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Krypton on graphite: Microstructure at zero temperature

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We have calculated the energy associated with different possible configurations of a krypton monolayer on graphite using a microscopic model for the Kr-Kr and Kr-graphite interactions. In the latter case, there is considerable uncertainty with regard to the choice of potential, and calculations have been carried out for a range of parameters. For a potential which is weakly modulated parallel to the graphite plane (such as the one suggested by Steele) the lowest energy per atom is found to be a hexagonal nonregistered configuration. If the modulation is increased by a factor of 2, the $(\sqrt{3}\times\sqrt{3})$ registered configuration becomes the lowest-energy configuration and there will also then be a regime in which hexagonal and striped phases differ in energy by less than 1 K. For the range of potentials of interest, the domain walls are found to be broad and in agreement with predictions from continuum theory.

I. INTRODUCTION

Monolayer krypton on graphite has served as an important model system for the experimental study of phase transitions in two dimensions. To this end it is important to know the properties of the ground state and other low-energy configurations pertaining to this surface.

It is the purpose of this paper to employ currently available model potentials, for the dominant interactions, to estimate which of several proposed orderings are energetically favorable and to discuss some properties of the corresponding configurations. Of particular interest are the answers to the following questions:

(a) Does the registered $(\sqrt{3}\times\sqrt{3})$ structure yield the lowest energy per adsorbed atom? The experimental work of Nielsen *et al.*[1] indicates that the registered $(\sqrt{3}\times\sqrt{3})$ structure is the low-pressure configuration for temperatures as low as 40 K. The best known krypton-graphite potential is the one suggested by Steele.[2] When this potential is used, our calculations give a lowest-energy state per adsorbed atom for a compressed state with a coverage of about 1.1. There is, however, a considerable uncertainty in the magnitude of the modulations of the Kr-graphite potential. An increase by a factor of 2 is sufficient to change qualitatively our results and the registered state is then the lowest-energy configuration.

(b) How can the system best be described when compressed beyond the registered structure? One possibility is that the Kr atoms are near registry except for thin domain walls.[3–7] This approach fits the framework of the charge-density-wave theory of McMillan.[8] It is thus natural to describe the adsorbate in terms of quantities such as wall, wall-wall, and wall-crossing energies.

An alternative approach is to consider the krypton monolayer as a triangular lattice with spacing corresponding to coverage. This lattice is then weakly modulated by the substrate potential. A model using this picture was constructed by McTague and Novaco.[9] Their calculations were based on a lowest-order perturbation expansion in the substrate potential. By making a continuum approximation, Shiba[10] was able to accommodate both the domain-wall and weak-modulation limits, although for thin walls the continuum approximation will not be accurate. The fact that higher-order satellites have not been reported in diffraction studies[11] indicates that the weak-modulation limit is most appropriate experimentally. A curious aspect of calculations in this limit is that the adsorbate lat-

tice in general will be rotated with respect to the substrate. Such a rotation has been observed,[12] but is so small that the effect cannot be of significance for the energetics in the case of Kr on graphite. We have not pursued the question of orientational epitaxy here. The present calculations suggest that the wall thickness is of the order of 10 krypton spacings, and that therefore the modulations will be too smooth for the domain-wall picture to be pertinent except very close to the transition from the $\sqrt{3}\times\sqrt{3}$ registered phase.

(c) Will hexagonal or striped arrays of discommensurations (or modulations) be favored in the compressed state? Several authors[4–7,10] have considered phase transitions involving these two types. We find that when the modulations of the substrate potential are weak enough to favor nonregistered phases, the hexagonal phase has the lowest energy. The reason for this is that the mean spacing, parallel to the stripes, is too far from optimum. When the modulation strength exceeds a critical value the registered configuration will have the lowest energy per atom. For a given compression the striped phase will be slightly [less than (1 K)$/k_B$ per atom] lower in energy than the hexagonal phase. The smallness of this energy difference is in agreement with a prediction by Talapov.[13] Villain[5] has shown that entropy considerations favor the hexagonal structure. Experimentally, only the hexagonal phase has been found.[11]

II. MODEL POTENTIALS

The accuracy of the present calculation is limited by our ability to choose realistic potentials. We need to consider both the krypton-graphite and krypton-krypton interactions. In the latter case, it is necessary also to take into account graphite-mediated interactions. The graphite layers are taken to be rigid.

