LOW TEMPERATURE BEHAVIOR OF KRYPTON MONOLAYERS ON GRAPHITE

by

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ABSTRACT

The low temperature behaviour of a system of incommensurate krypton monolayers on graphite was analysed. The free energy was calculated for a variety of monolayer configurations and the misfit and orientation of the minimum energy configuration determined as a function of the temperature and chemical potential of the system. The free energy did not vary significantly over the temperature range from 0 K to 4 K. The zero point energy contributes significantly to the free energy and could not be neglected.

The lowest energy vibrational modes were determined; these modes correspond to motion of the domain walls. For configurations with clearly separated domain walls the vibrational modes separated into groups of three (triads). In the lowest energy triad, the lowest energy mode was a compressional mode. The second and third lowest modes were shearing modes. These three modes describe the fundamental forms of domain wall motion. The modes of the higher energy triads are more energetic forms of the lowest energy triad.

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1.

INTRODUCTION

(I)

MOTIVATION

Rare gas physisorbed systems have been extensively studied because of the two dimensional (2D) nature of the surface film. Experimental results have indicated a large number of possible 2D phases and this has prompted considerable interest. One such system is krypton on graphite.

At low temperatures, graphite will physisorb krypton, and under suitable conditions, a monolayer film of krypton is formed. In addition to the gas and liquid phases of the monolayer, a commensurate and an incommensurate solid phase occurs. The purpose of this work is to study the incommensurate phase of krypton on graphite.

Krypton is a rare gas and therefore it interacts very weakly with its surrounding environment. The interactions result from fluctuations of the atomic moments (London - van der Waals forces). Since no charge exchange occurs, three body effects can be treated as perturbations. The forces present at the atomic (microscopic) level can thus be ascribed either to the substrate or to the individual neighbouring krypton atoms. Moreover, because rare gas atoms are spherical, from a theoretical point of view, the number of parameters required to describe the microscopic nature of the system is reduced. An excellent discussion of the interactions present in a physisorbed system is provided by Bruch¹.

Experimentally, exfoliated graphite substrates with many large, defect free surfaces can be prepared². Large surface areas minimize the impact of finite size on the study of monolayer phase transitions. The great number of such surfaces in exfoliated graphite magnifies the measurable properties of the films. Furthermore, by controlling the temperature of the system and the vapour pressure of the gas above the films the monolayer can be driven between its various phases.

Volumetric studies³ observed a 2D gas phase, a 2D liquid phase, and indicated the possibility of two 2D solid phases⁴. Early diffraction studies⁵ found only one solid phase where the adatoms formed a triangular lattice with spacing of 4.26 Å. This spacing is not favoured by krypton atoms as their interaction energy is minimized for a triangular lattice with a smaller spacing. (From the form of the adatom interaction used in this thesis the spacing is calculated to be 4.02 Å.) A spacing of 4.26 Å reflects the fact that the substrate does not exert a uniform attraction over its surface. The variation in the attraction causes certain adsorption sites on the graphite to be favoured (Figure 1). The bond length of the carbon atoms in the graphite plane is 1.42 Å. Since the adsorption sites are at the centers of the hexagons formed by the carbon bonds, they form a triangular lattice with spacing $\sqrt{3} \times 1.42$ Å. The observed spacing of the monolayer reflects the fact that $\sqrt{3} \times 1.42$ Å is too close a packing for the Kr atoms to fill every adsorption site. Instead, the atoms choose to fill every third

adsorption site so that their positions form a triangular sublattice with spacing 4.26 Å. This phase, which is commensurate with the substrate, is known as the commensurate or the $\sqrt{3} \times \sqrt{3}$ registered phase.

Further experimental work⁶, however, revealed a second solid phase which is characterized by a shift of the main diffraction peak away from its commensurate location. The shift results from a discrepancy, otherwise known as the misfit, between the averaged adatom spacing in this incommensurate phase and that of the commensurate phase. The precise definition of the misfit is provided by equation 2.8. The incommensurate phase is more dense than the commensurate phase. The incommensurate monolayer can also be rotated with respect to the commensurate configuration⁷; the degree of rotation is termed the orientational epitaxy⁸. Satellite peaks are observed and their positions indicate that the adatoms within the monolayer have a hexagonal superlattice structure⁹. The monolayer can be driven from the commensurate phase to the incommensurate phase by increasing the vapour pressure of the gas above the monolayer. The misfit, $M\%$, is observed to vary with the chemical potential μ as

$$M\% \propto (\mu - \mu_c)^\beta \quad (1.1)$$

where $\beta \approx 1/3$ and μ_c is the chemical potential of the commensurate phase⁹. This relationship is found to be

independent of the temperature of the system⁷. For small misfits the monolayer is not rotated with respect to the substrate; however, for misfits greater than 3.5% the monolayer is rotated¹⁰.

Many theories were developed to explain the behavior of the incommensurate monolayer. A calculation was performed by Novaco and McTague⁸ for a system where the substrate interaction is nearly uniform across its surface. For this system, the substrate can be considered to be a perturbing influence on the positions of the adatoms and the interaction can be linearized. The results of this calculation indicate that the incommensurate monolayer will be rotated with respect to the substrate. For krypton on graphite, however, the substrate interaction is significantly modulated and as shown by Shiba¹¹, its influence can not be regarded as being linear. Shiba's calculations predicted that the monolayer would form a uniaxial phase as the density increases from its commensurate value. With a further increase in the density, the monolayer will form a hexagonal phase that be aligned and then will start to rotate with respect to the substrate when the density exceeds a threshold value. Although the rotational behaviour predicted by Shiba matched the observed misfit-dependent orientation of the incommensurate monolayer¹⁰, the uniaxial phase has never been observed experimentally.

Shiba's theory considered the adatom interaction to be harmonic, an approximation that will compromise the results¹².

Calculations for the energy of the static configuration that do not require approximations to the adatom pair interaction involve a relaxation process whereby the positions of the adatoms are shifted until a static force-free configuration is achieved. Gooding et al.¹³ have performed relaxation studies for the non-rotated configurations of krypton monolayers and conclude that the configuration with lowest energy per adatom is dependent on the magnitude of the substrate corrugation. If the substrate corrugation is greater than 11.0 K, the monolayer will be registered with the substrate, otherwise the configuration will be incommensurate. The incommensurate configuration has regions where the adatoms are registered with the substrate that are separated by higher density domain walls. These configurations can have a hexagonal or uniaxial (striped) symmetry. For values of the substrate corrugation large enough for the monolayer to be registered at zero temperature, the monolayer upon compression will form a striped phase¹³. The striped phase is not observed experimentally, therefore the higher entropy of the domain walls in the hexagonal configuration¹⁴ has been expected to be significant enough to influence the equilibrium configuration of the monolayer.

Molecular dynamic calculations by Abraham et al.¹⁵⁻¹⁸ describe the classical behaviour of the system at finite temperatures. The periodic boundary conditions were chosen so that the monolayer could form either a uniaxial or a hexagonal

superlattice structure. No striped phases were observed, although their existence could not be ruled out for configurations close to the commensurate transition¹⁷. The monolayer was found to form a honeycomb domain wall network that approached hexagonal periodicity at low temperatures and coverages¹⁷.

The relaxation and molecular dynamics calculations are limited by computational constraints and hence cannot evaluate the behavior of the monolayer through the transition to a commensurate phase. The results of these studies can, however, be extended to the commensurate limit¹⁸ by using a phenomenological description of the system based on the renormalized system of domain walls¹⁹.

The concept of describing the properties of the monolayer in terms of domain wall structures followed from early work on soliton systems by Frenkel and Kontorova²⁰. Interactions present within the monolayer can provide a system of equations which determine the positions of the adatoms (Appendix B). Frank and van der Merwe²¹ recognized that, for systems where the adatom seeks to have a spacing different from that of the adsorption point spacing, these equations can have soliton solutions. These solitons produce domain walls which separate regions where the adatoms are registered. The energy of the configuration can be determined entirely from the separation of the domain walls, and a renormalized description of the system based on the positions of the domain walls is possible. When

this renormalized description was extended phenomenologically to include wall intersections¹⁹, hexagonally symmetric phases where the domain walls form a honeycomb network could also be analyzed. An excellent review of this theory is provided by Villain and Gordon²².

The monolayer is expected to form a striped incommensurate phase if the intersection of the walls is energetically unfavourable. The monolayer will then have a continuous transition from the commensurate phase to a striped incommensurate phase, which is followed by a hexagonal phase as the density is increased. If wall intersections are energetically favourable, the monolayer will not form a striped phase and the transition from the commensurate phase to the hexagonal incommensurate phase will be first order. As noted above, the striped phase has never been observed. Experimental evidence by Nielsen et al.²³ suggests that the transition is first order, although this has not been substantiated. The latest experimental evidence²⁴ suggests that the monolayer has a continuous transition from a commensurate to a hexagonal incommensurate configuration, although near the transition the domain wall structures appear to become disordered²⁵. This disordering of the domain wall structures has been discussed by Coppersmith et al.²⁶. Their calculations indicate that both the striped and honeycomb domain wall networks are susceptible to dislocations which destroy their structure.

Theories have been developed²⁷ which describe configurations

with domain walls arranged in patterns other than striped or honeycomb wall networks. Because each registered domain has the adatoms situated at every third adsorption site, the domains can be identified as being an a, b, or c, $\sqrt{3} \times \sqrt{3}$ sublattice of the substrate. The domain walls correspond to the boundary between domains of differing sublattices with the simplest type of wall involving a shift of only one adsorption site between domains. Assuming that the walls are constrained to lie along the $0, \pm 120^\circ$ symmetry directions of the substrate, only two types of heavy walls (and light walls) are possible (Figure 2). A system so constrained can be described as a, b, and c patches of adatoms, and its energy will depend solely on the types of domain walls which separate the patches. This situation can be renormalized to a 3 state Potts model where the patches are treated as particles and the domain walls represent their interactions. Potts model calculations are useful for examining the various phases, and the transitions between them, that the monolayer can have. In particular, near the commensurate phase transition, Caflisch et al.²⁸ predict that the domain walls will become fluid.

The intent of this thesis is to calculate the free energy of the system of an incommensurate krypton monolayer adsorbed on graphite and to determine the impact of the monolayer's dynamics on the behaviour of the system at low temperatures. The calculation is based on the microscopic interactions of the adatoms within the monolayer and takes into account the

quantized nature of the adatom motion. This calculation differs from molecular dynamic calculations in that molecular dynamic calculations assume that the motion of the adatoms is classical. The vibrational modes associated with the motion of the domain walls are studied, and their contribution to the free energy of the monolayer is determined.

The thermodynamics of the system is discussed in the following section. Chapter 2 considers the energy of the static configuration. The microscopic interactions present within the monolayer are discussed. The average potential energy per adatom is calculated and its dependence on the configuration of the monolayer is shown. Chapter 3 considers the dynamic aspects of the system. The dynamical matrix for the motion of the adatoms is presented with a discussion of the approximations required in its derivation. The zero point energy is calculated and its impact on the configuration of the monolayer is analysed. Chapter 4 considers the low energy vibrational modes of the domain walls. The behaviour of these modes is discussed and their influence at finite temperatures on the free energy of the monolayer is examined. Chapter 5 presents a concluding discussion that ties the results of the previous sections together and states the original contribution of the author of this thesis.

(II)

FORMALISM

The behaviour of the monolayer must be considered in the context of the total system of krypton vapour, graphite substrate and condensed krypton film. The equilibrium configuration is the configuration that minimizes the total free energy of this system. An exact calculation for the total free energy which considers all aspects of the system simultaneously is not practical. However, approximations can be made which separate the free energy into several independent components thus reducing the complexity of the problem. This separation has been considered by Villain and Gordon²² and their arguments are repeated here so that a consistent terminology may be established.

The general system is taken to be a sealed chamber of volume V containing N_T krypton atoms and a graphite substrate. The temperature of the system is maintained at T . Under appropriate conditions the krypton will condense onto the substrate to form a solid monolayer. The configuration of the monolayer will depend on the temperature and pressure of the gas above the substrate.

Consider the system, at temperature T , when N krypton atoms are adsorbed onto the graphite leaving $N_T - N$ atoms as vapour. In order to determine the properties of the system it is necessary to construct the partition function

$$Z = \sum_S e^{-\beta E_S} \quad (1.2)$$

where s ranges over all possible states of the system (given the constraints V, N_T), E_S is the energy of the state, and $\beta = 1/k_B T$. When the vapour is dilute, the vapour and condensed atoms are weakly interacting so that the energy can be split into two components

$$E_S(N) = E_V + E_C \quad (1.3)$$

where E_V is the energy of the vapour and

E_C is the energy of the condensed krypton and the graphite substrate.

This separates the partition function into contributions due to the vapour and to the condensed system. By using the chemical potential of the gas μ to describe the contribution of the vapour, the partition can be given as

$$Z = \sum_{N=0}^{N_T} e^{-\beta \mu (N_T - N)} \sum_{S_C} e^{-\beta E_C(N)} \quad (1.4)$$

In practice, the chamber is taken to be sufficiently large that the chemical potential of the gas is constant over the range in N relevant to the formation of the solid monolayer phases. This allows the partition function to factorize as

$$Z = Z_V Z_C$$

$$\text{where } Z_V = e^{-\beta \mu N_T} \quad (1.5)$$

$$\text{and } Z_C = e^{-\beta \Lambda_C} = \sum_{N=0}^{N_T} \sum_{s_C} e^{-\beta (E_C - \mu N)}$$

Because the monolayer is large, only one configuration will be significant and the summation over N can be neglected. The equilibrium state will then be the state that minimizes the free energy Λ_C ,

$$\Lambda_C = F_C - \mu N \quad (1.6)$$

where F_C is the Helmholtz free energy of the condensed phase. The study is therefore restricted to an examination of the condensed system. The effect of the vapour on the total system is provided by the chemical potential μ which is treated as a parameter.

The energy of the condensed system will involve both potential and kinetic energies. Because the components of the system are quite massive, the dynamic aspects of the condensed phase are, at low temperatures, expected to provide only minor corrections to the information obtained from calculations of the static properties. The potential energy of the condensed system is considered first and the dynamical contributions are

discussed later.

2.

POTENTIAL ENERGY

(I)

MICROSCOPIC CONSIDERATIONS

The potential energy of the condensed system can be divided into two parts. The first is the potential energy of the bare substrate; the second is the energy change when krypton is adsorbed onto the surface. The calculation can be restricted to consider only the potential energy change due to the monolayer because constant terms have no impact on the equilibrium configuration.

A given adatom will be influenced by pair interactions with neighbouring krypton atoms and the interaction with the substrate. The interaction between krypton atoms is due to fluctuations in the multipole moments which, on average, create an attractive potential. A parameterized form for this potential can be determined from the bulk properties of the rare gas²⁹. Sinanoglu and Pitzer noted that the substrate, because of its metallic nature, acts as a mirror to the dipole moments of the krypton atoms³⁰. This creates an additional quadrupole moment which modifies the interaction between krypton atoms in the monolayer. A more exact form for this modifying effect has been determined by McLachlan³¹. Additional influences have been discussed in detail by Bruch¹ with the conclusion that they do have an impact on the

configuration of the monolayer. Thus, the interaction energy of an adatom with its neighbours can be determined by a summation of pair potentials. In this study, the pair potential is taken to be the bulk potential of Aziz²⁹ and the parameters of Rauber et al.³² have been used in the McLachlan³¹ form for the substrate modification.

The substrate interaction, which involves the attraction between substrate carbon atoms and the adsorbed krypton, is however, not as easily described. The charge distribution within the substrate, due to chemical bonding between carbon atoms, complicates the interaction to the extent that it has not yet been modelled reliably. Because of this, a parameterized form of the substrate potential that reflects the symmetry of the substrate is used in the calculation. As shown in figure 1, the substrate has a Bravais lattice with basis vectors

$$\begin{aligned}\vec{B}_1 &= \frac{3}{2} 1.42 \hat{x} - \frac{\sqrt{3}}{2} 1.42 \hat{y} \\ \vec{B}_2 &= \frac{\sqrt{3}}{2} 1.42 \hat{y}\end{aligned}\tag{2.1}$$

where the units are Angstroms.

If we define $\vec{g}$ to be a reciprocal lattice vector of the lattice, the substrate potential has the form

$$V(\vec{r}, z) = V_a(z) - \sum_{\vec{g}} V_{\vec{g}}(z) e^{i\vec{g} \cdot \vec{r}} \quad (2.2)$$

where z is the height of the krypton atom above the substrate and $\vec{r}$ is a vector confined to the plane of the substrate having its origin at an adsorption site. The summation proceeds over all reciprocal lattice vectors of the substrate.

The dominant term in (2.2), $V_a(z)$, is the surface average of the potential energy $V(\vec{r}, z)$. The remaining terms in (2.2) provide the lateral variation of the substrate potential. As shown by Steele³³, the lateral variation in the substrate potential influences the adsorbed atoms in two ways: Firstly, the substrate can exert a lateral force on the adatoms, and secondly, the height z at which each atom sits varies as a function of its lateral position $\vec{r}$. For the commensurate monolayer, each atom sits above an equivalent site on the substrate and the monolayer is planar. For the incommensurate monolayers, however, the adatoms are not all situated at equivalent sites of the substrate and the monolayer will therefore not be planar.

Gooding et al.¹³ have considered the variation in the height of the adatoms in the monolayer. They find that because the positions of the adatoms $(\vec{r}, z)$ are smoothly modulated, the difference in heights between an adatom and its neighbours will be negligible. The interactions between the adatoms can therefore be calculated as though the monolayer was planar; the

heights of the adatoms are dependent only on the substrate interaction.

