

Model of the commensurate-incommensurate transitions of CH₄/graphite

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A quantitative, anharmonic, finite-temperature model is presented for the pressure- and temperature-driven commensurate-incommensurate (C-I) transitions of an adsorbed layer of methane on graphite. The statistical thermodynamic properties of the system are calculated and free-energy constructions predict the C-I transitions to be of first order. The incommensurate phases are free-floating two-dimensional "solids" without domain walls. At $T=0$ K, a $\sqrt{3}\times\sqrt{3}$ registered phase is predicted.

A registered $\sqrt{3}\times\sqrt{3}$ adlayer of methane adsorbed 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 of registry by increasing the two-dimensional (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 2D solid methane adsorbed on graphite (CH₄/graphite). The statistical thermodynamic properties of the CH₄/graphite system, calculated by quantum cell theory (QCT) and quasiharmonic lattice dynamics (QHT), indicate 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.

Previously,⁷ it was shown that empirical intermolecular potentials can be built by representing the interaction of CH₄ molecules within the adlayer or with the graphite as a superposition of Lennard-Jones [LJ(12,6)] atom-atom pair potentials. The LJ(12,6) potential parameters ϵ_{xy} and σ_{xy} used in this study are the modified set of Severin and Tildesley⁸ which give reasonable results for the heights of rotational tunneling barriers.^{9,10} The adlayer interaction potential for both the QHT and QCT calculations is for a spherical molecule with a LJ(12,6) form.¹¹ Above 20 to 30 K, the methane molecules are in a rotationally diffusing state.¹² For the translational properties, the methane pair potential is represented by $\sigma_m = 3.6814$ Å with $\epsilon_m/k_B = 137$ K. This value of σ_m is well within the range of uncertainties and results in the same lattice constant for a potential-energy minimum as the atom-atom intermolecular potential. The McLachlan interaction for the substrate-mediated effects¹³ and the Axilrod-Teller-Muto triple-dipole interaction are added but surface dipole interactions are believed to be small and are omitted. The C_{s1} and C_{s2} parameters in the McLachlan interaction are given by Rauber, Klein, Cole, and Bruch.¹⁴ The triple-dipole coefficient was calculated by Margoliash, Proctor, Zeiss, and Meath.¹⁵

This report contains two types of calculations: (1) potential-energy mappings by static lattice sums and (2) statistical thermodynamic properties by quasiharmonic theory¹⁶ (QHT) of lattice dynamics and quantum cell theory (QCT).^{17,18} Zero-temperature results for the first calculation are given below and followed by the finite-temperature methods and results.

The minimum potential-energy structure for the atom-atom interaction potentials without the McLachlan and triple-dipole terms is predicted from the static lattice sums

calculations. For a single methane molecule, the minimum structure is a tripod position with the carbon atom of the molecule 3.28 Å above the plane of the surface carbons and sitting in an atop site (carbon above carbon) with the tripod legs oriented toward the centers of the three adjacent graphite hexagons (−1663 K/molecule). This energy value is less than 3% above the experimental value of Thomy and Duval¹⁹ for the isosteric heat in the low coverage limit. The potential energy of the molecule to the adlayer is an additional −914 K/molecule. The potential energy rises 11 K/molecule if the molecule is above a graphite hexagon center at the same height and orientation (center site) and 22 K/molecule higher if the molecule is between two adjacent graphite carbons (bridge site). The uncompressed adlayer of methane molecules forms a 2D hexagonal lattice with the energy minimum occurring at an adlayer lattice constant of $L = 4.09$ Å. The methane molecules pack closely so that the tripod legs of one molecule always nest into the vertex of the angle between the tripod legs of its nearest neighbors. Estimates of the zero-point energies in the uncompressed layer are 109 K/molecule for the vertical degree of freedom, 105 K/molecule for the librational,²⁰ and 88 K/molecule for the translational motions.