A. Krypton-substrate interaction

The best-known potential is that of Steele.[2] He modeled the krypton-graphite interaction by a sum of Lennard-Jones potentials between krypton and carbon atoms. In a plane, a distance z from the exposed graphite layer, and parallel to it, the potential can be written as

$$V(\vec{r},z)=V_0(z)+\sum_{\vec{g}} V_g(z)e^{i\vec{g}\cdot\vec{r}}\,, \tag{1}$$

where the $\vec{g}$'s are the two-dimensional graphite reciprocal-lattice vectors. Using the parameter values suggested by Steele,[2] we find the krypton potential-energy minimum at a distance $z_0=3.46$ Å above the honeycomb center. We obtain $V_0(z_0)/k_B=-1112.34$ K and $V_g(z_0)/k_B=-4.43$ K for $\vec{g}$ in the first shell. Only the first set of reciprocal-lattice vectors and the carbon atoms in the graphite layer closest to the krypton plane need to be taken into account to describe the potential modulation at distances as large as z_0. The function $V_g(z)$ varies rapidly with z and the height at which the potential minimum occurs increases by approximately 0.06 Å as a krypton atom is moved from above a honeycomb center to a position above a corner. Let ΔV be the increase in energy at this position. A reasonable two-dimensional potential can be constructed by replacing $V_g(z)$ in (1) by $\Delta V/9$. [This would give (5.2 K)k_B in the case of the Steele potential.] The value of 3.46 Å for z_0 is close to $z_0=3.35\pm0.1$ Å reported by Shaw *et al.*[14] using low-energy electron diffraction (LEED) and the x-ray absorption fine-structure (EXAFS) result 3.3 ± 0.1 Å quoted by Bouldin and Stern.[15] Because of the dramatic dependence of $V_g(z)$ on z the effective two-dimensional modulation would be considerably larger if z_0 were to lie toward the lower end of the experimental uncertainty. It has also been suggested by Bonino *et al.*[16] that the anisotropy in the graphite polarizability could lead to an increase in the potential modulation by a factor of the order of 2. For this reason we will here treat V_g as an adjustable parameter.

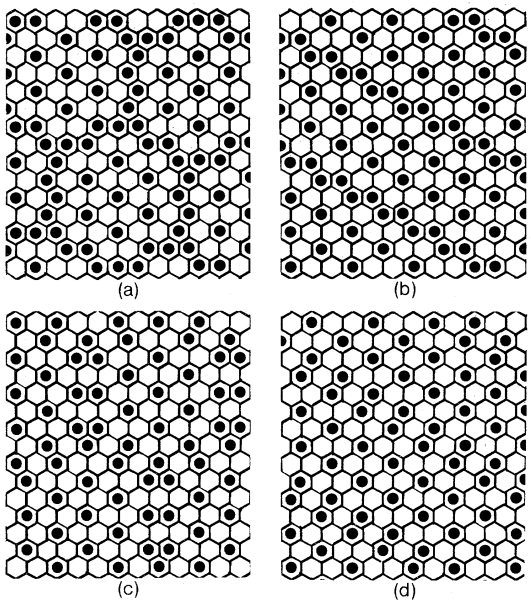

FIG. 1. Typical periodic configurations in the lattice-gas limit. (a) Hexagonal superheavy walls with $l=3$. (b) Striped superheavy walls with $l=4$. (c) Hexagonal heavy walls with $l=3$. (d) Striped heavy walls with $l=4$.

B. Krypton-krypton interactions

We use the potential derived by Aziz[17] to describe the Kr-Kr pair interaction. This potential describes quite well the dilute bulk properties of Kr. When the gas is adsorbed on graphite one must also include the substrate-mediated potential which arises from a three-body effect where the entire graphite structure is treated as the third body (for a review see Steele[2]). We have chosen the Sinanoglu-Pitzer[18] form

$$V(r)=C/r^3 \tag{2}$$

for this term. We use $C/k_B=1595$ Å^{3}K to agree with the observation of Freeman[19] that the substrate-mediated interaction reduces the pair potential-well depth U_0 by about 12.3%. This gives $U_0/k_B=175$ K. This potential is in fairly good agreement with the potential recently reviewed by Bruch.[20] In our calculation we take into account Kr-Kr interactions up to a distance of 12.22 Å when the potential is approximately 0.1% of U_0.