Because the substrate potential determines the heights z of the adatoms as a function $z(\vec{r})$ of their position $\vec{r}$, the monolayer's configuration is determined entirely from the lateral positions $\vec{r}$ of the adatoms. This does not imply that the monolayer can be assumed planar, rather that the adatoms lie on the surface defined by the function $z(\vec{r})$. On this surface the potential of the substrate can be expressed exclusively as a function of $\vec{r}$, with the resulting potential $V(\vec{r})$ having a form similar to (2.2). The variation in the substrate potential is so smooth on this surface, however, that summation over reciprocal lattice vectors can be truncated after the first shell³³. This leads to a simplified form

$$V(\vec{r}) = V_0 + V_g \sum_{\vec{g}} \left(1 - e^{i\vec{g} \cdot \vec{r}} \right) \quad (2.3)$$

where the summation involves only the first shell reciprocal lattice vectors. V_g is a parameter, known as the substrate corrugation, which provides the lateral variation in the substrate interaction. Because of the symmetry of the interaction, V_g is a constant that can be factored from the summation.

Given the pair potential $\phi(\vec{r})$, which describes the interaction between krypton atoms in the monolayer, and the

substrate potential $V(\vec{r})$, which gives the interaction between a krypton atom and the substrate, the potential energy of the monolayer can be calculated.

$$E = \frac{1}{2} \sum_{\substack{\vec{r}, \vec{r}' \\ \vec{r} \neq \vec{r}'}} \phi(\vec{r}' - \vec{r}) + \sum_{\vec{r}} V(\vec{r}) \quad (2.4)$$

where $\vec{r}$ and $\vec{r}'$ are positions of the adatoms within the monolayer, and the first summation excludes the possibility that both positions coincide.

The potential energy is minimized for configurations of the monolayer in which the positions of the adatoms satisfy the condition

$$0 = \sum_{\substack{\vec{r}' \\ \vec{r}' \neq \vec{r}}} \vec{\nabla} \phi(\vec{r}' - \vec{r}) + \vec{\nabla} V(\vec{r}) \quad (2.5)$$

As before, the summation excludes the possibility of coincidence. Equation (2.5) reflects the fact that the static forces felt by the adatoms are zero when the positions of the adatoms minimize the potential energy. More generally, the right hand side of this equation describes the force felt by an adatom at $\vec{r}$ due to its neighbouring adatoms and the substrate. This force, if non-zero, will accelerate the adatoms and the resulting behaviour of the monolayer can be analysed by molecular dynamics calculations.

The density modulations due to the domain walls are not as sharp as shown in figure 2; instead, the registered regions smoothly blend into the higher density walls¹³. The adatoms in the monolayer always maintain a hexagonal packing configuration. Their positions $\vec{r}$ have slight displacements $\vec{u}$ from the averaged triangular lattice of vectors $\vec{R}$

$$\vec{r} = \vec{R} + \vec{u}(\vec{R}) \quad (2.6)$$

The primitive lattice vectors, $\vec{d}_1$ and $\vec{d}_2$, for the triangular lattice of vectors $\vec{R}$, have their length determined by the averaged spacing of the adatoms in the monolayer. For the commensurate phase $\vec{u}(\vec{R})=0$, and the basis vectors are the same as the substrate vectors $\vec{D}_1$ and $\vec{D}_2$, defined from (2.1) to be

$$\vec{D}_1 = 2\vec{B}_1 + \vec{B}_2 \quad (2.7)$$

$$\vec{D}_2 = -\vec{B}_1 + \vec{B}_2$$

The experimentally measured quantities of misfit $M\%$ and orientation θ are related to these basis vectors by

$$M\% = \left(1 - \frac{|\vec{d}_1|}{|\vec{D}_1|} \right) \times 100 \quad (2.8)$$

with θ being the angle between the two vectors $\vec{d}_1$ and $\vec{D}_1$.

These quantities are also related to the size and arrangement of the domain network.

Molecular dynamics calculations show that the monolayer forms a honeycomb network of domain walls at low temperatures¹⁷. The domain walls are not pinned to the substrate³⁴ and move easily. For systems with fixed coverage, this behaviour can be described in terms of domain wall vibrations about a perfect honeycomb. The lowest energy deviation of the domain walls from the perfect honeycomb configuration is a breathing distortion which varies the size of the registered domains without changing the total length of the domain walls in the monolayer¹⁴. If energy is not required to breathe the domain walls, the potential energy will be the same for all breathed configurations and can be calculated from the configuration that is periodic. If the breathing motion requires energy, the periodic configuration will be the configuration of minimum energy. If the periodic configuration has vibrational modes that are unstable, then another configuration will be lower in energy. Thus, the energy of the monolayer at a given misfit and orientation can be calculated with the assumption that the configuration is periodic. This assumption is tested when the vibrational modes of the system are calculated.

Assuming the static incommensurate monolayer has superlattice periodicity, figure 3 shows that an adatom in one

registered region will be separated from its identical counterpart in another registered region by a distance

$$\vec{R}_1 = n\vec{D}_1 + m\vec{D}_2 + \ell\vec{B}_1 + k\vec{B}_2 \quad (2.9a)$$

$n\vec{D}_1 + m\vec{D}_2$ is the position of the counterpart adatom in the absence of the intervening wall; $\ell\vec{B}_1 + k\vec{B}_2$ is the shift in its position due to the domain wall.

Given the periodic nature of the system, there will be many possible separations between identical counterpart adatoms, and $\vec{R}_1$ can be taken to be one of the lattice vectors which generate this group. By symmetry, the other primitive lattice vector $\vec{R}_2$ will be

$$\vec{R}_2 = -m\vec{D}_1 + (n-m)\vec{D}_2 - k\vec{B}_1 + (\ell-k)\vec{B}_2 \quad (2.9b)$$

These superlattice vectors are also related to the primitive lattice vectors for the averaged adatom positions by

$$\begin{aligned} \vec{R}_1 &= n\vec{d}_1 + m\vec{d}_2 \\ \vec{R}_2 &= -m\vec{d}_1 + (n-m)\vec{d}_2 \end{aligned} \quad (2.10)$$

The integers n and m specify the size of the domains and ℓ and k indicate the type of walls that separate the domains.

This thesis has been restricted to superlattice

configurations with walls that correspond to shifts of only one substrate adsorption site. The discrete set of possible misfits and orientations of the monolayers that conform to this restriction is given in figure 4. Setting $\ell=1$ and $k=0$ does not reduce the ability to generate this set.

This set of misfits and orientations can be augmented by considering values of ℓ and k which correspond to shifts of more than one adsorption point. The extension to an arbitrary value of misfit and rotation can be obtained by a procedure analogous to the extension of a sequence of rational numbers to an irrational limit. However, at low misfits and small rotation angles, restricting the calculation to configurations for which $\ell=1$ and $k=0$ (figure 4) provides a dense enough sampling that the general behaviour of the monolayer can be determined.

Because further work will involve summations of various quantities (all of which require summation indices), the integer variables ℓ , k , m and n will be used in different contexts. To remove confusion, all further mention of the monolayer configuration will be in terms of misfit and orientation; the integers ℓ , k , m and n (aside from appendix A) will not be associated with the configuration of the system. The relationship between the various geometric properties of the monolayer and these integer variables is described in Appendix A.

(II)

SIMPLIFICATIONS

From (2.2) the adatoms will be forced to lie on a surface $z(\vec{r})$. The positions of the adatoms on this surface will be determined by the substrate's corrugation, which imposes a lateral force on the adatoms, and the interactions between the adatoms. The variation in height z of the adatoms is so slight, that the adatom pair interactions can be calculated as if the monolayer was planar¹³. Also, with the form of the substrate interaction (2.3) the lateral positions $\vec{r}$ of the adatoms can be calculated as though the monolayer was planar. The heights of the adatoms can be subsequently calculated from (2.2). This simplifies the calculation.

In addition, only periodic configurations, where the registered domains are separated by domain walls which shift only one adsorption site, need be considered in order to determine the variation of the monolayer's potential energy as a function of its misfit and orientation. This reduces the calculation, because the potential energy of the monolayer can be determined by examining only the adatoms in one of the periodic domains. Further simplifications to the calculation are possible, because the displacements of the adatoms $\vec{u}(\vec{R})$ are smoothly modulated and the distances between adatoms remain close to the averaged spacings $\vec{R}$ determined from the misfit. This allows the adatom pair potentials used in (2.4) and (2.5) to be expanded as a Taylor series about the averaged spacing.

Given (2.6), this contribution to the potential of an adatom at $\vec{r}(\vec{R})$ can be expressed as

$$E_a(\vec{R}) = \frac{1}{2} \sum_{\vec{R}'} \left(1 + (\vec{u}-\vec{u}') \cdot \vec{\nabla} + \frac{1}{2} ((\vec{u}-\vec{u}') \cdot \vec{\nabla})^2 + \frac{1}{6} ((\vec{u}-\vec{u}') \cdot \vec{\nabla})^3 + \dots \right) \phi(\vec{R}-\vec{R}') \quad (2.11)$$

where the summation excludes the possibility that $R=R'$. From (2.6) $\vec{u}$ and $\vec{u}'$ are functions of $\vec{R}$ and $\vec{R}'$ respectively, and the gradient operator works on the argument $\vec{R}$ of the function ϕ .

The contribution of the pair interactions to the force felt by a given adatom at $\vec{r}$ is likewise

$$\vec{F}_a(\vec{R}) = - \sum_{\vec{R}'} \left(1 + (\vec{u}-\vec{u}') \cdot \vec{\nabla} + \frac{1}{2} ((\vec{u}-\vec{u}') \cdot \vec{\nabla})^2 + \dots \right) \vec{\nabla} \phi(\vec{R}-\vec{R}') \quad (2.12)$$

These series can be truncated after the first few terms because the distances between the adatoms remain near the spacings of the triangular lattice. The most frequently used truncation for analytic studies excludes the anharmonic terms. Within the continuum approximation (appendix B), the displacements of the adatoms must solve a second order nonlinear system of equations. These approximations have been discussed in a previous work¹² with the conclusion that the expansion of (2.11) must include at least the cubic terms to produce agreement with relaxation studies. Other studies³⁵ on similar

systems have considered the quartic term and have concluded that truncating (2.11) at the cubic is adequate. Therefore, to allow the influence of pair interactions to be calculated rapidly, all terms past the cubic are neglected.

Another benefit of the smooth modulation in the adatom positions is that the amount of information required to describe the configuration of the monolayer can be reduced¹¹. From the periodicity of the monolayer, the displacements of adatoms $\vec{u}(\vec{R})$ can be expressed as a Fourier sum^{11,36}

$$\vec{u}(\vec{R}) = \sum_{\vec{\lambda}_m} \vec{u}_{\vec{\lambda}_m} e^{i\vec{q}_{\vec{\lambda}_m} \cdot \vec{R}} \quad (2.13)$$

where $\vec{q}_{\vec{\lambda}_m} = \vec{\lambda}_1 \vec{q}_1 + m \vec{q}_2$ is a reciprocal lattice vector of the superlattice (A.5). The Fourier series can be truncated after the first few long wavelength shells because the displacements have such a smooth spatial modulation. The exact criteria for the truncation is established in section IV of this chapter. The resulting reduction in the amount of information required to describe the system makes the computations for the displacements $\vec{u}$ more efficient.

When the expansion (2.13) is inserted into (2.12), the force due to the adatom interactions becomes

$$\vec{F}_a(\vec{R}) = \sum_{L,M} \vec{f}_{L,M} e^{i\vec{q}_{LM} \cdot \vec{R}} \quad \text{where} \quad (2.14)$$

$$\vec{f}_{L,M} = -\vec{u}_{L,M} \cdot \vec{Q}_{L,M} + \frac{i}{2} \sum_{\ell,m} \vec{u}_{\ell,m} \vec{u}_{L-\ell, M-m} : (\vec{R}_{L-\ell, M-m} - \vec{R}_{L,M} + \vec{R}_{\ell,m})$$

$$\text{and} \quad \vec{Q}_{L,M} = \sum_{\vec{h}} 2 \sin^2(\vec{q}_{LM} \cdot \vec{h}) \vec{\nabla} \vec{\nabla} \phi(\vec{h})$$

$$\text{with} \quad \vec{R}_{L,M} = \sum_{\vec{h}} -\sin(\vec{q}_{LM} \cdot \vec{h}) \vec{\nabla} \vec{\nabla} \vec{\nabla} \phi(\vec{h})$$

the $\vec{h}$ summations range over the triangular lattice generated by the basis vectors $\vec{d}_1$ and $\vec{d}_2$ (A.2).

Similarly, when (2.13) is inserted into (2.11), the average energy per adatom due to the contribution of the pair interactions is

$$U_a = U_0 + \sum_{L,M} \left(\frac{1}{2} \vec{u}_{L,M} \vec{u}_{-L,-M} : \vec{Q}_{L,M} + \frac{i}{6} \vec{u}_{L,M} \sum_{\ell,m} \vec{u}_{\ell-L, m-M} \vec{u}_{-\ell,-m} : (\vec{R}_{L-\ell, M-m} - \vec{R}_{L,M} + \vec{R}_{\ell,m}) \right) \quad (2.15)$$

where $U_0 = \sum_{\vec{h}} \phi(\vec{h})$ is a summation of the pair potentials over the averaged triangular lattice.

From (2.3), the force exerted on a given adatom due to the substrate is

$$\vec{F}_S(\vec{R}) = -\vec{\nabla}V(\vec{r}) = v_g \sum_{j,k} -i\vec{g}_{jk} e^{i\vec{g}_{jk} \cdot \vec{R}} e^{i\vec{g}_{jk} \cdot \vec{u}(\vec{R})} \quad (2.16)$$

where $\vec{g}_{jk} = j\vec{g}_1 + k\vec{g}_2$ (A.4) and the summation over j and k is restricted to the first shell reciprocal lattice vectors of the substrate. Because of the superlattice periodicity, functions of $\vec{u}(\vec{R})$ can be expressed as

$$e^{i\vec{g}_{jk} \cdot \vec{u}(\vec{R})} = \sum_{L,M} A_{L,M}^{jk} e^{i\vec{q}_{LM} \cdot \vec{R}} \quad (2.17)$$

Equations (2.17) and (A.7) allow (2.16) to have the form

$$\vec{F}_S(\vec{R}) = - \sum_{L,M} \left(i v_g \sum_{j,k} \vec{g}_{jk} A_{L-j, M-k}^{jk} \right) e^{i\vec{q}_{LM} \cdot \vec{R}} \quad (2.18)$$

where the summation over j and k maintains the restrictions of (2.16).

Similarly, the average potential per adatom due to the substrate becomes

$$U_S = V_0 + 6V_g - v_g \sum_{j,k} A_{-j, -k}^{jk} \quad (2.19)$$

If the displacements of the adatoms are known, the sum of (2.19) and (2.15) will provide the total potential energy per

adatom. The displacements are determined from the force-free solutions of (2.5). From the results of (2.14) and (2.18), the force-free solution requires that

$$\vec{F}(\vec{R}) = - \sum_{L,M} \vec{F}_{LM} e^{i\vec{q}_{LM} \cdot \vec{R}} = \vec{0} \quad \text{where} \quad (2.20a)$$

$$\begin{aligned} \vec{F}_{LM} = & \vec{u}_{L,M} \cdot \vec{Q}_{LM} + \frac{i}{2} \sum_{\lambda,m} \vec{u}_{\lambda,m} \vec{u}_{L-\lambda, M-m} : (\vec{\bar{R}}_{L-\lambda, M-m} - \vec{\bar{R}}_{L,M} + \vec{\bar{R}}_{\lambda,m}) \\ & + v_g \sum_{j,k} \vec{g}_{jk} A_{L-j, M-k}^{jk} \end{aligned} \quad (2.20b)$$

Given that values of $\vec{u}_{\lambda m}$ and A_{LM}^{jk} are defined over the first Brillouin zone, the summations over λm and jk in (2.20b) will extend the values of $\vec{F}_{LM}$ past the zone edge. As a consequence, the force-free condition (2.20a) does not imply $\vec{F}_{LM}=0$ for all LM, rather the summation of $\vec{F}_{LM}$ over the set of similar points LM of all Brillouin zones is zero. From (2.20b), this requirement will provide enough equations to match the number of variables $\vec{u}_{\lambda m}$ and the system of equations can, in theory, be solved. However, considering that the monolayer structure is so smooth spatially, the higher shell coefficients of $\vec{u}_{\lambda m}$ and A_{LM}^{jk} are negligible and the coefficients of $\vec{F}_{LM}$ which extend beyond the first Brillouin zone can be ignored. Thus $\vec{F}_{LM}$ is taken to be zero in (2.20b). This provides a simpler system of equations, the solution of which will provide, to all intents and purposes, the general force-free configuration.

The following three sections relate purely to the numerical analysis and describe in detail the method for calculating the values of the coefficients $\vec{u}_{\lambda m}$. Given these values the energy of the configuration is obtained from (2.15 and 2.19). The discussion of the physical properties of the system resumes in section VI of this chapter.

