

## Potential expansion for molecules adsorbed or scattered on a surface

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We present an analytical potential expansion for a molecule interacting with a two-dimensional lattice of atoms which is convenient in quantum-mechanical scattering and lattice-dynamics calculations. It combines the following three ingredients: a spherical expansion in symmetry-adapted free-rotor functions of the molecule which represents the anisotropy of the potential explicitly, a translational-displacement expansion that goes beyond the harmonic approximation, and a two-dimensional Fourier expansion, which reflects the translational symmetry parallel to the substrate. As an example, we show some numerical results for  $N_2$  on graphite which illustrate the convergence of the various expansions. The potential anisotropy is visualized explicitly. At an adsorption site, the in-plane anisotropy appears to be negligible with respect to the out-of-plane anisotropy. The anharmonic terms in the molecular-displacement expansion are so important that they will influence the out-of-plane translational vibrations.

### I. INTRODUCTION

The interaction between molecules and substrates plays an important role in many interesting physical phenomena. It can be probed by molecular-beam surface-scattering experiments.<sup>1,2</sup> Furthermore, it leads to the adsorption of molecules or molecular layers on the surface, which can take part in many interesting processes. Adsorbed layers are (quasi-) two-dimensional systems which occur in a rich variety of phases<sup>3</sup> that can differ strongly from the ordinary bulk phases. Of course, in an adsorbed layer the admolecule-admolecule and the substrate-mediated interactions<sup>4,5</sup> must also be taken in account. The competition between all types of interactions determines, for instance, whether an adsorbed molecular layer is commensurate or incommensurate with the underlying crystal.<sup>6,7</sup> However, in this paper we concentrate on the molecule-substrate interactions.

In order to calculate the dynamics of adsorbed or surface-scattered molecules, one needs expansions of the total molecule-substrate potential. First we summarize what is available in the literature. Steele<sup>8</sup> has derived a powerful expansion for the interaction between an atom and a two-dimensional lattice of substrate atoms, adopting an atom-atom pair-potential model. Because of the two-dimensional translation symmetry, the sum over pair potentials can be replaced by a rapidly convergent Fourier series. Steele has given explicit formulas for the Fourier transforms in the case of a Lennard-Jones 12-6 atom-atom potential. The extension to exponential potentials has been made by Belak.<sup>9</sup> Both types of Fourier series have proved to be valuable in various classical molecular-dynamics and harmonic-lattice-dynamics calculations on adsorbed molecular layers.<sup>10,11</sup> In these calculations the interaction between an adsorbed molecule and a substrate atom is considered to be a sum of atom-atom potentials, so that the total molecule-substrate potential can be written as a sum over atom-substrate Fourier expansions. The lowest-order term of such a

molecule-substrate Fourier expansion only depends on the height of the atoms above the substrate. Sokolowski, in his calculations of second virial coefficients and other properties of adsorbed linear molecules, has expanded this term into spherical harmonics and numerically evaluated the expansion coefficients.<sup>12,13</sup> Further, we remark that the atom-substrate Fourier series has been expanded with respect to atomic-displacement coordinates in order to get harmonic force constants.

Another type of expansion which is useful in molecule-molecule scattering calculations and in dynamical calculations of molecular complexes (van der Waals molecules) and molecular bulk solids, is the so-called spherical expansion.<sup>14</sup> Such an expansion represents explicitly the anisotropy of an intermolecular potential. If the intermolecular potential is given as a sum of atom-atom potentials, this spherical expansion can be obtained with the aid of analytical transformation formulas which are known for inverse-power-law<sup>15</sup> and exponential atom-atom-potential types.<sup>16</sup> However, spherical expansions are much more general than atom-atom-potential models and they can be used to fit experimental or *ab initio* data directly. They can also be further expanded with respect to translational-molecular-displacement coordinates,<sup>17</sup> which is useful for the calculation of the vibrational states in molecular complexes or solids. Combined spherical and displacement expansions have proved to be valuable, for example, in quantum-mechanical lattice-dynamics calculations on solid nitrogen and oxygen.<sup>18</sup>

In the present paper we are interested in molecule-substrate interactions and we combine the two ingredients, atom-substrate potentials and molecule-molecule potentials, in order to derive new formulas for molecule-substrate potentials. We combine the advantages of spherical, molecular-displacement, and Fourier expansions.

In Sec. II we describe a general method to obtain a molecule-substrate Fourier potential series starting from

a spherical expansion for molecule-atom pair potentials. In Sec. III we derive an alternative method, which is applicable and preferable in the special case that the pair interaction can be approximated by an atom-atom-potential model. In Sec. IV we give some quantitative examples.

## II. GENERAL METHOD

### A. Spherical expansion of anisotropic molecule-atom potentials

Consider a molecule interacting with a substrate that consists of discrete atoms or ions. The total interaction between the molecule and the substrate is assumed to be the sum of molecule-atom pair potentials. Three-particle and higher-order terms are neglected. In order to represent the anisotropic behavior, we use a spherical expansion to describe the molecule-atom pair potentials:

$$V(\mathbf{R}, \omega) = \sum_{l=0}^{\infty} \sum_{m'=-l}^l v_{lm'}(R) \times \sum_{m=-l}^l (-1)^m C_{-m}^{(l)}(\hat{\mathbf{R}}) D_{mm'}^{(l)}(\omega)^* . \quad (1)$$

This is a special case of the more general expansion for two interacting molecules given by Van der Avoird *et al.*,<sup>14</sup> which follows easily when one of the molecules is replaced by an atom. In a forthcoming paper we will use the more general spherical expansion in order to derive analytical expressions for the interaction between an electrostatic multipole and a two-dimensional lattice of multipoles. In Eq. (1)  $C_m^{(l)}$  is a Racah spherical harmonic and  $D_{mm'}^{(l)}$  is a Wigner  $D$  function in the active convention.<sup>19</sup> These angle-dependent functions are coupled. The result is a scalar, which ensures the invariance of the total expansion with respect to an overall rotation of the system. Furthermore, the vector  $\mathbf{R} = \{R, \hat{\mathbf{R}}\}$  connects both centers of mass, pointing from the atom to the molecule, and the molecular orientation is described by the Euler angles  $\omega = (\alpha, \beta, \gamma)$ . For a linear molecule these angles are the polar angles  $\omega = (\varphi, \vartheta, 0)$ . In that case the sum over  $m'$  must be omitted and the complex-conjugated Wigner  $D$  functions have to be replaced by Racah spherical harmonics according to Ref. 19:

$$C_m^{(l)}(\vartheta, \varphi) = D_{m0}^{(l)}(\varphi, \vartheta, 0)^* . \quad (2)$$

In the special case that the molecule consists of a single atom, the expansion of Eq. (1) reduces to an isotropic ( $l=0$ ) atom-atom potential.

If the molecule possesses a molecular symmetry group  $G$  of order  $n_G$ , then the total molecule-atom pair-potential expansion must be invariant under all operations of this group. It is convenient to exploit this property with the aid of the totally symmetric projection operator:<sup>17</sup>

$$\hat{S} = \frac{1}{n_G} \sum_{g \in G} \hat{P}(g) . \quad (3)$$

The molecular symmetry operators  $\hat{P}(g)$  act on  $D$  functions according to the Wigner convention.<sup>20</sup> It can be shown that the corresponding symmetry-adapted functions are linear combinations of  $D$ -functions:

$$G_{mm'}^{(l)}(\omega) = \hat{S} D_{mm'}^{(l)}(\omega)^* = \sum_n c_{nm}^{(l)} D_{mn}^{(l)}(\omega)^* . \quad (4)$$

An example of symmetry-adapted functions can be found in Ref. 17, where the tetrahedral rotation functions are listed for  $l \leq 10$ . Using the symmetry-adapted functions from Eq. (4), we can write the spherical expansion of a molecule-atom potential as

$$V(\mathbf{R}, \omega) = \sum_l \sum_{m'} \Phi_{lm'}(R) \sum_{m=-l}^l (-1)^m C_{-m}^{(l)}(\hat{\mathbf{R}}) G_{mm'}^{(l)}(\omega) . \quad (5)$$

There may be more than one symmetric linear combination of  $D$ -functions for a fixed value of  $l$ . In Eq. (5), the summation over  $m'$  has to be performed over different combinations only.

It is assumed that the expansion coefficients  $\Phi_{lm'}$ , occurring in Eq. (5), are (analytical) functions of the intermolecular distance  $R$ . These functions are usually obtained by an analytical fit of *ab initio* or experimental data. The simplest and most popular forms are of the inverse-power or exponential type, but many other forms have been used.<sup>21</sup> The functions  $\Phi_{lm'}$  can also be derived from an atom-atom-potential model, with the aid of explicit formulas, as given in, for instance, Refs. 15 and 16. This does not imply, however, that a spherical expansion is always equivalent to a sum of atom-atom potentials. On the contrary, it is much more general.

### B. Molecular-displacement expansion

In dynamical calculations on adsorbed molecules which perform small oscillations around an equilibrium configuration, one often needs an expansion with respect to molecular-displacement coordinates. For this reason we make the following Taylor expansion of the pair potential given by Eq. (5):

$$V(\mathbf{R} + \mathbf{u}, \omega) = \sum_{\alpha=0}^{\infty} \frac{(\mathbf{u} \cdot \nabla)^{\alpha}}{\alpha!} V(\mathbf{R}, \omega) , \quad (6)$$

where  $\mathbf{u}$  denotes a small molecular-displacement vector. The substrate is considered to be rigid.

