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Methane adsorbed on graphite. I. Intermolecular potentials and lattice sums

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The potential-energy surface for methane adsorbed on the basal plane of graphite is determined from two different atom-atom intermolecular interaction models. Static lattice sums are calculated for solid adlayer films in which the structure is varied in a systematic search for potential-energy minima. The potential-energy barriers to desorption, translations, and rotations are calculated, and a structure with two molecules per unit cell is investigated. Estimates of the translational, librational, and vibrational zero-point energies are given. Comparisons to experiments are discussed.

I. INTRODUCTION

The physisorption of small molecules on smooth substrates has been the subject of a number of recent experiments.[1–7] Structural and thermodynamics data resulting from these experiments are now generally available and provide a measured set of facts to qualitatively test models of intermolecular interaction. The calculation of statistical-thermodynamic properties requires both realistic intermolecular potentials and practical calculational methodologies. Our study is the investigation of proposed interaction models applied to an adlayer of methane adsorbed on the basal plane of graphite (CH_4/graphite) and to the development of computational procedures. The potentials discussed in this paper (I) will be used in the following paper (II) to study the commensurate-incommensurate transitions of the CH_4/graphite system.

The approach is parallel to the calculation of the structural properties of two-dimensional (2D) solids with Lennard-Jones [LJ(12-6)] interactions[8,9] or with realistic potentials for xenon on silver [Xe/Ag(111)].[10–14] We calculate the zero-temperature properties of the CH_4/graphite system as the first step toward a realistic parametrization of the interactions. It is necessary to find a potential that reasonably predicts the features of the static lattice configuration before going on to finite-temperature effects, substrate-mediated interactions, and transitions between phases. Since the potential energy is a term in the Helmholtz free energy, this study (paper I) is an integral part of the finite-temperature investigation (paper II).

Specifically, our purpose is to report the results of static lattice sums over a methane adlayer adsorbed of the basal plane of graphite. We obtain, in effect, a potential-energy map. From the map, we make estimates of the adsorption energy, and of the barriers to translation, rotational diffusion, and rotational tunneling. We also report on the static lattice sums of a proposed[15] structure with two molecules per unit cell.

Physical adsorption has been previously reviewed by Dash,[16] Steele,[17] and Webb and Bruch.[18] A brief summary of CH_4/graphite experiments includes heats of adsorption and the higher-temperature regions of the phase diagram.[4,7] Recent work has measured the mobilities for 2D methane fluids,[4] established the existence of a low-temperature solid phase,[3] and observed changes between orientational phases.[3,19] Other studies have investigated commensurate-incommensurate transitions[1,4,5] and 2D melting.[4,5] Static lattice sums have been computed for some configurations[20] and computer simulations[19] have added to the literature for this system. Small hydrocarbon molecules adsorbed on graphite provide diverse systems abundant in structural and thermodynamic information. In this work, we attempt to calculate a number of properties in order to establish reasonable limits on the applicability of these empirical potentials. In Sec. II we present the intermolecular interaction models used in this work. Section III is a description of the two lattice summing methods employed. Section IV is a discussion of the results.

II. INTERMOLECULAR POTENTIAL

The problem of calculating the lattice energy of a molecular crystal is often reduced to only the consideration of van der Waals interactions. In this study we make such an assumption. It is, however, interesting that some of our results are similar to those of O'Shea and Klein[19] and Righini *et al.*[21] who include an electric octapole interaction.

An assumption, in the early studies by London,[22] requiring the molecule to be spherically symmetric cannot adequately explain some of the data from modern experiments. Attempts to overcome this limitation by dividing the molecule into force centers[23] have produced useful models. The parameters in these models are empirically derived.[24,25] The intermolecular interactions are assumed to be a superposition of van der Waals atom-atom interaction between atom pairs of interacting molecules.