(III)

METHOD OF SOLUTION

A Newton step method is chosen to solve the nonlinear system of equations (2.20b). This method is an iterative process where the values of $\vec{u}_{\ell m}$ approach the solution in a series of steps. An initial estimate is made for the values of $\vec{u}_{\ell m}$, and the forces $\vec{F}_{LM}$ are calculated from (2.20b). The response of the $\vec{F}_{LM}$ to a small perturbation $\Delta\vec{u}_{\ell m}$ is then considered. By expanding the force coefficients algebraically in terms of $\Delta\vec{u}_{\ell m}$ and retaining only the linear terms

$$\vec{F}_{LM}(\vec{u} + \Delta\vec{u}) = \vec{F}_{LM}(\vec{u}) + \sum_{\ell, m} \bar{\vec{D}}_{LM, \ell m} \cdot \Delta\vec{u}_{\ell m} \quad (2.21)$$

where

$$\begin{aligned} \bar{\vec{D}}_{LM, \ell m} = & -\bar{\vec{Q}}_{LM} \delta(L-\ell) \delta(M-m) - \frac{i}{2} \vec{u}_{L-\ell, M-m} : \left(\bar{\vec{R}}_{L-\ell, M-m} - \bar{\vec{R}}_{L, M} + \bar{\vec{R}}_{\ell, m} \right) \\ & + v_g \sum_{j, k} \vec{g}_{jk} \vec{g}_{jk} A_{L-\ell-j, M-m-k}^{jk} \end{aligned} \quad (2.22)$$

and advantage is taken of the fact that

$$\begin{aligned} e^{i\vec{g}_{jk} \cdot (\vec{u}(\vec{R}) + \Delta\vec{u}(\vec{R}))} &= e^{i\vec{g}_{jk} \cdot \vec{u}(\vec{R})} (1 + i\vec{g}_{jk} \cdot \Delta\vec{u}(\vec{R}) + \dots) \\ &= \sum_{L, M} \left(A_{LM}^{jk} + \sum_{\ell, m} i\vec{g}_{jk} \cdot \Delta\vec{u}_{\ell m} A_{L-\ell, M-m}^{jk} \right) e^{i\vec{q}_{LM} \cdot \vec{R}} \end{aligned} \quad (2.23)$$

The perturbations $\Delta \vec{u}_{\lambda m}$ are taken to be the values for which $\vec{F}_{LM}(\vec{u} + \Delta \vec{u}) = 0$ (2.21) and therefore must solve the linear set of equations

$$\vec{F}_{LM}(\vec{u}) = - \sum_{\lambda, m} \vec{D}_{LM, \lambda m} \cdot \Delta \vec{u}_{\lambda m} \quad (2.24)$$

These perturbations are added to the $\vec{u}_{\lambda m}$ values and the process of (2.20b), (2.22) and (2.24) is then used to determine, from these new values, the next set of perturbations. This process is repeated until the change in the energy, ΔU determined from

$$\Delta U = \sum_{L, M} \vec{F}_{LM}(\vec{u}_{\lambda m}) \cdot \Delta \vec{u}_{LM} \quad (2.25)$$

falls below a specified value. The minimum energy (or force-free) configuration can thus be determined as accurately as required.

The above discussion presents the Newton step method in its most straightforward form. However, the system under consideration is not quite so easily handled. As has been discussed previously, the adatoms will have extremely soft phonon modes, in fact two modes are acoustic, due to motion of the domain walls. Since the matrix D in (2.24) is simply the dynamical matrix of the system calculated at the Brillouin zone center, the matrix is singular and (2.24) does not have a unique solution. This causes the Newton step method to fail.

To resolve this problem, a specific configuration must be selected and the Newton step method restricted so that it seeks only this solution. The configuration chosen has an adatom situated at the center of the hexagonal domains formed by the domain walls. Since the centers of the domains are registered, the central adatoms are at adsorption sites of the graphite. Given the hexagonal symmetry of the superlattice and the symmetry of the substrate, the minimum energy configuration should be invariant under rotations of 60° about these central adatoms. It is therefore reasonable to impose invariance under rotations of 180° (or inversion symmetry) on the solutions to (2.24). This restriction forces the values of $\vec{u}_{00}$ and $\vec{F}_{00}$ to be zero and their contributions to the system of equations in (2.24) can be neglected. The resulting reduced matrix is nonsingular.

An additional benefit of imposing inversion symmetry is that the $\vec{u}_{\ell,m}$ values are totally imaginary and $\vec{u}_{\ell,m} = -\vec{u}_{-\ell,-m}$. A similar requirement applies to the $\vec{F}_{LM}$, and only one quarter of the matrix D need be considered in (2.24) to obtain a full solution. Therefore, inversion symmetry is imposed to ease the calculation since it not only allows a unique solution of (2.24) to be obtained, it also significantly reduces the amount of computation necessary.

The Newton step method was selected because, with an accurate starting point, it converges rapidly. All nonlinear search methods require a calculation of the $\vec{F}_{LM}$ values; a

numerically tedious process. Therefore, repeated computations should be minimized. This criteria eliminates the other commonly used secant and gradient methods because the system has low energy phonon modes associated with domain wall motion. Even after eliminating the degeneracy in the configuration due to the acoustic modes, the low energy optical modes still allow large fluctuations to be made in the displacements of the adatoms without significant impact upon the calculated energy of the configuration. This can severely slow gradient methods which take steps according to the direction and magnitude of the current force, and can cause stability problems in secant methods. Modified secant methods are stable, but each step requires more computation than those of the Newton step method.

(IV)

NUMERICAL APPROXIMATIONS

The following section is concerned with approximations made to facilitate efficient calculation of the adatom displacements. These approximations will introduce errors into the calculated quantities. However, these errors will be shown to be controllable.

The first numerical approximation concerns the number of adatom shells included in the summation of (2.11). Since the adatom interaction is short range, the summation can be truncated to involve only the first few nearest neighbour shells. This is equivalent to setting bounds on h used in the calculation for $\vec{Q}_{L,M}$ and $\vec{R}_{L,M}$ in (2.14) and for U_0 in (2.15). Once the misfit, $M\%$, for the configuration is specified, U_0 can be calculated and the effect of the truncation examined. Because the error in truncating the calculation for U_0 reflects the error in truncating (2.11), this provides a means of establishing bounds for the summation in (2.11) and correspondingly, the summations over h required in (2.14).

Another numerical approximation concerns equation (2.13) where the displacements of the adatoms are described by a Fourier series summation. From the preceeding section a method of determining the values of $\vec{u}_{\ell m}$ has been established. Because the displacements are smoothly modulated, the first few long wavelength terms are sufficient to describe the system. Exactly how many terms are needed depends on the accuracy

required for the calculated values of the energy (2.15 and 2.19). A trial and error method of determining the number of terms is inefficient, and therefore, an analytic method is sought.

Truncation of the Fourier series restricts the ability to describe sharp structures in the monolayer. Apart from the vertices, the sharpest structures in the monolayer will be the domain walls. The effect of truncating the Fourier series can be examined by considering how the calculated energy of the domain wall changes as the truncation is changed. For this analysis the simpler system of uniaxial domain walls is suitable. Corrections for the vertices will be discussed later.

The theoretical work by Frank and van der Merwe²¹ provides an analytic description of a uniaxial system of domain walls. This is reviewed in appendix B to establish the equations required in the context of this thesis. For the case where the monolayer has a single domain wall, displacements of the adatoms will be given as (B.3 and B.6)

$$\vec{u}(\vec{R}) = \frac{\vec{B}_1}{2\pi} 4 \tan^{-1}(e^{\alpha S}) \quad (2.26)$$

where $S = \vec{B}_1 \cdot \vec{R}$ and $\vec{B}_1$ is a basis vector of the substrate.

For the solution (2.26) the energy of a given adatom (B.4) can be reduced to

$$E(\vec{R}) = E_0 + a(\theta'(S))^2 + b\theta'(S) \quad (2.27)$$

where $\theta(S)$ is defined by (B.6). This provides an analytic form for the energy associated with a domain wall, and the impact of truncating the Fourier series (2.13) can be tested.

Given the definition of $\theta(S)$ in (B.6), in the limit $Q \rightarrow \infty$, the function $\theta'(S)$ can be expressed as

$$\theta'(S) = \int_{-Q}^Q f(q) e^{iqS} dq \quad (2.28)$$

where $f(q)$ is

$$f(q) = \frac{2\alpha}{\pi} \frac{e^{-q\pi/2\alpha}}{1 + e^{-q\pi/\alpha}} \quad (2.29)$$

The error due to truncating the Fourier series is then determined by considering the impact of finite values of Q on the total energy of the system determined from (2.27). The portion of the total energy which is dependent on the value of Q is

$$E(Q) = a \int_{-\infty}^{\infty} (\theta'(S))^2 dS \quad (2.30)$$

where $\theta'(S)$ varies with Q as defined by (2.28).

From (2.29)

$$E(Q) = a \frac{2\alpha^3}{\pi^4} \left(1 - \frac{2e^{-Q\pi/\alpha}}{1 + e^{-Q\pi/\alpha}} \right) \quad (2.31)$$

The relative error $\% \delta(Q)$ introduced by having a finite value of Q is then

$$\% \delta(Q) = \frac{2}{1 + e^{Q\pi/\alpha}} \quad (2.32)$$

The Q sensitive terms present in the calculation of the energy will be the harmonic and cubic terms of (2.15) and the substrate corrugation terms of (2.19). Since the derivation of (2.32) has neglected the vertices present in the monolayer's structure, the resulting estimate of the error may not be accurate. To test the estimate provided by (2.32), sample calculations were performed to obtain the energy per adatom when the summation (2.13) was truncated to include only terms with $|\vec{q}_{2m}| \leq Q$. For configurations with large misfits, because the reciprocal lattice vectors $\vec{q}_1$ and $\vec{q}_2$ are large only a few reciprocal lattice vectors $\vec{q}_{2m}$ are required, for configurations with smaller misfit values, however, the reciprocal lattice vectors are spaced closer together and more are required. A variety of configurations were considered; the calculation was repeated for each configuration with a variety of cut off values for Q . In all cases, expression (2.32) accurately

estimated the error associated with the cut off value of Q . Thus, the estimate of (2.32) allows bounds to be set, in advance, for the number of coefficients $\vec{u}_{\ell m}$ required to calculate the energy of the monolayer to a specified accuracy.

The final numerical approximation required is for the evaluation of A_{LM}^{jk} in (2.17). Analytically, these coefficients can be obtained by taking sums and products of Bessel functions³⁶. From (2.13)

$$\begin{aligned}
 e^{i\vec{g}_{jk} \cdot \vec{u}(\vec{R})} &= \prod_{\ell m} \left(e^{i\vec{g}_{jk} \cdot \vec{u}_{\ell m}} e^{i\vec{q}_{\ell m} \cdot \vec{R}} \right) \\
 &= \prod_{\ell m} \left(\sum_{\nu} J_{\nu}(i\vec{g}_{jk} \cdot \vec{u}_{\ell m}) e^{i\nu\vec{q}_{\ell m} \cdot \vec{R}} \right)
 \end{aligned}
 \tag{2.33}$$

The coefficients $\vec{u}_{\ell m}$ are small, and the summation over Bessel functions can therefore be truncated after the first few terms. Moreover, for the higher shell terms, the Bessel summation can be truncated after the first term because the magnitude of the coefficients $\vec{u}_{\ell m}$ decreases rapidly for increasing $|\vec{q}_{\ell m}|$. This is equivalent to replacing the $\vec{u}_{\ell m}$ in (2.13) by the truncated set which involves only the significant low order shells. This lack of sharp structure is also reflected in the values of $A_{\ell m}^{jk}$ which can be assumed to be zero for the higher order shells. With this restriction the number of coefficients $A_{\ell m}^{jk}$ and the computation required to

determine them can be reduced.

However, even with these reductions, the numerical evaluation of (2.33) for $A_{\lambda m}^{jk}$ becomes increasingly tedious as the number of coefficients $\vec{u}_{\lambda m}$ is increased. The number of operations required in the calculation increases exponentially with the number of coefficients $\vec{u}_{\lambda m}$. Since a large number of coefficients may be required in the calculation, this method is not suitable.

A better method of evaluating (2.17) can be derived from the fact that a domain wall induces a shift of π in the phase of an adatom with respect to the substrate²¹. Because the displacements, $\vec{u}(\vec{R})$, of the adatoms are measured relative to the averaged spacing of the monolayer, the maximum value of $\vec{g}_{jk} \cdot \vec{u}(\vec{R})$ is $\frac{1}{2}\pi$. This bound on the values of $\vec{g}_{jk} \cdot \vec{u}(\vec{R})$ allows the expansion of

$$e^z = \sum_n \frac{1}{n!} z^n \quad \text{where } z = i\vec{g}_{jk} \cdot \vec{u}(\vec{R}) \quad (2.34)$$

to be truncated after the first few terms. Since this expression involves powers of z , the coefficients $A_{\lambda m}^{jk}$ can be evaluated by a short summation involving repeated convolutions of the coefficients $\vec{u}_{\lambda m}$. This can be further improved by utilizing self convolutions, which require half as many operations as the general case. From

$$e^z = (A_n)^{2^n} \quad \text{where} \quad e^{z/2^n} = A_n \pm \delta_n \quad (2.35)$$

A_n is obtained from a truncated Taylor series expansion (as in 2.34) with the resulting error δ_n . Since the argument will be much smaller than $\frac{1}{2}\pi$ for large values of n , the expansion can be truncated after fewer terms than (2.34). e^z is then obtained by performing n repeated squares of the summation's result. The error in e^z due to this method can be calculated from

$$(A_n \pm \delta_n)^{2^n} \approx A_n^{2^n} \left(1 \pm 2^n \frac{\delta_n}{A_n} \right) \quad (2.36)$$

$$\approx A_n^{2^n} \left(1 \pm 2^n \delta_n \right) \quad \text{since} \quad A_n \rightarrow 1$$

If the series for A_n is truncated after m terms, the error δ_n will be

$$\delta_n \approx \frac{1}{m!} \left(\frac{z}{2^n} \right)^m \quad (2.37)$$

with the relative error % δ in the value for e^z due to this method of calculation being

$$\% \delta \approx \frac{z^m}{m! (2^{m-1})^n} \times 100 \quad (2.38)$$

The computational effort for obtaining the set $A_{\lambda_m}^{jk}$ using the above scheme will involve m general convolutions of the set $\vec{u}_{\lambda_m}$ and n self convolutions. Because the displacements are smoothly modulated, the set of $\vec{u}_{\lambda_m}$ and the set of $A_{\lambda_m}^{jk}$ are restricted so that only the long wavelength coefficients are non-zero. Given these conditions, the number of operations required to calculate the values $A_{\lambda_m}^{jk}$ varies as the square of the number of coefficients. This rate of increase is more reasonable than the exponential increase of the Bessel series approach.

From the expression for $\% \delta$ in (2.38), it would appear that the least amount of computation would result if the number of self convolutions is greater than the number of general convolutions (i.e. $m=2$ and n large). However, due to machine rounding, the error is more significant for large values of n than it is for large values of m . Because of this, the actual errors due to this method were calculated for several representative configurations of the monolayer; the general rule was established that the best accuracy and the least work occurs when $m=4$ and n is varied to suit the specified error bound $\% \delta$. With the condition that $z \leq \frac{1}{2}\pi$, and for the specified error bound $\% \delta$, the value of n must be the smallest integer that satisfies

$$n \geq \frac{\log\left(\frac{(\pi/2)^4}{4! \% \delta}\right)}{\log(8)} \quad (2.39)$$

This value of n can be larger than necessary, since some smoothly modulated configurations have maximum values of z that are well below $\frac{1}{2}\pi$. Thus a criterion that also takes into account the configuration of the monolayer provides the most efficient scheme. This is discussed in appendix C.

(V)

CALCULATIONAL PROCEDURE

The potential energy of the monolayer configurations are calculated for various values V_g of the substrate corrugation at the points of misfit and orientation shown in figure 4. Since the Newton step method requires an accurate initial configuration to start, a means of estimating this configuration must be found. Furthermore, the calculation requires error bounds to be set for the various numerical approximations used in the calculation. The error bounds used to truncate the summation (2.13) and to calculate the A_{LM}^{jk} in (2.17) must be expressed as relative errors (2.32 and 2.38). Setting these relative error bounds also requires an estimate of the final result. A procedure whereby accurate estimates of the configuration are obtained prior to calculation is thus required.

From relaxation studies, the structure of the monolayer changes smoothly with misfit. As a result, the $\vec{u}_{\ell m}$ for one configuration closely approximates the $\vec{u}_{\ell m}$ of the configuration with a slightly smaller misfit. For large misfit configurations the domain walls blend together and the displacements of the adatoms are slight. For such a configuration the initial state can be taken to be the triangular lattice of the averaged positions (i.e. $\vec{u}_{\ell m} = 0$), and the error bounds (2.32) and (2.38) can be made more stringent without significant computational consequences. This

establishes a procedure whereby a large misfit configuration is calculated, so that the smaller misfit can be obtained sequentially using the results of one calculation to estimate the next configuration of smaller misfit. This is the same type of procedure as the bootstrap procedure used by Novaco³⁶.

A possible danger of this procedure is that the solutions may converge to metastable states. Such configurations will be force-free solutions to (2.20b), but they will not be the minimum energy configuration. For non-rotated configurations, such metastable states were sought by relaxation calculations¹³. Regardless of the initial state, the monolayer always relaxed to the configuration which was concluded to be the minimum energy configuration. Because the present calculational procedure matches the results of these relaxation studies, the method is considered to be accurate.

For rotated states, however, relaxation results were not available to test the calculation. Instead, tests for metastable states were made by sequentially solving for solutions along a variety of paths through the set of points in figure 4. More than one force-free solution was never found and it is therefore believed that the method finds the configuration of minimum energy. However, with increased rotation, there appears to be a sudden flip between domain wall systems with highly sheared domain walls and very smoothly modulated systems where commensurate domains are absent. This behaviour may be a result of stretching the cubic approximation

of (2.11) beyond validity. Fortunately these configurations, which are outside the range of values shown in figure 4, are quite high in energy and do not influence the choice of equilibrium configuration. They can therefore be disregarded. The configurations relevant to this study have misfits and orientations within the range of figure 4. Within this region the procedure for calculating the configurations is accurate.

