Anharmonicity in rare-gas monolayers

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We have calculated the energy and atomic positions of possible ground-state configurations of Kr and Xe monolayers physiadsorbed on graphite for different coverages. We do this by expanding in a Fourier series the modulation of the atomic positions. In so doing, we extend the previous work of Shiba by (1) using microscopic pair potentials, (2) taking into account the discreteness of the lattice, and (3) including anharmonic terms. It is found that the cubic term in the expansion of the rare-gas pair potential is significant for Kr, but not for Xe. Excellent agreement is found with previous calculations using a different approach.

Graphite will, at low temperatures, allow physisadsorption by rare gases such as Kr and Xe. Under suitable conditions, rare-gas monolayers are formed which exhibit solid phases that are either commensurate or incommensurate with the carbon substrate. It is of interest to study these phases as well as transitions between them (an excellent review is that of Villain and Gordon[1]). If the monolayer is slightly expanded or compressed beyond that of the $\sqrt{3}\times\sqrt{3}$ graphite configuration, then the interaction with the substrate will cause a modulation of the triangular lattice associated with the mean spacing. These modulations have the appearance of registered domains separated by discommensurations or domain walls. Model calculations for Kr (Ref. 2) and Xe (Ref. 3) indicate that the incommensurate phases contain very broad and smoothly varying structures (~ 35 Å for Kr and ~ 100 Å for Xe). Experimental diffraction studies[4,5] also indicate that there are no sharp domain walls. Under these circumstances, it is natural to make use of a method similar to that of Shiba.[6]

The present communication presents results for the ground-state properties of Xe and Kr. The approach taken generalizes Shiba's work in three respects: (i) We calculate the forces between the adatoms using microscopic pair potentials, instead of macroscopic stress tensors. (ii) When calculating the displacements of the adatoms, the continuation approximation is not made. (iii) Anharmonic contributions to the adatom pair potentials are taken into account.

The results of the present calculation are found to be in good agreement with those of Refs. 2 and 3. The present methods, however, are computationally considerably more efficient and therefore are more suited to further applications. We plan to present elsewhere results on the phonon modes, including the phonon contributions to the free energy.

In our study, we express the position of the ith adatom as

$$\vec{r}_i=\vec{R}_i+\vec{v}_i \ , \tag{1}$$

where $\vec{R}_i$ is a triangular lattice vector with lattice constant determined by the coverage, and $\vec{v}_i$ is the displacement relative to $\vec{R}_i$. We consider strain-free configurations that exhibit periodic superstructures of hexagonal symmetry. Let

$$\vec{q}_{lm}=l\vec{q}_1+m\vec{q}_2 \tag{2}$$

be a reciprocal lattice vector of the superlattice with primitive vectors $\vec{q}_1$ and $\vec{q}_2$. The displacement field can be expressed as

$$\vec{v}_i=\sum_{l,m}\vec{u}_{lm}e^{i\vec{q}_{lm}\cdot\vec{R}_i} \ . \tag{3}$$

For the rare-gas pair potential $\phi(\vec{r}_i-\vec{r}_j)$, we have used the potential of Aziz.[7] This potential was originally intended for Kr while in the case of Xe, we have rescaled the potential parameters as discussed in Ref. 3.

We used the McLachlan[8] expression as discussed by Rauber, Klein, and Cole[9] for the substrate mediated screening of the pair potential. In the case of Kr, calculations were also performed with Sinanoglu-Pitzer[10] form for ease of comparison with earlier work.[2]

The pair potentials are expanded in a Taylor series about the points $\vec{R}_i$, giving for the total adatom-adatom interaction energy

$$\begin{aligned}U&=\tfrac{1}{2}\sum_{i\neq j}\phi(\vec{r}_i-\vec{r}_j)\\&=\tfrac{1}{2}\sum_{i\neq j}\{1+(\vec{v}_i-\vec{v}_j)\cdot\vec{\nabla}+\tfrac{1}{2}[(\vec{v}_i-\vec{v}_j)\cdot\vec{\nabla}]^2\\&\quad+\tfrac{1}{6}[(\vec{v}_i-\vec{v}_j)\cdot\vec{\nabla}]^3+\ldots\}\phi(\vec{r}_i-\vec{r}_j) \ .\end{aligned} \tag{4}$$