III. CALCULATIONS

We have calculated the energy per atom for different strain-free configurations using the adatom-adatom and adatom-substrate interactions discussed in the preceding section. These configurations were obtained by letting the adsorbed atoms move in the direction of the net force acting on them until the strain is effectively zero. As the adatom coverage is

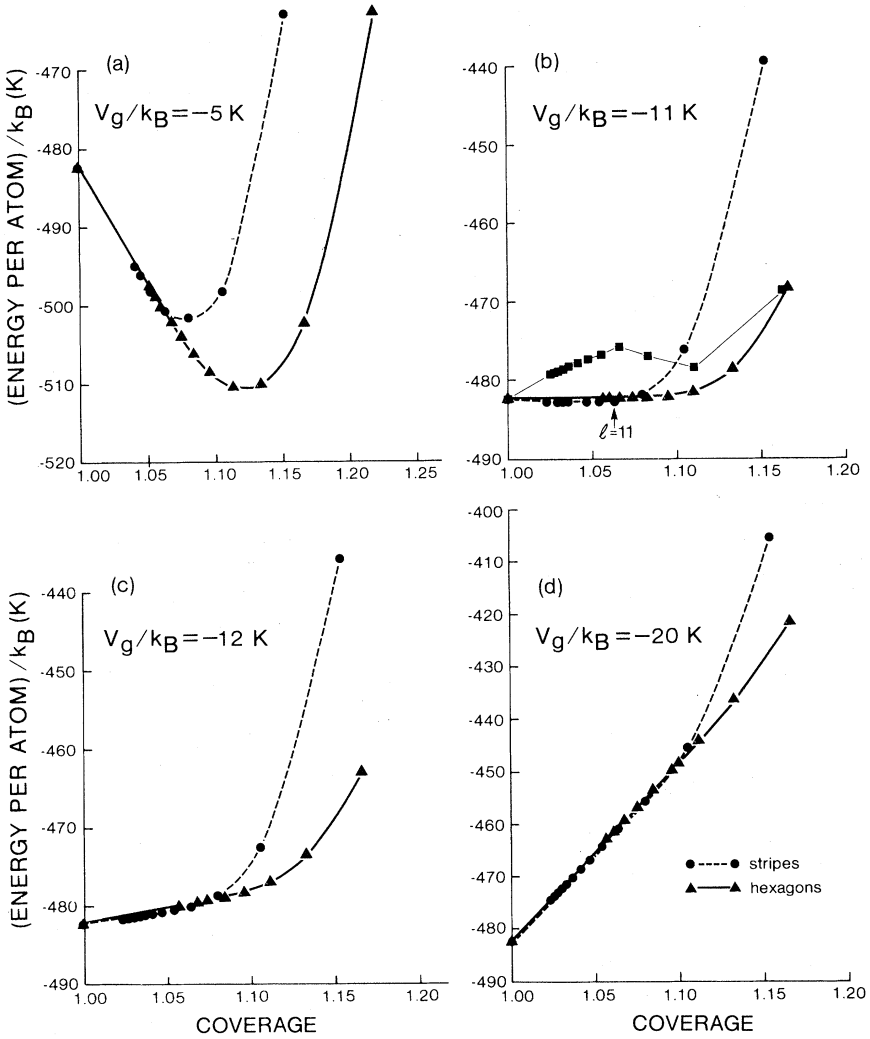

FIG. 2. Energy per atom for different relaxed configurations starting from superheavy walls. The points marked by squares in (b) have hexagonal heavy walls as starting point. The lines are only intended as guide to the eye. The energies are all in K and the zero of energy is the minimum energy of a single Kr on the graphite surface. The $\sqrt{3}\times\sqrt{3}$ registered phase has an energy of $-(482.19\text{ K})/k_B$ (or -41.5 meV) per atom.

varied we expect the ground-state configurations to include a set of discrete points consisting of high-order commensurate phases. In analogy with the situation which pertains to the one-dimensional case, we expect these commensurate phases to form a "devil's staircase."[21,22] Prime candidates to the status of being a ground-state configuration at the appropriate coverage are structures which can be obtained by relaxing periodic arrays of registered domains separated by walls. The simplest symmetries of the network of walls are honeycombs and stripes. In the former case, a uniform compression will, in the lattice-gas limit, lead to what Kardar and Berker[7] call superheavy walls. These are also the outcome of a uniaxial compression leading to a striped phase [see Figs. 1(a) and 1(b)]. A periodic array of hexagonal domains of equal size separated by "superheavy" walls can be constructed for the discrete set of coverages