We separately use the exponential-sixth form with Williams parameters[24] and the Lennard-Jones interaction with parameters obtained from dense fluid-methane data[26] as modified by Severin and Tildesley.[25]

A. Exponential-sixth potential model

The potential between the *j*th atom of the reference molecule and the *i*th atom of another molecule or of a carbon atom in the graphite substrate is

$$\Phi_{ij}(r_{ij})=A_{ij}r_{ij}^{-6}+B_{ij}\exp(-C_{ij}r_{ij}) , \tag{1}$$

where r_{ij} is the separation distance. We use the values

TABLE I. Parameters for the exponential-sixth atom-atom interactions. See Ref. 24.

Interaction	A_{ij} (Å^6 kcal/mole)	B_{ij} (kcal/mole)	C_{ij} (Å^{-1})
C-C	−535	74 460	3.60
C-H	−139	9411	3.67
H-H	−36	4000	3.74

given by Williams[24] for the parameters A_{ij}, B_{ij}, and C_{ij} (see Table I). Williams required the interatomic potential to vanish beyond a certain cutoff length. We employed these cutoffs in our sums, 6.0 Å for the carbon-carbon interaction, 5.0 Å for the hydrogen-hydrogen, and 5.5 Å for the carbon-hydrogen interactions. Note that the second graphite layer is beyond the cutoff distance. Consequently, this particular model considers only a single carbon layer to be the graphite substrates.

B. Lennard-Jones potential model

In the second model, the atom-atom potential function is taken to be the LJ(12-6) equation. The potential energy of the ith atom of the reference molecule to the jth atom of the substrate or adlayer molecule is

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

where the parameters ϵ_{ij} and σ_{ij} are estimated empirically by comparisons to the experimental data.

In a molecular dynamics study of a single methane molecule on a graphite surface, Severin and Tildesley[25] investigated the potential parameters used in the LJ(12-6) atom-atom interaction. They started with two different sets of parameters: one from a study of dense fluid methane by Murad and Gubbins[26] and the other from matching the well depth and collision diameters of the Williams[24] work to the ϵ and σ of the LJ(12-6) potential. The Lennard-Jones parameters for the carbon-to-carbon interaction in graphite are obtained from compressibility measurements[27] and inert gas on graphite investigations.[28] Methane-to-graphite parameters were determined by the usual mixing rules[29]

$$\sigma_{ij}=(\sigma_i+\sigma_j)/2 \tag{3}$$

and

$$\epsilon_{ij}=(\epsilon_i\epsilon_j)^{1/2} . \tag{4}$$

Severin and Tildesley adjusted these parameters to produce comparable results to experiments determining rotational barrier heights,[3] second virial coefficients,[30] and isotropic enthalpy at zero coverage.[30,31] The two original sets of parameters and the adjusted set are compared in Table II.

Any empirical model for intermolecular intersections with parameters fitted to experimental data is subject to limitations. Our purpose is not to further refine the adjustments made by Severin and Tildesley in what is admittedly an *ad hoc* construction. Instead, we calculated a number of potential sensitive properties in an attempt to discover any gross inconsistencies between the predictions of the model and observations. We have required all of our results to be quite computationally precise beyond any reasonable physical interpretation. In doing so, we have very good cross-checks on methodology and on inherent defects of a particular model. For example, the cutoffs of the Williams construction cause shallow local minimums and small jumps in the potential energy as the methane molecule is moved in the scanning procedure.

TABLE II. Parameters of the LJ(12-6) atom-atom interaction. This table is from the study by Severin and Tildesley (Ref. 25).

	ϵ_{ij}/k_B (K)			σ_{ij} (Å)		
Interaction	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]
CH_4-CH_4						
C_m-C_m	51.198	47.68	51.198	3.35	3.35	3.35
C_m-H_m	23.798	24.46	23.798	2.995	2.99	2.99
H_m-H_m	8.631	4.87	4.87	2.813	3.12	2.61
Graphite						
C_g-C_g	28.00			3.40		
CH_4-graphite						
C_g-C_m	37.862	47.68	47.68	3.375	3.35	3.30
C_g-H_m	15.54	24.46	17.00	3.107	2.99	2.98

[a] From dense fluid-methane data.
[b] From the Williams study (Ref. 24).
[c] From the adjusted set of Severin and Tildesley (the set used in this work).

