Molecular-Dynamics Simulations of the Incommensurate Phase of Krypton on Graphite Using More than 100 000 Atoms

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The incommensurate phase of krypton on graphite is studied by use of the molecular-dynamics simulation technique for systems with graphite substrate dimensions comparable to present-day laboratory capabilities. At low temperature and for all coverages, honeycomb networks of "heavy" domain walls are observed for the first time. With increasing temperature, distortion from the perfect honeycomb structure becomes more prevalent, characterized by significant fluctuations from the symmetry directions, wall thickening, and wall roughening.

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The nature of the incommensurate (IC) phase of krypton on graphite and its transition to the $\sqrt{3}\times\sqrt{3}\,R30°$ commensurate (C) phase are being extensively investigated theoretically,[1-9] experimentally,[10-13] and by computer simulation.[14,15] For Kr on graphite, the domain walls may be in three different directions because of the hexagonal substrate structure. If wall intersections are energetically unfavorable, a *striped* phase might be expected where walls are only in one direction.[4] However, Villain has noted that a *honeycomb* array of walls has a degeneracy in which the hexagons of the array can expand or contract without changing the total wall length or the number of nodes (i.e., wall crossings).[1,2] Hence, Villain argues that this additional contribution to the entropy stabilizes the honeycomb phase relative to the striped phase and that the IC-C transition is first order. Expanding upon the Villain picture, Coppersmith *et al.*[5,6] have predicted that the *slightly* incommensurate phase is unstable to dislocations and conclude that sufficiently close to the IC-C transition the hexagonal overlayer will be a fluid at all temperatures, provided that the IC-C transition is weakly first order. The order of the transition has not been resolved experimentally.[10-12] However, Moncton *et al.*[11] have found the *high-temperature*, weakly incommensurate phase to be disordered with correlation lengths on the order of 100 Å. Computer simulation has reproduced the experimental measurements of this high-temperature phase and has established the microstructure of this "domain-wall liquid."[15] Such a demonstration suggests that computer experiments should be valuable in determining the incommensurate phase microstructure for all temperatures and coverages.

In this present investigation, we report on the structure of the incommensurate phase of krypton on graphite as a function of temperature and coverage using the molecular-dynamics simulation technique for systems of 103 041 and 161 604 krypton atoms. Hence, graphite substrate dimensions up to 1700 Å are realized and are essentially identical to present-day laboratory capabilities. We observe that the incommensurate phase consists of commensurate islands separated by a interconnecting network of incommensurate domain walls, the structure of this network being a sensitive function of temperature and coverage. At low temperature, Villain's honeycomb network of domain walls is observed for all coverages. Following the definition of Huse and Fisher,[7] all of the walls are *heavy* and are in agreement with the prediction of Kardar and Berker.[8] A low-temperature fluid phase or an incommensurate striped phase is not seen. With increasing temperature, distortions from the perfect honeycomb structure become more prevalent. At high temperatures, the individual domain walls fluctuate significantly from the symmetry directions while possessing boundary roughness and a greater wall thickness. But before we present the details of our findings, we briefly outline certain aspects of the simulation procedure.

Our numerical simulation method for studying rare-gas adsorption on graphite has been presented[15,16] and will not be described here. However, an additional feature of employing Hockney and Eastwood's[17] chain-link method to set up Verlet tables[18] for all atoms was adopted,[19] the table update being executed every ten time steps, each time step being 0.025 ps. Similar to our previous study,[15] we use the Lennard-Jones 12:6 pair potential to represent the interaction between the various atoms of the krypton-graphite system. The Lennard-Jones parameters are taken to be $\epsilon/k = 170$ K and $\sigma = 3.6$ Å for the krypton-krypton

interaction and $\epsilon/k = 64.83$ K and $\sigma = 3.22$ Å for the krypton-carbon interaction, respectively. Simple pairwise additivity of the atomic interactions is assumed, and the carbon atoms defining the semi-infinite solid are fixed at their lattice sites. In order to reduce the computer memory requirement, we constrain the movement of the krypton atoms to a plane parallel to the graphite surface. Thus, in contrast to our earlier studies, we are dealing with a two-dimensional system in the external field of the graphite substrate. However, a detailed comparison between a two-dimensional simulation and the previous, quasi-two-dimensional simulation shows no physically relevant differences.[19] The external field of the graphite is reproduced to a very good approximation by the expression[20]

