Phonon-mediated indirect interactions between adatoms on surfaces

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A general formulation for the phonon-mediated indirect interaction between adatoms on the surface of a solid is given in terms of the lattice dynamics of the substrate. The result is expressed in terms of the interaction of the adatoms with the rigid substrate and the vibrational Green's functions of the clean surface. Detailed calculations are presented for two model systems: pairs of As dimers on the Si(100) surface and H adatoms on the reconstructed W(100) surface. For Si(100) the Keating model is used for the lattice dynamics, and the interaction of the As dimer with the rigid substrate is extracted from recent pseudopotential calculations. For W(100) a central-force-constant model with forces chosen appropriately for the reconstructed surface is used. It is found that the phonon-mediated interactions on these surfaces can be substantial in magnitude, can vary nonmonotonically as a function of adatom separation, and depend on the direction of the adatom separation with respect to the surface. These features are different from the results of simple elasticity theory.

I. INTRODUCTION

There are two kinds of interactions between adatoms on surfaces: the direct interaction between the adatoms, and the indirect interaction, which is mediated through the substrate. The indirect interaction can arise from elastic distortions of the substrate or from perturbation of the electronic structure of the substrate due to the presence of the adatoms on the surface. The strength, sign, and anisotropy of the indirect interaction at small adatom separations is of interest in studies of adsorbate-induced surface reconstruction, surface phase transitions, clustering of adatoms, and kinetic phenomena on surfaces.

Existing work on the indirect elastic interaction is all based on a treatment of the substrate using the continuum approximation of elasticity theory. Lau and Kohn[1] have investigated the interaction between two adatoms, and they found that the adatom-adatom interaction energy varies as $R_{\parallel}^{-3}$, where $R_{\parallel}$ is the projection of the separation between the two defects onto the surface plane. They found for identical adatoms that the interaction is repulsive, and for different adatoms it may be either attractive or repulsive. In addition, Lau[2] has studied cubic anisotropic substrates using the continuum model. He has found for identical adatoms that the interaction is either attractive or repulsive depending on the angle between $R_{\parallel}$ and the cubic axes of the substrate.

Stoneham[3] also has studied the indirect substrate-mediated elastic interactions for defects on continuum substrates and has found results similar to those of Lau and Kohn[1] and of Lau.[2] Stoneham notes that the indirect elastic interaction varies as $R_{\parallel}^{-3}$ when $R_{\parallel}$, which is the separation between the adatoms, is much larger than the range of the defect forces. He then argues that the elastic interaction has longer range than the indirect electronic interaction, which behaves roughly as $R_{\parallel}^{-5}$, as calculated by Einstein and Schreiffer.[4] Thus at large adatom-adatom separations the elastic interaction will dominate over the electronic interaction.

Maradudin and Wallis[5] have studied the indirect substrate-mediated elastic interaction for an isotropic substrate, where the height of the adatoms relative to the surface may be varied. They found again that the interaction energy varies as $R_{\parallel}^{-3}$. They also found that the interaction energy for identical adatoms is repulsive when $\bar{R}_{\perp} < R_{\parallel}/2\sqrt{2}$, and attractive when $\bar{R}_{\perp} > R_{\parallel}/2\sqrt{2}$, where $\bar{R}_{\perp}$ is the average height of the adatoms below the surface.

Kappus[6] has found a similar large distance behavior which varies as $R_{\parallel}^{-3}$ and similar anisotropic results to those of Lau.[2] However, in order to generate finite results for the integral over the two-dimensional Brillouin zone, Kappus introduces a smooth cutoff function with the cutoff parameter of the order of the inverse lattice constant. Kappus found that for $R_{\parallel}$ less than a few lattice constants, the interaction energy was sensitive to the choice of the cutoff function. At large $R_{\parallel}$ he found the interaction energy to be independent of the choice of cutoff function and obtained the usual $R_{\parallel}^{-3}$ dependence. In addition, Kappus found that in the isotropic case, the interaction would change from being attractive at small $R_{\parallel}$ to repulsive at large $R_{\parallel}$. The sensitivity to the choice of the cutoff function is an indication of the breakdown of the continuum elastic model at short length scales, and the change in the interaction from attractive at small distances to repulsive at large distances that Kappus observed is somewhat unrealistic.

In the present study we are concerned with the indirect substrate-mediated elastic interaction. We are interested

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primarily in the regime when $R_{\parallel}$ is less than or of the order of a few lattice constants and in the anisotropic character of the interaction. In addition, we want to include the local structure of both the substrate and the adsorbate. Thus a lattice-dynamics analysis of the substrate and not a continuum elasticity approach is needed. In the next section, we will present a derivation of these interactions within a lattice-dynamics approach.