This expansion is most conveniently performed with the aid of the spherical gradient formula,<sup>22</sup> as demonstrated by Briels *et al.*<sup>17,18</sup> Since the formulas given in Ref. 17 are very complex, we summarize the result in a compact notation:

$$V(\mathbf{R} + \mathbf{u}, \omega) = \sum_{\Lambda} E_{\Lambda}(\mathbf{R}) u^{\alpha} C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) G_{mm'}^{(l)}(\omega) , \quad (7)$$

where the combined index  $\Lambda$  is defined by

$$\Lambda = (l, m, m', \alpha, l_1, m_1), \quad 0 \leq l_1 \leq \alpha, \quad l_1 + \alpha \text{ even} . \quad (8)$$

In Eq. (7), the coefficients  $E_{\Lambda}(\mathbf{R})$ , which depend on the equilibrium intermolecular vector, appear to be given by

$$E_{\Lambda}(\mathbf{R}) = E_{lm'm'al_1m_1}(\mathbf{R}) \\ = \frac{1}{\alpha!} \sum_{l_2} \sum_{m_2} \begin{Bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{Bmatrix} W_{lm';l_1l_2}^{(\alpha)}(\mathbf{R}) C_{m_2}^{(l_2)}(\hat{\mathbf{R}}). \quad (9)$$

Here, the summation over  $l_2$  and  $m_2$  is limited to a few terms because of the selection rules that can be obtained

$$W_{lm';l_1l_2}^{(\alpha+1)}(\mathbf{R}) = (2l_1+1)(-1)^{l+1} \sum_{j_1} \sum_{j_2} \begin{Bmatrix} j_1 & 1 & l_1 \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l_2 & l_1 & l \\ j_1 & j_2 & 1 \end{Bmatrix} \hat{A}_{j_2l_2}(\mathbf{R}) W_{lm';j_1j_2}^{(\alpha)}(\mathbf{R}), \quad (11)$$

where the operator  $\hat{A}_{j_2l_2}(\mathbf{R})$  is defined by

$$\hat{A}_{j_2l_2}(\mathbf{R}) = (-1)^{j_2} \left[ \delta_{l_2, j_2-1} \left[ \frac{j_2(2j_2-1)}{2j_2+1} \right]^{1/2} \left[ \frac{d}{dR} + \frac{j_2+1}{R} \right] - \delta_{l_2, j_2+1} \left[ \frac{(j_2+1)(2j_2+3)}{2j_2+1} \right]^{1/2} \left[ \frac{d}{dR} - \frac{j_2}{R} \right] \right]. \quad (12)$$

See Ref. 17 for further details.

We have now obtained a useful potential expansion, see Eq. (7), for the interaction between a molecule and an atom. As we have mentioned before, this expansion represents explicitly the anisotropy of the pair potential. Furthermore, it includes an expansion with respect to molecular displacements that goes beyond the harmonic approximation.

### C. Fourier transformation of the pair potential sum

As a final step, the total molecule-substrate interaction can be obtained as a sum over the expanded molecule-atom pair potentials. In most practical cases the substrate atoms are ordered in lattice planes, so that the molecule-substrate potential shows a two-dimensional periodicity parallel to the substrate surface. This symmetry property can be exploited by transforming the sum over pair potentials into a two-dimensional Fourier series, as will be demonstrated in this subsection.

Assume, for simplicity, that the molecule is interacting with a single two-dimensional lattice of substrate atoms. We choose a global reference frame, so that the  $xy$  plane coincides with the lattice plane. Further, it is assumed that there are  $n_s$  different substrate sublattice types  $s$ , which are translated by a vector  $\tau_s$  with respect to the origin. The position of a single substrate atom, of type  $s$ , can then be written as

$$\tau_{sk_1k_2} = \tau_s + k_1 \mathbf{a}_1 + k_2 \mathbf{a}_2 \quad (1 \leq s \leq n_s), \quad (13)$$

where  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the two-dimensional lattice vectors and  $k_1$  and  $k_2$  are integers. Let  $\mathbf{x}$  denote the (equilibrium) position of the molecular center of mass. The total molecule-substrate potential

$$U(\mathbf{x} + \mathbf{u}, \omega) = \sum_{\Lambda} F_{\Lambda}(\mathbf{x}) u^{\alpha} C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) G_{mm'}^{(l)}(\omega) \quad (14)$$

is assumed to be the sum of two-particle interactions only, so that

$$F_{\Lambda}(\mathbf{x}) = \sum_{s=1}^{n_s} \sum_{k_1=-\infty}^{+\infty} \sum_{k_2=-\infty}^{+\infty} E_{\Lambda}(\mathbf{x} - \tau_{sk_1k_2}), \quad (15)$$

from the Wigner  $3j$  symbol. For a fixed combination of  $l$  and  $m'$  the distance-dependent functions  $W_{lm';l_1l_2}(\mathbf{R})$  in Eq. (9) can be calculated by means of the initialization

$$W_{lm';l_1l_2}^{(0)}(\mathbf{R}) = \delta_{l_1 0} \delta_{l_2 l} \sqrt{2l+1} \Phi_{lm'}(\mathbf{R}) \quad (10)$$

and the recurrence relation

where we have used Eq. (7). The combined index  $\Lambda$  is defined in Eq. (8). The function  $F_{\Lambda}$  is invariant under a lattice translation parallel to the substrate surface. For this reason, the following two-dimensional Fourier transformation is possible:

$$F_{\Lambda}(\mathbf{x}) = \sum_{\mathbf{g}} \tilde{F}_{\Lambda}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}} \quad (16)$$

with  $\boldsymbol{\tau}$  denoting the projection of  $\mathbf{x}$  on the  $xy$  plane, so that  $\mathbf{x} = \boldsymbol{\tau} + z\mathbf{e}_z$ . The summation has to be performed over all wave vectors  $\mathbf{g}$ , which are linear combinations of the reciprocal-lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$ :

$$\mathbf{g} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 \quad (\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}), \quad (17)$$

where  $n_i$  is an integer.

It appears, in analogy with Ref. 8, that the  $z$ -dependent Fourier coefficients are given by means of the Fourier transformation

$$\tilde{F}_{\Lambda}(\mathbf{g}|z) = \frac{1}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g}\cdot\boldsymbol{\tau}_s} \right] \int_{\sigma_{xy}} E_{\Lambda}(\boldsymbol{\tau} + z\mathbf{e}_z) e^{-i\mathbf{g}\cdot\boldsymbol{\tau}} d\boldsymbol{\tau}, \quad (18)$$

in which the parameter  $\sigma_c$  equals the substrate unit-cell area and where the integration has to be performed over the whole  $xy$  plane  $\sigma_{xy}$ . In the following, we will reduce the two-dimensional integral of Eq. (18) to a simpler form. To this end, we separate the integrand into a radial and an angular-dependent part, using the following cylindrical expansion of a two-dimensional plane wave:

$$e^{i\mathbf{g}\cdot\boldsymbol{\tau}} = \sum_{n=-\infty}^{+\infty} i^n J_n(g\tau) e^{in\varphi_g} e^{-in\varphi_{\boldsymbol{\tau}}}, \quad (19)$$

which comprises the Bessel functions  $J_n$  of the first kind.<sup>23</sup> The symbols  $\varphi_g$  and  $\varphi_{\boldsymbol{\tau}}$  denote the angles of the vectors  $\mathbf{g}$  and  $\boldsymbol{\tau}$  with respect to the  $x$  axis. Further, it can be shown, with the aid of Eq. (9), that

$$E_{\Lambda}(\boldsymbol{\tau} + z\mathbf{e}_z) = \Psi_{\Lambda}(\boldsymbol{\tau}, z) e^{-i(m+m_1)\varphi_{\boldsymbol{\tau}}}, \quad (20)$$

with

$$\Psi_{\Lambda}(\tau, z) = \frac{1}{\alpha!} \sum_{l_2} \sum_{m_2} (-1)^{m_2} \left[ \frac{(l_2 - m_2)!}{(l_2 + m_2)!} \right]^{1/2} \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} W_{lm'; l_1 l_2}^{(\alpha)} ((z^2 + \tau^2)^{1/2}) P_{l_2}^{m_2} (z / (z^2 + \tau^2)^{1/2}) . \quad (21)$$

Here, the associated Legendre function  $P_{l_2}^{m_2}$  and some of the algebraic factors originate from the following expression for the Racah harmonics:<sup>19</sup>

$$C_{m_2}^{(l_2)}((\tau + z\mathbf{e}_z) / |\tau + z\mathbf{e}_z|) = (-1)^{m_2} \left[ \frac{(l_2 - m_2)!}{(l_2 + m_2)!} \right]^{1/2} P_{l_2}^{m_2} (z / (z^2 + \tau^2)^{1/2}) e^{im_2\varphi_{\tau}} . \quad (22)$$

The argument of  $P_{l_2}^{m_2}$  equals the cosine of the angle between the vector  $\mathbf{x}$  and the  $z$  axis. Note that the  $3j$  symbol in Eq. (21) can only be nonzero if  $m_2 = -(m + m_1)$ , which explains the argument of the exponential function in Eq. (20). After substitution of Eqs. (19) and (20) into Eq. (18), we obtain the following expression for the total molecule-substrate potential:

$$U(\mathbf{x} + \mathbf{u}, \omega) = \sum_{\Lambda} \left[ \sum_{\mathbf{g}} \tilde{F}_{\Lambda}(\mathbf{g}|z) e^{i\mathbf{g} \cdot \boldsymbol{\tau}} \right] u^{\alpha} C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) G_{mm'}^{(l)}(\omega) . \quad (23)$$

This expansion is a combination of a spherical, a displacement, and a Fourier expansion. The Fourier coefficients are given by

$$\tilde{F}_{\Lambda}(\mathbf{g}|z) = \frac{2\pi}{\sigma_c} \left[ \sum_s e^{-i\mathbf{g} \cdot \boldsymbol{\tau}_s} \right] \tilde{\Psi}_{\Lambda}(\mathbf{g}|z) e^{-i(m + m_1)\varphi_{\mathbf{g}}} , \quad (24)$$

with

$$\tilde{\Psi}_{\Lambda}(\mathbf{g}|z) = \frac{1}{\alpha!} \sum_{l_2} \sum_{m_2} i^{m_2} \left[ \frac{(l_2 - m_2)!}{(l_2 + m_2)!} \right]^{1/2} \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} \int_0^{\infty} J_{m_2}(g\tau) W_{lm'; l_1 l_2}^{(\alpha)} ((z^2 + \tau^2)^{1/2}) P_{l_2}^{m_2} (z / (z^2 + \tau^2)^{1/2}) \tau d\tau . \quad (25)$$

We have now transformed the sum over pair potentials, occurring in Eq. (14), into a two-dimensional Fourier series with Fourier coefficients that can be calculated with the aid of Eqs. (24) and (25). Thus, the two-dimensional lattice sum has vanished, but some one-dimensional Fourier integrals, see Eq. (25), remain to be calculated for each wave-vector length  $g$ . These integrals can be evaluated numerically using a Gauss-Legendre quadrature. For special cases, analytical expressions can be given, as shown below.

#### D. Analytical Fourier transforms

If we want to evaluate the radial Fourier transforms of Eq. (25) analytically, a problem arises because the integrand contains a product of a cylindrical Bessel function  $J_{m_2}$  and an associated Legendre function  $P_{l_2}^{m_2}$ . Unfortunately, integrals with such a combination of functions in the integrand are very difficult. However, there are two special cases in which either  $J_{m_2}$  or  $P_{l_2}^{m_2}$  is a constant function, so that an analytical solution of the problem exists for some special types of pair potentials. We will give some examples in the following.