For the results presented in this chapter, the energies were calculated to an accuracy of 0.005 K. Because there are four sources of error to be controlled within the calculation, the total of the four estimated uncertainties was set to be 0.005 K. By portioning out the error, the summation over nearest neighbour adatoms in (2.11) is required to be accurate to 0.0005 K. The bounds are set so that the error due to truncating the Fourier expansion in (2.13) is less than 0.003 K, the error involved in calculating the influence of the substrate corrugation (C.8) is less than 0.0005 K, and the error (2.26) associated with limiting the number of Newton steps is less than 0.001 K.

It is recognized that these errors are interrelated, and that separating them out as indicated can underestimate the final uncertainty in the calculation. However, performing sample calculations with a variety of error bounds indicates that portioning out errors as shown provides a value of the energy accurate to 0.005 K with a minimum of computational effort. For a more accurate calculation of the energy, the

error bounds can be uniformly scaled smaller.

(VI)

RESULTS AND DISCUSSION

The monolayer's energy is found to vary primarily with the misfit. In comparison, the variation in energy for different orientations of the monolayer is quite minor. The lowest energy configuration is found to be non-rotated for small misfits, and rotated when the misfit exceeds a value which varies with the substrate corrugation V_g . However, when the energy of the rotated configuration is compared to the energy of the non-rotated configuration of same misfit, the difference is extremely slight. Thus, the change with misfit in the energy of the monolayer can be determined by considering only the non-rotated configurations.

Plots of energy versus misfit for the non-rotated configurations are shown in figures 5a-f. The solid lines indicate the potential energy per adatom in the monolayer. The calculations have been performed for substrate corrugations ranging up to 11.0 K and the most representative plots have been shown. Since rotating the monolayer does not cause any significant decrease in the potential energy, the general result remains that the monolayer forms incommensurate islands if the substrate corrugation is less than 9.8 K^{12} . This value differs from the value of 11.0 K quoted by Gooding et al.¹³ because a different form of the substrate screening is used in the calculation¹².

As noted in the introduction (1.1), the equilibrium

configuration of the monolayer depends on the chemical potential μ of the vapour above its surface. The critical exponent β of (1.1) is found experimentally to be approximately 0.3⁹. The chemical potential μ of the vapour, which is also the chemical potential of the monolayer, can be determined by taking derivatives of the total energy of the monolayer with respect to the number of adatoms in the monolayer. This is equivalent to seeking the minimum of (1.5). To fit these calculated values of μ to (1.1), because there is no data near the commensurate phase, μ_c is not known accurately and both β and μ_c are treated as parameters.

Unfortunately, given the latitude of values for μ_c and for deciding which data points should be considered, linear log fits could be made for a wide range of β values. β was found to lie anywhere between 0.28 and 0.33. Furthermore, the value of β is insensitive to the value chosen for the substrate corrugation. This remains true even when points are included that correspond to nonphysical configurations calculated for $V_g < 9.8$ K which would require negative spreading pressures to exist.

The orientational epitaxy has been analysed for three different substrate corrugations which represent the general behaviour of the monolayer. Selective data has been calculated for other V_g to confirm the trends illustrated. As noted above, the energy of the monolayer is relatively insensitive to its orientation. In order to separate out the orientational

behaviour from the misfit-dependent behaviour, the results are displayed as energy differences between the rotated configuration and the non-rotated configuration. For the specified substrate corrugations, the energies are calculated for all the points of misfit and orientation shown in figure 4. The energy differences are mapped out as contours on a surface of possible misfits and orientations (figures 6a-c). When the substrate corrugation has a value $V_g = 5.0$ K the minimum energy path matches quantitatively the behaviour described by Shiba¹¹. This is expected since harmonic theories are found to be adequate for such a corrugation¹². However, for larger corrugations the behaviour changes and the monolayer rotates at misfits much smaller than Shiba's theory would predict. Furthermore, the line shape of the minimum energy configuration rotation verses misfit curve will not match the Shiba result even if arbitrary scaling of Shiba's parameters is used. To understand this behaviour, the structure of the monolayer must be considered.

For configurations with substrate corrugations greater than 10.0 K the rotated configurations at small misfits that would correspond to the higher energy contours of figure 6c did not converge. Structures that would correspond to heavy domain walls (figure 4) could not be produced. This behaviour was also found by Gooding et. al.¹³ for striped heavy walls at high substrate corrugations since the relaxation calculation would not stabilize. The energies of these structures are expected

to be significantly higher in energy than the stable configurations that are less rotated. They will therefore not have an influence on the equilibrium configuration of the monolayer.

A general analysis of the structure of non-rotated monolayers having small misfits reveals that the density of the adatoms is constant at the center of the domains, it increases along the domain walls, and reaches a maximum at the vertices. This is in agreement with the concept of soliton density modulations arranged in a honeycomb network. The peak in density at the vertex is due to the focused compression of the domain walls which intersect at the vertex. The compression of the adatoms at the vertices becomes stronger for higher substrate corrugations resulting in the spacings of the adatoms at the vertex being less than 4.02 Å which is the spacing favoured by the floating monolayer. For example, when $V_g = 8.0$ K, the spacing at the vertex is found to be 3.99 Å and the monolayer is overcompressed. If the monolayer is allowed to rotate, the domain walls form a staggered intersection³⁷ and the compression due to the domain walls is diffused. The density of the adatoms at the vertices for rotated configurations is not as high as that for the non-rotated configuration and spacings closer to 4.02 Å are found. This decreases the interaction energies of the adatoms at the vertices, and since the change in the substrate energy due to diffusing the vertex is negligible, the rotated configuration

will have vertices of lower energy. When the domains are small the monolayer will have many vertices and the rotated configurations will be energetically more favourable.

For larger domains the preferred configuration is non-rotated despite the overcompression of the vertices. This is due to the fact that the number of adatoms at the vertices becomes significantly less than the number of adatoms on the domain walls. Since the domain walls for rotated configurations must contain a shear as well as a compression, the domain wall adatoms would favour a non-rotated configuration. At smaller misfits, the adatoms on the domain walls dominate the adatoms at the vertices and the monolayer becomes non-rotated.

This describes the orientational behaviour found in figures 6b,c. However, this behaviour must be verified as real and not an artifact of the constraints of the calculation. The configurations examined have inversion symmetry about the domain centers. By breaking this inversion symmetry, the vertices can be diffused. This possibility has been examined by Duesbery and Joos³⁸ who concluded that breaking the inversion symmetry does not change the energy significantly. The orientational behaviour observed in figure 6 is thus considered to be correct even with symmetry breaking. The consequences to the orientational behaviour of forcing the monolayer to be periodic are discussed in the section on phonon modes.

As noted previously, the orientational behaviour does not completely agree with the calculations of Shiba¹¹. This discrepancy is directly attributable to the anharmonic terms present in the approximation to the pair potential (2.11). In harmonic theories the sharp potential minimum of the adatom interaction is not well modelled, however, including the cubic terms improves the fit considerably. Additional terms in the Taylor series expansion will add to the accuracy, but as noted previously, their contribution will be slight compared to the impact of including the cubic term. Thus, for a periodic system, the orientational behaviour predicted by this calculation is expected to be real; additional improvements in the theory due to including more Taylor series terms will only cause slight changes in the misfit value for the onset of rotation.

Gordon and Lancon³⁷ have considered the diffusion of the vertex in relaxation calculations. They conclude that spreading the vertex does not cause any observable change in the energy. However, as seen in figures 6 the energy difference is very slight and within the accuracy of their calculation they may not have detected this effect.

Experimentally the orientational behaviour is observed to match the results of Shiba¹¹. Since the measurements were taken at fairly high temperatures (> 30 K), the thermal motion of the adatoms should diffuse the vertices and allow the non-rotated phases to be favoured where the zero temperature

results shown in figure 6 would indicate otherwise. This is not unreasonable since the domain walls are predicted to broaden with temperature^{22,39}. Furthermore, the thermal broadening of the vertices is suggested by the molecular dynamics study of Schobinger and Abraham¹⁸. They find that at finite temperatures, hexagonal phases are energetically more favourable than striped phases for configurations that at zero temperature are predicted to be striped¹³.

3. DYNAMICAL ASPECTS

(I)

BACKGROUND

The previous chapter has treated the system classically and the configurations of minimum energy assumed that the krypton atoms are stationary. This is an incomplete description of the system since the krypton and carbon atoms vibrate about their equilibrium positions (even at zero temperature) and a calculation of the free energy must also consider this motion.

For the commensurate configuration of the monolayer de Wette et al.⁴⁰ have performed extensive calculations, with the harmonic approximation, for the system's dynamics. They found that the in-plane motion of the adatoms is decoupled from the out-of-plane motion and can be calculated using the rigid substrate approximation (2.2). The out-of-plane long wavelength modes of the monolayer are heavily coupled to the motion of the substrate, and, for the out-of-plane motion, the rigid substrate approximation appears to be inappropriate.

The coupling between the out-of-plane motion of the monolayer and substrate, however, has not been observed in any rare gas physisorbed system⁴¹. Instead, the experimental results can best be explained (except for Xe on the highly corrugated KCl substrate⁴²) by treating the adatoms as independent Einstein oscillators acting under the holding potential $V_a(z)$ (cf 2.2) of a rigid substrate. For graphite

this result is reasonable since the substrate is quite rigid in comparison to the monolayer^{40,43}. If the substrate is assumed to be totally rigid, the holding potential $V_a(z)$ of the substrate so dominates the out-of-plane behaviour that the substrate corrugation and interactions of the surrounding adatoms are of little influence.

For Ag(111) Hall et al.⁴⁴ have performed calculations for an elastic substrate, which indicate that the monolayer's out-of-plane motion can become hybridized with the substrate Rayleigh modes. Furthermore, hybridization with the continuum of bulk modes of the substrate broadens the frequencies of the long wavelength modes. (Hall et al.⁴⁴ refer to this as radiative damping by the substrate.) However, when the dynamics of the substrate and monolayer is compared with that of the bare substrate, the difference is a motion of the monolayer, whose major frequency out of the plane is dispersionless except near the crossing point of the Rayleigh mode. Therefore the out-of-plane motion of the adatoms, relative to the substrate, would appear to be Einstein like.

In any case, experimental evidence indicates that the motion specific to the monolayer appears to be less sensitive to the substrate's dynamics than de Wette et al.⁴⁰ suggest. The discrepancy in de Wette's calculation may be due to the fact that only 13 sheets of graphite were used to model the substrate, and the monolayers may thus have an undue influence on dynamics of the total system. Apart from the fact that a

finite slab calculation can not describe radiative damping, it is expected that a calculation involving more sheets of graphite will produce frequencies which cluster closer to the dispersionless Einstein frequency.

In summary, it appears reasonable to separate the in-plane motion from the out-of-plane motion of the monolayer. For in-plane motion the substrate can be treated as rigid. For out-of-plane motion, most of the dynamics will be associated with the substrate. Out-of-plane motion specific to the monolayer is expected to be "Einstein like", although the Rayleigh mode and the long wavelength bulk modes of the substrate will alter the behaviour slightly. Because the intent of this work is to determine the equilibrium misfit and orientation of the monolayer, any quantity that does not vary with the monolayer's configuration will be irrelevant.

The short wavelength motion of the monolayer out of the plane is dispersionless, even if the long wavelength motion may not be^{40,41,44}. This implies that the adatom interactions are insignificant and can be neglected for these modes. For the incommensurate monolayers, having density fluctuations that do not overly compress the adatoms, this conclusion will be valid. Furthermore, Steele's³³ estimates of the substrate corrugation indicate that the influence of corrugation on the substrate interaction is totally overshadowed by the magnitude of the holding potential $V_a(z)$ and, for the out-of-plane behaviour, the substrate interaction can be regarded as

uniform. Thus, for motion perpendicular to the substrate, the adatoms move independently of each other and without regard to their location on the substrate. This removes any possible distinction between out-of-plane motion of adatoms in the commensurate and incommensurate monolayers, and the mode coupling between the monolayer and the substrate is expected to be, on average, the same regardless of the configuration of the monolayer. For very dense monolayers, the mass of krypton atoms on the surface will start to influence the motion even if the adatom interactions remain negligible. However, the intent of this work is to examine incommensurate phases near the commensurate transition and for such systems, the out-of-plane dynamics are not expected to influence the equilibrium configuration.

The average holding potential of the substrate, $V_a(z)$ in (2.2), which dominates the out-of-plane motion does not affect in-plane behaviour. The behaviour of adatoms within the plane is determined by the substrate corrugation and the interactions between the adatoms. Since the positions of the adatoms change with different configurations of the monolayer, the in-plane free energy contribution will be configuration dependant. Thus, the in-plane dynamics of the monolayer must be determined in order to find the equilibrium configuration.

The in-plane modes are of considerable interest, because the dynamics are significantly different for the commensurate and incommensurate monolayers. For the commensurate monolayer,

each adatom is at an adsorption site. This locks the monolayer onto the substrate and does not allow vibrational energies below a given band gap value. The incommensurate phase, however, contains domain walls which have a great deal of mobility and the monolayer will have low energy modes. Indeed, as mentioned in the introduction, Villain¹⁴ has predicted that a domain wall breathing mode could become completely soft with consequences for the commensurate - incommensurate phase transition²⁶.

Therefore, for the calculation of the dynamics, it is assumed that the motion of the monolayer can be split into in-plane and out-of-plane components. The out-of-plane motion is not expected to have any influence on the equilibrium misfit and orientation of the monolayer and will not be considered. However, the in-plane motion will influence the equilibrium configuration and must be considered. In the following sections, any further mention of dynamics or motion will refer to that within the plane of the monolayer.

(II)

HARMONIC APPROXIMATION

Krypton atoms are quite massive and at low temperatures their vibrational amplitudes relative to their nearest neighbours will be small. Calculations of the dynamics of floating monolayers indicate that anharmonic effects provide only small perturbations to the general results obtained from harmonic treatments⁴⁵. Thus, at low temperatures, the general behaviour of the adatoms in response to each other can be obtained if the motion is assumed to be harmonic.

For incommensurate monolayers, the adatoms are also influenced by the substrate. The domain wall motion causes significant movement of the adatoms relative to the substrate and the influence of the substrate interaction will be harmonic only for small displacements of the walls. Since the walls move freely³⁴, the energy associated with their motion will be small and the amplitude of their vibrations will be large even at zero temperature. Thus, the motion of adatoms cannot be calculated within the harmonic approximation. However, this does not imply that the mode frequencies cannot be calculated with the harmonic approximation.

From a renormalized description of the incommensurate monolayer, the properties of the monolayer can be determined entirely from the shape of its domain wall structures. The location of these structures on the substrate is not relevant since the pinning is so small. In the renormalized picture,

the domain walls will have vibrational modes associated with their motion. Since the behaviour of the domain walls is insensitive to their location on the substrate, anharmonic effects will result only from the walls colliding. The following calculation assumes that these collisions do not occur. The vibrational modes can then be determined by considering the behaviour of the system under infinitesimal perturbations of the domain walls. The consequences of this assumption will be discussed with the results.

For harmonic motion of the adatoms, the normal modes of the incommensurate monolayer can be calculated from the dynamical matrix. The frequencies of the modes will be the eigenvalues of the dynamical matrix. The low frequency motion of the domain walls will not, however, be given directly by the eigenvectors. Instead, the form of the domain wall motion must be interpreted from the movement of the adatoms on the domain walls.

The positions of the vibrating adatoms are defined to be

$$\vec{r}(\vec{R}, t) = \vec{r}(\vec{R}) + \vec{v}(\vec{R}, t) \quad (3.1)$$

where $\vec{r}(\vec{R})$ is the static force free position of (2.6) and $\vec{v}(\vec{R}, t)$ provides the time dependent behaviour. With the assumption of harmonic behaviour, the force felt by a given adatom will be linearly dependent on the motion of the adatoms in the monolayer. This force will cause the adatom to

accelerate; the resulting motion will obey

$$M_a \frac{\partial^2}{\partial t^2} \vec{v}(\vec{R}, t) = - \sum_{\vec{R}'} \bar{D}(\vec{r}(\vec{R}), \vec{r}(\vec{R}')) \cdot \vec{v}(\vec{R}, t) \quad (3.2)$$

where M_a is the mass of the adatom, and the summation over $\vec{R}'$ includes the point $\vec{R}$. The periodic nature of $\vec{r}(\vec{R})$ allows the matrix D in (3.2) to be expressed as

$$\bar{D}(\vec{r}(\vec{R}), \vec{r}(\vec{R}')) = \sum_{\vec{q}_m} \bar{D}_{\vec{q}_m}(\vec{h}) e^{i\vec{q}_m \cdot \vec{R}} \quad (3.3)$$

where $\vec{h} = \vec{R} - \vec{R}'$ and $\vec{q}_m$ is the reciprocal lattice vector as defined for (2.13).

