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Methane adsorbed on graphite. II. A model of the commensurate-incommensurate transitions

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A two-structure model is presented for the pressure- and temperature-driven commensurate-incommensurate (*C-I*) transitions of an adlayer of methane adsorbed on the basal plane of graphite. The statistical-thermodynamic properties of the system are calculated from an empirical intermolecular potential with substrate-mediated effects. Free-energy constructions predict transition temperatures and pressures in agreement with experiment. The quantitative anharmonic finite-temperature model demonstrates directly that the zero-temperature configuration is a $\sqrt{3}\times\sqrt{3}$ registered phase. The *C-I* transitions of the model are first order, and the incommensurate phases (compressed and expanded) are free-floating two-dimensional "solids" without domain walls. The model results are consistent with existing static theories of "misfit dislocations" in that a transition to a free-floating unwalled phase preempts the system from reaching the critical misfit necessary for the spontaneous formation of domain walls.

I. INTRODUCTION

A registered $\sqrt{3}\times\sqrt{3}$ adlayer on methane absorbed on the basal plane of graphite has been observed to undergo commensurate-incommensurate (*C-I*) transitions.[1-5] At low temperatures, the methane adlayer is compressed off registry by increasing the two-dimensonal (2D) spreading pressure. At low pressure, the adlayer is thermally expanded out of registry. This report describes a quantitative anharmonic finite-temperature model of the *C-I* transitions of a 2D solid of methane adsorbed on graphite (CH_4/graphite). The statistical-thermodynamic properties of the CH_4/graphite system, calculated by quantum-cell theory (QCT) and quasiharmonic theory (QHT) of lattice dynamics indicate that both *C-I* transitions proceed from the $\sqrt{3}\times\sqrt{3}$ registered phase to a floating 2D "solid"[6] phase without the formation of domain walls. The results are in agreement with experiment and a model[7-10] for misfit dislocations.

Methane, when adsorbed on graphite, is between krypton and xenon in size. An adlayer of krypton must experience significant thermal expansion before the periodic variations in the substrate potential sharply enhance the dilation of the 2D lattice.[10-12] In contrast, an adlayer of xenon must be compressed beyond the point of second-layer growth before the lattice constant is reduced sufficiently to allow $\sqrt{3}\times\sqrt{3}$ registry. This report shows that the ground-state lattice constant of 2D solid methane is within one-half percent of the registry length. The model predicts directly, at low temperatures and pressures, the stable structure to be an uncompressed $\sqrt{3}\times\sqrt{3}$ registered adlayer (or large islands). The following sections contain descriptions of an empirical atom-atom intermolecular potential (CH_4-CH_4) and a molecule to substrate potential, the role of substrate-mediated interactions, statistical-mechanics methods of calculating the free energies of each of the two states (registered and floating) of the 2D solid adlayer, Fourier decomposition of the adatom to substrate potential, calculation of the temperatures and pressures for the *C-I* transitions, reconciliation of the two-structure model to a quasistatic version of the Frank and van der Merwe theory,[7] and a discussion of the results.

II. INTERMOLECULAR POTENTIAL

In the preceding paper (I), it was shown that empirical intermolecular potentials can be built by representing the interaction of a CH_4 molecule with the adlayer or with the graphite as a superposition of Lennard-Jones [LJ(12-6)] atom-atom pair potentials. The static lattice sum for a reference molecule at $\vec{r}_0$ with orientation θ and ϕ taken over the lattice of the adlayer or substrate potential is

$$\Phi(\vec{r}_0,\theta,\phi)=\sum_n\sum_{i,j}\Phi_n(\sigma_{ij},\epsilon_{ij}r_{ij}(n))\ , \tag{1}$$

where

$$\Phi_n(\sigma_{ij},\epsilon_{ij},r_{ij}(n))=4\epsilon_{ij}\{[\sigma_{ij}/r_{ij}(n)]^{12}-[\sigma_{ij}/r_{ij}(n)]^6\}\ . \tag{2}$$