In the first case we consider the isotropic ( $\Lambda=0$ ) Fourier transforms that describe the interaction, without displacement expansion, of a structureless molecule, or an atom, with a substrate. In this case the associated Legendre function vanishes and the integrand can be fur-

ther reduced with the aid of Eq. (10). So, the isotropic Fourier integrals are given by

$$\tilde{\Psi}_0(\mathbf{g}|z) = \int_0^{\infty} J_0(g\tau) \Phi_0((z^2 + \tau^2)^{1/2}) \tau d\tau . \quad (26)$$

These integrals are known for isotropic inverse-power-law pair potentials

$$\Phi_{\nu;0}(R) = R^{-\nu}, \quad \nu \geq 3 \quad (27)$$

as shown by Steele.<sup>8</sup> The corresponding Fourier transforms can be calculated analytically with the aid of Ref. 23:

$$\tilde{\Psi}_{\nu;0}(\mathbf{g}|z) = \begin{cases} \frac{1}{\nu-2} z^{-\nu+2} & (g=0) , \\ \frac{1}{\Gamma(\nu/2)} \left[ \frac{g}{2z} \right]^{(\nu-2)/2} K_{(\nu-2)/2}(gz) & (g>0) . \end{cases} \quad (28)$$

Here,  $K_n$  is a modified Bessel function and  $\Gamma$  is the ordinary gamma function. An exponential pair potential

$$\Phi_{\text{exp};0}(R) = e^{-cR} \quad (c > 0) \quad (29)$$

is also commonly used.<sup>9</sup> In that case the isotropic Fourier integral equals<sup>24</sup>

$$\begin{aligned} \tilde{\Psi}_{\text{exp};0}(g|z) &= c(c^2 + g^2)^{-3/2} e^{-z(c^2 + g^2)^{1/2}} \\ &\times [(c^2 + g^2)^{1/2} z + 1]. \end{aligned} \quad (30)$$

The second example concerns the flat ( $g=0$ ) terms in the Fourier series. These terms describe the interaction of a molecule with a flat surface; in other words, the molecule is unaffected by the discrete atomic structure of the substrate layer. For a fixed displacement vector  $\mathbf{u}$ , the flat part of the Fourier series of Eq. (23) must be invariant

under a rotation of the molecule around an axis parallel to the global  $z$  axis and through the molecular center of mass. This property implies that the index  $m$  must be necessarily equal to zero. Further, because of the property<sup>23</sup>

$$J_{m_2}(0) = \delta_{m_2 0}, \quad (31)$$

the radial Fourier transform of Eq. (25) reduces to

$$\tilde{\Psi}_{\Lambda}(0|z) = \delta_{m_0} \delta_{m_1 0} \frac{1}{\alpha!} \sum_{l_2} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \int_0^\infty W_{l_1 l_2}^{(\alpha)}((z^2 + \tau^2)^{1/2}) P_{l_2}(z/(z^2 + \tau^2)^{1/2}) \tau d\tau. \quad (32)$$

We have derived an analytical expression starting with an inverse-power-law expansion function:

$$\Phi_{\nu;lm}(R) = a_{\nu;lm} R^{-\nu} \quad (\nu \geq 3) \quad (33)$$

in the pair potential of Eq. (5). In this case the functions  $W_{\nu;lm;l_1 l_2}^{(\alpha)}$ , occurring in the integrand, are also of the inverse-power-law type, according to

$$W_{\nu;lm;l_1 l_2}^{(\alpha)}(R) = w_{\nu;lm;l_1 l_2}^{(\alpha)} R^{-(\nu+\alpha)}, \quad (34)$$

where the coefficients  $w_{\nu;lm;l_1 l_2}^{(\alpha)}$  can be obtained with the aid of the recurrence relation of Eq. (12) together with Eq. (11). After substitution of Eq. (34) in (32), the remaining integrals are all of the type<sup>25</sup>

$$\begin{aligned} &\int_0^1 \rho^\mu P_\lambda(\rho) d\rho \\ &= \frac{\pi^{1/2} 2^{-\mu-1} \Gamma(\mu+1)}{\Gamma(1 + \frac{1}{2}\mu - \frac{1}{2}\lambda) \Gamma(\frac{3}{2} + \frac{1}{2}\mu + \frac{1}{2}\lambda)} \quad (\mu > -1), \end{aligned} \quad (35)$$

where the new integration variable  $\rho$  equals the cosine of the angle between the vector  $\mathbf{x}$  and the  $z$  axis, i.e., the argument of the Legendre polynomial in Eq. (32). It can be shown, with the aid of Eq. (35), that the resulting flat Fourier transform equals

$$\tilde{\Psi}_{\nu;\Lambda}(0|z) = \delta_{m_0} \delta_{m_1 0} b_{\nu;lm;l_1}^{(\alpha)} z^{-(\nu+\alpha-2)}, \quad (36)$$

where the coefficients  $b_{\nu;lm;l_1}^{(\alpha)}$  are given by

$$\begin{aligned} b_{\nu;lm;l_1}^{(\alpha)} &= \frac{\pi^{1/2} \Gamma(\nu+\alpha-2)}{2^{\nu+\alpha-2} \alpha!} \\ &\times \sum_{l_2} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \frac{w_{\nu;lm;l_1 l_2}^{(\alpha)}}{\Gamma(\frac{1}{2}\nu + \frac{1}{2}\alpha - \frac{1}{2}l_2 - \frac{1}{2}) \Gamma(\frac{1}{2}\nu + \frac{1}{2}\alpha + \frac{1}{2}l_2)}. \end{aligned} \quad (37)$$

We can draw the following conclusion from the examples described above. For some specific model pair potentials, the isotropic ( $\Lambda=0$ ) and flat ( $g=0$ ) Fourier integrals of Eq. (25) can be evaluated analytically. This means that either the molecule or the substrate is con-

sidered to be structureless, which is a good approximation for large distances  $z$  between the molecule and the substrate. However, for smaller values of  $z$ , the anisotropic ( $\Lambda \neq 0$ ) and corrugated ( $g \neq 0$ ) Fourier integrals are not negligible. As we have mentioned before, the latter types of integrals are difficult to handle analytically, because of the occurrence of a cylindrical Bessel function and an associated Legendre function in the integrand. So, in general, the anisotropic and corrugated Fourier transforms can only be calculated numerically. However, it appears that in the special case that the pair potential of Eq. (5) is equivalent to, or derived from, a sum of atom-atom potentials, all Fourier transforms can be tackled analytically with the aid of an alternative method. This will be proven in the next section.

### III. ALTERNATIVE METHOD FOR AN ATOM-ATOM PAIR-POTENTIAL MODEL

#### A. Atom-atom potential model

In this section we adopt an atom-atom model for the interaction between the molecule and a single substrate atom,

$$V(\mathbf{R}, \omega) = \sum_a \phi_a(|\mathbf{R} + \mathbf{r}_a(\omega)|), \quad (38)$$

which is of course less general than a spherically expanded molecule-atom potential. The vector  $\mathbf{R}$  connects the centers of mass of the molecule and the atom and  $\omega$  describes the orientation of the molecule, as in Sec. II. Further, the vectors  $\mathbf{r}_a$  denote the relative positions of the atoms  $a$  within the molecule with respect to the molecular center of mass. These vectors depend on  $\omega$  according to the relation

$$\mathbf{r}_a(\omega) = \mathbf{R}(\omega) \mathbf{r}_a^0, \quad (39)$$

where  $\mathbf{R}(\omega)$  is an active rotation matrix and  $\mathbf{r}_a^0$  is the position of atom  $a$  with respect to a body-fixed frame that coincides with the global frame for  $\omega=0$ .

In principle, it is possible to transform the sum of atom-atom potentials in Eq. (38) into a spherical expansion,<sup>26</sup> given by Eq. (5). Thus, the method of Sec. II can be applied in order to obtain a Fourier series for the total

molecule-substrate potential. The disadvantage of the latter method is that not all Fourier integrals can be calculated analytically, as appears from Sec. II D. The main reason for this problem is that the spherical expansion of the atom-atom potentials introduces associated Legendre functions which cause problems in the Fourier transformation. On the other hand, if the Fourier transformation is performed first and the spherical expansion afterwards, then only isotropic Fourier integrals are needed. Such integrals can be handled analytically for an inverse-power-law or an exponential pair potential, as appears from Eqs. (28) and (30), respectively. So, it seems to be profitable to write the total molecule-substrate potential first as a sum of atom-substrate potentials:

$$U(\mathbf{x} + \mathbf{u}, \omega) = \sum_a f_a(\mathbf{x} + \mathbf{r}_a(\omega) + \mathbf{u}), \quad (40)$$

where  $\mathbf{x}$  denotes the equilibrium position of the molecule and  $\mathbf{u}$  is a small displacement vector, in accordance with Sec. II. The Fourier series

$$f_a(\mathbf{x}_a) = \sum_{\mathbf{g}} \tilde{f}_a(\mathbf{g}|z_a) e^{i\mathbf{g} \cdot \mathbf{r}_a}, \quad (41)$$

describing the interaction between atom  $a$  and the substrate, is isotropic. So, it follows from Eqs. (24) and (26) that the Fourier coefficients can be written as

$$\tilde{f}_a(\mathbf{g}|z_a) = \frac{2\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g} \cdot \mathbf{r}_s} \right] \tilde{\psi}_a(\mathbf{g}|z_a), \quad (42)$$

with

$$\tilde{\psi}_a(\mathbf{g}|z_a) = \int_0^\infty J_0(\mathbf{g}\tau) \phi_a((z_a^2 + \tau^2)^{1/2}) \tau d\tau, \quad (43)$$

where  $\phi_a$  denotes the atom-atom pair potential, as in Eq. (38).

The main goal of this section is to write Eq. (40) explicitly in terms of the molecular orientation  $\omega$  and the molecular displacement  $\mathbf{u}$ . Thus we obtain a form similar to Eq. (23), with alternative formulas for the Fourier coefficients  $\tilde{F}_\Lambda(\mathbf{g}|z)$  that will be given analytically. In order to obtain the desired result we have to perform two expansions of the atom-substrate Fourier series, one for the vector(s)  $\mathbf{r}_a$  and one for  $\mathbf{u}$ , as will be demonstrated in the next two subsections.

### B. Spherical expansion of atom-substrate Fourier series

In first instance, the molecular-displacement vector  $\mathbf{u}$  is considered to be zero, so that we have to make the following expansion of the atom-substrate Fourier series:

$$f(\mathbf{x} + \mathbf{r}) = \sum_{\mathbf{g}} \tilde{f}(\mathbf{g}|z + \mathbf{r} \cdot \mathbf{e}_z) e^{i\mathbf{g} \cdot \mathbf{r}} e^{i\mathbf{g} \cdot \mathbf{r}}, \quad (44)$$

where we have omitted the label  $a$  and the explicit dependence on  $\omega$ .

