melting properties of fractional and complete monolayers of N_2 on graphite. In particular, the large difference in melting temperature between these two cases will be described as a consequence of different boundary conditions. This and other features of the N_2 melting curve are common to a large number of adlayer systems,[6,15] including Kr, He, CH_4, and H_2 on graphite, and the possibility that they derive from a generically common root will be discussed.

At all surface densities up to monolayer completion, N_2 adlayers form a $\sqrt{3} \times \sqrt{3}$ registered structure,[2] which persists until melting. The N_2 molecular centers are located above the centers of every third graphite hexagon. Thus, fractional monolayers form registered $\sqrt{3} \times \sqrt{3}$ islands, and the surface is completely covered at monolayer completion, where $\rho = 1$, in units of 0.0636 molecule/Å^2. Estimates[2,16] are that the fractional monolayer islands may contain from 10^2 to 10^3 molecules. The melting curve[1,2,7,11] is nearly constant at $T_M \simeq 48$ K for all surface densities substantially less than monolayer coverage but near this density it rapidly increases to $T_M \simeq 85$ K. There has been a suggestion[7] that the large change in T_M is a consequence of edge effects associated with the submonolayer islands, which reduces the melting temperature. No other explanation has previously been presented.

We postulate that the fundamental distinction between melting of partial and complete monolayers is that there are many vacancies between islands of the former that promote thermal fluctuations in the plane of the substrate which, in turn, facilitates self-diffusion, thermal expansion, and melting at T_M. For the latter case all lattice sites are occupied and thermal expansion in the plane is eliminated by the boundary of the experimental apparatus and/or possibly by grain boundaries. Thus, only fluctuations in the $\hat{z}$ direction, normal to the plane, can provide space sufficient to initiate 2D melting. This is important because forces impeding thermal expansion normal to the plane are about an order of magnitude larger than those in the plane. Melting should therefore occur at a higher temperature for monolayers than for partial monolayers. These ideas are not entirely new and vacancy-induced melting is implicit in many theories. Indeed, the considerable effect of edge pinning on melting has been demonstrated by Novaco[9] in a highly idealized calculation, and recent calculations of multilayer O_2 on graphite[17] have some similar features in common.

The Monte Carlo (MC) procedure employed in this work utilizes both the (N,P,T) and (N,ρ,T) ensembles, with and without deformable, periodic boundary conditions. Here N, P, and T are the number of molecules, the 2D pressure, and the temperature, respectively. Calculations were made with $N = 16$, 64, and 256 molecule MC cells, and lattice sums were taken out to 9 Å with continuum corrections beyond. Thermodynamic averages were determined over 2×10^4 steps, after neglecting the first 10^4 to minimize initial transients. Each step consists of randomly moving all $5N$ molecular coordinates and the three in-plane MC cell parameters, where the boundary conditions are changed using the Parrinello-Rahman[18] method. There are no boundary conditions in the $\hat{z}$ direction normal to the substrate.

The N_2-N_2 interaction is represented by our fit with *ab initio* and electron-gas calculations, which includes overlap, dispersion, and electric multipole terms. It has proven to be a highly accurate representation over a wide range of (P,T) for both 2D and 3D systems.[19] The interaction with the substrate is represented by the substrate-mediated dispersion expression, the interaction between charges charcterizing the electric multipole distribution on the N_2 molecules and their images formed by the presence of graphite substrate, and an overlap-dispersion interaction between the carbon and nitrogen atoms. The latter is determined from combining rules and is represented by the Fourier expansion of Steele.[20] The E_1 term in this expansion, which reflects the periodicity of the substrate-N_2 interaction, is given by the recent representation of Carlos and Cole.[21] Details of all interactions are given in Ref. 19.

The objective of our calculations is to establish boundary conditions that best reflect the experimental system.