Temperature-induced commensurate-incommensurate transition of submonolayer krypton on graphite

S. W. Koch
Institut für Theoretische Physik, Universität Frankfurt, D-6000 Frankfurt/Main, Federal Republic of Germany

Farid F. Abraham
IBM Research Laboratory K33/281, 5600 Cottle Road, San Jose, California 95193
(Received 11 July 1985)

The thermal expansion of submonolayer krypton on graphite is investigated using molecular-dynamics computer simulations. With increasing temperature a pronounced incommensurate-to-commensurate transition is found for parameter values corresponding to Steele's interatomic potential. The results indicate that this transition might be of first order.

The commensurate-incommensurate transition of krypton on graphite is mostly studied for coverages slightly above one commensurate monolayer. Here, the discrete translational symmetry of a perfectly commensurate krypton film is broken by the adsorption of additional atoms onto the surface. The microstructure of this "weakly incommensurate phase" is well described as a more or less regular array of commensurate honeycombs which are separated by incommensurate domain walls. The domain-wall concept has been introduced in low-temperature theoretical studies[1] and has been confirmed, e.g., by molecular-dynamics computer simulations.[2,3]

In the majority of the theoretical and numerical studies of krypton on graphite, a pairwise-additive interatomic Lennard-Jones potential between all atoms is assumed. Quite recently, the role of the magnitude of the krypton-graphite potential parameters has been investigated systematically and it has been shown that the zero-temperature commensurate phase does not yield the lowest energy per atom for a too weakly modulated graphite surface potential.[4] In particular, it has been pointed out that the widely used krypton-graphite parameter values suggested by Steele[5] might cause an insufficient corrugation. Furthermore, a zero-temperature calculation of the angular averaged atomic structure factor has been presented[4] for different values of the coupling strength. The structure factor shows a main peak, whose width is determined by the size of the commensurate honeycombs, together with two satellites whose intensity depends significantly on the corrugation.

The more pronounced first satellite of the atomic structure factor has been observed in synchrotron-x-ray scattering experiments.[6,7] However, these measurements have been done for temperatures above 70 K and therefore allow no direct comparison with the zero-temperature theoretical predictions. Moreover, very recent calculations seem to indicate,[8] that at higher temperatures (above 30–40 K) the strength of the graphite surface corrugation might be less important than anticipated from the zero-temperature results of Ref. 4. Gordon and Villain[8] investigate the role of anharmonicity on the commensurate phase of krypton on graphite and find that thermal expansion stabilizes the commensurate state at temperatures higher than T_{IC}. This transition temperature, T_{IC}, is determined from the condition that the commensurate phase becomes stable at the temperature at which the free energy for creating an incommensurate domain wall changes its sign from negative (at low temperatures) to positive. They estimate $T_{IC} \cong 34$ K for Steele's potential parameters. This thermally induced incommensurate-commensurate transition has not yet been observed experimentally for monolayer krypton on graphite.

To investigate the importance of the krypton-graphite potential parameters at finite temperatures and to test the theoretical ideas, we performed a series of molecular-dynamics computer simulations for a two-dimensional system modeling krypton on graphite. The details of the simulated system and our numerical procedure have been described elsewhere.[9,10] For the krypton-graphite interaction potential we used Eq. (1) of Ref. 9, where $V_g \simeq 0.054\epsilon$, $\epsilon/k_B = 170$ K, is derived for Steele's potential parameters.[11] In order to eliminate the possible influence of the periodic boundary conditions, which might lead to the stabilization of a perfectly commensurate monolayer, we studied in the present simulation submonolayer coverage by placing the krypton atoms as an isolated cluster onto the surface (total coverage $\theta = 0.56$). We simulated clusters of $N = 144$ and $N = 2304$ atoms to investigate possible size effects. The initial atomic density within the clusters was varied from a value corresponding to a completely commensurate layer (effective coverage of the cluster only; $\theta_{\text{eff}} = 1$), up to the density corresponding to the effective coverage $\theta_{\text{eff}} = 1.08$. (As usual, all coverages are given in units of commensurate monolayers.)

An overview of the simulation results for Steele's potential parameters is presented in Fig. 1. Here we plot the respective percentage of commensurate atoms as function of the constant mean temperature $k_B T/\epsilon$. As in our previous studies,[2,3,9] we adopted the criterion that a krypton atom is commensurate if its average position is inside a circle with radius $0.2a_0$ around the nearest adsorption site ($a_0 = 2.46$ Å, graphite lattice constant). For each set of parameter values we run the simulations very long, i.e., for a minimum of 50 000 up to 100 000 timesteps, until either equilibrium or a stationary metastable state was reached. For the 144-atom system we observe a smooth incommensurate-to-commensurate transition for $0.10 \lesssim k_B T/\epsilon \lesssim 0.15$ (17 K $\lesssim T \lesssim$ 25.5 K). The bars at the values for $N = 144$ (filled circles in Fig. 1) indicate the spread of the results obtained from different initial conditions. In agreement with the theoretical predictions of Gordon and Villain,[8] we observe a thermal stabilization of the