The radial distance $r_{ij}(n)$ is the location of the jth atom in the nth molecule of the adlayer (or substrate carbon atom) relative to the ith atom of the reference molecule. The parameters ϵ_{ij} and σ_{ij} are the LJ(12-6) values for the particular atomic species i and j. Sets of proposed species-dependent ϵ_{ij} and σ_{ij} combinations exist but our study (paper I and Ref. 13) determined that only the modified set of Severin and Tildesley[14] gave reasonable results for the heights of rotational tunneling barriers[15,16] (see Table I in the preceding paper I). The calculations contained in this report use these parameters.

III. SUBSTRATE-MEDIATED INTERACTIONS

Interactions making additional contributions to the lateral energy of a physisorbed adlayer have been formalized,[17] and the results of a quantitative calculation[18] of thermodynamic properties compare well with experiments.[19] The largest of these, the MacLachlan[20] interaction for the energy of two adatoms both at height L above the substrate and separated by distance r, is

$$\Phi_M(r)=\frac{C_{s1}[\frac{4}{3}-4L^2/(r^2+4L^2)]}{[r(r^2+4L^2)^{1/2}]^3}-\frac{C_{s2}}{(r^2+4L^2)^3} \ . \tag{3}$$

For methane, the parameters $C_{s1}=4.360\times10^5$ K/Å^6 and $C_{s2}=2.301\times10^5$ K/Å^6 are given by Rauber *et al.*[21] Surface dipoles for this system (CH_4/graphite) are believed to be small and are not included. The Axilrod-Teller-Muto triple-dipole interaction is available but quite small, it is included in these calculations. The triple-dipole coefficient ν was calculated by Margoliash *et al.*[22] In the static lattice sums of the preceding paper (I), the atom-atom intermolecular potential is used to establish potential-energy minimums and barrier heights. In the dynamical finite-temperature calculations of the present work, I use a spherical molecule approximation and a LJ(12-6) intermolecular potential with $\sigma=3.6814$ Å and $\epsilon/k_B=137$ K. The Boltzmann constant is k_B. Above 20–30 K, the methane molecules are in a rotationally diffusing state.[23] This value of σ is well within the range of the uncertainties[24] and gives the same lattice constant for a potential-energy minimum as the atom-atom intermolecular potential. The thermodynamic properties of the system are calculated by two different methods using this composite potential, i.e., the LJ(12-6) pair potential with the MacLachlan term and the triple-dipole energy.

IV. STATISTICAL-MECHANICS METHODS

The statistical-thermodynamics properties of both structures (registered and free-floating 2D solids) are calculated using QHT (Ref. 25) of lattice dynamics (0–10 K) and QCT (Refs. 26 and 27) (0–60 K). It is from these resulting properties that the sublimation line, free-energy constructions, and *C-I* transitions are determined.

The details of the quasiharmonic theory and the quantum-corrected cell theory of 2D triangular crystals were given previously[25] for LJ(12-6) systems. Applying QHT to a monolayer of xenon on silver[18] (Xe/Ag) with realistic pair potentials and substrate-mediated interactions gives thermal properties in good agreement with experiment[19] at low temperatures. At higher temperatures, the quantum-corrected cell theory agrees quite well with the same experiments and with Monte Carlo simulations.[25,26] The calculation of the thermal expansion of the Xe/Ag system gives the lattice constant at 1 K within 0.01 Å of experiment by QHT and at 80 K within 0.02 Å of experiment by quantum-corrected cell theory. Between the two methods 2D crystals of the larger rare-gas atoms are well described. For 2D neon and to a lesser extent argon, these methods are unable to account for the increasing role of quantum-mechanical effects and anharmonicity.[26,27]