Similarly, the force on a given adatom is

$$\begin{aligned}\vec{F}_j=-\sum_i\{1+(\vec{v}_i-\vec{v}_j)\cdot\vec{\nabla}+\tfrac{1}{2}[(\vec{v}_i-\vec{v}_j)\cdot\vec{\nabla}]^2+\ldots\}\\\times\vec{\nabla}\phi(\vec{r}_i-\vec{r}_j) \ .\end{aligned} \tag{5}$$

Calculations have been performed in the harmonic approximation and for the case where the cubic anharmonic term is included. In the harmonic case, we have also considered the effect of the continuous approximation. In this approximation, the displacement field is considered to be a continuously varying function $\vec{v}(\vec{R})$. Thus $\vec{v}_i-\vec{v}_j$ in Eqs. (4) and (5) is replaced by

$$\vec{v}_i-\vec{v}_j=\{(\vec{R}_i-\vec{R}_j)\cdot\vec{\nabla}+\tfrac{1}{2}[(\vec{R}_i-\vec{R}_j)\cdot\vec{\nabla}]^2+\ldots\}\vec{v}(\vec{R}_j) \ . \tag{6}$$

In the harmonic approximation, only terms up to second order are retained in (6). In what we call the discrete approach, no use is made of the expansion (6).

The rare-gas–substrate interaction is treated as in Refs. 2 and 3. We construct a two-dimensional potential $V(\vec{r}_i)$ to describe the interaction where

$$V(\vec{r}_i) = V_0 + \sum_{\vec{g}} V_{\vec{g}} e^{i\vec{g}\cdot\vec{r}_i} . \tag{7}$$

$\vec{g}$ is a substrate reciprocal lattice vector and only the first shell of $\vec{g}$'s are considered in the summation. Similarly, the force of a given adatom due to the substrate is

$$\vec{F}(\vec{r}_i) = -\sum_{\vec{g}} i\vec{g} V_{\vec{g}} e^{i\vec{g}\cdot\vec{r}_i} . \tag{8}$$

The total force on a given adatom can be obtained by summing Eqs. (5) and (8). From the assumed periodicity, we can express this force as a Fourier series

$$\vec{F}(\vec{r}_i) = \sum_{l,m} \vec{F}_{lm} e^{i\vec{q}_{lm}\cdot\vec{r}_i} .$$

In this way, the coefficients $\vec{F}_{lm}$ can be expressed as an implicit function of the set $\{\vec{u}_{lm}\}$ defined by Eq. (3). In all cases considered, it was found that the contribution to the displacements from Fourier coefficients beyond the order $m,l = \pm 3$ gave rise to a negligible contribution. If one wishes to consider coverages very close to registered $\sqrt{3}\times\sqrt{3}$ configuration, it would be necessary to include more coefficients. The present calculations involve solving a coupled set of nonlinear equations obtained by setting the coefficients $\vec{F}_{lm}$ equal to zero. We used a multidimensional Newton step method because it provided rapid convergence for initial states close to the force-free state. The calculations were carried out sequentially for coverages approaching registry using the coefficients of each previous calcula-

