Molecular-Dynamics Computer Simulation of the Weakly Incommensurate Phase of Monolayer Krypton on Graphite

Farid F. Abraham, S. W. Koch,[a] and W. E. Rudge

IBM Research Laboratory, San Jose, California 95193

The weakly incommensurate phase of monolayer krypton adsorbed on graphite has been investigated by employing the molecular-dynamics simulation technique for a 22 212-krypton-atom system. The coverages and temperatures chosen correspond to the region of the phase diagram experimentally studied by Moncton *et al.* The simulation results are in very good agreement with the laboratory measurements. The atomic nature of the weakly incommensurate disordered phase may be described as a "domain-wall liquid."

From a very-high-resolution synchrotron-x-ray study, Moncton *et al.*[1] have found that the experimental (10) diffraction profiles through the incommensurate-commensurate (C → IC) transition of monolayer krypton graphite behave in an entirely unexpected manner and conclude that, in contrast to expectation, the weakly incommensurate phase arising from this transition is disordered (IC-D). However, Moncton *et al.* point out that this disordered phase is unusually well correlated for a liquid, but it is clearly not a two-dimensional (2D) solid (IC-S). In their Fig. 2 diffraction profiles are presented at various temperatures for a closed-cell experiment where the measured phase transitions from liquid to commensurate solid (L → C-S) and from commensurate solid to incommensurate disordered phase (C-S → IC-D) occur at 112.9 and 97.24 K, respectively. At 96.37 K, there is a "reemergence" of a prominent peak, indicating that at large incommensurability the system is apparently near a transition to an incommensurate 2D solid; i.e., the completion of the IC-D → IC-S transition occurs in this temperature neighborhood. Motivated by this experiment, Coppersmith *et al.*[2] studied the stability of weakly incommensurate two-dimensional solid phases described by periodic arrays of discommensurations and found that they are unstable with respect to the spontaneous creation of dislocations. They concluded that such phases are consequently "liquids," suggesting an explanation for the disordered phase in the experiment of Moncton *et al.* but warning that the details of the theoretical calculation probably do not apply in the region of the phase diagram studied thus far with high-resolution synchrotron radiation.

Stimulated by these experimental and theoretical developments, we have investigated the commensurate-incommensurate transition of monolayer krypton adsorbed on graphite by employing the molecular-dynamics simulation technique. The coverages and temperatures chosen correspond to the region of the phase diagram experimentally studied by Moncton *et al.*[1] We find that the simulation experiments are in very good agreement with the laboratory measurements, and this allows us to ascertain the atomic nature of the weakly incommensurate disordered phase. But before we discuss the details of our findings, we give a terse summary of the simulation procedure.

We have adopted the well-known Lennard-Jones 12:6 pair potential to represent the van der Waals interaction between the various atoms of the krypton-graphite system. The interatomic parameters ϵ and σ are determined empirically; the krypton-krypton parameters are taken to be $\epsilon/k = 170$ K and $\sigma = 3.6$ Å, and the krypton-carbon parameters are taken to be $\epsilon/k = 66.6$ K and $\sigma = 3.35$ Å. Simple pairwise additivity of the interatomic interactions is assumed, and the carbon atoms defining the semi-infinite graphite solid are fixed at the lattice sites. In order to reduce computational time in the evaluation of the forces, certain approximations and procedures are implemented. The krypton-krypton interaction is truncated at 3σ. Furthermore, the "chain/link" method is employed so that the tests for locating atoms within 3σ of any particular atom need only be performed over a small subset of the total number of the krypton atoms.[3] This is very important for our simulations using 22 212 atoms. The krypton-graphite substrate interaction is evaluated with a fast and efficient algorithm recently proposed by Dion, Barker, and Merrill.[4] The atomic carbon positions of the graphite surface define the basal plane of the computational