With the definitions of (2.13) and (2.17), and limiting the expansion of the adatom pair interaction to only cubic terms as in (2.11), $D_{\vec{q}_m}(\vec{h})$ can be calculated from

$$\bar{D}_{\vec{q}_m}(\vec{h}) = \varepsilon(\vec{q}) \varepsilon(\vec{m}) \left[\nabla \nabla \phi(\vec{h}) - \varepsilon(\vec{h}) \sum_{\vec{h}'} \vec{\nabla} \vec{\nabla} \phi(\vec{h}') \right] +$$

$$\varepsilon(\vec{h}) \left[v_g \sum_{j,k} \vec{g}_{jk} \vec{g}_{jk} A_{\vec{q}-j, m-k}^{jk} \right] +$$

$$\varepsilon(\vec{h}) \left[\sum_{\vec{h}'} (1 - e^{-i\vec{q}_m \cdot \vec{h}'}) \vec{u}_{\vec{q}_m} \cdot \vec{\nabla} \vec{\nabla} \phi(\vec{h}') \right] +$$

$$(1 - e^{-i\vec{q}_{\ell m} \cdot \vec{h}}) \vec{u}_{\ell m} \cdot \vec{\nabla} \phi(\vec{h}) \quad (3.4)$$

where $\delta(\ell)$ and $\delta(m)$ are integer delta functions, $\delta(\vec{h})$ is a vector delta function, and $\phi(\vec{h})$ is the adatom pair interaction.

For harmonic systems, the equilibrium positions of the adatoms will be the force free positions $\vec{r}(\vec{R})$ of the static configuration. From the periodicity of the static configuration, $\vec{v}(\vec{R}, t)$ must have the form

$$\vec{v}(\vec{R}, t) = \sum_{\vec{k}} \sum_{\ell m} \vec{v}_{\ell m}(\vec{k}) e^{i(\vec{k} + \vec{q}_{\ell m}) \cdot \vec{R} - i\omega(\vec{k})t} \quad (3.5)$$

where $\vec{k}$ can be restricted to the first Brillouin zone of the superlattice and $\vec{q}_{\ell m}$ is defined above.

For equation (3.2) to be satisfied, the coefficients $\vec{v}_{\ell m}(\vec{k})$ in (3.5) must solve

$$M_a \omega^2(\vec{k}) \vec{v}_{LM}(\vec{k}) = \sum_{\ell m} \vec{v}_{\ell m}(\vec{k}) \cdot \sum_{\vec{h}} \bar{D}_{L-\ell, M-m}(\vec{h}) e^{i(\vec{k} + \vec{q}_{\ell m}) \cdot \vec{h}} \quad (3.6)$$

This identifies the dynamical matrix of the incommensurate monolayer

$$\bar{D}_{LM, \ell m}(\vec{k}) = \sum_{\vec{h}} \bar{D}_{L-\ell, M-m}(\vec{h}) e^{i(\vec{k} + \vec{q}_{\ell m}) \cdot \vec{h}} \quad (3.7)$$

The summation over $\vec{h}$ involves nearest neighbour shells of the surrounding adatoms and includes the case when $\vec{h}=0$. Since the adatom interactions are short range, the terms in (3.4) decrease rapidly away from the origin and the summation can be truncated after the first few shells. This is equivalent to assuming that $D_{L-\ell, M-m}(\vec{h})$ is zero for values of $|\vec{h}|$ past a given cut off value.

The possible solutions to equation (3.6) can be calculated and provide the in-plane normal modes $(\omega_s(\vec{k}), \vec{v}_{\ell m}(s, \vec{k}))$ of the system. The index s is used to identify the mode. Since the system is two dimensional, the number of modes will be twice the number of adatoms per domain. With these normal mode frequencies, the in-plane component of the average Helmholtz free energy per adatom is

$$f_C = U_C + \frac{\hbar}{2} \frac{1}{N} \sum_{s, \vec{k}} \omega_s(\vec{k}) + \frac{1}{N\beta} \sum_{s, \vec{k}} \ln(1 - e^{-\beta \hbar \omega_s(\vec{k})/2}) \quad (3.8)$$

where $F_C = Nf_C$ for equation (1.6), and U_C is the energy per adatom of the static configuration (equations 2.15 plus 2.19).

Equation (3.8) has split the free energy into a static energy contribution, a zero point energy, and a temperature dependent contribution. The static energy, U_C , has been calculated in the previous section. The calculation for the zero point energy, E_0 , is given in the following section. The calculation for the temperature dependent contribution, E_T ,

are presented later in chapter 4 which considers the low energy phonon modes.

(III)

ZERO POINT ENERGY

From (3.8) the zero point energy can be obtained by solving for the eigenvalues of the dynamical matrix and then summing for all values of wavevector $\vec{k}$ in the Brillouin zone. For incommensurate monolayers, the number of adatoms per domain increases dramatically as the density of the configuration approaches the commensurate limit. As an example, the non-rotated configuration with a misfit of 2.22% has 675 adatoms per domain and thus 1350 in-plane normal modes. Solving for the eigenvalues of such a large system is computationally unwieldy. Furthermore, calculating the eigenvalues for several $\vec{k}$ points compounds the problem. Therefore, a more practical method of calculating E_0 is required.

If the eigenvalues of (3.6) are defined to be $\lambda_S(\vec{k})$, the frequency $\omega_S(\vec{k})$ of the mode can be determined from

$$\lambda_S(\vec{k}) = M_a \omega_S^2(\vec{k}) \quad (3.9)$$

The zero point energy can then be expressed as

$$E_0 = \frac{\hbar}{2M_a} \int_{\lambda_0}^{\lambda_m} g(\lambda) \lambda^{1/2} d\lambda \quad (3.10)$$

where λ_m and λ_0 are the upper and lower bounds of $\lambda_S(k)$

respectively, and $g(\lambda)$ is the density of states

$$g(\lambda) = \frac{1}{N} \sum_{\vec{s}, \vec{k}} \delta(\lambda - \lambda_{\vec{s}}(\vec{k})) \quad (3.11)$$

The density of states, being a function of λ , can be expanded as a sum of orthogonal polynomials. In the case of two dimensional systems, $g(\lambda)$ is non-zero at its minimum λ_0 and maximum λ_m . Functions of this form are well described using Legendre polynomials⁴⁶

$$g(\lambda) = \sum_{n=0}^{\infty} a_n P_n\left(\frac{2(\lambda - \lambda_a)}{\lambda_d}\right) \quad (3.12)$$

where $\lambda_a = \frac{\lambda_m + \lambda_0}{2}$, and $\lambda_d = \lambda_m - \lambda_0$

Since (3.12) must satisfy (3.11), a_n must have the form

$$a_n = \frac{1}{N} \frac{(2n+1)}{\lambda_d} \sum_{\vec{s}, \vec{k}} P_n\left(\frac{2(\lambda_{\vec{s}}(\vec{k}) - \lambda_a)}{\lambda_d}\right) \quad (3.13)$$

Using the form (3.12) for $g(\lambda)$ in (3.10) produces

$$E_0 = \frac{\hbar}{2\sqrt{M_a}} \sum_{n=0}^{\infty} a_n c_n(\lambda_m, \lambda_0) \quad (3.14)$$

where

$$c_n(\lambda_m, \lambda_0) = \int_{\lambda_0}^{\lambda_m} \lambda^{1/2} P_n\left(\frac{2(\lambda - \lambda_a)}{\lambda_d}\right) d\lambda \quad (3.15)$$

Thus E_0 can be calculated once the orthogonal polynomial moments a_n of the dynamical matrix are determined. While many moments may be required to accurately describe the density of states $g(\lambda)$ (3.12), calculations of smooth averages (3.14) require relatively few moments⁴⁶.

The method of Wheeler and Blumstein⁴⁷ allows the summation over s in (3.13) to be expressed as the trace of an orthogonal polynomial matrix. Because of the form of the dynamical matrix in (3.7), the orthogonal polynomial matrix must have the form

$$\bar{P}_{LM, \ell m}^{(n)}(\vec{k}) = \sum_{\vec{h}} \bar{P}_{L-\ell, M-m}^{(n)}(\vec{h}) e^{i(\vec{k} + \vec{q}_{\ell m}) \cdot \vec{h}} \quad (3.16)$$

The recurrence relation to provide these orthogonal polynomial matrices is

$$\begin{aligned} (n+1) \bar{P}_{L, M}^{(n+1)}(\vec{h}) &= (2n+1) \sum_{\ell m, \vec{h}'} \left[\frac{2}{\lambda_d} (\bar{D}_{L-\ell, M-m}(\vec{h}') - \lambda_a \bar{I}_{L-\ell, M-m}(\vec{h}')) \right. \\ &\quad \left. \cdot \bar{P}_{\ell, m}^{(n)}(\vec{h}-\vec{h}') e^{i\vec{q}_{\ell m} \cdot \vec{h}'} \right] \\ &\quad - n \bar{P}_{L, M}^{(n-1)}(\vec{h}) \end{aligned} \quad (3.17)$$

where $\bar{P}_{L,M}^{(0)}(\vec{h}) = \bar{I}_{L,M}(\vec{h})$ and $\bar{P}_{L,M}^{(-1)}(\vec{h}) = \bar{0}_{L,M}(\vec{h})$ start the recurrence process. ($I_{L,M}(\vec{h})$ is defined to be the 2×2 identity matrix if L, M and h are zero, otherwise it is the 2×2 null matrix; $0_{L,M}(\vec{h})$ is defined to be the null matrix for all L, M and $\vec{h}$.)

Since

$$\frac{1}{N} \sum_{\vec{k}, \vec{q}_m} e^{i(\vec{k} + \vec{q}_m) \cdot \vec{h}} = \delta(\vec{h}) \quad (3.18)$$

performing the summations of (3.13) on the trace of the matrix in (3.16) will result in a_n being given by

$$a_n = \frac{2n+1}{\lambda_d} \text{Tr} \left[\bar{P}_{0,0}^{(n)}(\vec{h}=0) \right] \quad (3.19)$$

(IV)

CALCULATION

The method for calculating the zero point energy, presented above, allows several approximations to be made which improve the execution speed of the calculation without degrading the accuracy of the results. Firstly, the summation in (3.14) can be truncated after the first few terms because it converges rapidly given an appropriate choice of λ_0 and λ_m . Furthermore, as n increases, the weights $c_n(\lambda_m, \lambda_0)$ decrease in magnitude and an increasing error in the moments a_n can be permitted without significant loss of accuracy in E_0 . This increasing tolerance of error in a_n allows approximations to be made to the recurrence process (3.17).

The recurrence process in (3.17) involves a summation over $\vec{h}$ and a summation over ℓ and m . Advantage can be taken of the form of $D_{\ell m}(\vec{h})$ in (3.4) which allows the summations to be separated. If each of these summations can be limited, the amount of computation required by the recurrence process is significantly reduced.

From (3.4), the summation over $\vec{h}'$ in (3.17) will depend on the magnitude of the adatom pair interaction. Because the pair interaction is short range the summation can be truncated after the first few shells. Furthermore, the resulting values of the $P_{L,M}(\vec{h})$ will diminish rapidly with $|\vec{h}|$ and, as in (3.7), the summation of (3.16) can be truncated. This is equivalent to the assumption that the values of $P_{L,M}(\vec{h})$ are zero for values

of $|\vec{h}|$ larger than a given cutoff. With the cutoff value set, the accuracy of (3.16) (and the subsequent accuracy of (3.19)) decreases with increasing n because (3.17) involves a convolution over $\vec{h}$ and the successively generated polynomials have values that are significant beyond the cutoff.

The recurrence process (3.17) also involves a summation over ℓ and m . Because the monolayer has a smoothly modulated structure, terms in (3.4) will decrease rapidly with $|\vec{q}_{\ell m}|$. This behaviour is numerically analogous to the rapid decrease with $|\vec{h}|$ in the terms of (3.4), and similar consequences result. The summation over ℓm in (3.17) can thus be restricted to the long wavelength shells, and the values of the resulting orthogonal polynomials $P_{L,M}(\vec{h})$ can be taken to be zero for $|\vec{q}_{LM}|$ larger than a given cutoff. As with the truncation for $\vec{h}$, the truncation for ℓm will cause increasing inaccuracy in the higher moments.

The moments a_n decline in accuracy at a rate which is dependent on the values of bounds set for $|\vec{h}|$ and $|\vec{q}_{\ell m}|$ in the recurrence process. When the bounds are set low, only a few moments will have significant accuracy. If many accurate moments are required, the bounds must be set higher. Since high bound values increase the amount of computation required by the recurrence process, it is desirable to calculate E_0 with as few moments as possible.

Given that E_0 must be calculated to within a specified uncertainty, the number of moments required is determined by

the convergence of the summation in (3.14) and the rate of convergence of (3.14) depends on the values of λ_0 and λ_m . The most rapid convergence occurs when λ_0 and λ_m are, respectively, the minimum and maximum eigenvalues of the system.

Unfortunately, the approximations in the recurrence process due to the truncations for $\vec{h}$ and $\vec{q}_{\lambda_m}$ cause the method to become unstable if λ_0 and λ_m are exactly the minimum and maximum eigenvalues. This instability arises from the description of the density of states $g(\lambda)$ in (3.12). Should $g(\lambda)$ be non-zero beyond the interval defined by λ_0 and λ_m , the polynomial moments calculated will diverge to infinity. Because the recurrence process has been approximated, the resulting density of states will extend beyond the bounds set by the maximum and minimum eigenvalues, and the calculated moments a_n will diverge. To stabilize the method, values for λ_0 and λ_m must be chosen which are outside the range of possible eigenvalues. This will have the consequence that the summation of (3.14) will not converge as quickly as expected, but given a reasonable choice of λ_0 and λ_m , the convergence will not be significantly slower. The system does not have eigenvalues less than zero, and therefore, λ_0 is chosen to be slightly negative. λ_m should be slightly larger than the maximum eigenvalue, but determining this value is numerically tedious and not necessary because only an estimate is required. Instead, λ_m is set to be twice the maximum frequency of a floating monolayer which has a density equal to the highest

density present in the monolayer; the point of highest density is at the center of the domain wall vertices. This value for λ_m can be easily calculated and provides a reasonably rapid convergence for (3.14).

Given these values for λ_0 and λ_m , E_0 can be calculated to within 0.0005 K with only 11 moments. For these moments to have sufficient accuracy, the bounds on h must be set so that $|\vec{h}| \leq 25$ A. The bounds on $\vec{q}_{\lambda m}$ are adequately set if they are taken to be the same as the bounds used to calculate U_C to the accuracy of 0.0005 K.

To check the results, the calculation was performed with more than 11 moments and with larger bounds on $\vec{h}$ and $\vec{q}_{\lambda m}$. The values for E_0 were confirmed to be accurate to within the prescribed error of 0.0005 K. A more general test for the convergence of the method was performed for the easily handled commensurate configuration and the bounds indicated above produced the required accuracy when compared to the results of direct summation of the eigenvalues.

(V)

RESULTS AND DISCUSSION

For several different values of the substrate corrugation, the zero point energies have been calculated for a variety of misfits and orientations. The zero point energy is relatively insensitive to the orientation of the monolayer. Given the accuracy of the calculation, E_0 appears invariant over the range of orientations in figure 4. Thus the zero point energy of the monolayer will not influence the orientational behaviour of the monolayer. The zero point energy does have significant variation with the misfit of the monolayer. As shown in figures 5a-f, the zero point energy increases with the density of the monolayer. This is not unexpected because as the adatoms become more closely packed, the force constants, and thus the frequencies, increase. Since the zero point energy does not change as the monolayer rotates, it would appear that a calculation based on a floating monolayer with an averaged substrate influence should duplicate these results. Such a calculation was performed and although the general behaviour agreed, the values of E_0 could not be made to match. Thus, compression of the monolayer produces the general trend in the zero point energy but the actual values are subject to more rigorous considerations.

The most significant consequence of these results is that the zero point energy changes the value of the substrate corrugation at which the monolayer switches from an

incommensurate ground state to a commensurate ground state. From consideration of the static energy of the monolayer alone, the critical value of substrate corrugation is 9.8 K. This value is higher than that predicted by theories which calculate the substrate corrugation from the microscopic interactions between the adatom and the substrate¹⁸. Vidali and Cole⁴⁸ have provided the latest estimate of $V_g = 7.4$ K. When the zero point energy is considered, the critical value of substrate corrugation is reduced to 7.0 K (figure 5c). For a substrate corrugation of 7.4 K, the monolayer should be commensurate unless it is forced to be incommensurate. This is in agreement with the experimental evidence that the monolayer can be driven from a commensurate solid to an incommensurate solid by increasing the chemical potential⁶.

The potential between the adatoms is approximated by a Taylor series that is truncated past the cubic term. The zero point energy depends on the second derivative of the pair potential and the cubic approximation may not be valid. To test the effect of this approximation, the adatom pair interaction was replaced by cubic polynomials fit to the segments over which the nearest neighbours range. This is an alternative description to the truncated Taylor series expansion and the differences are displayed in figure 7. For a substrate corrugation of 7.0 K the two calculations produce the same behaviour of the system (figure 8).

Though the behaviour of the adatoms can generally be

described as harmonic, anharmonic influences will alter the results slightly. From self-consistent calculations for the floating monolayer⁴⁵, the zero temperature motion of the adatoms causes the zero point energy to be 6% higher than the value obtained under the harmonic approximation. The increase in energy can be attributed to the interactions of the adatoms since the force constants increase faster upon compression than they decrease on dilation.

The incommensurate monolayer is more complex since its structure allows many different phonon modes. Some of these modes correspond to domain wall motion and move blocks of adatoms as a unit. These modes do not contribute significantly to the zero point energy since they are low in energy and, as will be seen in the following section, few in number. The modes which do contribute significantly to the zero point energy are the higher energy modes which involve motion of the adatoms relative to their neighbours. For these modes the anharmonic effects will be the same as those for the commensurate configuration. Therefore, the zero point energies in figures 5a-e of the incommensurate configurations near the commensurate transition will actually be higher by 6%. Away from the commensurate transition, the density of the monolayer is greater and, from the nature of the adatom interaction, the anharmonic contribution to the zero point energy should decrease. It is anticipated that this decrease will not have a significant impact on the general trend of the zero point

energy. As a result, where the zero point energy calculated with the harmonic approximation predicts that the critical substrate corrugation value is 7.0 K (figure 5c), the anharmonic contribution to the zero point energy will shift the value to be slightly greater than 7.0 K.