Expanding Eq. (42), it follows that

$$\tilde{f}(\mathbf{g}|z + \mathbf{r} \cdot \mathbf{e}_z) = \frac{2\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g} \cdot \mathbf{r}_s} \right] \sum_{\beta=0}^{\infty} \frac{(\mathbf{r} \cdot \mathbf{e}_z)^\beta}{\beta!} \tilde{\psi}^{(\beta)}(\mathbf{g}|z), \quad (45)$$

with

$$\tilde{\psi}^{(\beta)}(\mathbf{g}|z) = \frac{\partial^\beta}{\partial z^\beta} \tilde{\psi}(\mathbf{g}|z). \quad (46)$$

It appears to be possible to rewrite the expansion of Eq. (44), in combination with (45), in spherical tensor form, as will be shown in the sequel. As a first step we substitute into Eq. (42) the following spherical expansion:<sup>27</sup>

$$(\mathbf{r} \cdot \mathbf{e}_z)^\beta = r^\beta \sum_{\lambda_1=0}^{\beta} \frac{\beta!(2\lambda_1+1)}{(\beta-\lambda_1)!(\beta+\lambda_1+1)!} \times \sum_{\mu_1=-\lambda_1}^{\lambda_1} C_{\mu_1}^{(\lambda_1)}(\hat{\mathbf{e}}_z) C_{\mu_1}^{(\lambda_1)}(\hat{\mathbf{r}})^* \quad (\lambda_1 + \beta \text{ even}), \quad (47)$$

and

$$C_{\mu_1}^{(\lambda_1)}(\hat{\mathbf{e}}_z) = \delta_{\mu_1 0}. \quad (48)$$

Further, we make use of the well-known spherical expansion of a three-dimensional plane wave<sup>28</sup>

$$e^{i\mathbf{g} \cdot \mathbf{r}} = \sum_{\lambda_2} \sum_{\mu_2} i^{\lambda_2} (2\lambda_2+1) j_{\lambda_2}(gr) C_{\mu_2}^{(\lambda_2)}(\hat{\mathbf{g}}) C_{\mu_2}^{(\lambda_2)}(\hat{\mathbf{r}})^*, \quad (49)$$

where  $j_{\lambda_2}$  is a spherical Bessel function of the first kind. After substitution of Eqs. (45) and (49) into Eq. (44), the  $\hat{\mathbf{r}}$ -dependent Racah harmonics are recoupled with the aid of Gaunt's rule:<sup>22</sup>

$$C_{\mu_1}^{(\lambda_1)}(\hat{\mathbf{r}})^* C_{\mu_2}^{(\lambda_2)}(\hat{\mathbf{r}})^* = \sum_l \sum_m (2l+1) \begin{pmatrix} \lambda_1 & \lambda_2 & l \\ \mu_1 & \mu_2 & m \end{pmatrix} \begin{pmatrix} \lambda_1 & \lambda_2 & l \\ 0 & 0 & 0 \end{pmatrix} C_m^{(l)}(\hat{\mathbf{r}}). \quad (50)$$

Finally, the explicit dependence of the expansion on the molecular orientation  $\omega$  is introduced with the aid of<sup>19</sup>

$$C_m^{(l)}(\hat{\mathbf{r}}) = \sum_{m'} C_m^{(l)}(\hat{\mathbf{r}}^0) D_{mm'}^{(l)}(\omega)^*, \quad (51)$$

where  $\hat{\mathbf{r}}$  and  $\hat{\mathbf{r}}^0$  are related to each other via Eq. (39). As a result we obtain

$$f(\mathbf{x} + \mathbf{r}(\omega)) = \sum_{\Lambda'} \left[ \sum_{\mathbf{g}} \tilde{S}_{lm}(\mathbf{g}|z, r) e^{i\mathbf{g} \cdot \mathbf{r}} \right] \times C_m^{(l)}(\hat{\mathbf{r}}^0) D_{mm'}^{(l)}(\omega)^*. \quad (52)$$

Here, the summation is performed over the combined index

$$\Lambda' = (l, m, m'), \quad (53)$$

which can be considered as a special value of  $\Lambda$  [see Eq. (8)] with  $\alpha = l_1 = m_1 = 0$ . In Eq. (52), the Fourier transforms  $\tilde{S}_{lm}$  appear to be

$$\tilde{S}_{lm}(\mathbf{g}|z, r) = \frac{2\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g} \cdot \mathbf{r}_s} \right] \times \sum_{\beta=0}^{\infty} \tilde{\psi}^{(\beta)}(\mathbf{g}|z) \tilde{\chi}_{lm}^{(\beta)}(\mathbf{g}|r), \quad (54)$$

with

$$\begin{aligned} \tilde{\chi}_{lm}^{(\beta)}(\mathbf{g}|r) &= (2l+1)r^\beta \sum_{\lambda_1=0}^{\beta} \frac{(2\lambda_1+1)}{(\beta-\lambda_1)!(\beta+\lambda_1+1)!!} \\ &\times \sum_{\lambda_2} i^{\lambda_2} (2\lambda_2+1) j_{\lambda_2}(gr) \begin{bmatrix} \lambda_1 & \lambda_2 & l \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \lambda_1 & \lambda_2 & l \\ 0 & -m & m \end{bmatrix} C_{-m}^{(\lambda_2)}(\hat{\mathbf{g}}) \quad (\lambda_1+\beta \text{ even}). \end{aligned} \quad (55)$$

After summation over all atoms within the molecule, the total expansion can be written in terms of totally symmetric symmetry-adapted functions  $G_{mm'}^{(l)}$  with the aid of<sup>17</sup>

$$\sum_{a \in \kappa} \sum_{m'} C_m^{(l)}(\hat{\mathbf{r}}_a^0) D_{mm'}^{(l)}(\omega)^* = \sum_{m'} d_{m'\kappa}^{(l)} G_{mm'}^{(l)}(\omega). \quad (56)$$

Here  $\kappa$  denotes a class of symmetry-related atoms with the same distance  $r_\kappa$  to the molecular center of mass. In Eq. (56), the Racah harmonics are constant coefficients which must obey the molecular symmetry. As a result, the total molecule-substrate-potential expansion becomes

$$U(\mathbf{x}, \omega) = \sum_{\Lambda'} \left[ \sum_{\mathbf{g}} \tilde{F}_{\Lambda'}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}} \right] G_{mm'}^{(l)}(\omega), \quad (57)$$

with an alternative formula for the Fourier coefficients:

$$\begin{aligned} \tilde{F}_{\Lambda'}(\mathbf{g}|z) &= \frac{2\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g}\cdot\boldsymbol{\tau}_s} \right] \\ &\times \sum_{\kappa} d_{m'\kappa}^{(l)} \sum_{\beta=0}^{\infty} \tilde{\psi}_{\kappa}^{(\beta)}(\mathbf{g}|z) \tilde{\chi}_{lm}^{(\beta)}(\mathbf{g}|r_\kappa). \end{aligned} \quad (58)$$

This equation does not contain difficult anisotropic Fourier integrals, which is, from an analytical point of view, a remarkable simplification with respect to Eqs. (24) and (25) for  $\Lambda = \Lambda'$ .

### C. Molecular-displacement expansion

As a final step, the Fourier series of the molecule-substrate potential [see Eq. (57)] is expanded with respect to molecular-displacement coordinates, according to

$$U(\mathbf{x} + \mathbf{u}, \omega) = \sum_{\alpha=0}^{\infty} \frac{(\mathbf{u}\cdot\nabla)^\alpha}{\alpha!} U(\mathbf{x}, \omega). \quad (59)$$

We will perform the expansion with the aid of the following gradient formula:

$$\begin{aligned} (\mathbf{u}\cdot\nabla) \tilde{F}_{\Lambda'}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}} \\ = u e^{i\mathbf{g}\cdot\boldsymbol{\tau}} \sum_{\sigma=-1}^{+1} [\hat{A}_\sigma(\mathbf{g}) \tilde{F}_{\Lambda'}(\mathbf{g}|z)] C_\sigma^{(1)}(\hat{\mathbf{u}}), \end{aligned} \quad (60)$$

where the operator  $\hat{A}_\sigma(\mathbf{g})$  is defined by

$$\hat{A}_\sigma(\mathbf{g}) = \begin{cases} \frac{\partial}{\partial z}, & \sigma = 0 \\ i\mathbf{g} C_\sigma^{(1)}(\hat{\mathbf{g}})^*, & \sigma = -1, 1. \end{cases} \quad (61)$$

It can be proved, with the aid of the recoupling formula (50), that successive application of the gradient formula results in the following expansion for the  $z$ - and  $\tau$ -

dependent part of Eqs. (57) and (58):

$$\begin{aligned} \tilde{\psi}^{(\beta)}(\mathbf{g}|z + \mathbf{u}\cdot\mathbf{e}_z) e^{i\mathbf{g}\cdot(\boldsymbol{\tau} + \mathbf{u})} \\ = \sum_{\alpha=0}^{\infty} \frac{1}{\alpha!} \sum_{l_1=0}^{\alpha} \sum_{m_1=-l_1}^{l_1} [\tilde{W}_{l_1 m_1}^{(\beta; \alpha)}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}}] \\ \times u^\alpha C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) \quad (\alpha + l_1 \text{ even}), \end{aligned} \quad (62)$$

in which the expansion functions  $\tilde{W}_{l_1 m_1}^{(\beta; \alpha)}$  can be calculated by means of the initialization

$$\tilde{W}_{l_1 m_1}^{(\beta; 0)}(\mathbf{g}|z) = \delta_{l_1 0} \delta_{m_1 0} \tilde{\psi}^{(\beta)}(\mathbf{g}|z) \quad (63)$$

and the recurrence relation for fixed  $\beta$ ,  $\mathbf{g}$ , and  $z$ :

$$\begin{aligned} \tilde{W}_{l_2 m_2}^{(\beta; \alpha+1)}(\mathbf{g}|z) &= (-1)^{m_2} (2l_2 + 1) \\ &\times \sum_{l_1} \sum_{m_1} \sum_{\sigma} \begin{bmatrix} l_1 & 1 & l_2 \\ m_1 & \sigma & -m_2 \end{bmatrix} \\ &\times \begin{bmatrix} l_1 & 1 & l_2 \\ 0 & 0 & 0 \end{bmatrix} \hat{A}_\sigma(\mathbf{g}) \\ &\times \tilde{W}_{l_1 m_1}^{(\beta; \alpha)}(\mathbf{g}|z). \end{aligned} \quad (64)$$

Defining, in agreement with Eq. (8),

$$\Lambda = (\Lambda', \alpha, l_1, m_1) = (l, m, m', \alpha, l_1, m_1), \quad (65)$$

we obtain from Eqs. (57), (58), and (62) the final expression for the Fourier series of the molecule-substrate potential:

$$\begin{aligned} U(\mathbf{x} + \mathbf{u}, \omega) &= \sum_{\Lambda} \left[ \sum_{\mathbf{g}} \tilde{F}_{\Lambda}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}} \right] \\ &\times u^\alpha C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) G_{mm'}^{(l)}(\omega), \end{aligned} \quad (66)$$

which is indeed equivalent to Eq. (23) with

$$\begin{aligned} \tilde{F}_{\Lambda}(\mathbf{g}|z) &= \frac{2\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g}\cdot\boldsymbol{\tau}_s} \right] \frac{1}{\alpha!} \\ &\times \sum_{\kappa} d_{m'\kappa}^{(l)} \sum_{\beta=0}^{\infty} \tilde{W}_{l_1 m_1; \kappa}^{(\beta; \alpha)}(\mathbf{g}|z) \tilde{\chi}_{lm}^{(\beta)}(\mathbf{g}|r_\kappa). \end{aligned} \quad (67)$$

The results of the alternative method, described above, can be summarized as follows. Starting from an atom-potential model, we have derived an alternative formula for the Fourier transforms  $\tilde{F}_{\Lambda}(\mathbf{g}|z)$  [see Eq. (58)] which is valid for  $\Lambda = \Lambda'$ . The extension to  $\Lambda \neq \Lambda'$  has been made with the aid of the recurrence relation (64). In the next subsection we will show that the new expressions

can be evaluated analytically for the most commonly used atom-atom potentials.