box, this base being a parallelogram compatible with the triangular lattice of a close-packed, two-dimensional crystal. Periodic boundary conditions are imposed at the four faces of the computational cell which pass through the sides of the basal parallelogram at normal incidence to the surface. The basal plane of the computational box must be compatible with the graphite structure, as otherwise periodic replication creates unphysical size dependences. A reflecting wall is placed at the top of the computational box at an 8-Å height, but no krypton atoms reached this normal distance for the simulations performed. Conventional molecular dynamics is employed and consists of numerically integrating Newton's equations of motion to obtain trajectories of the atoms. The time step for the simulations of this study is equal to 0.05 ps. The atomic velocities are renormalized at every numerical time step so that the mean kinetic energy corresponds to the specified temperature. For equilibrium states, time averaging of the state variables over a sufficiently large configuration and/or a sufficiently long interval of the temporal evolution of the system will yield proper equilibrium properties.

A series of isothermal simulations has been performed for various coverages, the temperature being set equal to 97.5 K. In this Letter, we will report on only those simulations where we have established the effects of system size (i.e., computational cell dimension) on the measured physical properties, in particular the pair correlation function and its Fourier transform (the structure factor). As usual, careful attention is given to determining that the system is in "local equilibrium" (stable or metastable) when taking statistics for the quantities of interest. In order to obtain the equilibrium properties, it was typical to perform 20 000 to 40 000 time steps for a given coverage. Finally, the structural information is in terms of the atom configurations projected onto a plane parallel to the graphite surface.

In Fig. 1(a), we demonstrate the inverse square-root dependence of the structure factor's peak width on the system size for a finite commensurate crystal (coverage equal to unity). A similar behavior exists for a finite floating-incommensurate solid. A theoretical analysis of this behavior due to size truncation is given by Dutta and Sinha[5] and Imry.[6] For a quasi two-dimensional "disordered" phase where the structure of the pair distribution function dies out long before the dimension of the system is reached, there is no
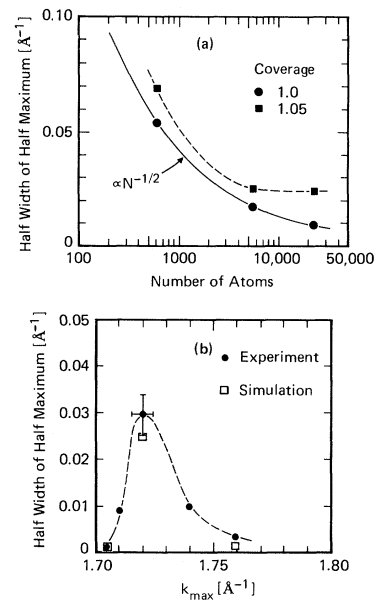

FIG. 1. (a) The half-width at half maximum (HWHM) of the atomic structure factor as a function of the number of atoms in simulations for two different coverages. (b) The experimental results of Moncton et al. (Ref. 1) for the HWHM (solid circles) vs peak position in comparison with the computer simulation results (open squares). Note that the numerical HWHM for the commensurate monolayer (k_{max}= 1.702 Å^{-1}) and for the incommensurate monolayer (k_{max}= 1.76 Å^{-1}) are scaled to the experimental graphite-particle size of 2300 Å (see text).

system size dependence for the peak width of the structure factor. The classic example of this feature is an atomic liquid. While this limit is not achievable for a coverage of unity (the commensurate solid phase), we note in Fig. 1(a) that for a coverage of 1.05 the width of the structure factor has become size independent for a krypton system greater than approximately 5000 atoms. We make special note that a system of 22 212 atoms was followed for 20 000 time steps in order to establish the convergence of the structure-factor width with increasing system size. This was no small computational feat! In order to be compared with the experimental findings of Moncton et al., our measured structure-factor widths with the inverse-square-root dependence on system size have to be scaled to the particle size of their ZYX exfoliated graphite, which is 2300 Å. Hence, the widths for the commensurate solid (coverage = 1.00) and the incommensurate solid (coverage = 1.09) are scaled by the factor of (620 Å)/(2300 Å) = 0.27. This is in contrast to our "disordered" phase at a coverage of 1.05 where

no scaling is performed. In Fig. 1(b), compari-son between the molecular-dynamics simulation results and laboratory measurements[1] demon-strates excellent agreement.