4. LOW ENERGY PHONON MODES

(I) HELMHOLTZ FREE ENERGY

The first two terms in (3.8) for the Helmholtz free energy were determined in the previous chapters, and represent the energy of the monolayer at zero temperature. The third term, identified as E_T , provides the temperature dependence of the free energy.

$$E_T = \frac{1}{N\beta} \sum_{s,k} \ln(1 - e^{-\beta \hbar \omega_s(\vec{k})/2}) \quad (4.1)$$

where N is the number of adatoms in the monolayer and $\beta=1/k_B T$.

At low temperatures only the lowest energy modes of the monolayer will be significant in this expression. The commensurate monolayer with all the adatoms locked in adsorption sites will not have any modes with energies below a band gap value. The incommensurate monolayer, on the other hand, has highly mobile domain walls and low energy modes are possible. From (4.1) configurations with extremely soft modes could have a large free energy; the misfit or orientation of the monolayer may thus change significantly with temperature even when the chemical potential μ is kept constant in (1.6). It is therefore interesting to determine the magnitude of E_T at different temperatures for various configurations of the

monolayer.

E_T can be calculated by the polynomial expansion method which was used to calculate E_0 . However, (4.1) is seen to be a rapidly varying function as $\omega \rightarrow 0$. The coefficients $c_n(\lambda_m, \lambda_0)$ calculated for this expression would cause the summation, corresponding to (3.14), to converge very slowly. Thus, many moments a_n must be calculated and the viability of the method is reduced.

Fortunately, the low energy modes, because of their nature, allow approximations to be made to (3.6) which do not compromise the accuracy of the resulting eigenvalues and eigenvectors. These approximations overcome the previously discussed difficulties associated with the large size of the dynamical matrix and allow a practical solution for the eigenvalues and eigenvectors of (3.6). Thus (4.1) can be evaluated through a direct summation of eigenvalues.

(II)

NORMAL MODE CALCULATION

The static incommensurate structure of the monolayer is known to be smoothly modulated¹³. In the previous chapters this fact has allowed approximations to be made to the description of the adatom positions (2.13) so that the static configuration and the corresponding energy per adatom can be calculated efficiently. It is therefore assumed that a comparable approximation can be made for the low energy motion of the adatoms (3.5).

The motion of the adatoms is described by the truncated expression

$$\vec{v}(\vec{R}, t) \approx \sum_{\vec{k}} \sum_{\substack{|\vec{\ell}| \leq n \\ |\vec{m}| \leq n}} \vec{w}_{\ell m}(\vec{k}) e^{i(\vec{k} + \vec{q}_{\ell m}) \cdot \vec{R} - i\omega(\vec{k})t} \quad (4.2)$$

The cutoff parameter n , determines the accuracy of the approximation, and will be discussed below. If this assumption is correct, then only a portion of the dynamical matrix (3.7) will be of significance in determining the low energy modes. The linear set of equations (3.6) can then be reduced to consider only these relevant terms.

The significant portion of the dynamical matrix will be the submatrix S where

$$\begin{aligned}\bar{\bar{S}}_{LM,\ell m}(\vec{k}) &= 0 \text{ for } |\ell|, |m|, |L| \text{ or } |M| > n \\ \bar{\bar{S}}_{LM,\ell m}(\vec{k}) &= \bar{\bar{D}}_{LM,\ell m}(\vec{k}) \quad \text{otherwise}\end{aligned}\tag{4.3}$$

This produces the reduced set of equations

$$M_a \lambda^2 \vec{w}_{LM}(\vec{k}) = \sum_{\ell m} \bar{\bar{S}}_{LM,\ell m}(\vec{k}) \cdot \vec{w}_{\ell m}(\vec{k})\tag{4.4}$$

with

$$\vec{w}_{LM}(\vec{k}) = 0 \quad \text{if } |L| > n \text{ or } |M| > n\tag{4.5}$$

The eigenvalues $\lambda^2(\vec{k})$ and eigenvectors $\vec{w}_{\ell m}(\vec{k})$ of (4.4) can be treated as trial solutions to (3.6). The values λ^2 of these trial solutions are close to being the actual eigenvalues ω^2 of (3.6). In fact⁴⁹,

$$M_a |\omega^2 - \lambda^2| \leq \epsilon\tag{4.6}$$

where

$$\epsilon = \left| \sum_{\ell m} [\bar{\bar{D}}_{LM,\ell m}(\vec{k}) \cdot \vec{w}_{\ell m}(\vec{k}) - m \lambda^2 \vec{w}_{LM}(\vec{k})] \right|\tag{4.7}$$

Using (4.4), equation (4.7) can be reduced so that ϵ can be calculated from

$$\epsilon^2 = \sum_{\substack{|L| > n \\ \text{or } |M| > n}} \left| \sum_{\substack{|\lambda| \leq n \\ |m| \leq n}} \bar{D}_{LM, \lambda m}(\vec{k}) \cdot \vec{w}_{\lambda m}(\vec{k}) \right|^2 \quad (4.8)$$

From (4.2), the accuracy of the approximation should increase as n is increased, thus the value of ϵ will depend on the value chosen for n . For a given choice of n the value of ϵ will also depend on the energy of the phonon mode. From the preceding work, the ground state configuration of the monolayer is known to be smoothly modulated and $D_{LM, \lambda m}(\vec{k})$ (calculated from (3.7) and (3.4)) must decrease rapidly in magnitude for increasing values of $|L-\lambda|$ and $|M-m|$. This has the consequence that ϵ in (4.8) will depend on how rapidly $\vec{w}_{\lambda m}(\vec{k})$ decreases for increasing $|\lambda|$ and $|m|$. The low energy modes of the monolayer correspond to motion of the domain walls, and since the domain walls are smoothly modulated structures, $\vec{w}_{\lambda m}(\vec{k})$ will decrease rapidly with $|\lambda|$ and $|m|$. With increasing phonon energies, however, the modes will be associated with structural variations that are much sharper and $\vec{w}_{\lambda m}(\vec{k})$ will not decrease as rapidly. Thus ϵ increases as the energy of the phonon mode increases and the accuracy of the trial values λ will decrease. Fortunately, only the low energy modes are significant in determining the temperature dependence of the Helmholtz free energy (4.1). For these modes the eigenvalues and eigenvectors can be determined accurately from (4.4) for values of n small enough to make the calculation practical.

From the preceding discussion, the approximating system of

equations (4.4) will produce solutions that are within a determinable error of the solutions to (3.6). This does not imply, however, that all the low energy modes of the system can be determined by this method. To show that the trial solutions from (4.2) do indeed provide the complete set of low energy solutions to (3.6) it is necessary to show a one-to-one correspondence.

The approximate (4.2) and exact (3.6) system of equations agree when the substrate is not corrugated, i.e. $V_g = 0$, and a one-to-one correspondence exists between the exact and approximate modes. Since the dispersion curves of the normal modes are continuously deformable as a function of corrugation strength V_g , this one-to-one correspondence must be maintained for all values V_g . Thus all frequencies ω for the low energy modes of the monolayer can be determined to within the accuracy of (4.6) by this method. The eigenvectors can also be calculated from (4.2); however, when the mode frequencies are close together the eigenvectors calculated may be a linear combination of the corresponding nearly degenerate modes of (3.6).

Dispersion curves are calculated for a range of superlattice configurations. The accuracy of the values calculated is determined by varying the parameter n . It is apparent that the error bound ϵ is generous, since the eigenvalues change very little with n for values of n much less than the value of ϵ would suggest. This overly large error bound is a result of

the sharp cutoff at n present in the eigenvectors $\vec{w}_{LM}(\vec{k})$. A linear mix of the eigenvectors $\vec{v}_{LM}(\vec{k})$ is required to describe this cutoff, resulting in $\vec{w}_{LM}(\vec{k})$ being less than a pure match to its corresponding eigenvector $\vec{v}_{LM}(\vec{k})$. This discrepancy between $\vec{w}_{LM}(\vec{k})$ and $\vec{v}_{LM}(\vec{k})$ would not ordinarily be noticed, but in equation (4.6) it becomes significant. The eigenvalue λ , however, can be expected to be a closer match to ω than the value of ϵ suggests, since $\vec{w}_{LM}(\vec{k})$ is predominantly in the direction of $\vec{v}_{LM}(\vec{k})$. A better indication of the error in λ is obtained by examining the values of the two lowest phonon branches at the Γ point. These values are found to approach zero as n is increased and, for a given n , their computed values give an indication of the absolute error in the eigenvalues of the low energy phonon modes.

For the dispersion curves calculated, the parameter n was chosen so that ϵ is small enough that all but the three softest modes are accurate to better than 0.1% . For the three softest modes an analysis at the Γ point is necessary to obtain the error bounds. The frequencies are given by the square root of the calculated eigenvalues and because the absolute error in the eigenvalues is roughly constant for the low energy phonon modes considered, the percent error in the calculated frequencies will be proportional to $1/\omega$ for frequencies of ω away from zero.

(III)

REVIEW OF PREVIOUS WORK

In a previous paper³⁴, the behaviour of the three lowest phonon modes was discussed for monolayer configurations with misfit values between 1.75% and 2.22%. For reasonable values of the substrate corrugation, the domain walls will be clearly separated at these misfits. These misfit values are large enough that the calculation for the low energy normal modes is practical, and given the renormalized nature of the domain walls, the information obtained about these domain wall modes will apply to incommensurate monolayers in the limit of the commensurate transition.

A typical dispersion curve for the incommensurate monolayer is shown in figure 9. Of the normal modes possible for the monolayer, three modes are significantly softer than the rest. For the wavevector k at M , figures 10a-c illustrate each of the three lowest modes of figure 9; the dashed lines show the deformation of the walls about their equilibrium positions (solid lines). The scale is provided so that the size of the domains can be determined, although the magnitudes of the deformations are scaled arbitrarily to make the modes clearly visible. The value used for the scaling of the wall deformations is, however, consistent in all of figures 10. From figure 10a the softest mode is the breathing mode predicted by Villain¹⁴, with the other acoustic mode and the optical mode producing a shearing of the domain walls.

When the configuration of the monolayer was rotated the two shear modes were found to increase in energy. The dispersion of the breathing mode, however, did not significantly change. When the misfit of the monolayer was decreased, the breathing mode became significantly softer, while the shear modes showed little change.

(IV) QUANTIZED NATURE OF WALL MOTION

The previous paper³⁴ concentrated on the three lowest energy modes as these modes are expected to be the most significant influence on the temperature dependance of the Helmholtz Free energy. The forms of the higher energy modes were not considered. Figure 11 shows the dispersion curves calculated at a misfit of 1.75% . The dispersion curves form a triad grouping of modes. The shape of the dispersion curves for the higher energy triads repeats the shape of the triad for the lowest energy mode.

The form of the domain wall motion calculated at the Γ point is shown in figure 12a for the third lowest and in figure 12b for the sixth lowest mode. It is clear that the higher energy mode is a more energetic version of the lower energy mode. Where the low energy mode causes the domain walls to vibrate with two nodes (at the vertices) the corresponding mode at the higher energy causes the domain walls to vibrate with three nodes. Furthermore, the ninth lowest energy mode (not shown) is found to have the same type of motion except the domain walls vibrate with four nodes.

As an alternate example, the motion of the domain walls at the M point for the lowest energy mode figure 10a can be compared with the motion of the fourth lowest energy mode figure 13a. The fourth lowest mode is clearly a more energetic form of the lowest energy mode. Because this mode causes the

domain walls to vibrate with a wavelength that is twice their length, the frequency of the mode provides the velocity at which vibrations will propagate along the domain walls. The form of this mode is constant through to the Γ point (figure 13b), and should therefore be dispersionless. Further confirmation for the value of the domain wall's wavevelocity can be obtained by examining the seventh mode (figure 11). This mode is twice as energetic as the fourth mode and causes the domain walls to vibrate with a wavevector equal to their length.

Since no contradictions to this quantized behaviour were found, the general conclusion can be made that the domain wall modes are quantized according to the motion of a fundamental triad of modes. The motion of a domain wall mode can be determined according to which of the three triad modes it corresponds to, and the number of the triad's group. This behaviour is expected to break down when the energy of the modes approaches the band gap energy of the commensurate monolayer. At this energy the adatoms in the registered regions also vibrate and the monolayer will have vibrational modes other than domain wall modes.

(V)

DOMAIN WALL INSTABILITIES

From the static results, at misfits greater than 2.5% the monolayer will be rotated when the substrate corrugation is greater than 8.0K. The non-rotated configuration, because of the overcompression of the vertices, will be energetically unfavourable. This observed rotation, however, may be an artifact of the calculation since it is possible to diffuse the vertices by breaking the inversion symmetry imposed on the monolayer. This allows the domain walls to shift relative to the substrate so that the domain walls no longer meet at a point. Should the monolayer seek to form a less energetic configuration by shifting the domain walls, the translational modes calculated for the monolayer with inversion symmetry should be unstable. Within the accuracy of the calculation, unstable translational modes have never been observed. The monolayer does, however, have other modes which can become unstable.

Figure 14a shows the dispersion curves calculated for the non-rotated monolayer with misfit 3.33% and substrate corrugation 8.0 K. It is apparent that one of the modes becomes unstable at the M point. This mode is shown in figure 15 and corresponds to a shearing of the domain walls. Since the energy of the monolayer will decrease with rotation (figure 6b), this suggests that the monolayer is trying to rotate. Alternately, the instability may indicate that the

domain wall periodicity imposed on the monolayer will be broken so that the monolayer can stay non-rotated.

However, this is not likely since the unstable mode (figure 15) indicates that the domain walls wish to be sheared. Because the rotated configuration imposes a shear on the domain walls the non-rotated configuration can not resist being rotated. This is contrary to the behaviour of the monolayer at misfits below 2.5%. At these misfits the shear mode is not unstable and the domain walls resist shearing.

The non-rotated configurations of the monolayer are unstable when the substrate corrugation is greater than 7.0 K and the misfit is between 2.5% and 3.5% . This instability is also found to a lesser degree in some configurations that are slightly rotated. For a given misfit the rotated configurations of lowest energy from figure 6 will be stable as will configurations that are rotated further (figure 14b). For misfits larger than 3.5% , the monolayer no longer has distinct domain walls and it becomes smoothly modulated; this eases the localized overcompression at the vertices and the motion of the monolayer is stabilized. Despite this fact, the lowest energy configuration will still be rotated. The dispersion curves for the non-rotated configuration with misfit 3.7% is shown in figure 16.

In summary, overcompression of the vertices is expected to be a significant influence, not only on the static energy of the monolayer, but also on the stability of the configuration.

The monolayer will seek to ease the overcompression by rotating or breaking the periodicity imposed on the configuration. At higher temperatures, thermal motion of the adatoms is expected to diffuse the vertices so that the periodic non-rotated configurations become stable. Such an effect requires a self-consistent phonon calculation, and confirmation of this prediction awaits further work.

(VI) FREE ENERGY CALCULATION

The expression (4.1) which determines E_T involves a summation over all modes of the monolayer. In order to calculate E_T it is necessary to separate (4.1) as

$$E_T = \frac{1}{N_d} \sum_{\vec{k}} f(\vec{k}) \quad (4.9)$$

where

$$f(\vec{k}) = \frac{1}{N_p} \sum_s \frac{1}{\beta} \ln(1 - e^{-\beta \hbar \omega_s(\vec{k})/2}) \quad (4.10)$$

The total number of adatoms in the monolayer N has been factored into the number of adatoms per domain N_p and the number of domains N_d . For temperatures near zero only the lowest energy modes of the monolayer need be considered. Since it is possible to calculate the frequencies of these modes, $f(\vec{k})$ can be determined. From (3.6), $f(\vec{k})$ is a periodic function with reciprocal lattice vectors $\vec{q}_{lm}$ being those of the superlattice (A.5).

Equation (4.9) can be described as an average of $f(k)$ evaluated at all points $\vec{k}$ in the first Brillouin zone of the superlattice. For a monolayer of infinite extent, the summation in (4.9) is actually an integral. Chadi and Cohen⁵⁰

have devised a method for numerically integrating periodic functions that are analytic. With their method, equation (4.9) becomes a weighted sum of the function $f(\vec{k})$ evaluated at a discrete set of special points $\vec{k}$. The set of special points appropriate to (4.9) have been determined by Cunningham⁵¹. The number of points in the set and their positions vary according to the accuracy required for the numerical integration. This method is reviewed in appendix D.

Unfortunately, $f(\vec{k})$ determined from (4.10) is not analytic. The acoustic modes of the monolayer cause $f(k)$ to diverge logarithmically whenever $\vec{k}$ approaches a reciprocal lattice vector $\vec{q}_{\ell m}$. In order to use the numerical integration scheme discussed, $f(\vec{k})$ must be modified so that it is analytic.