It has been established that 2D solids with significant quantum effects are quite anharmonic.[27] Since cell theories are well suited for anharmonic systems, the quantum-cell model is a good approximation for the CH_4/graphite system. The deBoer parameter, $\Lambda=2\pi\hbar[\sigma(m\epsilon)^{1/2}]$, for methane is 0.245. This is intermediate to neon (0.591) and argon (0.187). The CH_4/graphite system is well within the range where quantum-mechanical considerations are important. The CH_4/graphite system's thermal properties are, to a good approximation, derivable from QCT (Ref. 26) in the temperature range from zero to near the triple-point melting. As applied in this work, the quantum-cell model is non-self-consistent and therefore does not include correlation effects. The model is a collection of anharmonic Einstein oscillators. The classical self-consistent cell model has been treated by Barker.[28] Since the differences in thermal properties of two structures determine the transitions, the small correlation entropy contributions of these calculations nearly cancel and the uncorrelated cell model is reasonable. For 2D systems with parameters near those of neon and argon, the leading term of the quantum-cell approximation is taken to be the anharmonicity. Under these constraints, the QCT calculations are quite satisfactory.

The thermodynamic properties of the adlayer are calculated in the QCT approximation by determining the energy eigenvalues $E_{n,l}$ of the 2D Schrödinger equation in polar coordinates

$$-d^2u(r)/dr^2+[(2m/\hbar^2)\omega(r)+(l^2-\tfrac{1}{4})/r^2]u(r) =(2m/\hbar^2)E_{n,l}u(r) \ , \tag{4}$$

where n and l are the energy and angular-momentum quantum numbers, respectively. The cell potential $\omega(r)$ is the circularly averaged potential of the molecule in the cell composed from 36 shells of its neighbors in the adlayer[18,25] and with substrate-mediated interactions. In Eq. (4), $u(r)=r^{1/2}\psi(r)$, where $\psi(r)$ is the radial wave function. The cell potential $\omega(r)$ is quite anharmonic and Eq. (4) is not analytically integrable. The differential equation is written as a difference equation and the eigenvalues are determined in a vector space with a basis of plane waves.[29]

The details of the numerical methods are outlined in Ref. 26 including an efficient technique for treating the singularity at the origin. The partition function sums over the energy eigenvalues of Eq. (4) as follows:

$$Z=\sum_i g_i \exp(-E_i/k_BT) \ , \tag{5}$$

with g_i the degeneracy of the ith level. The Helmholtz free energy per particle is

$$F/Nk_B=-T\ln Z \ , \tag{6}$$

and the specific heat at constant area is

$$C/Nk_B=[1/(k_BT)^2](\langle E^2\rangle-\langle E\rangle^2) \ . \tag{7}$$

The spreading pressure ϕ and the isothermal compressibility K_T are calculated by a five-point numerical derivative of the Helmholtz free energy with respect to the area.

In order to understand the *C-I* transitions in the CH_4/graphite system, the thermodynamic properties are calculated for two structural states of the adlayer: (1) a uniform free-floating 2D solid without domain walls (mass-density waves or solitons) but with substrate effects being the addition of the MacLachlan and triple-dipole interactions, and (2) a solid adlayer constrained to the $\sqrt{3}\times\sqrt{3}$ registered structure with the MacLachlan and triple-dipole interactions included and with the periodic substrate potential found by the lattice sums of the previous paper (I). Free-energy constructions of these two phases determine which is the stable structure for a given temperature and spreading pressure. For a given dilation of the lattice, the force constants and consequently the vibrational properties of the two structures are similar. The small difference in the thermodynamic properties between the two models approximates the effects of the periodic substrate on this anharmonic finite-temperature system.

The first consideration in the study of thermal effects is registry at low temperatures and pressures. Will this model of the uncompressed adlayer at low temperatures have the lattice constant $L_0=4.26$ Å required for the $\sqrt{3}\times\sqrt{3}$ registry to be observed? The answer is yes. It is interesting to note that unless substrate-mediated interactions between molecules in the adlayer are included, the system must be at relatively high temperatures and have undergone sizeable thermal expansion to reach registry. Zero-point vibrations alone only expand the system halfway from the 4.09-Å lattice constant of the static sums minimum, found in paper I, to the required registry distance.