#### D. Analytical derivatives of isotropic Fourier integrals

In order to use the alternative formulas for the Fourier transforms  $\bar{F}_\Lambda(\mathbf{g}|z)$ , we need the derivatives of isotropic atom-substrate Fourier integrals, as appears from Eq. (58) for  $\Lambda = \Lambda'$  and from the relations (63) and (64) for  $\Lambda \neq \Lambda'$ . All other factors in both equations are independent of the atom-atom potential and are easy to calculate. So, the only remaining problem is the evaluation of the derivatives of the isotropic Fourier integrals.

First, we start with an exponential atom-atom potential type:

$$\phi_{\text{exp}}(\rho) = e^{-c\rho} \quad (c > 0). \quad (68)$$

In this case the isotropic Fourier integral is given by Eq. (30), which is a product of a linear and an exponential function. With the aid of

$$\frac{\partial^\beta}{\partial z^\beta}(ze^z) = (z + \beta)e^z, \quad (69)$$

it is not difficult to prove that the derivatives of the isotropic Fourier integrals are given by

$$\begin{aligned} \bar{\psi}_{\text{exp}}^{(\beta)}(\mathbf{g}|z) &= (-1)^\beta c (c^2 + g^2)^{(\beta-3)/2} \\ &\times [(c^2 + g^2)^{1/2}z + 1 + \beta] e^{-(c^2 + g^2)^{1/2}z}. \end{aligned} \quad (70)$$

Second, we consider the more difficult case of an inverse-power-law atom-atom potential

$$\phi_n(\rho) = \rho^{-n}, \quad n \geq 3. \quad (71)$$

The corresponding isotropic Fourier integrals

$$\bar{\psi}_n(\mathbf{g}|z) = \int_0^\infty J_0(g\tau) (z^2 + \tau^2)^{-n/2} \tau d\tau \quad (72)$$

are products of inverse-power-law and modified Bessel functions of  $z$ , as appears from Eq. (28). In principle, it is possible to make use of the well-known differentiation formulas for the modified Bessel functions,<sup>23</sup> but this results in some tedious algebra. It is easier to use the relation

$$\frac{\partial}{\partial z} \bar{\psi}_n(\mathbf{g}|z) = -nz \bar{\psi}_{n+2}(\mathbf{g}|z), \quad (73)$$

which can be proved by exchanging the differentiation and the integration. After successive application of Eq. (73), the isotropic Fourier derivatives can be written as a sum over zeroth-order integrals:

$$\bar{\psi}_n^{(\beta)}(\mathbf{g}|z) = \sum_{i=0}^{E(\beta/2)} c_i^{(\beta)} z^{\beta-2i} \bar{\psi}_{n+2\beta-2i}(\mathbf{g}|z), \quad (74)$$

where  $E$  denotes the entire function. The coefficients  $c_i^{(\beta)}$  can be calculated with the aid of the initialization

$$c_0^{(0)} = 1 \quad (75)$$

and the recurrence relation

$$c_i^{(\beta+1)} = -(n + 2\beta - 2i)c_i^{(\beta)} + (\beta + 2 - 2i)c_{i-1}^{(\beta)}, \quad (76)$$

where  $c_i^{(\beta)}$  is defined as zero if  $i$  is negative or greater than  $\beta/2$ . Although Eq. (74) is also applicable for  $g=0$ , in which case the Fourier integrals are inverse-power functions of  $z$ , the corresponding derivatives can be better calculated directly with the aid of

$$\bar{\psi}_n^{(\beta)}(0|z) = (-1)^\beta \frac{(n + \beta - 3)!}{(n - 2)!} z^{-n-\beta+2}. \quad (77)$$

So we have derived analytical expressions, see Eqs. (70), (74), and (77), for the derivatives of the isotropic Fourier integrals starting from an exponential or an inverse-power-law atom-atom potential. After substitution of these derivatives into Eq. (63), the Fourier transforms  $\bar{F}_\Lambda(\mathbf{g}|z)$  can be obtained analytically with the aid of Eq. (67). We conclude that, at least for an exponential and inverse-power-law atom-atom-potential model, all Fourier transforms can be calculated analytically. This is an important improvement with respect to the general method, described in Sec. II.

#### IV. A POTENTIAL EXPANSION FOR N<sub>2</sub> ON GRAPHITE

In Secs. II and III two methods have been described to obtain a combined spherical, displacement, and Fourier expansion for a molecule interacting with a two-dimensional substrate of regularly ordered atoms. In this section we will show some numerical results for N<sub>2</sub> on graphite which illustrate the convergence of the various expansions. As far as the isotropic ( $l=0$ ) part of the potential expansion is concerned, our results are similar to those of Steele for noble-gas atoms on substrates.<sup>8</sup> However, with the aid of the potential-expansion terms with  $l > 0$  we can visualize the potential anisotropy explicitly. Further, with the aid of the included displacement expansion the importance of anharmonic terms in the molecule-substrate potential can be demonstrated

Adsorbed monolayers of N<sub>2</sub> molecules on graphite can occur in a rich variety of interesting quasi-two-dimensional phases. Neutron-scattering experiments,<sup>29-31</sup> low-energy electron diffraction,<sup>32-34</sup> and heat-capacity measurements<sup>35</sup> have shown that the low-temperature ground state of a N<sub>2</sub> adlayer on graphite is an orientationally ordered phase with a commensurate ( $\sqrt{3} \times \sqrt{3}$ )R30° center-of-mass structure. This is confirmed by molecular dynamics<sup>10</sup> and Monte Carlo simulations.<sup>36,37</sup> For this ground-state structure two classical harmonic lattice-dynamics calculations are reported,<sup>38,39</sup> which are valuable for the determination of, as yet unknown, experimental adlayer phonon frequencies. The molecule-substrate force constants, used in these calculations, are derived from a sum of atom-substrate potentials. In a forthcoming paper we will present a quantum-mechanical lattice-dynamics calculation, where the molecule-substrate-potential expansion of the present paper will be used.

##### A. Spherical, displacement, and Fourier expansion of atom-atom potentials

Before we show the numerical results for N<sub>2</sub> on graphite we will first derive further analytical expansion formu-



las for a homonuclear diatomic molecule on a substrate, using a Lennard-Jones 12-6 atom-atom potential model:

$$\phi(\rho) = \sum_{n=6,12} \frac{c_n}{\rho^n}. \quad (78)$$

So, the molecule-atom interaction is a special case of Eq. (38), where the sum over atom-atom potentials is restricted to two terms:

$$V(\mathbf{R}, \omega) = \phi(|\mathbf{R} + \mathbf{r}(\omega)|) + \phi(|\mathbf{R} - \mathbf{r}(\omega)|). \quad (79)$$

As previously defined, the vector  $\mathbf{R}$  connects the molecular center of mass with a substrate atom and  $\omega = (\vartheta, \varphi)$  denotes the molecular orientation in polar angles  $\vartheta$  and  $\varphi$ . Further, the position of one atom within the molecule with respect to the molecular center of mass is described by the orientation-dependent vector  $\mathbf{r}(\omega)$  with length  $r$ .

In the sequel we will first apply the general method of Sec. II in order to obtain an explicit expression for a combined spherical and displacement expansion of the molecule-atom pair potential. This expression can be used to calculate the total molecule-substrate-potential expansion as a sum of pairwise contributions. With the aid of the pair-potential-expansion formulas we will also derive an explicit analytical expression for the Fourier transform with  $g=0$ , describing the interaction with a flat surface. However, as we have explained previously, the Fourier transforms with  $g \neq 0$  are difficult to evaluate analytically with the method of Sec. II. A solution to this problem is provided by the special method of Sec. III,

which can be applied in this case because we have started with an atom-atom-potential model. We will show that the method of Sec. III results, of course, in the same Fourier transform with  $g=0$ , as obtained with the method of Sec. II. Although the Fourier transforms with  $g \neq 0$  cannot be tackled analytically with the method of Sec. II, the latter method is not useless in this example for it results in formulas for the sum of molecule-atom expansions that can be used to check the convergence of the Fourier series numerically.