$$\varphi_{\mathrm{Kr-G}} = -V_g[\cos 2\pi s_1 + \cos 2\pi s_2 + \cos 2\pi(s_1+s_2)], \quad (1)$$

where $V_g = 0.08\epsilon_{\mathrm{Kr-Kr}}$ and s_1, s_2 are the basis vectors of the graphite unit cell. The planar x-y geometry of the computational cell is the same as described in Ref. 16, with the exception that our Cartesian coordinate system is now rotated by 90° about the origin. The 161 604 Kr atom system requires approximately 13 megabytes of memory and executes 110 time steps per central-processing-unit hour on the IBM/370 3081 computer.

We have performed two series of simulations: one in which the coverage was fixed at $\theta = 1.013$ and the *reduced* temperature was varied from $T^* \equiv kT/\epsilon_{\mathrm{Kr-Kr}} = 0.05$ to 0.9; the other in which the temperature was fixed at $T^* = 0.05$ and the coverage was varied from 1.013 to 1.086. At the lowest temperature, the Kr system was initialized in a perfect incommensurate triangular lattice, and the atoms were assigned a velocity distribution corresponding to a temperature $T^* = 0.05$. Equilibrium was determined by monitoring the energy, the ratio of commensurate to incommensurate atoms, the ratio of the commensurate atoms in the three degenerate ground states, and the domain microstructure as a function of time. For the higher-temperature simulations, we slowly heated the system over 2000 time steps to the next higher temperature and repeated the equilibration procedure. Equilibration times were typically less than 1000 time steps and therefore very rapid. For a given temperature and coverage, 4000 to 8000 total time steps were performed. We have adopted the criterion that a krypton atom is commensurate if its average position is inside a circle with a radius $\delta = 0.2$ around the nearest adsorption site, in units of the graphite lattice constant $a = 2.46$ Å.

Figure 1 shows the principal results of our simulations for the 103 041 atom system. The incommensurate and commensurate regions are shown as solid black and solid white areas, respectively; in actual fact, we plotted the incommensurate atoms as points but the lack of graphical resolution merged the points to make a solid region. We first consider the case where the temperature is fixed at the low value of 0.05 and the coverage is varied. We note that for all coverages a honeycomb network of domain walls is established, the network consisting of straight walls with smooth boundaries which are aligned to the three symmetry directions of the graphite substrate. The commensurate regions form an array of honeycomb domains, the individual hexagons not being identical in size or shape. This honeycomb domain structure with *breathing* freedom is direct conformation of Villain's[1] picture of the incommensurate phase, and this is the first direct observation of this structure. At fixed temperature, the percentage Kr atoms that are commensurate (%C) decreases linearly with increasing coverage (90, 80, 75, 60, and 37 percent, respectively), while the domain-wall thickness remains essentially constant at 18 Å. This low-temperature wall thickness is in agreement with recent calculations.[9,21] This decrease of the commensurate percentage is associated with an increase of the total length of domain walls, and this gives rise to smaller and more numerous commensurate domains. For krypton on graphite, there exist two configurationally distinct types of walls,[7,8] sometimes referred to as heavy and light walls.[7] All of the domain walls in the low-temperature honeycomb network are the heavy type, and this is in agreement with the theoretical calculation of Kardar and Berker.[8] One can visualize two extremes for the atomic microstructure of the incommensurate state: (1) the Kr atoms are near registry except for thin domain walls, or (2) the Kr monolayer is a lattice that is weakly modulated by the substrate field. In Fig. 2, we present the honeycomb picture for $T^* = 0.05$, $\theta = 1.025$ and for the three commensurate-radius cutoff criteria $\delta = 0.1$, 0.2, and 0.3. We conclude that at this low temperature the Kr lattice is significantly modulated. However, with increasing coverage, this modulation will de-