V. THE FOURIER DECOMPOSITION OF THE SUBSTRATE POTENTIAL

It is necessary in this calculation to express the periodic substrate potential in analytic form. The quantitative results of paper I for the potential-energy map of an adsorbed molecule to the basal plane of the graphite crystal can be written as a Fourier-series expansion. Two features are obtained from the expansion: (1) a functional form of the potential to be added to the cell potential and (2) averaged barrier height to omnidirectional translation V_0.

The substrate potential is expressed as a Fourier decomposition[30]

$$V(\vec{r},z)=\sum_{\vec{G}_j} V_{\vec{G}_j}(z)\exp(j\vec{G}_j\cdot\vec{r})\ , \tag{8}$$

which is incorporated into the circularly averaged cell potential $\omega(r)$. In Eq. (8) $\vec{r}$ is the position vector in the plane of the surface, z is the height of the molecule above the surface, and the $\{\vec{G}_j\}$ is a set of reciprocal-lattice vectors of the graphite surface. The substrate potential given in Eq. (8) is within 0.5-K agreement with the static lattice sums of paper I throughout the surface plane. The leading factor of the Fourier-series expansion is $V_0=19.25$ K, which is taken to be the effective barrier height to translation for the adlayer rather than the 22-K maximum or the 11-K saddle-point values given by the lattice sums.

The height z of the adlayer above the graphite plane is set at the equilibrium value ($z_0=3.28$ Å) determined in paper I. The vertical thermal expansion for similar systems is known to be small and the calculations in this work are all for $z=z_0$.

VI. FREE-ENERGY CONSTRUCTIONS

The internal energy, heat capacity, Helmholtz free energy, entropy, and isothermal compressibility of the free-floating solid model are calculated for a range of temperatures at a given dilation of the lattice. The lattice dilation is varied from a highly-compressed system to a greatly expanded lattice. The equilibrium lattice constant for the free-floating structure is determined by finding the lattice dilation for which the Helmholtz free energy is a minimum (see Fig. 1). The thermal properties along the sublimation line are given in Table I and Figs. 2 and 3. For the registered system (see Table II), the dilation is set at the registry value and the properties are determined for the full range of temperatures relevant to the stable 2D solid. The differences in the thermodynamic properties of these two structures relate directly to the effects of the periodic substrate potential to the adlayer structure. There are vibrational modes not included in these thermodynamic properties, e.g., vertical oscillations, molecular rotational diffusion, and intramolecular vibrations. This model takes as an approximation that these modes, although contributing to the system totals, do not couple with sufficient strength to make significant differences in the translational C-I transition under discussion. This approximation is reasonable since the oscillation in the substrate potential is less than 1% of the heat of adsorption and at a given lattice dilation the vibrational spectra of the structures are nearly the same.

The calculation for the temperature-driven C-I transition is carried out for zero spreading pressure along the solid-vapor equilibrium line. The transition criterion is

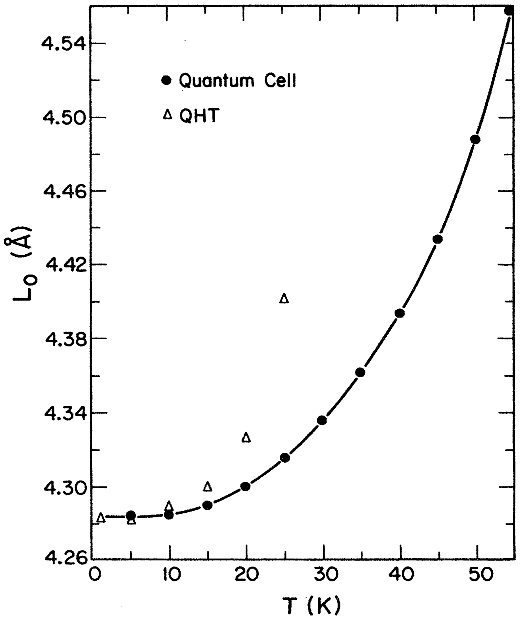

FIG. 1. Equilibrium lattice constant along the sublimation line for the CH_4/graphite system in the 2D floating solid structure. The symbols denote results of calculations with the (●) QCT and (△) QHT.