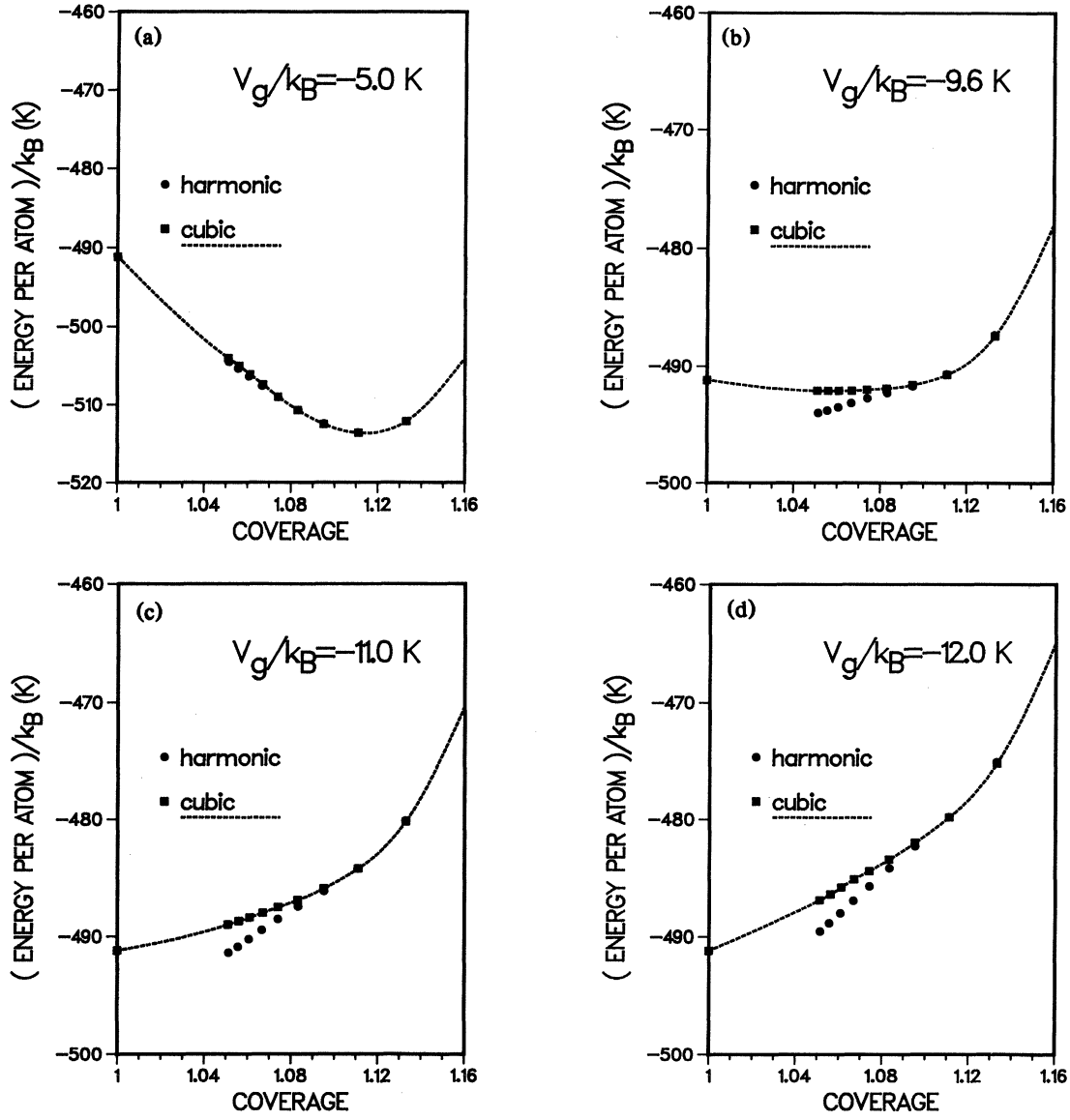

FIG. 1. Lowest-energy configurations for Kr on graphite as a function of coverage for different values of the substrate potential parameter $V_{\vec{g}}$.