We have neglected any subtrate-mediated effects in the lateral adsorbate-adsorbate interaction.[18] Triple-dipole effects are also omitted. Righini *et al.*[21] estimate the three-body effects to be 8% in three-dimensional (3D) solid methane. In 2D, there are fewer triplets and the effect will be inherently less. In paper II, substrate-mediated effects and the triple-dipole term are added to the intermolecular potential.

III. CALCULATIONS

In this section we present the calculational procedures of four lattice-sum studies. The first two use the Williams potential model and the next two use the Lennard-Jones potential model.

A. Williams potential and the CH_4/graphite system

Our study began by applying the methodology used by Hansen and Taub[2] for other hydrocarbons on graphite to the methane on graphite system. Using the exponential-sixth interaction of Eq. (1) with the parameters of Williams, we performed direct computer lattice sums for two different problems. The first was to vary the structure of an ordered methane adlayer in search of a potential-energy minimum.

The basic problem is the calculation of the total potential energy per adsorbed molecule, as two sums

$$\Phi=\Phi_1+\Phi_2 \; . \tag{5}$$

The first term, Φ_1, is a static lattice sum between a reference molecule and the graphite substrate, the second term, Φ_2, is over the asorbate film. The potential energy, relative to the basal plane of a semi-infinite graphite crystal, of a methane molecule whose center (C atom) at r is height z above a point (x,y) on the graphite surface is given by

$$\Phi_m(\vec{\mathrm{r}};\theta,\phi)=\sum_i \sum_j \Phi_{ij}(r_{ij};\theta,\phi) \; , \tag{6}$$

where $m=1,2$. With $m=1$, the outer sum is over the lattice sites of the graphite substrate from an atomic site of the methane. The inner sum is over the individual atom sites within the methane molecule. The orientation of the methane molecule is specified by the spherical coordinates θ and ϕ. The potential energy Φ_2 of the reference molecule interacting with the molecules of the lattice of an ordered methane film is also given by Eq. (6) with $m=2$. The outer sum is taken over the atoms making up the molecules of the rest of the film.

B. Two molecules per unit cell and the Williams potential model

The second problem was an attempt to resolve a question about a two molecule unit-cell structure suggested by Maki and Nosé.[15] In a crystal-field theory calculation they found inverted alternate rows of methane to be a favored structure. Equation (6) is adapted to apply to a two-molecule unit cell where the relative positions within the unit cell are fixed, the unit-cell potential energy is calculated, and then the same scanning procedure over the lattice is executed, as described above. The internal coordinates of the unit cell are systematically varied and the search for potential-energy minimum is initiated again.

C. Lennard-Jones potential model and the CH_4/graphite system

Because of several limitations to the Williams model when applied to condensed systems, we again search for potential-energy minimums but using the Lennard-Jones interaction as the atom-atom potential between molecules. The potential parameters were based upon the radius and well depth of the corresponding Williams interaction but revised by Severin and Tildesley.[25]

Lattice sums over the adsorbate-substrate system, in the rigid-lattice approximation, are calculated by two quite different methods: an Ewald summation technique[32] and a direct sum. For identical lattices and potential parameters, the two methods give the same values to six figures. The energy sum for the reference molecule to the substrate is

$$\Phi_1(\vec{\mathrm{r}};\theta,\phi)=4\sum_i \sum_{j=1}^{5} \epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12}-(\sigma_{ij}/r_{ij})^{6}]+\Phi' \; , \tag{7}$$

with $m=2$. The outer sum is over the lattice sites of the top five layers of the graphite substrate and the inner sum is over the individual atom within the methane molecule. The last term,

$$\Phi' \simeq (\pi\epsilon\rho\sigma^6)/[3(z_0')^3] \; , \tag{8}$$

is the integrated continuum tail correction for the deeper-lying layers of the graphite. In Eq. (8), ρ is the density of graphite atoms and

$$z_0'=z_0+d_0 \; ,$$

where z_0 is the height of the carbon atom of the methane molecule above the graphite surface, and d_0 is the depth of the first five layers of the discrete sum of Eq. (7). Directional effects are, in fact, small for the second layer of graphite. Laterally, we have arbitrarily cut off the discrete sum at distances which ensure precision to six digits. The potential energy of a methane reference molecule relative to the rest of an ordered triangular lattice of methane molecules is given by