TABLE I. Thermodynamic properties of the floating CH_4/graphite system along the sublimation curve. Interactions include the MacLachlan and triple dipole terms.

T (K)	L_0[a] (Å)	K_T[b] ($Å^2$/eV)	U/Nk_B[c]	C/Nk_B[d]	F/Nk_B[e]	S/Nk_B[f]	Φ/Nk_B[g]
5.0	4.2846	38.9678	−290.190 61	0.002 63	−290.191 84	0.000 25	−344.816 02
10.0	4.2854	39.2915	−289.829 29	0.209 00	−290.254 63	0.042 53	−344.816 02
15.0	4.2903	41.3459	−287.621 07	0.657 14	−290.850 14	0.215 27	−344.272 83
20.0	4.3006	45.8268	−282.899 00	1.035 84	−292.572 15	0.483 66	−342.563 77
25.0	4.3162	52.0770	−276.071 24	1.276 95	−295.718 35	0.785 88	−340.111 13
30.0	4.3364	55.5280	−267.951 97	1.414 50	−300.386 32	1.081 14	−337.476 93
35.0	4.3621	71.3644	−257.670 32	1.495 03	−306.586 88	1.397 62	−332.482 29
40.0	4.3938	86.5972	−246.560 48	1.53104	−314.313 02	1.693 81	−327.069 91
45.0	4.4340	114.7321	−233.204 21	1.537 05	−323.575 17	2.008 24	−318.760 08
50.0	4.4876	164.8997	−217.543 56	1.515 02	−334.430 29	2.337 73	−307.213 63
55.0	4.5599	228.3972	−198.715 94	1.450 17	−346.999 68	2.696 07	−290.396 10

[a] Equilibrium lattice constant along the sublimation curve.
[b] Isothermal compressibility at the given temperature and lattice constant.
[c] Internal energy given in units of kelvin.
[d] Heat capacity at constant area ($\phi=0$), given in units of kelvin.
[e] Helmholtz free energy given in units of kelvin.
[f] Entropy given in units of kelvin.
[g] Static lattice sum per particle given in units of kelvin.

taken to be the temperature T_c for which the entropy difference of the two structures is equal to the barrier height V_0 divided by the temperature. Table III shows the results of such a comparison of the entropy difference to the barrier height V_0. The prediction is $T_c \simeq 41$ K, considering the empirical potential this is in fair agreement with the experimental observation of 48 K.[3−5] The inclusion of communal entropy would improve the comparison.

To predict the conditions for a pressure-driven C-I transition, the temperature was set at 5 K and the critical spreading pressure was calculated from a free-energy construction (chemical potential versus spreading pressure) for the two models. The chemical potential μ_i of the ith phase is

$$\mu_i = F_i + \phi A ,$$

where the F_i is the Helmholtz free energy of the ith phase, ϕ is the spreading pressure, and A is the area per molecule for the appropriate structure. The intersection of the two chemical potentials gives the critical spreading pressure ϕ_c at which the C-I transition takes place (see Fig. 4). This procedure could, of course, be carried out at any appropriate temperature (see Fig. 5). At 5 K, the critical spreading pressure is 10.6 K $Å^2$. If the registered system is subjected to this constant spreading pressure, it compresses 0.01 Å in the lattice constant and assumes an incommensurate free-floating 2D solid configuration. This compression is consistent with a corresponding states