$$n_H = \frac{9l^2-9l+3}{9l^2-15l+7} n_0 \ . \tag{3}$$

Here l is the number of atoms per side of the hexagon (giving $3l^2-3l+1$ as the number of atoms per unit cell) and n_0 corresponds to the $\sqrt{3}\times\sqrt{3}$ configuration. Similarly, a regular array of superheavy stripes can occur for coverages

$$n_S = \frac{3l}{3l-2} n_0 \ . \tag{4}$$

We have also carried out calculations for hexagonal configurations corresponding to "heavy walls" in the notation Kardar and Berker[7] [see Figs. 2(c) and 2(d)]. In this case the coverage, expressed in terms of the number l of atoms along a hexagon, is given by

$$n_H = \frac{9l^2-9l+3}{9l^2-12l+4} n_0 \ . \tag{5}$$

In Fig. 2 we plot the energy per atom in relaxed configurations corresponding to coverages given by (3)–(5). The zero of energy corresponds to an isolated Kr atom sitting at the energy minimum above a honeycomb center. The calculations have been carried out for a range of values for the strength parameter V_g defined in Eq. (1). The line through the points is only intended as a guide to the eye.

In Fig. 3 we show the displacement of the atoms in a direction from a domain center perpendicular to the domain wall in a hexagonal structure for three values of the strength parameter. The lines are solutions to the one-dimensional sine-Gordon equation (x is the row number):

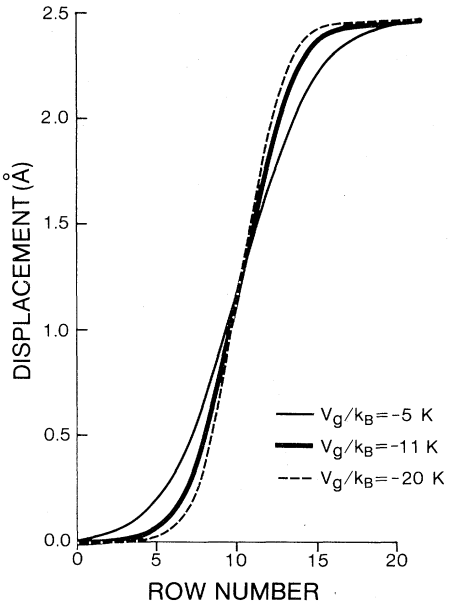

FIG. 3. Atomic displacements from $\sqrt{3}\times\sqrt{3}$ registered positions. Actual atomic positions correspond to integer values of the abscissa. The calculations were carried out for a superheavy hexagonal domain structure with $l=11$ (coverage 1.066) and in a direction bisecting a wall.

$$\frac{1}{a\sqrt{3}} \frac{d^2u}{dx^2} = \frac{\pi}{2l_0^2} \sin\left[\frac{2\pi u}{a\sqrt{3}}\right] \tag{6}$$

with fitted values of the strength parameter l_0. This equation yields the strain-free solution for a linear harmonic chain on a sinusoidal substrate[23] within the continuum approximation. The domain size is $l=11$.

In Fig. 4 we plot the angular average of the structure factor

$$S(\vec{q}) = \left| \frac{1}{N} \sum_j e^{i\vec{q}\cdot R_j} \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2 . \tag{7}$$

Here $\vec{R}_j$ is the coordinate of the jth domain, N is the number of domains, and $\vec{r}_i$ is the position of the ith atom within a domain. We have again chosen $l=11$ and smeared the δ functions by Gaussians of width $0.01g$, where g is the first reciprocal-lattice vector of the $\sqrt{3}\times\sqrt{3}$ structure. Only the intensity of the first satellite depends significantly on the strength parameter V_g, while the width of the main peak is determined by the domain size (coverage).