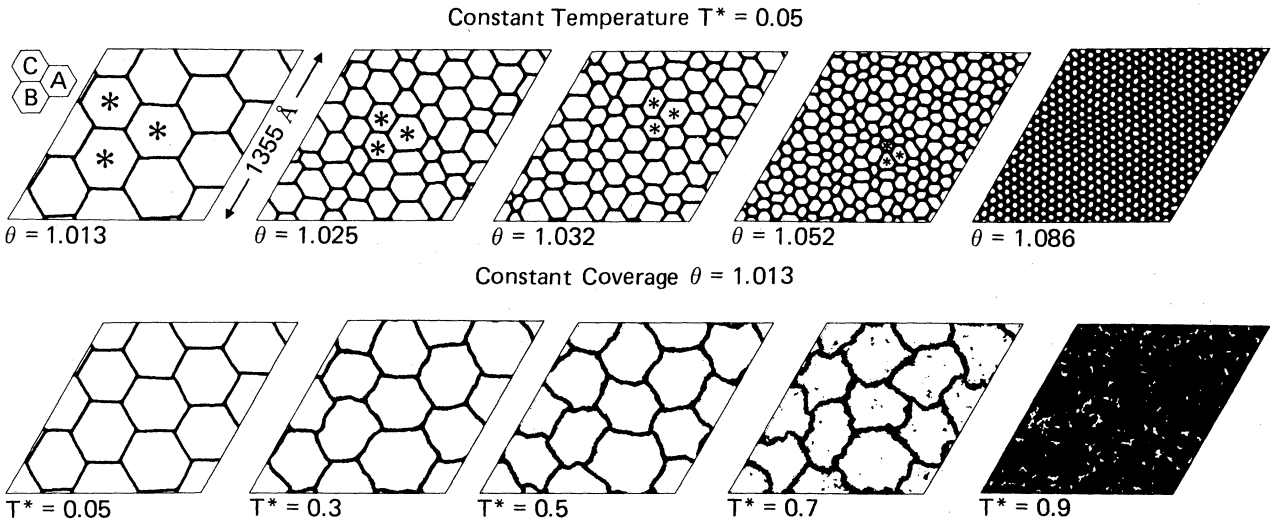

FIG. 1. Pictures of the domain-wall network for an equilibrium configuration of the incommensurate phase as a function of coverage θ at fixed temperature $T^*=0.05$ and as a function of temperature at a fixed coverage $\theta=1.013$. 103 041 Kr atoms on graphite.

crease; i.e., when the wall separation approaches the thickness of an individual wall.

In order to test the prediction of Coopersmith *et al.*[5,6] (i.e., the slightly incommensurate phase is unstable to dislocations sufficiently close to the IC-C transition and the hexagonal overlayer will be a *fluid* at all temperatures), we simulated as large a system as we felt was practical within the constraint of our computer resources—a 161 604 Kr atom system. The temperature and coverage are 0.05 and 1.005, respectively. In Fig. 3, we again see the incommensurate honeycomb structure and hence no evidence of a fluid phase at this low temperature. Furthermore, we do not observe the *striped* phase or two-phase coexistence between the commensurate and incommensurate phases, which would be indicative of a first-order transition when the total coverage is held constant in the two-phase region. Of course, the nonexistence of these features may be a consequence of our system not being sufficiently weakly incommensurate; i.e., a coverage may have to be much lower in order to observe these features. This same limitation exists for laboratory experiments.

Returning to Fig. 1, we now consider the series of simulations where the coverage was held fixed at 1.013. With increasing temperature, the overall appearance of the incommensurate phase remains that of the domain-wall network which becomes increasingly distorted, the walls becoming broader and the wall boundaries roughening considerably. One who feels compelled to classify the walls into the heavy- and light-wall catagories will note that the wall orientations favor the three symmetry directions, and those walls which can

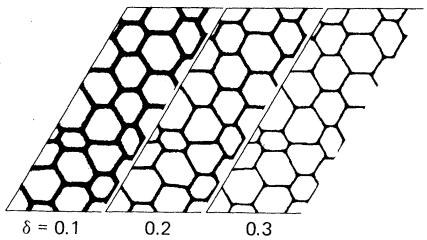

FIG. 2. Pictures of the domain-wall network for an equilibrium configuration of the incommensurate phase at a coverage $\theta=1.025$ and temperature $T^*=0.05$, for various values of the commensurate-radius cutoff criterion δ.