$$\Phi_2(\vec{\mathrm{r}};\theta,\phi)=\sum_n \sum_{i,j} \Phi_n(\sigma_{ij},\epsilon_{ij},r_{ij}(n)) \; , \tag{9}$$

where

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

The vector distance $r_{ij}(n)$ is measured from the ith atom of the reference molecule to the jth atom of the nth molecule in the film. The reference molecule is oriented by θ,ϕ with respect to the ordered molecules making up the adsorbate. The potential energy of the reference molecule in a particular static configuration is the sum of Eqs. (7) and (9) in Eq. (5). The minimum-energy structure is determined by computing the potential energy for the system as the film is moved over the substrate, and the structure within the film is varied. Energy barriers to molecular rotations are calculated by evaluating the lattice sums while moving the reference molecule in the static field of the ordered film and substrate.

D. Analytic sum techniques and the Lennard-Jones potential model

The second method utilizes an analytic approach given by Fumi and Tosi,[32] which reduces Eqs. (7) and (9) to a reciprocal-lattice sum. The fundamental computational problem is the evaluation of the sum $\sum r_{ij}^{-s}$ over the atom sites of a 2D triangular lattice of methane molecules. We have incorporated some analytical techniques to improve the computational efficiency of the potential-energy mapping. Three types of sums are involved: (1) when the j site is a lattice point, (2) when the jth site is not a lattice point but lies in the plane of the lattice, and (3) when the jth site is not in the plane of the lattice. The lattice point at the origin is the jth site in the first type of sum but the origin must be excluded in the second and third types. The sum over a graphite plane hexagonal lattice viewed as the difference between the sum over a triangular lattice of lattice constant a and one with lattice constant $\sqrt{3}a$. The first type of sum occurs when the atom-atom interaction is calculated between corresponding atoms in the adlayer. The second type occurs for different tripod-leg hydrogens in two different molecules. The third type is more general and applies to summing over the graphite lattice or adlayer molecules with respect to a nonplanar atom of the reference molecule. The algorithms are successively more involved and computation efficiency is realized by making use of these distinctions.

The sum over triangular lattice from its origin (type 1) can be written

$$\sum_i r_i^{-s} = (1/a^s) \sum_{m,n=-\infty}^{+\infty}{}' (m^2 + +mnn^2)^{-(s/2)} , \quad s > 2 \tag{10}$$

where the prime means that the origin is excluded ($m = n = 0$) and the jth site is taken to be the origin. Zucker[33] showed that

$$\sum_i r_i^{-s} = (1/a) \left[\sum_n (1/n^{s/2}) \right] \left[\sum_m [(3m+1)^{-(s/2)} - (3m+2)^{-(s/2)}] \right] = (1/a)\zeta(s/2) g(s/2) , \tag{11}$$

where $\zeta(s/2)$ is the Riemann ζ function and $g(s/2)$ is an easily tabulated function.

The next sum (type 2) can be evaluated by an extension of the Madelung method. Fumi and Tosi[32] give the sum at the point of the jth site (x,y) in the plane of a linear lattice as

$$S_s(x,y) = \sum_n r_n^{-s} = \frac{\pi^{1/2}\Gamma((s-1)/2)}{a\Gamma(s/2)x^{s-1}} + \frac{2\pi^{1/2}}{a\Gamma(s/2)(2x)^{(s-1)/2}} \sum_m{}' (2\pi m/a)^{(s-1)/2} K_{(s-1)/2}(2\pi m x/a) \exp(i 2\pi m y/a) \tag{12}$$

where $\Gamma(s)$ is the Γ function and $K(kx)$ is the modified Bessel function of the second kind. The point (x,y) cannot be a lattice point. Letting $n = i$ and defining the linear lattice as $x_n = na$ with n as an integer, we can extend Eq. (12) to be a sum over the successive rows of a triangular lattice.