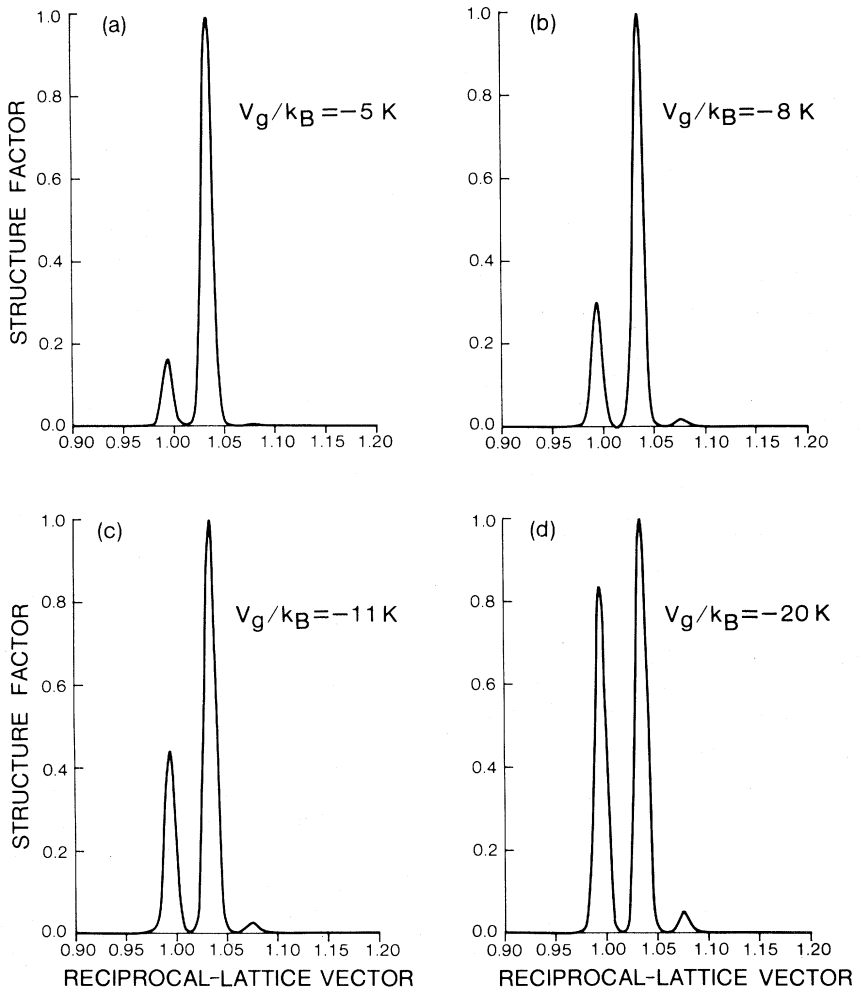

FIG. 4. Angular average of structure factor $S(q)$ for a hexagonal structure with $l=11$ and different values of V_g. The calculated δ-function distributions have been smeared by a Gaussian of width $\sigma=0.01g$.

IV. RESULTS

A. $V_g/k_B=-5$ K

We see from Fig. 2(a) that the substrate potential in this case is too weakly modulated for the state with the lowest energy per atom to be the $\sqrt{3}\times\sqrt{3}$ structure. Instead the system will, at very low temperatures, be expected to contract to a structure with domain walls. Interestingly, the hexagonal configuration is always lower in energy than the striped phase. The reason is that when the substrate modulation is so weak the energy cost of maintaining the registry distance between atoms in the direction parallel to the walls becomes significant. In contrast, the interatomic spacing is almost uniform in the hexagonal case. The lowest energy per atom is $E_H=-(510.5\text{ K})k_B$ and occurs at $n=1.125$. This energy is 28 K lower than that of the registered configuration ($E_R/k_B=-482.19$ K).

B. $V_g/k_B=-11$ K

As can be seen from Fig. 2(b), we are now close to the transition to the situation where the $\sqrt{3}\times\sqrt{3}$ configuration has the lowest energy per atom. There is now a substantial range of coverages $[(n=1)$–$(n=1.1)]$ for which the energy changes by less than 1 K, and there is very little energy difference between the striped and hexagonal structures. For coverages near registry the energy is ~ -483 K/atom. From Fig. 3(b) we see that the domain walls are still very thick, $l_0\approx 11$, and the good fit to the Frank and Van der Merwe theory in-

dicates that the continuum model of Shiba[10] would still be quite good.

C. $V_g/k_B = -12$ K

We have now entered the regime where the $\sqrt{3}\times\sqrt{3}$ configuration is the lowest-energy state, but the compressibility is still quite large for moderate compressions. We have not shown the displacement pattern or the structure factor for this V_g since the results are essentially the same as for $V_g = -11$ K. The main satellite in the structure factor is still relatively weak and the higher satellites negligibly small. The distortions across the domain walls are well described by the continuum model.