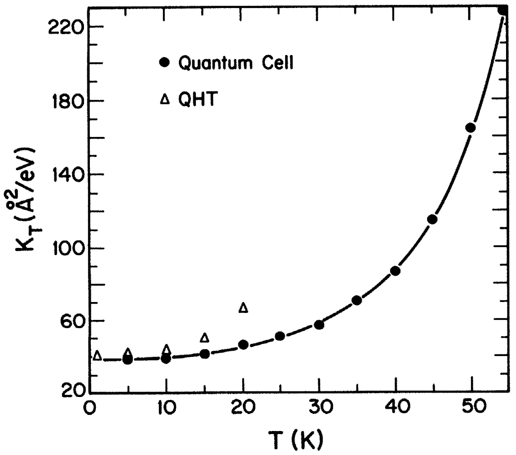

FIG. 2. Isothermal compressibility K_T as a function of temperature for the CH_4/graphite system along the sublimation line. The symbols denote results with (●) QCT and (△) QHT.

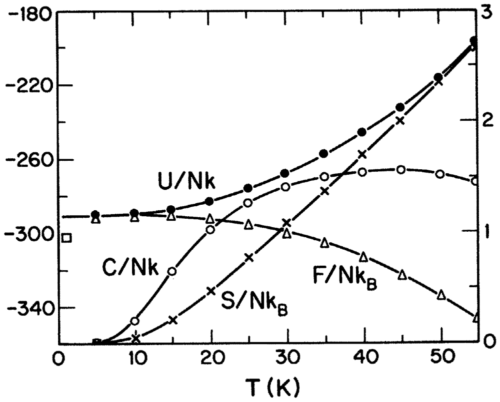

FIG. 3. QCT results for the thermodynamic properties of the 2D floating solid structure and the CH_4/graphite interactions. The data are given in Table I. The scale for the Helmholtz free energy (F/Nk_B) and the internal energy (U/Nk_B) is on the left-hand side in units of kelvin. The heat capacity at constant area ($\phi=0$) and the entropy (S/Nk_B) are given on the right hand side. A square box at 1 K is the Helmholtz free energy calculated by the QHT of lattice dynamics.

TABLE II. Thermodynamic properties of the registered CH_4/graphite system at the $\sqrt{3}\times\sqrt{3}$ lattice constant. Interactions include the MacLachlan and triple dipole terms.

T (K)	L_0[a] (Å)	K_T[b] (Å^2/eV)	U/Nk_B[c]	C/Nk_B[d]	F/Nk_B[e]	S/Nk_B[f]	Φ/Nk_B[g]
5.0	4.26	34.0771	−288.322 29	0.001 21	−288.322 81	0.000 11	−347.773 96
10.0	4.26	34.2208	−288.076 35	0.153 48	−288.362 35	0.028 60	−347.773 96
15.0	4.26	34.9368	−286.347 97	0.551 07	−288.796 84	0.163 26	−347.773 96
20.0	4.26	35.7669	−282.646 40	0.911 17	−290.121 21	0.373 74	−347.773 96
25.0	4.26	36.4765	−277.427 86	1.158 89	−292.568 10	0.605 61	−347.773 96
30.0	4.26	37.0013	−271.201 96	1.319 86	−296.167 58	0.832 19	−347.773 96
35.0	4.26	37.3237	−264.321 99	1.424 82	−300.865 15	1.044 09	−347.773 96
40.0	4.26	37.5596	−257.012 04	1.494 54	−306.580 37	1.239 21	−347.773 96
45.0	4.26	37.6171	−249.413 81	1.541 77	−313.230 21	1.418 14	−347.773 96
50.0	4.26	37.5403	−241.618 76	1.574 26	−320.737 28	1.582 37	−347.773 96
55.0	4.26	37.4593	−233.687 60	1.596 85	−329.032 15	1.73354	−347.773 96

[a] Lattice constant for the $\sqrt{3}\times\sqrt{3}$ registered structure.

[b] Isothermal compressibility at the given temperature and lattice constant.

[c] Internal energy given in units of kelvin.

[d] Heat capacity at constant area given in units of kelvin.

[e] Helmholtz free energy given in units of kelvin.

[f] Entropy given in units of kelvin.