In order to apply the general method of Sec. II, we must first transform the molecule-atom pair potential of Eq. (79) into a spherical expansion similar to Eq. (5). For a linear molecule, the symmetry-adapted rotation functions  $G_{mm}^{(l)}$  of Eq. (5) are simple Racah harmonics  $C_m^{(l)}$ , as follows from Eq. (2). So, Eq. (5) reduces to

$$V(\mathbf{R}, \omega) = \sum_l \Phi_l(R) \sum_{m=-l}^l (-1)^m C_{-m}^{(l)}(\hat{\mathbf{R}}) C_m^{(l)}(\omega), \quad (80)$$

where the summation over  $l$  is limited to even values because the molecule possesses an inversion center. Further, the radially dependent functions  $\Phi_l$ , occurring in Eq. (80), can be evaluated analytically with the aid of so-called one-center spherical-expansion formulas (see for instance Ref. 15) applied to Eq. (79). The result is

$$\Phi_l(R) = \sum_{n=6,12} \sum_{\nu=n+l}^{\infty} \frac{a_{n\nu;l}}{R^\nu} \quad (\nu \text{ even}) \quad (81)$$

with  $r$ -dependent expansion coefficients

$$a_{n\nu;l} = \frac{2c_n(2l+1)(\nu-2-l)!(\nu-2+l)!!r^{\nu-n}}{(n-2)!(\nu-n+l+1)!(\nu-n-l)!(\nu-2-l)!!}. \quad (82)$$

Secondly, we expand the molecule-atom pair potential of Eq. (80) with respect to a molecular-displacement vector  $\mathbf{u}$ , using Eq. (9) substituted into Eq. (7):

$$V(\mathbf{R} + \mathbf{u}, \omega) = \sum_{\Lambda} \left[ \frac{1}{\alpha!} \sum_{l_2} \sum_{m_2} \begin{Bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{Bmatrix} W_{l;l_1l_2}^{(\alpha)}(R) C_{m_2}^{(l_2)}(\hat{\mathbf{R}}) \right] u^\alpha C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) C_m^{(l)}(\omega). \quad (83)$$

Here, a summation has to be performed over the combined index  $\Lambda = (l, m, \alpha, l_1, m_1)$ , as defined in Eq. (8). In Eq. (83), the radially dependent functions  $W_{l;l_1l_2}^{(\alpha)}$  determine the potential derivative of order  $\alpha$  with respect to the intermolecular vector. These functions are, just as  $\Phi_l$  in Eq. (81), of the inverse-power-law type according to

$$W_{l;l_1l_2}^{(\alpha)}(R) = \sum_{n=6,12} \sum_{\nu=n+l}^{\infty} \frac{w_{n\nu;l;l_1l_2}^{(\alpha)}}{R^{\nu+\alpha}} \quad (\nu \text{ even}). \quad (84)$$

The coefficients  $w_{n\nu;l;l_1l_2}^{(\alpha)}$  in this equation can be computed with the aid of the recurrence relation of Eq. (11), starting with the initialization condition of Eq. (10). However, in this case it is also possible to derive an explicit analytical expression for these coefficients if one considers the combined spherical and displacement expansion of Eq. (83) from another point of view. To this end, we write

$$V(\mathbf{R} + \mathbf{u}, \omega) = \phi(|\mathbf{R} + \mathbf{u} + \mathbf{r}(\omega)|) + \phi(|\mathbf{R} + \mathbf{u} - \mathbf{r}(\omega)|) \quad (85)$$

and perform a so-called double spherical expansion of the two atom-atom potentials. With the aid of analytical double-spherical-expansion formulas (see Ref. 17) Eq. (83) can be obtained almost immediately. After some elementary algebra, we arrive at the desired explicit expression for the expansion coefficients:

$$w_{n\nu;l;l_1l_2}^{(\alpha)} = \begin{Bmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{Bmatrix} \frac{2c_n \alpha! (-1)^l (2l_1+1)(2l_2+1)(2l+1)(\nu+\alpha-l_2-3)!(\nu+\alpha+l_2-2)!! r^{\nu-n}}{(n-2)!(\nu-n+l+1)!(\nu-n-l)!(\alpha+l_1+1)!(\alpha-l_1)!!}. \quad (86)$$

So far, we have obtained explicit analytical expressions for the molecule-atom pair-potential expansion. Summation over all pairs results in the following useful combined spherical and displacement expansion for the total molecule-substrate interaction:

$$U(\mathbf{x} + \mathbf{u}, \omega) = \sum_{\Lambda} F_{\Lambda}(\mathbf{x}) u^{\alpha} C_{m_1}^{(l_1)}(\hat{\mathbf{u}}) C_m^{(l)}(\omega), \quad (87)$$

which is a special case of Eq. (14). In Eq. (87), the vector  $\mathbf{x}$  represents the position of the molecular center of mass with respect to a global frame as defined in Sec. II. Further, the functions  $F_{\Lambda}$  contain a sum over pair contributions similar to Eq. (15), that can be replaced by a two-dimensional Fourier series [see Eq. (16)]:

$$F_{\Lambda}(\mathbf{x}) = \sum_{\mathbf{g}} \tilde{F}_{\Lambda}(\mathbf{g}|z) e^{i\mathbf{g}\cdot\boldsymbol{\tau}}, \quad (88)$$

with  $\boldsymbol{\tau}$  denoting the projection of  $\mathbf{x}$  on the  $xy$  plane, so that  $\mathbf{x} = \boldsymbol{\tau} + z\mathbf{e}_z$ . In Sec. II it has been demonstrated that the Fourier coefficients with  $g = 0$  can be evaluated analytically for the inverse-power-law pair-expansion functions of Eq. (84). Using Eqs. (24), (36), and (37), we obtain

$$\tilde{F}_{\Lambda}(0|z) = \delta_{m_0} \delta_{m_1, 0} \frac{2\pi n_s}{\sigma_c} \sum_{n=6, 12} \sum_{\nu=n+l}^{\infty} \frac{b_{n\nu; l; l_1}^{(\alpha)}}{z^{-(\nu+\alpha-2)}}, \quad (89)$$

where  $n_s$  is the number of substrate sublattices. Further, the coefficients  $b_{n\nu; l; l_1}^{(\alpha)}$  are given by

$$b_{n\nu; l; l_1}^{(\alpha)} = \frac{2c_n (-1)^{l_1} (2l+1)(2l_1+1)(\nu+\alpha-3) l r^{\nu-n}}{(n-2)!(\nu-n+l+1)!(\nu-n-l)!(\alpha+l_1+1)!(\alpha-l_1)!}. \quad (90)$$

As we have explained in Sec. II, the higher-order Fourier components ( $g \neq 0$ ), are difficult to evaluate analytically because the radial Fourier integral of Eq. (25) contains a product of a cylindrical Bessel function and an associated Legendre function in the integrand. However, in this example we have started with an atom-atom-potential model, so that the method of Sec. III can also be applied. The application of this alternative method is rather straightforward and results in the following expression for the Fourier coefficients:

$$\begin{aligned} \tilde{F}_{\Lambda}(\mathbf{g}|z) &= \frac{4\pi}{\sigma_c} \left[ \sum_{s=1}^{n_s} e^{-i\mathbf{g}\cdot\boldsymbol{\tau}_s} \right] \frac{1}{\alpha!} \\ &\times \sum_{n=6, 12} \sum_{\nu=n}^{\infty} \tilde{W}_{l_1 m_1}^{(\nu-n; \alpha)}(\mathbf{g}|z) \tilde{\chi}_{lm}^{(\nu-n)}(\mathbf{g}|r), \end{aligned} \quad (91)$$

which is a special case of Eq. (67). The coefficients  $\tilde{\chi}_{lm}^{(\nu-n)}(\mathbf{g}|r)$  are defined in Eq. (55) and the functions  $\tilde{W}_{l_1 m_1}^{(\nu-n; \alpha)}$  can be calculated with the aid of the recurrence relation Eq. (64) together with the initialization condition of Eq. (63). Of course, the Fourier coefficients of Eq. (89), derived with the general method of Sec. II, must be equivalent to Eq. (91), i.e., the result of the special method of Sec. III. In order to check this equality we use Eq. (55), which reduces to

$$\tilde{\chi}_{lm}^{(\nu-n)}(0|r) = \delta_{m_0} \frac{(2l+1)r^{\nu-n}}{(\nu-n-l)!(\nu-n+l+1)!} \quad (\nu-n=l, l+2, \dots). \quad (92)$$

From Eqs. (63) and (77) we conclude that

$$\tilde{W}_{l_1 m_1}^{(\nu-n; 0)}(0|z) = \delta_{l_1, 0} \delta_{m_1, 0} \frac{c_n (\nu-3)!}{(n-2)! z^{\nu-2}}. \quad (93)$$

After substitution of Eqs. (92) and (93) in Eq. (91) we obtain Fourier transforms similar to Eq. (89) without molecular-displacement expansion ( $\alpha=0$ ) and with coefficients

$$b_{n\nu; l; l_1}^{(0)} = \delta_{l_1, 0} \frac{2c_n (2l+1)(\nu-3) l r^{\nu-n}}{(n-2)!(\nu-n+l+1)!(\nu-n-l)!} \quad (94)$$

in accordance with Eq. (90). The higher-order terms with  $\alpha > 0$  fulfill the recurrence relation of Eq. (64), which can be simplified to

$$b_{n\nu; l; l_1}^{(\alpha)} = -\frac{(\nu+\alpha-3)}{\alpha} \left[ \frac{l_1}{2l_1-1} b_{n\nu; l; l_1-1}^{(\alpha-1)} + \frac{l_1+1}{2l_1+1} b_{n\nu; l; l_1+1}^{(\alpha-1)} \right], \quad (95)$$

where  $b_{n\nu; l; l_1}^{(\alpha)}$  equals zero by definition if  $l_1$  is negative or greater than  $\alpha$ . It is not difficult to prove that the coefficients of Eq. (90) obey the recurrence relation of Eq. (95). So, the methods of Secs. II and III result in the same flat ( $g=0$ ) Fourier transform. However, the method of Sec. III is more powerful because with the aid of Eq. (91) the Fourier transforms with  $g \neq 0$ , which describe the surface corrugation, can also be evaluated analytically.

## B. Numerical results

In the following we present some numerical results for a  $N_2$  molecule interacting with a single graphite layer. In order to obtain a real physical molecule-substrate system, with graphite consisting of several layers, we have to consider a sum of such single-layer contributions. It is instructive to start with one substrate layer, because this illustrates clearly which terms in the total potential expansion

sion can be neglected for the subsequent layers.

The C atoms in one graphite layer are ordered in a two-dimensional two-sublattice structure ( $n_s=2$ ) with primitive cell vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  of equal length (0.246 nm) which make an angle of  $60^\circ$ . We choose the origin of the global frame in the center of a graphite hexagon and orient the  $x$  axis along the lattice vector  $\mathbf{a}_1$ . With respect to this reference frame the two substrate atoms within the primitive unit cell are positioned at

$$\boldsymbol{\tau}_s = \frac{s}{3}\mathbf{a}_1 + \frac{s}{3}\mathbf{a}_2 \quad (s=1,2). \quad (96)$$

Further, we use the empirically determined atom-atom-potential parameters  $c_6 = -1.469 \text{ J mol}^{-1} \text{ nm}^6$  and  $c_{12} = 2.050 \text{ mJ mol}^{-1} \text{ nm}^{12}$  corresponding with a minimum  $\epsilon = 0.2631 \text{ kJ mol}^{-1}$  of the N-C potential at a distance  $\rho = 0.375 \text{ nm}$ .<sup>38</sup> The parameter  $r$ , occurring in the expansion formulas, equals half the bond length of the  $\text{N}_2$  molecule which is  $2r = 0.1094 \text{ nm}$ .