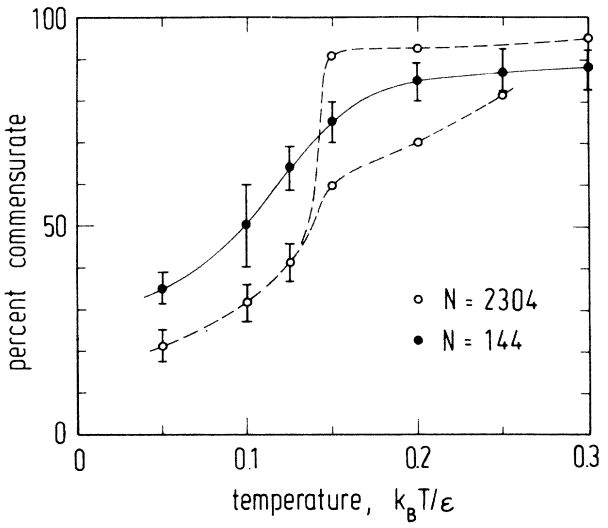

FIG. 1. Percentage of commensurate atoms as function of temperature. The bars indicate the spread of the results obtained from different initial conditions (see text).

commensurate ground state. Our numerical value for the transition temperature is, however, slightly below the theoretical estimate.

Our simulations of the 2304-atom cluster (open circles in Fig. 1) show a large hysteresis loop. The upper branch, indicating a high percentage of commensurate atoms, is obtained after initializing the system at each temperature in a perfectly commensurate state. For temperatures $k_B T/\epsilon$ larger than 0.15 the cluster simply remains commensurate, whereas for temperatures below 0.125 we observe a rapid relaxation to a weakly modulated incommensurate state. In comparison to the results for the 144-atom cluster, the transition occurs considerably more pronounced, indicating that this phase change might be of first order.

The lower branch of the hysteresis loop for 2304 atoms in Fig. 1 is obtained after initializing the atoms in the cluster for each temperature at the effective coverage $\theta_{\text{eff}} = 1.02$. Our earlier simulations[2,3,9] of a monolayer system (with periodic boundary conditions) at this coverage $\theta = 1.02$ showed a breathing honeycomb network for temperatures from $k_B T/\epsilon = 0.01$ up to $k_B T/\epsilon = 0.7$. In this state the system populates the three degenerate commensurate ground states with equal probability, forming domain walls between neighboring regions. A similar situation occurs in our 2304-atom cluster. At low temperatures, $k_B T/\epsilon < 0.125$, the cluster is incommensurate with slight modulations. At $k_B T/\epsilon = 0.15$, commensurate regions corresponding to different ground states are more pronounced. They are separated by incommensurate walls; however, we do not find a well-defined honeycomb wall structure. The system is in a configuration which can only relax to the completely commensurate structure if all atoms move into the same ground state. For the total times of our simulations, this becomes possible only for higher temperatures, $k_B T \gtrsim 0.25$. For the 144-atom cluster we did not observe the coexistence of different commensurate regions since the system is sufficiently small to prevent the formation of an incommensurate domain wall.

To summarize, we simulated the temperature-induced commensurate-incommensurate transition using Steele's interatomic potential parameters. We verified the theoretical prediction of Gordon and Villain that thermal expansion stabilizes the commensurate phase at higher temperatures even for a weakly corrugated graphite surface potential. We find pronounced hysteresis for larger clusters and a size-dependent sharpening of the transition which suggests that this phase change may be first order.

For a krypton-graphite coupling strength $V_g = 0.08\epsilon$, i.e., roughly 1.5 times larger than Steele's value, we observe a commensurate cluster which is stable even at the lowest temperatures. For example, for the 144-atom system we find 75% commensurate atoms at $k_B T/\epsilon = 0.05$ which continuously increases to 90% at $k_B T/\epsilon = 0.2$. For the 2304-atom cluster we obtain 90% commensurate atoms already at $k_B T/\epsilon = 0.05$. As pointed out, e.g., by Vidali and Cole,[12] it is believed that Steele's potential is insufficiently corrugated to be consistent with the recent analysis of experimental data. However, our simulations show that data obtained at higher temperatures might not be conclusive to test the krypton-graphite coupling strength. A very decisive experimental test would be a search for the existence of a commensurate (sub-)monolayer krypton on graphite at temperatures below the transition temperature $T_{\text{IC}} \simeq 30$–40 K obtained for Steele's potential parameters.

S.W.K. wants to thank M. B. Gordon, J. Villain, and M. Schöbinger for stimulating discussions. Furthermore, he gratefully acknowledges financial support from IBM Germany, IBM San Jose, and from the Deutsche Forschungsgemeinschaft.

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