Out-of-the-plane sums (type 3) are calculated by another form of the Fumi and Tosi method. The reference point is at a height z above the planar position $\vec{r}$. The sum is over the planar lattice $\vec{r}_1 = l_1\vec{a}_1 + l_2\vec{a}_2$ with the integers l_1 and l_2, and the 2D triangular lattice vectors $\vec{a}_1$ and $\vec{a}_2$. The reciprocal-lattice vectors are $\vec{G} = g_1\vec{A}_1 + g_2\vec{A}_2$ with the integers g_1 and g_2 and $\vec{a}_i \cdot \vec{A}_j = 2\delta_{ij}$. Transforming the sum to the reciprical-lattice space and summing gives

$$\sum_i r_i^{-s} = S_s(\vec{r},z) = \frac{\pi}{\omega\Gamma((s/2)-1)z^{s-2}} + \frac{2\pi}{\omega\Gamma(s/2)(2z)^{(s/2)-1}} \sum_{g_1,g_2}{}' |\vec{G}|^{(s/2)-1} K_{(s/2)-1}(|\vec{G}|z) \exp(i\vec{G}\cdot\vec{r}) , \tag{13}$$

where $\omega = |\vec{a}_1 \times \vec{a}_2|$, $z > 0$, and $s > 2$. Equation (13) is evaluated for the graphite layers and relevant planes of adlayer atoms. The sums for the potential energy of a given configuration use all three of the above methods for both the sixth and twelfth powers.

Calculating the lattice sums of the CH_4/graphite system by two completely independent methods was very useful for cross-checks against errors. Equations (12) and (13) converge rapidly but for reciprocal-sixth and -twelfth powers of a well-written direct-sum algorithm is faster for a reasonable number of significant figures. The evaluation of the special functions in Eqs. (12) and (13) in our program was slower than our direct sums. The extended Madelung approach will be more helpful for systems with power-law interactions closer to a cubic than the sixth and twelfth of the LJ(12-6) potential. When the reference molecules are translated or rotated in a fixed field of the adlayer, the direct-sum method [Eqs. (7) and (9)] is more convenient.

The zero-point energy estimates for the vertical and librational oscillations of an adsorbed molecule in the potential of the substrate and adlayer neighbors was made in the harmonic approximation with the elastic constants derived from the derivatives of the potential. The translational zero-point energy was calculated by lattice dynamics (quasiharmonic theory)[8] assuming the methane to be a spherical molecule.

IV. RESULTS

The minimum-potential-energy structure for the LJ(12-6) atom-atom interaction potentials is predicted from the static lattice sums calculation described above. For a single molecule, the minimum structure is in a tripod position with the carbon atom of the molecule 3.28 Å

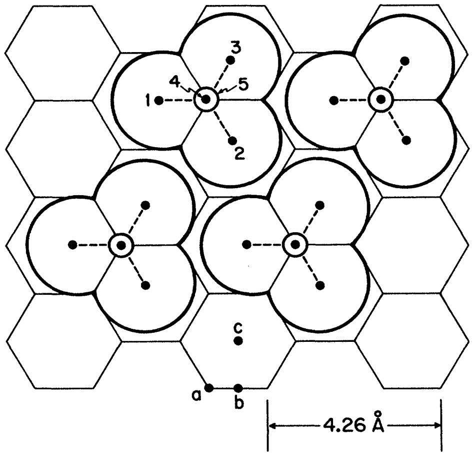

FIG. 1. Schematic diagram of the CH_4/graphite system in the $\sqrt{3}\times\sqrt{3}$ structure. Position *a* is the atop site, *b* is the bridge site, and *c* is the center site of the text. The solid circles 1, 2, and 3 prepresent the hydrogens of the tripod legs closest to the graphite basal plane and 4 is the vertical hydrogen standing above the other atoms of the methane molecule. The open circle 5 represents the carbon atom at the center of the methane tetrahedron.