The nesting of the hydrogens of the tripod legs in an uncompressed 2D adlayer precludes free rotations at very low temperatures. Inelastic neutron scattering experiments^{9,10} show this system experiences rotational quantum tunneling. A theory by Smalley, Huller, Thomas, and White¹⁰ allows the data to be interpreted in terms of the potential-energy barriers to the rotation. The potential of the present work gives a minimum potential-energy barrier for rotation 4% below the experiment for the z-axis rotation and 13% below for the rotation about a tripod leg. The librational zero-point energies have been subtracted out.

It has been established that 2D solids with significant quantum effects can be quite anharmonic.¹⁷ The deBoer parameter, $\Lambda^* = 2\pi\hbar/[\sigma(m\epsilon)^{1/2}]$, for methane is 0.245 which is between neon and argon. The CH₄/graphite system is well within the range where quantum-mechanical considerations are important. Its thermal properties are, to a good approximation, derivable from QCT¹⁷ 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 correlational effects.²¹ The model is a collection of anharmonic Einstein oscillators. For 2D systems with parameters near those of neon and argon, the leading correction of the quantum cell approximation is the anharmonicity.¹⁷

The thermodynamic properties of the adlayer are calculated in the QCT approximation by determining the energy eigenvalues $E_{n,1}$ of the 2D Schrödinger equation, where n and l are the energy and angular momentum quantum numbers, respectively. The cell potential $\omega(r)$ (Ref. 17) is the circularly averaged potential of the molecule in the cell composed from 36 shells of its neighbors in the adlayer¹⁶ and with substrate-mediated interactions.¹³ The Schrödinger equation is written as a difference equation and solved in a vector space with a basis of plane waves.²²

In order to describe the C-I transitions in the CH₄/graphite system, the thermodynamic properties are calculated for two structural states of the adlayer: (1) a uniform free-floating 2D solid without domain walls, and (2) a solid adlayer constrained to the $\sqrt{3}\times\sqrt{3}$ registered structure with the periodic substrate potential found by the lattice sums mentioned earlier.

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 (see Table I). 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 minimizing the Helmholtz free energy. For the registered system, 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 (see the values in parentheses in Table I).

The periodic substrate potential is written as a Fourier decomposition²³ and incorporated into the circularly averaged cell potential $\omega(r)$. Free-energy constructions determine which is the stable structure for a given temperature and spreading pressure. The leading factor of the Fourier expansion is $V_0=19.25$ K which is taken to be the effective barrier height to translation for the adlayer. For a given dilation of the lattice, the vibrational properties of the two structures do not differ greatly. The small difference in the thermodynamic properties between the two models approxi-

mates the effects of the periodic substrate on this anharmonic finite-temperature system.

The calculation for the temperature-driven C-I transition is carried out for zero spreading pressure along the solid-vapor equilibrium line. The C-I transition temperature is determined by comparing the entropy difference between the two phases with the barrier height divided by the temperature V_0/T . To predict the conditions for a pressure-driven C-I transition, the temperature was set at 5K and the critical spreading pressure is calculated from a free-energy construction (chemical potential versus spreading pressure) for the two models. The chemical potential of the i th phase is $\mu_i = F_i + \phi A$, where the F_i is the Helmholtz free energy of the i th phase, where $\phi = -(\partial F_i/\partial A)$ is the spreading pressure, and A is the area per molecule for the appropriate structure. The intersection of the two chemical potentials gives the transition spreading pressure ϕ_c for the C-I transition.

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 preempts the appearance of a domain-walled (light or heavy) incommensurate phase. I estimate the critical misfit δ_c for this system by a quasistatic interpretation of the theory of Frank and van der Merwe.²⁴ For a given dilation of the adlayer lattice, the critical misfit satisfies the condition $l_0\delta_c = 2/\pi$, where $l_0 = (\kappa a^2/2V_0)^{1/2}$, with the force constant of the adlayer at the given lattice dilation

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

“ a ” is the registry distance, and V_0 is as defined. The natural 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

TABLE I. The thermodynamic properties of the floating and registered CH₄/graphite system. The interactions include the McLachlan and triple-dipole terms. The data in brackets are for the $\sqrt{3}\times\sqrt{3}$ registered structure.