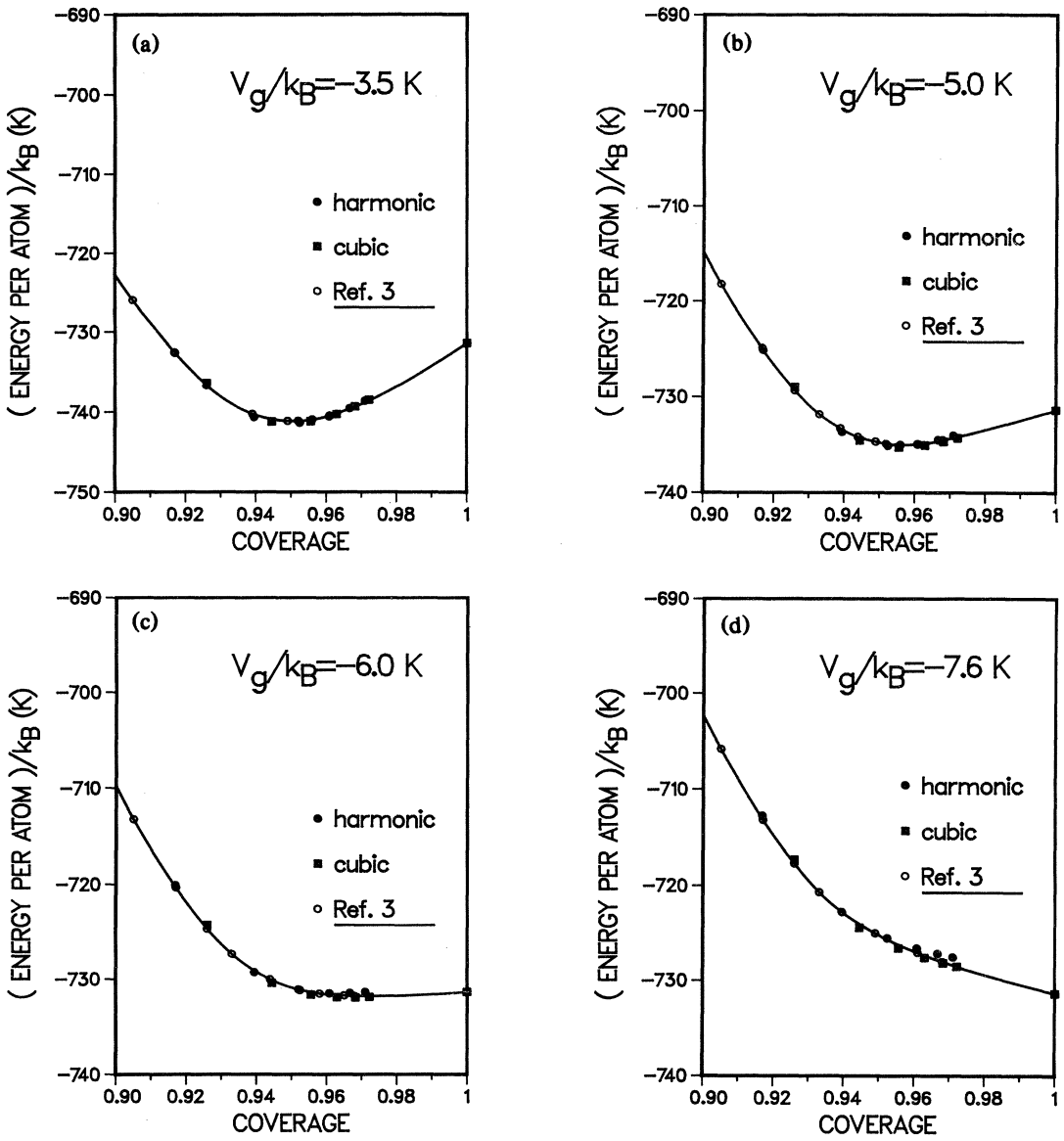

FIG. 2. As in Fig. 1, but for Xe.

tion as input for the initial state of the next calculation. For the first calculation in each sequence, an initial state with zero displacements was used.

We show in Fig. 1 results for Kr using the discrete harmonic and cubic approximations using McLachlan screening. In this calculation, the radial cutoff is set to include the shells up to a distance of 30 Å. The results from the continuum approximation are indistinguishable from that of discrete treatment in the harmonic case and therefore not shown. It is seen that while the contribution from the cubic term is relatively small in magnitude, it is still significant in determining whether the registered configuration is energetically favored. Presumably the reason for this is that when the incommensurate configurations are compressed, the cubic term increases the domain-wall energy. We have repeated the calculations using the parameter values in Ref. 2. The results were found to agree within 1 K for the calculation that took into account the cubic approximation.

In Fig. 2, we show results for Xe. In this case, the effect of the anharmonic terms are found to be qualitatively insignificant. The reason for this is that the domain walls are very broad and smooth for Xe.

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