The asymptotic behaviour of the acoustic frequencies $\omega_{\sigma}(\vec{k})$ with $\vec{k}$ near $\vec{q}_{\ell m}$ is

$$\omega_{\sigma}(\vec{k}) \rightarrow c_{\sigma} |\vec{k} - \vec{q}_{\ell m}| \quad (4.11)$$

The mode index σ corresponds to either the longitudinal or the transverse acoustic mode. If $f(\vec{k})$ is expressed as

$$f(\vec{k}) = \frac{1}{N_P \beta} \ln \left(\frac{\prod_S (1 - e^{-\beta \hbar \omega_S(\vec{k})/2})}{\prod_{\ell m} \prod_{\sigma} (1 - e^{-\beta \hbar c_{\sigma} |\vec{k} - \vec{q}_{\ell m}|/2})} \right) + \quad (4.12)$$

$$\frac{1}{N_P} \sum_{\ell m} \sum_{\sigma} \frac{1}{\beta} \ln(1 - e^{-\beta \hbar c_{\sigma} |\vec{k} - \vec{q}_{\ell m}|/2})$$

the logarithmically divergent portion of $f(k)$ can be separated out and integrated over $\vec{k}$ analytically. The remaining portion of $f(\vec{k})$ is now analytic and can be integrated using the Cunningham special points⁵¹.

(VII)

RESULTS AND DISCUSSION

At low temperatures, the magnitude of E_T is extremely sensitive to errors in the frequencies calculated for the low energy modes. With the present computer resources, when the misfit is small or the substrate corrugation is large, the low frequency values obtained from (4.4) will not be accurate³⁴. Thus the calculation must be constrained to configurations with larger misfit values or smaller substrate corrugations. This is unfortunate, because the configurations with small misfit or large substrate corrugation will have the softest phonon modes, and potentially the greatest E_T .

The free energy calculation is also not possible if the underlying static configuration is unstable. When the substrate corrugation is greater than 7.0 K, the non-rotated configurations become unstable when the misfit is between 2.5% and 3.5%. Thus the calculation for E_T is confined to stable configurations that permit the frequencies to be determined accurately.

The configurations chosen for this study have misfits of 2.8%, 3.0%, and 3.7%. When the misfit is 2.8% or 3.0%, only rotated configurations are considered. The substrate corrugation is taken to be 8.0K so that the domain walls are clearly separated at 2.8% misfit, while the configuration at 3.7% is a modulated structure. This allows the free energy associated with soft domain wall modes to be compared to the

more rigid system that does not have distinct domain walls.

The values E_T for these configurations are as follows:

Table 1.

Values of E_T calculated for various
temperatures and orientations when $M\%=3.7\%$

	T=0.5K	T=1.0K	T=2.0K	T=4.0K
0.00°	-0.0019K	-0.0086K	-0.0325K	-0.1329K
0.52°	-0.0011K	-0.0058K	-0.0252K	-0.1171K
0.79°	-0.0011K	-0.0055K	-0.0240K	-0.1145K
0.95°	-0.0009K	-0.0051K	-0.0231K	-0.1130K

Table 2.

Values of E_T calculated for various
temperatures and orientations when $M\%=3.0\%$

	T=0.5K	T=1.0K	T=2.0K	T=4.0K
0.09°	-0.0034K	-0.0116K	-0.0366K	-0.1419K
0.71°	-0.0020K	-0.0073K	-0.0260K	-0.1192K

Table 3.

Values of E_T calculated for various temperatures and orientations when $M\%=2.8\%$

	T=0.5K	T=1.0K	T=2.0K	T=4.0K
0.21°	-0.0022K	-0.0081K	-0.0276K	-0.0941K
0.68°	-0.0024K	-0.0080K	-0.0265K	-0.0916K

The immediate observation can be made that at low temperatures the contribution of E_T to the free energy will be negligible. The only impact that the domain wall modes can have is to change the equilibrium orientation of the monolayer. However, the temperatures required to make E_T significant may invalidate the harmonic approximation. Furthermore, the rapid softening of the domain wall modes does not cause any significant increase in the values.

The values of E_T have not been determined for temperatures greater than 4.0K. This limit has been imposed since no modes are calculated with energies greater than twice the commensurate band gap value of 11.0K. The commensurate band gap value is the lowest possible energy that the modes of the commensurate monolayer can have. Because the accuracy of the frequencies deteriorates with increasing energy, values with energies much greater than the band gap will be suspect. Furthermore, additional modes may be present in the monolayer

that are missed by the calculation. Thus the temperatures must be kept small so the inaccuracies caused by the approximate equations (4.4) are minimized.

The frequencies have been calculated under the assumption of harmonic motion. This approximation will not be valid if the domain walls collide with each other. Since collisions of the domain walls will increase the energy of wall modes, anharmonic effects are expected to diminish the values of E_T . Confirmation of this prediction awaits a self-consistent phonon calculation of the incommensurate monolayer.

The only mechanism that could soften the domain wall motion is the formation of domain wall dislocations²⁶. Further work based on the elastic constants of the renormalized domain wall system should be performed. In the absence of domain wall dislocations, however, at low temperatures domain wall motion should not influence the misfit and orientation for the equilibrium configuration of the monolayer.

To extend the results to the commensurate limit, it is necessary to estimate the change in E_T as the misfit decreases. From previous work³⁴, when the domain size is large the softest mode is the breathing mode. At low temperatures this mode will dominate the value of E_T and the variation of its contribution due to misfit should be examined.

The breathing mode is influenced by the domain wall interaction. The strength of this interaction will decrease as

$$U_w(L) = c L^\sigma e^{-\kappa L} \quad (4.13)$$

for increasing separation L of the domain walls²². The constants c , σ and κ are determined from the calculated energetics of the system. Correspondingly, the frequency of the breathing motion should decrease as

$$\omega(\vec{k}) = f(\vec{k}, L) e^{-\kappa L/2} \quad (4.14)$$

where $f(\vec{k}, L)$ is a function which is periodic in k and algebraic in L . To leading order, the contribution of this mode to (4.1) will decrease as

$$\frac{1}{N_p} \ln(e^{-\kappa L/2}) \quad (4.15)$$

with increasing L . Since N_p varies as L^2 , the contribution will decrease as $1/L$. This analysis assumes that the harmonic approximation for motion is valid. For low energy modes the vibrational amplitudes will be large even at zero temperature, and the domain walls may collide with each other. If collisions occur, the motion will not be harmonic and (4.15) will not be correct.

Coppersmith et al.²⁶ have presented a model which describes the domain walls as being free to move provided that their displacements do not exceed $L/4$. This ensures that the domain

walls move independently of each other, and to some extent, simulates the anharmonic repulsion between the domain walls. They predict that the free energy contribution of the domain wall breathing will decrease as $\ln(L)/L^2$. This is a more restricting limit than $1/L$ predicted by (4.15) and should be valid for configurations approaching the commensurate transition.

At higher temperatures, other domain wall modes begin to influence the value of E_T . More low energy domain wall modes appear as the domain size increases³⁴, and the value of E_T could be expected to increase as well. However, the number of these modes does not increase as quickly as the total number of modes N_p and, from (4.10), E_T is expected to remain small as the domain size increases.

The results presented are for configurations where the substrate corrugation is 8.0K. Because the domain wall modes decrease in energy as the value of V_g increases, E_T will increase with V_g . For reasonable values of V_g the change in E_T can be estimated from the renormalized description based on domain walls.

Increasing the substrate corrugation will sharpen the domain walls; from a renormalized description based on the continuum model, the configuration will resemble a configuration that has a lower value of V_g and smaller misfit. Because κ in (4.13) varies as $\sqrt{V_g}$, scaling considerations predict the ratio of the number of adatoms per domain N_p for these two configurations is

$$\frac{N_p}{N'_p} = \frac{V'_g}{V_g} \quad (4.16)$$

For the configuration with the larger V_g , the domain walls vibrate faster because they contain fewer adatoms and are less massive. The effect of this on (4.10), however, is expected to be minor compared to the impact of rescaling N_p . Because the substrate corrugation cannot be significantly greater than 8.0K, the values of E_T for these configurations should remain small. Correspondingly, it is obvious that decreasing the substrate corrugation will decrease the value of E_T .

5.

CONCLUSION

The purpose of this thesis is to determine the low temperature behaviour of krypton monolayers adsorbed on graphite. Of specific interest is the experimentally observed variation of the monolayer's misfit and orientation as a response to the chemical potential and temperature of the system. To understand this behaviour, the variation of the free energy with misfit and orientation must be calculated. The free energy of the system is dependent on the interactions in and between the krypton vapour, the adsorbed krypton monolayers, and the graphite substrate. To simplify the calculation, only the component of the free energy that varies with the configuration of the monolayer was considered. This component involves the interactions between krypton atoms in the monolayer, and the interactions between these adatoms and the substrate.

The interaction between adatoms was modelled by pair potentials. The form of the pair potential was obtained from the bulk properties of krypton and modified to include the screening of the substrate. Because the interaction between the krypton atoms and the substrate can not be determined accurately, a parameterized form for the substrate potential, that reflects the symmetry of the substrate, was used in the calculation. On account of the nature of the substrate interaction, only one parameter, the substrate corrugation, was

necessary to define the substrate potential. This parameter was varied so that the impact of the substrate corrugation on the properties of the monolayer could be determined.

The substrate corrugation influences the way the misfit and orientation of the monolayer varies with the temperature and chemical potential of the system. At constant chemical potential, over the range of temperatures considered in this thesis (0 - 4 K), the misfit does not change with temperature. When the substrate corrugation is greater than 7.0 K, the monolayer forms a commensurate solid that becomes incommensurate when the chemical potential of the system is increased. However, when the substrate corrugation is less than 7.0 K, the monolayer does not form a commensurate solid. The significance of this result is that the substrate corrugation value of 7.4 K calculated by Vidaldi and Cole⁴⁸ produces a commensurate solid at zero temperature. This produces agreement between a theoretically derived value for the substrate corrugation and the experimental evidence that the monolayer can form a commensurate solid. The misfit of the most energetically favourable configuration varies with the chemical potential as shown in (1.1), regardless of the substrate corrugation. This result agrees with experimental observations although the information does not provide corroboration that the substrate corrugation should be 7.4 K.

Monolayers with small misfit values are not rotated, however when the misfit exceeds a given threshold value, the monolayer

is rotated. The relationship between the orientation of the monolayer and its misfit is dependent on the substrate corrugation. For substrate corrugations less than 7.0 K, the orientational behaviour matches that predicted by Shiba¹¹. However, when the substrate corrugation is greater than 7.0 K the anharmonic nature of the adatom pair interaction causes Shiba's results to be inaccurate. The monolayer is rotated at misfit values less than those predicted by Shiba because the non-rotated configurations have adatoms that are overcompressed at the vertices of the domain walls. In fact, for a range of misfit values where the rotated configurations are energetically favourable, the overcompression at the vertices causes the non-rotated configurations to be unstable. The orientation of the monolayer is sensitive to the temperature of the system. As the temperature is increased, configurations that are rotated will become less rotated.

The calculation for the free energy required splitting the free energy into three components - the potential energy, the zero point energy, and a temperature dependent component. The most significant of these components is the potential energy which, for the range of temperatures considered in this study determines the orientation behaviour of the monolayer. The zero point energy of the monolayer is not negligible, and influences the relationship between the misfit of the lowest energy configuration and the chemical potential. Because of this, relaxation studies and low temperature molecular dynamics

calculations do not predict the correct ground state of the monolayer. The temperature dependent component of the free energy, which is determined by the low energy vibrational modes of the monolayer, is not significant in determining the configuration of the monolayer.

The low energy modes of the incommensurate monolayer were calculated and correspond to motion of the domain walls. A renormalized model based on domain walls would provide not only the static properties of the monolayer, but the dynamical properties as well. The lowest energy mode is the breathing mode predicted by Villain¹⁴, and though this mode and other domain wall modes are quite soft, the entropy associated with them does not contribute significantly to the free energy. The domain wall vibrational modes are grouped into triads with the motion of a given mode in the triad corresponding to one of three fundamental forms of domain wall motion. By specifying the triad group and the mode of the triad, the motion associated with the mode is determined.

In the course of the work for this thesis two papers were published^{12,34}. The first of these papers, Shrimpton et. al.¹² examined approximations that are made to calculate the static properties of the monolayer. The results of this paper indicated that for krypton on graphite theories which assumed that the adatom pair interactions were harmonic would not be quantitatively correct. The paper also established the validity of the techniques used in this work to calculate the

static configuration of the monolayer. The thesis extends the results presented in this paper to cases where the monolayer is rotated with respect to the substrate. The results indicate that harmonic theories may not describe correctly the rotation verses misfit behaviour of the monolayer either.

The second paper published, Shrimpton et. al.³⁴, concerned the dynamics of the incommensurate monolayer. Prior to this work there was no quantitative information about the in-plane motion of the adatoms in the incommensurate monolayer. The low energy mode predicted by Villain¹⁴ was verified and several other low energy modes were described. With this information about the low energy modes, and with other information calculated for the zero point energy, the free energy of the incommensurate monolayer was calculated. The results of the calculation for the free energy indicate that the low energy modes of the monolayer do not have a catastrophic impact on the extension of zero temperature calculations to finite temperatures. However, the results also indicate that the zero point energy of the monolayer influences the configuration of the monolayer, and calculations based solely on the static properties of the monolayer may not be correct.

APPENDIX A

The monolayer configurations are determined by the integer parameters m and n . From equation (2.9) the size of the superlattice domains are determined. However, this is not the only information that can be obtained directly from m and n , and this section will consider other geometric quantities. From equation (2.9), the restricted case of $\ell=1$ and $k=0$ produces a relationship between these parameters and the basis vectors $\vec{R}_1$ and $\vec{R}_2$ of the superlattice periodicity

$$[\vec{R}_1, \vec{R}_2] = [\vec{D}_1, \vec{D}_2] \begin{bmatrix} n & -m \\ m & n-m \end{bmatrix} + [\vec{B}_1, \vec{B}_2] \quad (\text{A.1})$$

This introduces the notation whereby two vectors are combined to form a 2x2 matrix. The top row contains the x components and the bottom row contains the y components.

From equation (2.10), with the help of equation (2.7), the averaged lattice vectors $\vec{d}_1$ and $\vec{d}_2$ can be determined from the commensurate lattice vectors $\vec{D}_1$ and $\vec{D}_2$ to be

$$[\vec{d}_1, \vec{d}_2] = [\vec{D}_1, \vec{D}_2] \left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix}^{-1} \begin{bmatrix} n & -m \\ m & n-m \end{bmatrix}^{-1} \right) \quad (\text{A.2})$$

Referring back to (2.8) the misfit and orientation can then also be determined in terms of m and n .

Given the periodicity of the superlattice from (A.1) the set of reciprocal lattice vectors with basis $\vec{q}_1, \vec{q}_2$ are defined by

$$\begin{bmatrix} \vec{q}_1 \\ \vec{q}_2 \end{bmatrix} \begin{bmatrix} \vec{R}_1 & \vec{R}_2 \end{bmatrix} = \begin{bmatrix} \vec{q}_1 \cdot \vec{R}_1 & \vec{q}_1 \cdot \vec{R}_2 \\ \vec{q}_2 \cdot \vec{R}_1 & \vec{q}_2 \cdot \vec{R}_2 \end{bmatrix} = 2\pi \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad (\text{A.3})$$

The notation for the matrix formed by the q vectors has the left column containing the x components of the vectors and the right column containing the y components. These conventions cause the matrix multiplication of the $\vec{R}$ and $\vec{q}$ vector sets to produce the indicated dot products between the vectors.

Given the R matrix from (A.1) the q matrix (and subsequent q_1 and q_2) can be determined by simple manipulation of matrices in equation (A.3).

By analogy to the previous procedure, the reciprocal lattice vectors $\vec{g}_1$ and $\vec{g}_2$ for the substrate can be defined so that

$$\begin{bmatrix} \vec{g}_1 \\ \vec{g}_2 \end{bmatrix} \begin{bmatrix} \vec{B}_1 & \vec{B}_2 \end{bmatrix} = 2\pi \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad (\text{A.4})$$

from which the reciprocal lattice vectors of the substrate for a given m and n can be calculated.

$$\begin{bmatrix} \vec{q}_1 \\ \vec{q}_2 \end{bmatrix} = \left(\begin{bmatrix} 1 & 1 \\ -2 & 1 \end{bmatrix} \begin{bmatrix} -m & -n \\ n-m & -m \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right)^{-1} \begin{bmatrix} \vec{g}_1 \\ \vec{g}_2 \end{bmatrix} \quad (\text{A.5})$$

One of the quantities that is of interest is the dot product between averaged lattice vectors of the adatoms and the reciprocal lattice vectors of the substrate. Any vector dot product can be determined from the dot products between the basis vectors of the two lattices. Given equation (A.2), with the help of (2.7) and (A.4),

$$\begin{bmatrix} \vec{g}_1 \\ \vec{g}_2 \end{bmatrix} [\vec{d}_1, \vec{d}_2] = 2\pi \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \left(\begin{bmatrix} n & -m \\ m & n-m \end{bmatrix}^{-1} + \begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix} \right) \quad (\text{A.6})$$

From (A.3) and (2.10) it is clear that

$$\begin{bmatrix} \vec{g}_1 \\ \vec{g}_2 \end{bmatrix} [\vec{d}_1, \vec{d}_2] = \begin{bmatrix} \vec{q}_1 \\ \vec{q}_2 \end{bmatrix} [\vec{d}_1, \vec{d}_2] + 2\pi \begin{bmatrix} 1 & 1 \\ -2 & 1 \end{bmatrix} \quad (\text{A.7})$$

APPENDIX B

Much early interest in the problem of mismatched spacings between an overlayer of adatoms and the underlying substrate stemmed from the fact that the displacements, $\vec{u}$, of the adatoms in the minimum energy configuration, given suitable approximations to the microscopic interactions, were obtained by solving a second order nonlinear set of differential equations²¹. By considering configurations where the displacements occur only along one direction, the displacements were found to have soliton variation. This variation produces regions where the adatoms are in registry with the substrate, separated by stripes of higher (or lower) density domain walls.