In Fig. 2(a) a "snapshot picture" of the incom-mensurate atoms for the 22 212-atom "disor-dered phase" (coverage of 1.05) is presented after 20 000 time steps into the simulation. We arbi-trarily define a krypton atom as being incommen-surate if its position is displaced from a graphite adsorption site by an amount that is greater than two-tenths of a graphite lattice constant. With this definition, approximately 56% of the krypton atoms are commensurate at this coverage. The substrate sublattices of the commensurate kryp-ton atoms are denoted by A, B, and C, respec-tively. We note a rather extensive network of intertwining domain walls defined by the incom-mensurate atoms. The domain walls are well de-

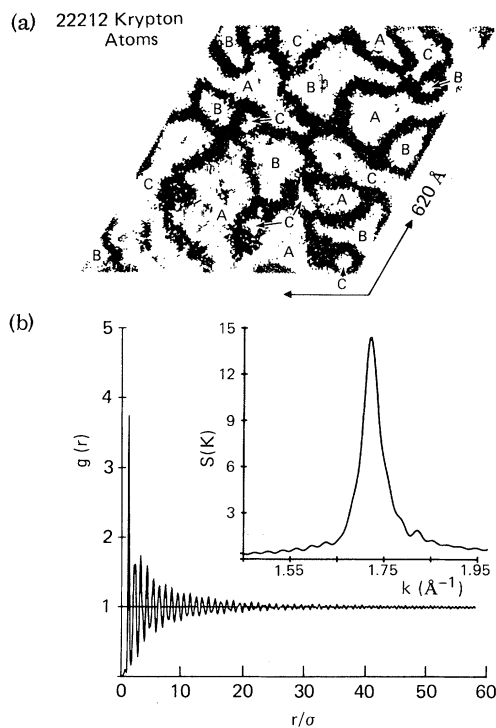(a) 22212 Krypton
        Atoms

(b)

FIG. 2. (a) A snapshot picture of the incommensurate krypton atoms (44%) for a 22 212-Kr-atom system on graphite at a coverage of 1.05, a temperature of 97.5 K, and a graphite linear dimension of 620 Å. The atom-ic configuration is for 20 000 time steps into the mole-cular-dynamics simulation. The occupied substrate sublattices of the commensurate krypton atoms are denoted by A, B, and C, respectively. (b) The radial distribution function $g(r)$ and the structure factor $S(k)$ of the 22 212-atom system depicted by the snapshot picture.

fined and have an approximate thickness of 30 Å. The "typical" dimension of a commensurate is-land is on the order of 100 Å. The presence of free dislocations, signaled by the misorientation of domain walls relative to each other, charac-terizes the "disordered" nature of this weakly incommensurate phase. By examining the tem-poral evolution of the individual atoms during the simulation process (i.e., a trajectory analysis), we have determined that there is no fluid mobility of the individual commensurate or incommensu-rate atoms. However, a series of snapshot pic-tures of the incommensurate atoms shows a slow temporal meandering of the domain walls. One may describe this phase as a "domain-wall liquid." In Fig. 2(b), the radial distribution function and its corresponding structure factor are presented and again show the loss of atomic correlation beyond a separation of 30σ or 100 Å for this very large system (620 Å).

In summary, the weakly incommensurate phase is characterized by large variations of separa-tion and orientation between domain walls, a broad distribution of commensurate islands in both size and relative location to one another, and the lack of any long-range atomic correlation. A consequence of this atomic feature is that the structure factor of this pseudorandomly mixed commensurate-incommensurate system appears "liquidlike" (but unusually well correlated for the ordinary atomic liquid phase). Also, domain-wall mobility is prevalent. This "domain-wall liquid" appears to be consistent with the general meaning of "liquid phase" in the study by Coppersmith et al.[7]

Future simulation studies may address the order of the commensurate-incommensurate transition in various regions of the coverage versus tempera-ture phase diagram,[8] the possibility of a chiral transition,[9] and the temperature dependence of the commensurability close to the commensurate-incommensurate transition. However, any one of these problems would demand excessive compu-tational resources in terms of present-day stan-dards.