In first instance we neglect the surface corrugation of the molecule-substrate interaction, i.e., we approximate the expansion coefficient  $F_\Lambda(\mathbf{x})$  in Eq. (87) by the lowest-order Fourier transform  $\bar{F}_\Lambda(0|z)$  that can be calculated with the aid of Eqs. (89) and (90). We observe that Sokolowski<sup>12,13</sup> has used similar potential-expansion coefficients in his calculations of the second virial coefficient and other statistical thermodynamics properties of  $\text{N}_2$  on graphite. Sokolowski, however, did not calculate the expansion coefficients with the aid of analytical formulas, but he evaluated the occurring integrals numerically. In Fig. 1 we have plotted some of the lowest-order coefficients  $\bar{F}_{lm}(0|z)$  with  $l \leq 12$  and  $\alpha = l_1 = m_1 = 0$  as a function of the distance  $z$  between the molecule and the substrate layer. In this case the index  $m$  is necessarily zero as appears from Eq. (89). From Fig. 1 we conclude that the flat ( $g=0$ ) isotropic ( $l=0$ ) coefficient is strongly

dominant, especially at large distances between the molecule and the substrate plane. Further, it has a relatively deep minimum of  $-7.2 \text{ kJ mol}^{-1}$  at a distance  $z = 0.36 \text{ nm}$ . Of course, the higher-order terms with  $l > 0$  in the potential expansion, including Racah harmonics that describe the anisotropy, have also to be taken into account in order to find the minimum of the flat ( $g=0$ ) part of the total potential expansion. These higher-order terms cause a shift of the flat potential minimum with respect to the isotropic minimum towards the substrate plane ( $z = 0.334 \text{ nm}$ ,  $\vartheta = 90^\circ$ ). Further, the  $l=2$  flat Fourier transform possesses also a recognizable minimum, although its depth is relatively small ( $-0.25 \text{ kJ mol}^{-1}$ ). Another interesting observation is that for all  $l$  values the spherical Fourier coefficients become strongly repulsive at short distances.

In order to investigate the influence of the surface corrugation on  $F_{lm}(\mathbf{x})$ , we have included the Fourier terms with  $g \neq 0$ . The projection of the molecular position  $\mathbf{x}$  on the substrate plane, the  $xy$  plane, is fixed in the center of a graphite hexagon, as is for instance the case in the two-dimensional commensurate  $(\sqrt{3} \times \sqrt{3})R 30^\circ \text{ N}_2$  adlayer.<sup>29</sup> The number of  $m$  values for which  $F_{lm}(\mathbf{x})$  does not vanish is limited because the molecule is positioned at the global  $z$  axis, which is a sixfold rotation axis so that  $m$  must be a multiple of 6. Further, the potential is also invariant under a reflection with respect to the  $xz$  plane so that all remaining expansion coefficients  $F_{lm}(\mathbf{x})$  are real numbers. From Fig. 2, which represents expansion coefficients  $F_{lm}(\mathbf{x})$  with  $l \leq 12$  and  $m=0$ , we observe that the  $l=0$  and  $l=2$  curves strongly resemble the corresponding curves of Fig. 1, apart from a small shift towards the substrate plane at short distances. However, for  $l \geq 4$  the higher-order Fourier contributions, describing the corrugation, have a great influence, probably caused by nearest-neighbor pair interactions. In Fig. 3 all

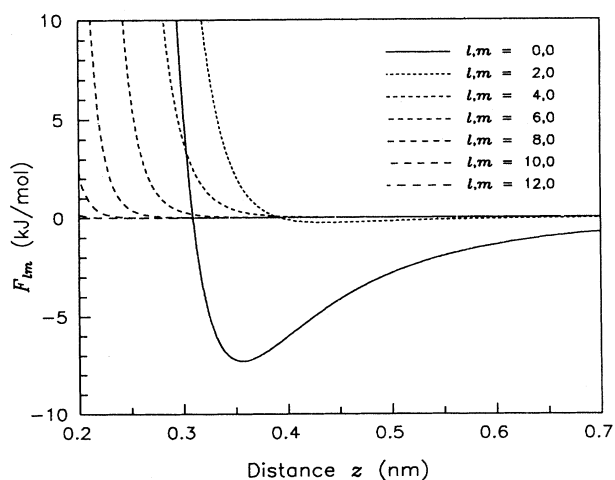


FIG. 1. Potential expansion coefficients  $F_{lm}$  with  $l \leq 12$ , describing the interaction between a  $\text{N}_2$  molecule and a single uncorrugated graphite layer, i.e., only the lowest-order Fourier coefficients with  $g=0$  are taken into account.

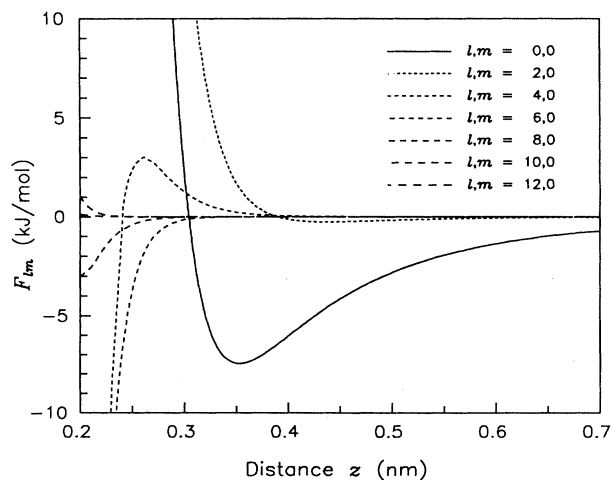


FIG. 2. Potential expansion coefficients  $F_{lm}$  with  $l \leq 12$  and  $m=0$  for a  $\text{N}_2$  molecule interacting with a single corrugated graphite layer. The molecule is positioned at a distance  $z$  above the center of a graphite hexagon.

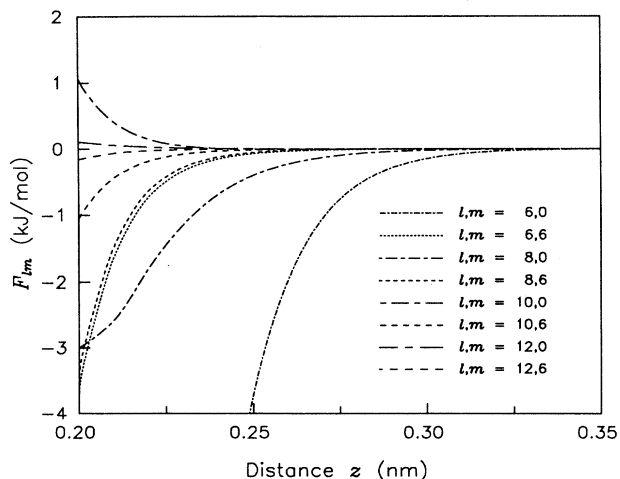


FIG. 3. Potential expansion coefficients  $F_{lm}$  with  $6 \leq l \leq 12$  and  $m=0,6$  with the same conditions as in Fig. 2.

independent expansion functions  $F_{lm}$  with  $l=6,8,10,12$ , and  $m=0,6$  are shown. The coefficients with  $m=12$  are omitted, because they are practically zero within the plot domain. From this figure we conclude that the  $m \neq 0$  terms, which are responsible for the  $\varphi$  dependence of the molecule-substrate potential, are negligible at distances greater than 0.3 nm. This is an important conclusion because it implies that if the  $N_2$  molecule is adsorbed beyond this critical distance, then the total molecule-substrate interaction cannot couple in-plane and out-of-plane rotational motions.

So far, we have considered the expansion coefficients  $F_{lm}(\mathbf{x})$  describing the interaction between a  $N_2$  molecule and a single graphite layer. For a corrugated surface, we have only presented results for the case that the molecule is positioned above the center of a graphite hexagon. As we have mentioned before, the potential expansion coefficients for a real graphite substrate, consisting of several layers with an interlayer distance of 0.337 nm, can be obtained as a sum of single-layer contributions. In this sum the Fourier coefficients with  $g \neq 0$  are negligible for the second- and lower-lying substrate layers, as can be concluded from Figs. 1 and 2, i.e., the lateral positions of the substrate atoms within these layers are of no influence. Further, in order to describe the interaction between a  $N_2$  molecule and a complete graphite substrate it appears to be sufficient to include only one corrugated top layer and ten flat ( $g=0$ ) layers. Minimizing the total molecule-substrate potential, we find that a single  $N_2$  molecule is adsorbed above the center of a graphite hexagon of the top layer, at a distance  $z=0.33$  nm, with equilibrium angles  $\vartheta=90^\circ$  and  $\varphi=0^\circ$ . The only  $\varphi$  dependence of the total potential originates from expansion terms containing coefficients  $F_{lm}(\mathbf{x})$  with  $m \neq 0$  resulting in a very weak sixfold barrier of  $0.5 \text{ J mol}^{-1}$  in the  $\varphi$  direction. On the other hand, the anisotropy in the  $\vartheta$  direction is relatively strong, as is illustrated by a rotational  $\vartheta$  barrier of  $10 \text{ kJ mol}^{-1}$ . So, at an adsorption site the  $\varphi$  anisotropy of the  $N_2$ -graphite interaction is negligible com-

pared with the  $\vartheta$  anisotropy, in agreement with a previous conclusion drawn from Fig. 3.

For quantum-mechanical lattice-dynamics calculations on a commensurate  $(\sqrt{3} \times \sqrt{3})R30^\circ N_2$  adlayer with two-dimensional space group  $p2gg$ , it is interesting to compare the anisotropy of the  $N_2$ -graphite interaction with the anisotropy of the  $N_2$ - $N_2$  interaction. We use the  $N_2$ - $N_2$  potential of Berns and Van der Avoird,<sup>40</sup> which is a spherical expansion of an *ab initio* potential surface. Because the molecule-molecule and molecule-substrate interaction are given in the same representation, they can be easily combined in the potential calculation, as well as in the lattice-dynamics calculation. Optimization of the adlayer crystal structure, assuming a rigid substrate and fixing the molecular centers of mass at adsorption sites, results in molecular axis orientations parallel to the substrate surface ( $\vartheta=90^\circ$ ). The equilibrium in-plane orientation for a molecule of the first sublattice becomes  $\varphi_1=48^\circ$ . A molecule of the second sublattice can be obtained from the first by means of a glide reflection, resulting in an equilibrium in-plane angle  $\varphi_2=132^\circ$ .