The minimum energy configuration is determined by finding the classical force free solution to the microscopic interactions. The adatom interaction ϕ is assumed to be harmonic and the substrate interaction is assumed to be sinusoidal (cf 2.3). According to these conditions the energy per adatom is

$$E(\vec{R}) = \sum_{\vec{R}'} \left[1 + (\vec{u} - \vec{u}') \cdot \vec{\nabla} + \frac{1}{2} ((\vec{u} - \vec{u}') \cdot \vec{\nabla})^2 \right] \phi(\vec{R} - \vec{R}') + V_0 + 2V_g \sum_{k=1}^3 (1 - \cos(\vec{g}_k \cdot \vec{R})) \quad (\text{B.1})$$

$\vec{g}_3$ is defined from $\vec{g}_1$ and $\vec{g}_2$ (cf A.4) to be $\vec{g}_3 = -\vec{g}_1 - \vec{g}_2$.

The continuum approximation is made which treats the

displacements as a continuous function of the averaged position $\vec{R}$. If the displacements are slowly varying, the following approximation can be made

$$\vec{u}' = \vec{u}(\vec{R}') = \left[1 + (\vec{R}' - \vec{R}) \cdot \vec{\nabla} + \frac{1}{2} ((\vec{R}' - \vec{R}) \cdot \vec{\nabla})^2 \right] \vec{u}(\vec{R}) \quad (\text{B.2})$$

With the assumption of uniaxial modulations, the displacements correspond to

$$\vec{u}(\vec{R}) = \frac{1}{2\pi} \theta(s) \vec{B}_1 \quad \text{with} \quad s = \vec{B}_1 \cdot \vec{R} \quad (\text{B.3})$$

where $\vec{B}_1$ is a basis vector for the substrate.

Using (B.3), and (B.2) which is substituted into (B.1), gives

$$E(\vec{R}) = E(s) = E_0 + \frac{1}{2} a \left(\frac{d\theta}{ds} \right)^2 + b \frac{d\theta}{ds} + 4V_g(1 - \cos\theta) \quad (\text{B.4a})$$

$$\text{where} \quad E_0 = \sum_{\vec{h}} \phi(\vec{h}) + V_0 \quad (\text{B.4b})$$

$$\text{and} \quad a = \frac{1}{(2\pi)^2} \sum_{\vec{h}} (\vec{h} \cdot \vec{B}_1)^2 (\vec{B}_1 \cdot \vec{\nabla})^2 \phi(\vec{h}) \quad (\text{B.4c})$$

$$\text{with} \quad b = \frac{1}{2\pi} \sum_{\vec{h}} (\vec{h} \cdot \vec{B}_1) (\vec{B}_1 \cdot \vec{\nabla}) \phi(\vec{h}) \quad (\text{B.4d})$$

Similarly, when the force on a given adatom is calculated the force free condition requires that the displacements satisfy

$$\frac{d^2\theta}{dS^2} = \alpha^2 \sin\theta \quad \text{where} \quad \alpha^2 = \frac{4V_0}{a} \quad (\text{B.5})$$

The solutions to (B.5) are solitons with the special case of a single soliton having the form

$$\theta = 4\tan^{-1}(e^{\alpha S}) \quad (\text{B.6})$$

This provides the shape of the domain wall soliton, with the other possible solutions, where the domain walls are well separated, corresponding to periodic repetition of the domain walls over the surface of the monolayer. From (B.6), if α is large, indicating a strongly corrugated substrate, the domain walls will be quite sharp; conversely if α is small, indicating strong interactions between the adatoms, the domain walls will be very broad.

APPENDIX C

From (2.38), the maximum error in (2.17) resulting from approximations in calculating the A_{LM}^{jk} can be determined. However, the quantity of interest is the energy of the monolayer and this must be calculated to a preset accuracy. The contribution of the substrate to this energy involves an average of all the individual adatom-substrate interaction energies. Thus an error bound which reflects the uncertainty in the average value of the adatom-substrate energy must be calculated.

In order to estimate the error, the displacements $\vec{u}$ are considered to be analytic functions of the mean positions $\vec{R}$. Two extreme cases for the behaviour of the displacements are considered with the assumption that the actual result will lie somewhere in between the two.

First, the domain walls are considered to be step functions. The displacements $\vec{u}$ vary linearly with $\vec{R}$, up to the edge of the domain, which for ease of calculation is taken to be circular.

$$\vec{u}(\vec{R}) = c\vec{R} \quad \text{if } |\vec{R}| \leq a \quad (\text{C.1})$$

where c is to be determined, and a is the radius of the domain.

The quantity of concern to (2.38) is

$$z = i \vec{g} \cdot \vec{u}(\vec{R}) \quad (\text{C.2})$$

Performing the average of $\langle z^2 \rangle$ using (C.1) over the area of the circle results in

$$\langle z^2 \rangle = \frac{1}{4} (a c |\vec{g}|)^2 \quad (\text{C.3})$$

The estimate of the error in the energy is $\langle \epsilon^2 \rangle$, from (2.38) and (C.1) it is calculated to be

$$\langle \epsilon^2 \rangle = \frac{\langle z^4 \rangle}{24 \cdot 8^n} = \frac{1}{8} \frac{(a c |\vec{g}|)^4}{24 \cdot 8^n} \quad (\text{C.4})$$

$$\text{with (C.3)} \quad = \frac{\langle z^2 \rangle^2}{12 \cdot 8^n}$$

The other extreme possibility is that the displacements of adatoms are so smoothly modulated that z can be given as

$$z = i c |\vec{g}| \sin\left(\frac{\pi}{a} |\vec{R}| \right) \cos(\theta) \quad \text{for } |\vec{R}| \leq a \quad (\text{C.5})$$

where θ is the angle between $\vec{R}$ and $\vec{g}$. For such a case $\langle z^2 \rangle$ is calculated to be

$$\langle z^2 \rangle = \frac{1}{4} (a c |\vec{g}|)^2 \quad (\text{C.6})$$

and the average error in $\langle \delta \rangle$ for such a system is

$$\langle \delta \rangle = \frac{3}{16} \frac{(ac|\vec{q}|)^4}{24 \cdot 8^n} \quad (C.7)$$

$$\text{with (C.6)} = \frac{\langle z^2 \rangle^2}{8 \cdot 8^n}$$

Because the configuration of the monolayer lies between the two extreme cases it is assumed that setting the uncertainty to be

$$\langle \delta \rangle = \frac{\langle z^2 \rangle^2}{6 \cdot 8^n} \quad (C.8)$$

will overestimate the actual error present in the calculated energy contribution of the substrate.

Equation (C.8) requires a value for $\langle z^2 \rangle$. From (2.13) this can be calculated by

$$\langle z^2 \rangle = - \sum_{\ell m} (\vec{g} \cdot \vec{u}_{\ell m}) (\vec{g} \cdot \vec{u}_{-\ell, -m}) \quad (C.9)$$

allowing an estimate of $\langle \delta \rangle$ to be determined from (C.8). The parameter value for n used to calculate the values A_{LM}^{jk} is chosen from the error bound δ to be the smallest integer that satisfies

$$n \geq \frac{\log\left(\frac{\langle z^2 \rangle^2}{6 \epsilon}\right)}{\log(8)} \quad (C.10)$$

where $\langle z^2 \rangle$ is given by (C.9).

It is realized that $\langle z^4 \rangle$ can be determined directly from (2.13). However, only a quick estimate of the uncertainty is required, and (C.8) with (C.9) is adequate to determine $\langle \epsilon \rangle$. Furthermore, the quantity (C.9) can be gleaned from the calculations required to evaluate the A_n of (2.34) whereas $\langle z^4 \rangle$ would have to be calculated separately.

The uncertainty in the calculation (C.8) has been deliberately chosen to be an overestimate from (C.4) and (C.7). This is necessary because the errors in calculating the A_{LM}^{jk} will influence the overall calculation of the displacements $\vec{u}_{\ell m}$. Since the values of $\vec{u}_{\ell m}$ are used to calculate the set of A_{LM}^{jk} , the error will be compounded. Thus (C.4) and (C.7) underestimate the consequences of a specific choice of n . By analysing the observed error in the substrate energy calculated for various n values, (C.8) is found to be a reliable estimate of the uncertainty, and given an error bound ϵ , (C.10) can be used to set the value of n .

APPENDIX D

Equation (4.9) requires integrating the periodic function $f(\vec{k})$ over the Brillouin zone of the superlattice. Chadi and Cohen⁵⁰ have developed a technique to evaluate such an integral numerically. The technique is reviewed here to establish the terminology.

$f(\vec{k})$ is a periodic function and can be expanded as

$$f(\vec{k}) = \sum_{\vec{R}} f_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \quad (D.1)$$

where $\vec{R}$ is a superlattice vector generated by (2.9). The symmetry of the superlattice allows the coefficients $f_{\vec{R}}$ to be combined so that (D.1) becomes

$$f(\vec{k}) = \sum_m f_m A_m(\vec{k}) \quad (D.2)$$

where

$$A_m(\vec{k}) = \sum_{|\vec{R}|=c_m} e^{i\vec{k} \cdot \vec{R}} \quad (D.3)$$

The values of c_m range over all possible values of $|\vec{R}|$ and are ordered to increase with m . If $f(\vec{k})$ varies smoothly with $\vec{k}$ the coefficients f_m in (D.2) will decrease rapidly with m .

A weighted summation of the $A_m(\vec{k})$ evaluated over a set of

points $\vec{k}_i$ can be performed so that

$$\sum_i \alpha_i A_m(\vec{k}_i) = 0 \quad (D.4)$$

for all m in the range $0 < m \leq N$. The weights α_i are normalized so that they total to unity. Given (D.2), performing the same weighted sum on the function $f(\vec{k})$ will result in

$$\sum_i \alpha_i f(\vec{k}_i) = f_0 + \sum_{m>N} f_m \sum_i \alpha_i A_m(\vec{k}_i) \quad (D.5)$$

Since f_m decreases rapidly with m , the right hand side of (D.5) will approach f_0 as N is increased. f_0 is the average value of $f(\vec{k})$ in the Brillouin zone. Thus,

$$\sum_i \alpha_i f(\vec{k}_i) \approx \frac{1}{A} \int f(\vec{k}) d\vec{k} \quad (D.6)$$

to increasing accuracy as N is increased.

For a given value of N there are many sets of points $\vec{k}_i$ that will satisfy (D.4). The points in the minimal set are called the special points of the Brillouin zone. As the value of N is increased, the number of special points increases. Chadi and Cohen⁵⁰ have devised a procedure whereby a set of special points is generated by point group operations on the points in

the two preceding sets. Cunningham⁵¹ has calculated the first few sets of special points appropriate a two dimensional lattice with hexagonal symmetry. By examining these special points, it is clear that when a given set of points is combined with all the preceding sets of points, a triangular lattice is formed. Furthermore, none of the lattice points belong to more than one set of special points. When the next successive set of special points is included, a more dense triangular lattice is formed of which the previous combined set forms a $\sqrt{3} \times \sqrt{3}$ sublattice.

For the calculation of (4.9), advantage has been taken of this fact. A triangular lattice is generated with spacing small enough that the special points derived from it will provide the required accuracy. The special points are extracted from the triangular lattice by subtracting from this set all points that are common with the $\sqrt{3} \times \sqrt{3}$ sublattice. The weight α_i associated with this set can be determined from the successive nature of the sets of special points. The weight for one set will be $1/3$ the weight of the previous set. By knowing the number of preceding sets of points, the weight can be calculated. It is remembered that the weight associated with points at the edge of the Brillouin zone must be modified.

Figure 1. Diagram of the graphite substrate. The honeycomb network indicates the carbon bonds, the adsorption sites are at the centers of the hexagons formed by the carbon bonds. $\vec{B}_1$ and $\vec{B}_2$ are the basis vectors which generate the set of adsorption sites. $\vec{D}_1$ and $\vec{D}_2$ are the basis vectors for the $\sqrt{3} \times \sqrt{3}$ sublattice.

Figure 2. Types of domain walls between the $\sqrt{3}\times\sqrt{3}$ lattices of krypton atoms. Krypton atoms in an a sublattice are identified by $\blacktriangle$. Atoms in a b sublattice are identified by a $\bullet$. Atoms in a c sublattice are identified by $\blacksquare$.

Figure 3. Typical positions of adatoms for an incommensurate monolayer with hexagonal symmetry. For this particular configuration $n=4$, $m=-4$, $k=0$, and $\ell=-1$ in equation (2.9).

Figure 4. Possible misfit and orientation values for hexagonally periodic incommensurate monolayers. The angle of rotation is given in degrees. The monolayers are constrained so that, over the length of the primitive lattice vectors, the adatoms are shifted by only one adsorption site relative to the commensurate monolayer. The configurations with super heavy domain walls are marked with circles, the configurations with heavy domain walls are marked with squares.

Figure 5(a). Energy per adatom of a nonrotated incommensurate monolayer as a function of its misfit when the substrate corrugation is 3.0 K. The dashed line shows the potential energy per adatom; the solid line shows the potential and zero point energy per adatom as is discussed in chapter 3.

Figure 5(b). As in figure 5(a) but with $V_g = 5.0$ K.

Figure 5(c). As in figure 5(a) but with $V_g = 7.0$ K.

Figure 5(d). As in figure 5(a) but with $V_g = 8.0$ K.

Figure 5(e). As in figure 5(a) but with $V_g = 9.0$ K.

Figure 6(a). Contour plot showing the difference in the potential energy per adatom between the rotated and nonrotated configurations. The angle of rotation is given in degrees. The solid contours show increments of 0.5 K. The dotted and dashed contours show decrements of 0.02 K. The substrate corrugation for this plot is 5.0 K.

Figure 6(b). As in figure 6(a) but with a substrate corrugation of 8.0 K.

Figure 6(c). As in figure 6(a) but with a substrate corrugation of 10.0 K.

Figure 7(a). A comparison of the adatom pair potential $\phi(r)$ (solid line) and the polynomial fit ar^3+br^2+cr+d (dashed line) for various values of r .

Figure 7(b). A comparison of the derivatives of the curves in figure 7(a) for various values of r . The solid line is $\phi'(r)$, the dashed line is $3ar^2+2br+c$.

Figure 7(c). A comparison of $\phi''(r)$ (solid line) and the polynomial fit $6ar+2b$ (dotted line) for various values of r .

Figure 7(d). A comparison of $\phi'''(r)$ (solid line) and the polynomial fit 6a (dotted line) for various values of r .

Figure 8. Energy per adatom as in figure 5(c) except in the calculation, the pair potential $\phi(r)$ is replaced by the polynomial fit ar^3+br^2+cr+d shown in figure 7(a).

Figure 9. Phonon energies as a function of wavevector for the nonrotated incommensurate monolayer with misfit 2.22%, and substrate corrugation 6.0 K. Γ is at the center of the hexagonal Brillouin zone, M is at the middle of an edge and K is at a corner.

Figure 10(a). Motion of the domain walls for the phonon mode at the point M of figure 9, having an energy of 0.011meV. In this picture, the direction of the wavevector is as shown in the Brillouin zone subdiagram. The dashed lines indicate the deformation of the walls about their central positions (solid lines).

Scale 10 nm

Phonon Energy=0.011meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Wave Vector

Figure 10(b). As in figure 10(a) but for a phonon mode with energy 0.021meV.

Phonon Energy=0.021meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Figure 10(c). As in figure 10(a) but for a phonon mode with energy 0.027meV.

Phonon Energy=0.027meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Wave Vector

Figure 11. Energies of the phonon modes as in figure 9 but for a nonrotated monolayer with misfit 1.75% . At this value of misfit the triad groupings of the domain walls are apparent.

Figure 12(a). Motion of the domain walls as in figure 10(a) but for a phonon mode with wavevector at the Γ point and energy 0.037 meV. From figure 9 this mode is the third lowest in energy and is identified as being the third mode of the first triad.

Phonon Energy=0.037 meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Wave Vector

Figure 12(b). As in figure 12(a) but for a phonon mode with energy 0.315 meV. This mode is the sixth lowest in energy and corresponds to the third mode of the second triad.

Phonon Energy=0.315 meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Wave Vector

Figure 13(a). Motion of the domain walls as in figure 10(a) but for a phonon mode having energy 0.201meV. From figure 9 this mode is the first mode of the second triad.

Phonon Energy=0.201meV

Misfit=2.22 % Rotation=0.00°

Substrate Corrugation $V_g=6.0K$

Figure 13(b). As in figure 13(a) but showing motion of the mode when the wavevector is at Γ .

Phonon Energy = 0.201 meV

Misfit = 2.22% Rotation = 0.00°

Substrate Corrugation $V_g = 6.0 \text{ K}$

Wave Vector

Figure 14(a). Phonon energies as a function of wavevector as in figure 9 but for a nonrotated monolayer with misfit 3.33% when the substrate corrugation is 8.0 K. The energy scale is extended to show imaginary values. The monolayer has an unstable mode.

Misfit 3.33% Angle 0.0°

Figure 14(b). As in figure 14(a) but for a rotated monolayer with slightly smaller misfit. The modes are not unstable.

Figure 15. Motion of the domain walls for the unstable phonon mode of figure 14(a) with wavevector at the M point.

Phonon Energy = $i0.026$ meV

Misfit = 3.33% Rotation = 0.00°

Substrate Corrugation $V_g = 8.0K$

Figure 16. Phonon energies as a function of wavevector as in figure 14(a), but for a monolayer with a misfit value of 3.7% .

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