T (K)	L_0 (Å) ^a	K_T (Å ² /eV) ^b	U/Nk ^c	C/Nk ^c	F/Nk ^c	S/Nk ^c	Φ/Nk ^c
5.0	4.2846 (4.26)	38.9678 (34.0771)	-290.19061 (-288.32229)	0.00263 (0.00121)	-290.19184 (-288.32281)	0.00025 (0.00011)	-344.81602 (-347.77396)
10.0	4.2854 (4.26)	39.2915 (34.2208)	-289.82929 (-288.07635)	0.20900 (0.15348)	-290.25463 (-288.36235)	0.04253 (0.02860)	-344.81602 (-347.77396)
20.0	4.3006 (4.26)	45.8268 (35.7669)	-282.89900 (-282.64640)	1.03584 (0.91117)	-292.57215 (-290.12121)	0.48366 (0.37374)	-342.56377 (-347.77396)
30.0	4.3364 (4.26)	55.5280 (37.0013)	-267.95197 (-271.20196)	1.41450 (1.31986)	-300.38632 (-296.16758)	1.08114 (0.83219)	-337.47693 (-347.77396)
40.0	4.3938 (4.26)	86.5972 (37.5596)	-246.56048 (-257.01204)	1.53104 (1.49554)	-314.31302 (-306.58037)	1.69381 (1.23921)	-327.06991 (-347.77396)
50.0	4.4876 (4.26)	164.8997 (37.5403)	-217.54356 (-241.61876)	1.51502 (1.57426)	-334.43029 (-320.73728)	2.33773 (1.58237)	-307.21363 (-347.77396)

^aThe equilibrium lattice constant along the sublimation curve.

^bThe isothermal compressibility at the given temperature and lattice constant.

^cThe internal energy, heat capacity at constant area ($\phi = 0$ for the floating model), Helmholtz free energy, entropy, and static lattice sum per particle. The internal energy, Helmholtz free energy, and the static lattice sum are given in Kelvin units.

of a realistic system.

The results from adding finite temperature to the model, through QCT and QHT, show the importance of thermal fluctuations in C-I transitions. Unless substrate-mediated interactions between molecules in the adlayer are included, the system must be at relatively high temperatures and have undergone sizable 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 to the required registry distance. When substrate mediation and temperature are included, the model quantitatively predicts the $\sqrt{3} \times \sqrt{3}$ registry structure for the uncompressed adlayer. The lattice constant at $T=0$ K is within 0.5% of registry length.

When the full model is applied to the temperature-driven C-I transition, the prediction is $T_c \approx 44$ K, which is in fair agreement with the experimental³⁻⁵ observation of 48 K. At this temperature, sufficient thermal energy is in the system that the fraction going into registry disassociation exceeds the barrier and the stable phase is a free-floating solid. For a pressure-driven C-I transition at $T=5$ K, the critical spreading pressure is $\phi_c = 10.6$ K/Å.² If the registered system is subjected to this constant spreading pressure, it compresses 0.01 Å in the lattice constant. This compression is consistent with a corresponding-states scaling of data from krypton on graphite and silver.^{25,26} Comparing the enthalpy difference between the two models with the V_0 of the sub-

strate potential is within a factor of 2 and error bars of 50%. 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) (Ref. 2) and an enthalpy 10% above V_0 .

These methods and results do not conflict at any point with previous theories.^{24,27} They do, however, extend them, through the use of QCT and QHT, to a particular system (CH₄/graphite) in a quantitative anharmonic calculation for a full range of temperatures. Given the likely case that domain walls are not present for the CH₄/graphite system, several results are clear: (1) substrate-mediated forces are sizable 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 predicted is a natural consequence of the theory; (3) the incommensurate phase is 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. Systems with a very small natural misfit near $T=0$ K may have C-I transitions that are describable in terms of these two simple structures of the present model.

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