[g] Static lattice sum per particle given in units of kelvin.

scaling of data from krypton on graphite and silver. Comparing the enthalpy difference between the two structures to the V_0 of the substrate potential is within a factor of 2 and error bars of 50%. A computational difficulty occurs because the strong repulsion between molecules under these relatively high spreading pressures causes the root search of two narrowly intersecting curves to have some imprecision. As a check on the method, a virtual dilation of the lattice (negative spreading pressure) was considered. In this case, the more slowly varying attractive intermolecular potential gave a lower pressure (-1.36 K/Å^2) and an enthalpy 10% above V_0.

VII. QUASISTATIC FRANK AND van der MERWE THEORY

The remaining question is whether the adlayer is compressed or thermally expanded sufficiently to achieve a misfit δ, relative to the substrate, sufficiently large ($\delta > \delta_c$) for the formation of domain walls. I estimate the critical misfit $\bar{\delta}_c$ for this system by a quasistatic interpretation of the theory of Frank and van der Merwe.[7-9] For a given dilation of the adlayer lattice, the critical misfit satisfies the condition

$$l_0 \delta_c = 2/\pi \tag{9}$$

where $l_0 = (\kappa a^2/2V_0)^{1/2}$ with κ as the force constant of the adlayer at the given lattice dilation

TABLE III. Temperature-driven C-I transition: Comparison of the entropy difference of the two-structure model and the averaged translation barrier.

T (K)	S/Nk_B[a]	V_0/T[b]
35.0	0.35	0.55
40.0	0.45	0.48
45.0	0.59	0.43
50.0	0.76	0.39

[a] The entropy difference between the registered structure (constrained to a fixed lattice constant $L = 4.26$ Å) and the floating solid structure thermally expanded but with zero spreading pressure.

[b] The averaged thermal-energy barrier determined in the Fourier decomposition ($V_0 = 19.25$ K) of the substrate potential divided by the temperature.

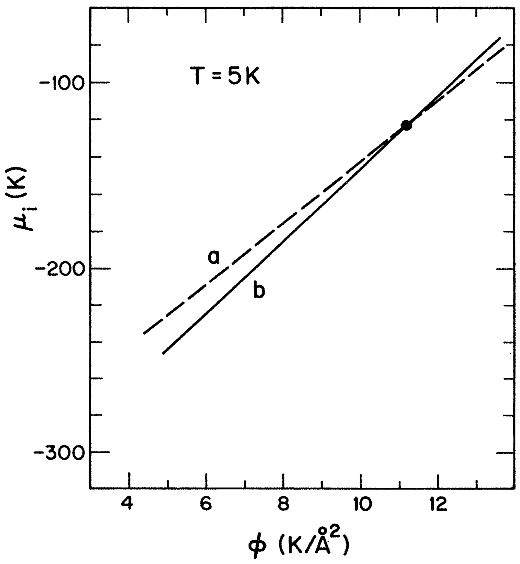

FIG. 4. Free-energy construction for the pressure-driven C-I transition at 5 K. The chemical potential in units of kelvin is plotted with the 2D spreading pressure (K/Å^2). The curve a is from the free-floating phase data and b is from the $\sqrt{3}\times\sqrt{3}$ registered phase. The intersection defines the critical spreading pressure of the first-order C-I transition.

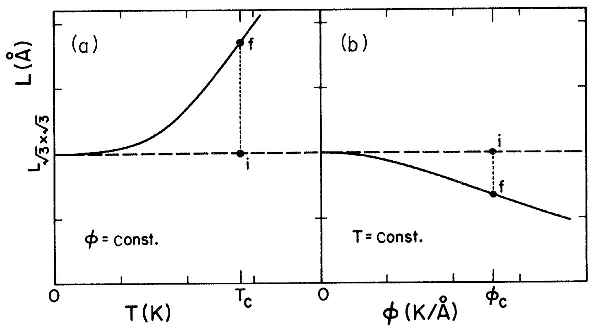

FIG. 5. Schematic representation of the (a) temperature-driven and the (b) pressure-driven *C-I* transitions. The horizontal line represents the $\sqrt{3}\times\sqrt{3}$ structure lattice constant. The curve represents the thermal expansion (a) and the lateral compression (b) of the free-floating structure. Points *i* and *f* represent the initial and final states of the transition. The calculations in this study follow the thermodynamic properties of the two structures to find the critical temperature (a) or the critical spreading pressure (b) of the *C-I* transition.