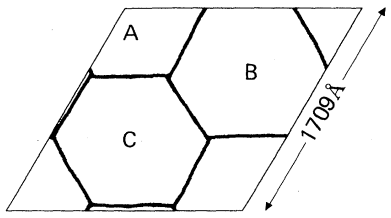

FIG. 3. A picture of the domain-wall network for an equilibrium configuration of the incommensurate phase simulated by 161 604 Kr atoms on graphite at a coverage $\theta=1.005$ and temperature $T^*=0.05$. The percentage of commensurate atoms is 96%.

be unambiguously classified are essentially heavy walls. Also, we note the marked increase in the wall thickness with increasing temperature, the wall thickness at $T^* = 0.7$ being approximately twice the wall thickness at $T^* = 0.05$. This is consistent with the gradual decrease of the percentage of commensurate atoms (90, 88, 85, and 81 percent, respectively). At the highest temperature, the system is mainly incommensurate since it is principally a liquid coexisting with very small patches of commensurate islands (%C = 26). This liquid is the familiar fluid state and not the fluid of Coopersmith *et al.*

Direct experimental confirmation of Villain's picture for the incommensurate phase of krypton on graphite has been achieved by simulating over 100 000 krypton atoms on a graphite substrate, thereby enabling us to study systems comparable to present-day laboratory experiments. A more detailed presentation including simulations of a smaller system (20 000 atoms) is forthcoming, where the variation of important quantities such as the wall thickness and average wall separation with temperature and coverage is presented.[19]

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[1]J. Villain, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980), p. 221.

[2]J. Villain and M. B. Gordon, Surf. Sci. 125, 1 (1983).

[3]P. Bak, Rep. Prog. Phys. 45, 587 (1982).

[4]V. L. Pokrovskii and A. L. Talapov, Phys. Rev. Lett. 42, 65 (1979).

[5]S. M. Coppersmith, D. S. Fisher, B. J. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. Lett. 44, 549 (1981).

[6]S. M. Coppersmith, D. S. Fisher, B. J. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. B 25, 349 (1982).

[7]D. A. Huse and M. E. Fisher, Phys. Rev. Lett. 49, 793 (1982).

[8]M. Kardar and A. N. Berker, Phys. Rev. Lett. 48, 1552 (1982).

[9]M. Schoebinger and S. W. Koch, to be published.

[10]M. D. Chinn and S. C. Fain, Phys. Rev. Lett. 39, 146 (1977).

[11]D. E. Moncton, P. W. Stephens, R. J. Birgeneau, P. Horn, and G. S. Brown, Phys. Rev. Lett. 46, 1533 (1981).

[12]M. Nielsen, J. Als-Nielsen, J. Bohr, and J. P. McTague, Phys. Rev. Lett. 47, 582 (1981).

[13]J. P. McTague, J. Als-Nielsen, J. Bohr, and M. Nielsen, Phys. Rev. B 25, 7765 (1982).

[14]F. Hanson and J. P. McTague, J. Chem. Phys. 72, 6363 (1980).

[15]F. F. Abraham, S. W. Koch, and W. E. Rudge, Phys. Rev. Lett. 49, 1830 (1982).

[16]S. W. Koch and F. F. Abraham, Phys. Rev. B 27, 2964 (1983).

[17]R. W. Hockney and J. W. Eastwood, *Computer Simulations Using Particles* (McGraw-Hill, New York, 1981).

[18]L. Verlet, Phys. Rev. 159, 98 (1967).

[19]S. W. Koch, W. E. Rudge, and F. F. Abraham, to be published.

[20]W. A. Steele, Surf. Sci. 36, 317 (1973).

[21]R. J. Gooding, B. Joos, and B. Bergerson, Phys. Rev. B 27, 7669 (1983).