We will now investigate the anisotropy of the crystal field, with and without  $N_2$ -graphite interaction, that is experienced by a molecule of the first sublattice, assuming that all other  $N_2$  molecules are fixed in their equilibrium positions and orientations. In Fig. 4 we have plotted the anisotropic part ( $l > 0$ ) of the intralayer crystal field, i.e., without substrate, as a function of the angles  $\vartheta$  and  $\varphi$ . From this contour plot we observe that the intralayer crystal field shows a strong  $\varphi$  anisotropy especially for  $\vartheta=90^\circ$  with a rotational barrier of  $5 \text{ kJ mol}^{-1}$ . Further, for  $\vartheta=90^\circ$  and  $\varphi=48^\circ$ , there is a saddle point, so that the

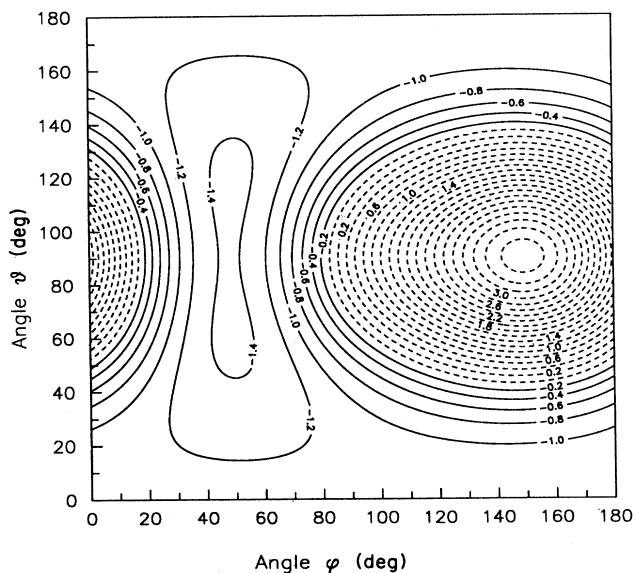


FIG. 4. Anisotropic part of the intralayer crystal field that is experienced by a  $N_2$  molecule within a commensurate  $(\sqrt{3} \times \sqrt{3})R30^\circ N_2$  adlayer as a function of the molecular angles  $\vartheta$  and  $\varphi$ . The molecule-substrate interaction is omitted and all other  $N_2$  molecules are fixed in their equilibrium positions and orientations (see text).

planar two-dimensional crystal structure is not stable without molecule-substrate interaction. In the neighborhood of this saddle point the  $\vartheta$  anisotropy is relatively weak compared with the  $\varphi$  anisotropy, in contrast with the anisotropic behavior of the  $N_2$ -graphite potential as discussed previously.

In Fig. 5 we have added the anisotropic part ( $l > 0$ ) of the  $N_2$ -graphite interaction to the intralayer crystal field of Fig. 4. Comparing these figures, we conclude that because of the strong anisotropy of the  $N_2$ -graphite interaction in the  $\vartheta$  direction, the saddle point in Fig. 4, obtained without substrate, is replaced by a minimum in Fig. 5. However, the  $\varphi$  anisotropy caused by the intralayer interaction is practically not influenced by the molecule-substrate interaction. Summarizing, we expect that in the commensurate  $(\sqrt{3} \times \sqrt{3})R 30^\circ N_2$  adlayer the out-of-plane rotational dynamics, described by the coordinate  $\vartheta$ , will be governed by the  $N_2$ -graphite interaction and the in-plane dynamical behavior, corresponding with motions in the  $\varphi$  direction, will be strongly determined by the  $N_2$ - $N_2$  interaction. This does not imply, however, that the  $\varphi$  anisotropy of the molecule-substrate interaction is always negligible. For example, in an incommensurate  $N_2$  adlayer,<sup>32</sup> where the molecules are not adsorbed above the centers of graphite hexagons, the corrugated part of the molecule-substrate interaction can cause a  $\varphi$  barrier of  $0.5 \text{ kJ mol}^{-1}$ , which is 10% of the intralayer value. On the other hand, the  $\vartheta$  anisotropy appears to be practically independent of the surface corrugation.

So far, we have fixed the molecular centers of mass in their equilibrium positions. In lattice-dynamics calculations, including the translational vibrations, the Taylor expansion of Eq. (87) with respect to molecular displacements  $\mathbf{u}$  is useful. Because the out-of-plane translational motions are, just as the out-of-plane rotations, strongly

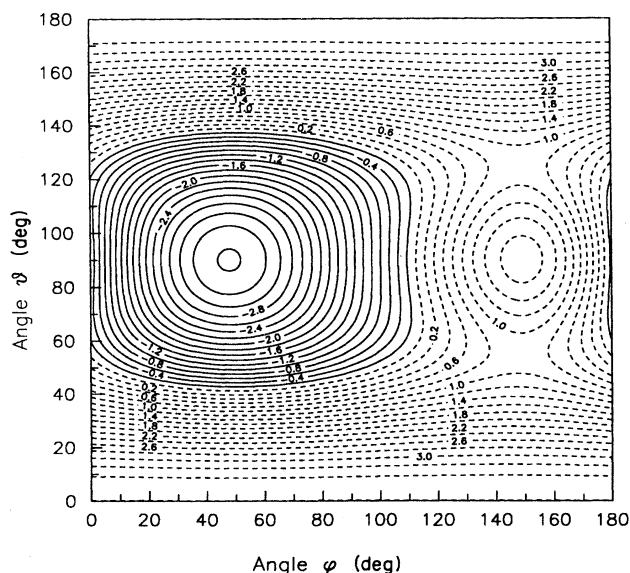


FIG. 5. Superposition of the anisotropic part of the  $N_2$ -graphite interaction and the intralayer crystal field of Fig. 4 within a commensurate  $(\sqrt{3} \times \sqrt{3})R 30^\circ N_2$  adlayer.

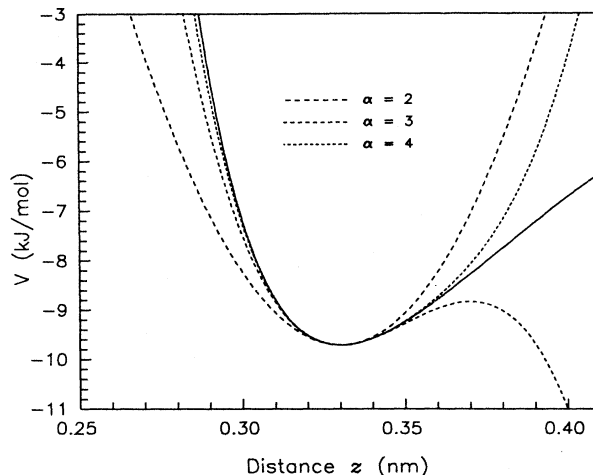


FIG. 6.  $N_2$ -graphite interaction as a function of the distance  $z$  with respect to the corrugated top layer. The molecule is positioned above the center of a graphite hexagon and the molecular orientation is fixed at angles  $\vartheta = 90^\circ$  and  $\varphi = 48^\circ$ . The dashed curves represent various Taylor approximations up to order  $\alpha = 2, 3$ , or  $4$ , inclusive.

determined by the molecule-substrate interaction, we will investigate the convergence of the Taylor expansion with respect to displacements perpendicular to the substrate surface. In Fig. 6 the solid curve represents the total  $N_2$ -graphite potential as a function of the distance  $z$  with respect to the substrate top layer. All other molecular coordinates are set equal to their equilibrium values in the optimized commensurate adlayer, although a variation of  $\varphi$  would not be visible on the energy scale used here. Within the harmonic approximation, represented by the dashed curve with  $\alpha = 2$  in Fig. 6, the bound-state energies can be characterized by a fundamental oscillator frequency of  $0.4 \text{ kJ mol}^{-1}$ . From Fig. 6 we conclude that the harmonic approximation is good if the molecule is in the ground state at  $-9.5 \text{ kJ mol}^{-1}$ , where it oscillates with a translational amplitude of  $0.01 \text{ nm}$  with respect to the potential minimum. However, for the first excited state at  $-9.1 \text{ kJ mol}^{-1}$ , corresponding with an amplitude of  $0.02 \text{ nm}$ , the harmonic approximation is not accurate enough. Although the third-order Taylor approximation ( $\alpha = 3$ ) is better within a greater domain, it is dangerous to use this approximation because the first excited state is nearly at the same level as the local maximum at  $z = 0.36 \text{ nm}$ . This implies that, at finite temperatures, the molecule can easily escape from the surface if the third-order Taylor approximation is used. Of course, this is an undesired artifact that is avoided if one only uses Taylor approximations of even order (see, for instance, the dashed curve corresponding with  $\alpha = 4$  in Fig. 6).

## V. CONCLUSION

We have elaborated on two methods to obtain an analytical potential expansion for a molecule interacting with a substrate that consists of atoms which are ordered in a two-dimensional lattice.

The most general method, shown in Sec. II, starts with a spherically expanded molecule-atom potential which represents the anisotropy explicitly. This pair potential is expanded with respect to molecular displacements. Finally, because of the two-dimensional translation symmetry parallel to the substrate surface, the lattice sum over the expanded molecule-atom pair potentials is replaced by a two-dimensional Fourier series. We have given analytical expressions for the isotropic ( $l=0$ ) and flat ( $g=0$ ) Fourier transforms. As far as the corrugated part of the molecule-substrate-potential expansion is concerned, the anisotropic Fourier transforms are difficult to evaluate analytically, however.

In Sec. III we have presented a special method that is applicable if an atom-atom model is used for the molecule-atom pair potential. This method starts with a Fourier transformation of isotropic atom-substrate potentials. After a spherical expansion of the atom-substrate Fourier series, followed by a translational displacement expansion, the final expression has a similar form as the result of the general method of Sec. II. A great advantage of the special method of Sec. III is that all expansion coefficients can be evaluated analytically for exponential and inverse-power-law atom-atom-potential types.

As an example, we have applied both methods for a homonuclear diatomic molecule on a substrate, resulting in some simplifications and further analytical formulas. In order to illustrate the convergence of the expansion, some numerical results have been shown for  $N_2$  on graph-

ite. At an adsorption site, the in-plane anisotropy of the  $N_2$ -graphite interaction, caused by the corrugation, appears to be negligible compared with the out-of-plane anisotropy. In the commensurate  $(\sqrt{3} \times \sqrt{3})R 30^\circ$  structure the out-of-plane crystal-field anisotropy is strongly determined by the  $N_2$ -graphite potential and the in-plane anisotropy is dominated by the  $N_2$ - $N_2$  interaction. The anharmonic terms in the molecular-displacement expansion are so important that they will influence the out-of-plane translational vibrations. Truncation of this expansion after the cubic terms should be avoided, since this produces the artifact that an adsorbed molecule can easily escape from the surface.

Finally we observe that the techniques developed in this paper can also be used to obtain general expressions for the interaction between electrostatic multipole moments and a two-dimensional lattice of multipoles. This will be treated in a forthcoming paper.

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