$$\kappa=\frac{1}{2}\sum_{\substack{i,j\\ i<j}}\nabla^2\Phi(R_{ij})\ , \qquad (10)$$

a is the lattice constant of the substrate registry positions, and V_0 is taken to be the leading factor of the Fourier decomposition of the substrate potential. The misfit of the free-floating model is $\delta=(b-a)/a$ where *b* is the lattice constant of the adlayer as predicted by the QCT or QHT calculation for a given temperature and spreading pressure combination. In this quantitative manner, the calculation includes the anharmonic nature of the intermolecular interactions and the finite temperatures of a realistic system.

In both *C-I* transitions considered here, the misfit δ is always less than the critical misfit δ_c, suggesting that the free-floating incommensurate phase may preempt the appearance of a domain-walled (light or heavy) incommensurate phase (see Table IV).

These methods and results do not generally conflict at any point with previous theories.[7-9] They do, however, extend previous theories, through the use of QCT and QHT, to a particular system (CH_4/graphite) in a quantitative anharmonic calculation for a full range of temperatures. Since the domain walls of the CH_4/graphite system should be far apart, I have not included the effects of wall interactions or crossings. I calculate the Novaco-McTague rotation of the adlayer to be 1.8° at 50 K. The thermal fluctuations considered in this finite-temperature model should be dominant in the free energies of the stable phase. In other systems with different adlayer elastic properties and substrate potential-energy variations, the domain-wall structures could be the stable phase within certain ranges of temperature and spreading pressure. The detailed results for the thermodynamic properties make possible the application of the uniaxial model of the Frank and van der Merwe criteria in a quasistatic manner to obtain an estimate of the misfit necessary for the spontaneous occurrence of domain walls. In light of the 2D Pokrovsky and Talapov[31] theory having the same critical misfit as Frank and van der Merwe and an expected low wall density for a weak periodic substrate potential such as the CH_4/graphite system, the estimate of the critical misfit should be a reasonable one.

TABLE IV. Comparison of the natural misfit with the critical misfit for the CH_4/graphite system.

T (K)	κ (K/Å^2)[a]	b (Å)[b]	δ[c]	δ_c[d]
1.0	774.31	4.2834	0.006	0.033
5.0	769.06	4.2846	0.006	0.033
40.0	389.44	4.3938	0.031	0.047
45.0	289.47	4.4340	0.041	0.055
50.0	181.26	4.4876	0.053	0.069

[a] Force constant calculated by Eq. (10).
[b] Equilibrium lattice constant of the unconstrained floating solid.
[c] Natural misfit δ as defined in the text.
[d] Critical misfit δ_c calculated by Eq. (9).

VIII. DISCUSSION

Given the likely case that domain walls are not present[7-9,30] in the *C-I* transition of the CH_4/graphite system, several results are clear: (1) substrate-mediated forces are sizeable and must be included to have results consistent with a variety of experiments, (2) the low temperature $\sqrt{3}\times\sqrt{3}$ registered phase configuration is predicted as a natural consequence of the theory, (3) the incommensurate phase expected to be a free-floating 2D solid without domain walls, and (4) the *C-I* transitions, both pressure and temperature driven, are first-order transitions. The two-structures model of *C-I* transitions applied to the CH_4/graphite system is generally suitable to physisorbed systems that have a very small natural misfit near the zero of temperature. Such systems must be compressed by spreading pressure or thermally expanded greatly before reaching the corresponding critical misfit for domain-wall formation. If the periodic oscillations of the substrate potential are small, the possibility exists that the *C-I* transition is directly to an unwalled free-floating 2D solid.

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