(a)Present address: Institut für Theoretische Physik, Universität Frankfurt, Frankfurt-am-Main, West

Germany.

[1] D. Moncton, P. Stephens, R. Birgeneau, P. Horn, and G. Brown, Phys. Rev. Lett. **46**, 1533 (1981).

[2] S. N. Coppersmith, D. S. Fisher, B. I. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. Lett. **46**, 549 (1981), and Phys. Rev. B **25**, 349 (1982).

[3] R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles*, (McGraw-Hill, New York, 1981), Secs. 8–4.

[4] D. R. Dion, J. A. Barker, and R. P. Merrill, Chem. Phys. Lett. **57**, 298 (1978).

[5] P. Dutta and S. K. Sinha, Phys. Rev. Lett. **47**, 50 (1981).

[6] Y. Imry, Crit. Rev. Solid State Mater. Sci. **8**, 157 (1979).

[7] D. S. Fisher, private communication.

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

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

Phason Dynamics of Incommensurate Crystals

R. Zeyher and W. Finger

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 26 July 1982)

It is shown that phase modulations (phasons) of the order parameters of incommensurate lattices are always diffusive at sufficiently large wavelengths λ. In general there is a crossover from diffusive behavior for $\lambda \gg \Lambda$ to propagating behavior for $\lambda \ll \Lambda$ where Λ is a mean free path due to nonlinear interactions. The present results explain why light- and neutron-scattering experiments probe different dynamical behavior of phasons.

In an incommensurably modulated crystal the equilibrium positions of the atoms are modulated with a wavelength which is, at least in one direction, incommensurate with the underlying basic structure.[1] Examples include quasi one- and two-dimensional metals (for instance $NbSe_2$) as well as insulating materials [for instance $BaMnF_4$ (Ref. 2) and biphenyl[3]].

An interesting property of incommensurate crystals is the invariance of the free energy with respect to changes in the relative position of modulation and basic structure. These changes are generated by space-independent shifts of the phase of the order parameter which describes the modulation.[1] This invariance is expected to hold true as long as the modulation can be described by analytic functions.[4] The existence of an associated collective mode, the phason, with zero excitation energy follows immediately.

It has generally been argued that the phase independence of the free energy implies the existence of a gapless branch of propagating phase modulations (phasons) with a linear dispersion in the long-wavelength limit.[1] This prediction seems to agree with inelastic neutron-scattering experiments in biphenyl[3] which showed the existence of propagating phase fluctuations. However, light-scattering experiments in $BaMnF_4$ (Ref. 2) found evidence that phase fluctuations are purely diffusive, giving rise to a central peak in the spectrum of scattered light with width Dq^2. The latter result was interpreted in terms of a time-dependent Ginzburg-Landau theory which has been developed for charge-density-wave systems.[5,6]

It is the purpose of this Letter to demonstrate that both the propagating and the diffusive regimes of phase fluctuations follow quite naturally and for general reasons from the nature of the incommensurate state once the nonlinearities in the Hamiltonian are properly taken into account.

We start from the general form of the Hamiltonian for an anharmonic lattice,

$$H = \frac{1}{2} \sum_{\vec{k},j} \dot{A}(\vec{k},j)\dot{A}(-\vec{k},j) + \sum_{\nu=0}^{\infty} \frac{1}{\nu!} \sum_{\vec{k}_1,j_1;\cdots;\vec{k}_\nu,j_\nu} \Phi^{(\nu)}(-\vec{k}_1,j_1;\ldots;-\vec{k}_\nu,j_\nu)A(\vec{k}_1,j_1)\cdots A(\vec{k}_\nu,j_\nu). \tag{1}$$

$A(\vec{k},j)$ denotes the normal coordinates, j is a branch index, and $\vec{k}$ is a wave vector within the first Brillouin zone of the basic structure. $\dot{A}(\vec{k},j)$ denotes the time derivative of $A(\vec{k},j)$ and $\Phi^{(\nu)}$ are the expansion coefficients of the adiabatic potential.