above the plane of the surface carbons and sitting in an atop site (see Fig. 1) 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 Duval[4] for the isosteric heat in the low-coverage limit. The potential energy of the molecule to the adlayer is an additional −914 K/molecule when the adlayer lattice constant is the $\sqrt{3}\times\sqrt{3}$ value. The potential energy rises to 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 molecular forms a 2D hexagonal lattice with the energy minimum occurring at an adlayer lattice constant of $L_0 = 4.09$ Å. The methane molecules pack so closely that the tripod legs of one molecule always nests 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,[19] 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[3] show that this system experiences rotational quantum tunneling. A theory by Hüller *et al.*[3] allows the data to be interpreted in terms of the potential-energy barriers to the rotation. The potential of this 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. In order to find the minimum barrier, the reference molecule is lifted out of the plane of the adlayer at the sacrifice of the substrate attraction to a height of 3.56 Å for the tripod leg rotation and 3.33 Å for the vertical axis rotation.

The results of the exponential-sixth potential Eq. (1) (the Buckingham potential with the Williams parameters) are significantly different from those of the LJ(12-6) potential. The lowest-lying-energy configuration of a single molecule is in a tripod position above a bridge site (see Fig. 1) with two tripod legs straddling the graphite carbon-carbon bond. The value is −1644 K/molecule. At the potential minimum, the vertical height of the methane carbon above the graphite plane is 3.32 Å. The potential energy of the molecule to the adlayer is −296 K/molecule when the adlayer is in the $\sqrt{3}\times\sqrt{3}$ structure. The total potential energy for this structure is −1940 K/molecule. A systematic scan over positions and orientations shows many local translational minima. Such minima also occur for small rotations away from symmetrical orientations. The effect is due to the relative short-range cutoffs in the Williams potential. Another problem with the cutoffs is that only one layer of the graphite is in the range. The rest of the semi-infinite crystal contributes 15% to the total in the LJ(12-6) model.

We use the LJ(12-6) potential to calculate the potential-energy minimum for the adlayer structure of alternating inverted rows of the methane.[15] This is a structure with two molecules per unit cell. We set the methane-methane distance to the $\sqrt{3}\times\sqrt{3}$ value. The results for the energy minimum are 3.56 Å for the adlayer height and a total energy of −2108 K/molecule. The CH_4-CH_4 interaction has a lower potential energy but the CH_4 to graphite is much higher. The 18% increase in the total potential energy indicates that this alternating inverted rows structure, in the presence of a substrate, is not the preferred structure.

In summary, we have investigated atom-atom models of intermolecular potentials by evaluating static lattice sums of systematically varied structures of an adlayer of methane adsorbed on the basal plane of graphite. The exponential-sixth interaction model with Williams parameters gives results that differ from experiment sufficiently to cause doubt in its usefulness. The bridge site, preferred by the exponential-sixth model, is the least favored by the LJ(12-6) potential. Symmetry arguments[34] for CF_4 give some indirect support for the atop-site result of the LJ(12-6) model. A similar potential-energy study[35] for CF_4, CCl_4, and CBr_4 predicts the atop sites for energy minima. Only CI_4 has the hexagonal center-site result. The adsorption energy comparisons are close for the exponential-sixth and the LJ(12-6) models but the alternate rows inverted structure differs considerably. The methane-methane interaction for the LJ(12-6) model is 3 times the Williams interaction result. The occurrence of local minima and the problems with the cutoffs are serious defects in the Williams model as applied to adsorbed systems. It should be pointed out that these difficulties arise in an application of the Williams model to systems far different from the original intention. The model works quite well on a number of molecular problems.[24]

The height of the adlayer above the graphite plane is well within experimental error for the LJ(12-6) and the exponential-sixth (Williams) results. The alternating inverted rows structure is located 9% higher than the experimental value of 3.30 + 0.02 Å. The total energy is 18% higher than the LJ(12-6) structure with a single molecule per unit cell. The adlayer height predictions of the calculated potential-energy minimum should compare reasonably well with experiment because the thermal expansion of this distance is generally quite small and less than the experimental error.

The results of our study tend to support the atom-atom intermolecular potential using the LJ(12-6) form with the parameters of Severin and Tildesley as being a reasonable representation of the CH_4/graphite system. This model is the best candidate for the finite-temperature considerations of the following paper (II) where we find good agreement with the transition temperatures and pressures for commensurate-incommensurate transitions.

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