D. $V_g/k_B = -20$ K

The compressibility is now much lower, and it might be easier to start a second layer than to compress the system. The main satellite in the structure factor is now too large to be compatible with experiment.[11] Nevertheless, we see from Fig. 3 that the distortions are still surprisingly well described by the continuum model with a wall-thickness parameter as large as $l_0 = 8$. The hexagonal and striped configurations are still very close in energy for moderate compressions.

E. Heavy walls

In addition to the "superheavy-wall" configurations, we have also carried out calculations with "heavy walls" [see Figs. 1(c) and 1(d)]. For small modulations (such as, e.g., $V_g/k_B = -5$ K), the relaxed energies lie on essentially the same smooth curve as the energies for superheavy walls. As the modulation $|V|_g$ increases, the heavy-wall configuration becomes energetically unfavorable as shown in Fig. 2 for $V_g/k_B = -11$ K.

F. Ground-state energy

We have plotted in Fig. 5 the value of the energy minimum (as a function of l) for different substrate modulations V_g. For large $|V|_g$ the registered phase gives the ground state while the hexagonal phase gives the lowest energy for small $|V|_g$. The striped phase gives a marginally lower energy near the transition.

V. CONCLUSIONS

If the krypton-graphite potential modulation had been as low as $V_g/k_B = -5.2$ K (the value which comes out as Steele's[2] choice of parameters), the lowest energy per atom would occur for an incommensurate hexagonal configuration with relatively high density. There is, however, no experimental evidence[1] that the registered configuration is unstable at low temperatures.

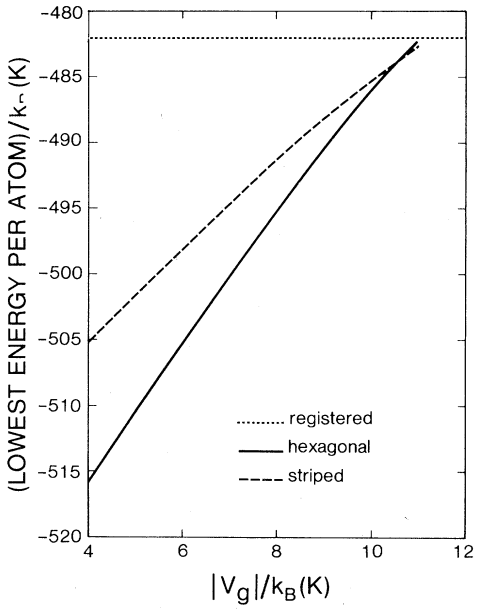

FIG. 5. Lowest energy per atom for different configurations as a function of V_g.

For $V_g/k_B < -11$ K the registered $\sqrt{3}\times\sqrt{3}$ configuration has lowest energy. We have seen that for $V_g/k_B \sim -11$ K there is very little difference in energy between the registered and compressed state and between striped and hexagonal configurations. We then expect thermal fluctuations to be very large and it will be difficult for the system to reach a thermal equilibrium configuration at low temperatures. This might explain why it has not been possible to perform well-characterized experiments at very low temperatures.

Whenever V_g is negative enough for the registered configuration to be lowest in energy, there is, for moderate compression, very little difference in energy between the striped and hexagonal configurations. By Villain's entropy argument the free energy will, at accessible temperatures, be lower for the hexagonal phase than for the striped phase, explaining why only the hexagonal phase is seen experimentally.

The prominent features of the calculated structure factors are a dominant peak and a main satellite. The former is essentially determined by the domain-wall density (which again is determined by the density). The intensity of the main satellite grows nearly linearly with the magnitude of the sub-

strate modulation V_g while the higher-order satellites are very weak (and not seen experimentally). Wall fluctuations at finite temperatures will reduce the satellite intensity. The first satellite was observed by Moncton *et al.*[11] up to $T=96$ K. This satellite was not observed by Abraham *et al.*[24] in their molecular-dynamics simulation. This suggests that they used a surface potential which was too weakly modulated (they used the potential suggested by Steele[2]). On the other hand, the satellite is almost as intense as the main peak for $|V_g|/k_B=20$ K suggesting that this value is too large.

Our analysis of the atomic displacements in the relaxed configurations show that the domain walls are very broad. Therefore, we expect that a continuum model will accurately simulate the strain-free configurations of the krypton monolayer. The sine-Gordon parameter is found to be ~ 10. We therefore expect little pinning by the substrate. Subtle effects such as orientational epitaxy can be studied most easily within the framework of a continuum model.

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