II. FORMALISM

Consider two adatoms located at positions R_1 and R_2 in the vicinity of the surface of a periodic crystal. The elastic energy of the system consisting of the substrate atoms plus the two adatoms is written

$$E = W[\{r_s\}] + V_1[\{r_s\};R_1] + V_2[\{r_s\};R_2] , \tag{1}$$

where the $\{r_s\}$ are the positions of the substrate atoms labeled by s, W is the potential governing the interactions among the substrate atoms in the absence of the adatoms, and V_ξ, $\xi = 1,2$, represent the interaction between the ξth adatom and a local region of substrate atoms in the vicinity of R_ξ. No direct adatom-adatom interactions are included in Eq. (1). In addition, the interactions V_ξ are not necessarily two-body interactions, but may include angle-bending interactions as well as other many body forces.

The substrate equilibrium positions $\{r_s^0\}$ when no defect is present are defined by the vanishing of the force on any substrate atom s',

$$\left. \frac{\partial W[\{r_s\}]}{\partial r_{s'}} \right|_{\{r_s^0\}} = 0 . \tag{2}$$

We next expand Eq. (1) about $\{r_s^0\}$ to harmonic order in the variables $u_s = r_s - r_s^0$ and find

$$\begin{aligned}
E = {} & W[\{r_s^0\}] + V_1[\{r_s^0\};R_1] + V_2[\{r_s^0\};R_2] \\
& + \sum_\lambda u_\lambda (V'_{1,\lambda}[\{r_s^0\};R_1] + V'_{2,\lambda}[\{r_s^0\};R_2]) \\
& + \frac{1}{2} \sum_{\lambda,\mu} u_\lambda u_\mu B_{\lambda\mu}[\{r_s^0\};R_1,R_2] .
\end{aligned} \tag{3}$$

In Eq. (3) the index λ labels both the substrate atom site s and the coordinate $i = x,y,z$, and $V'_{\xi,\lambda} = \partial V_\xi / \partial r_\lambda$. The tensor $B_{\lambda\mu}$ is defined through the equation

$$B_{\lambda\mu}[\{r_s^0\};R_1,R_2] = \frac{\partial^2}{\partial r_\lambda \partial r_\mu} (W[\{r_s\}] + V_1[\{r_s\};R_1] + V_2[\{r_s\};R_2]) \Big|_{\{r_s^0\}} , \tag{4}$$

with $B_{\lambda\mu} = B_{\mu\lambda}$.

The equilibrium positions $\{\bar{r}_s\}$ of the substrate atoms in the presence of the adatom defects are given by

$$\frac{\partial}{\partial r_s'} (W[\{r_s'\}] + V_1[\{r_s'\};R_1] + V_2[\{r_s'\};R_2]) \Big|_{\{\bar{r}_s\}} = 0 . \tag{5}$$

We write $u_\lambda = r_\lambda - r_\lambda^0 = \bar{u}_\lambda + p_\lambda$, where $\bar{u}_\lambda = r_\lambda - \bar{r}_\lambda$ and $p_\lambda = \bar{r}_\lambda - r_\lambda^0$. Note that the p_λ are the static distortions of substrate atoms between their equilibrium positions on the clean surface and their equilibrium positions in the presence of the adatom defects. We then substitute for $u_\lambda = \bar{u}_\lambda + p_\lambda$ in Eq. (3) to obtain

$$\begin{aligned}
E = {} & \sum_\lambda \left[\left[V'_{1,\lambda}(R_1) + V'_{2,\lambda}(R_2) + \sum_\mu B_{\lambda\mu}(R_1,R_2)p_\mu \right] \bar{u}_\lambda + [V'_{1,\lambda}(R_1) + V'_{2,\lambda}(R_2)]p_\lambda \right] \\
& + \frac{1}{2} \sum_{\lambda,\mu} B_{\lambda\mu}(R_1,R_2)(\bar{u}_\lambda \bar{u}_\mu + p_\lambda p_\mu) + W + V_1[R_1] + V_2[R_2] ,
\end{aligned} \tag{6}$$

where W, V_ξ, V'_ξ, and $B_{\lambda\mu}$ are evaluated about $\{r_s^0\}$. The fact that the linear term in Eq. (6) must vanish gives

$$V'_{1,\lambda} + V'_{2,\lambda} + \sum_\mu B_{\lambda\mu}p_\mu = 0 , \tag{7}$$

where we have suppressed the R_1 and R_2 dependence. Rearranging Eq. (7) we solve for p_ν and find

$$p_\nu = -\sum_\lambda (B^{-1})_{\nu\lambda}(V'_{1,\lambda} + V'_{2,\lambda}) . \tag{8}$$

Substituting for p from Eq. (8) into Eq. (6) yields

$$\begin{aligned}
E = {} & \frac{1}{2} \sum_{\lambda,\mu} B_{\lambda\mu} \bar{u}_\lambda \bar{u}_\mu \\
& - \frac{1}{2} \sum_{\lambda,\mu} (V'_{1,\lambda} + V'_{2,\lambda})(B^{-1})_{\lambda\mu}(V'_{1,\mu} + V'_{2,\mu}) \\
& + W + V_1 + V_2 .
\end{aligned} \tag{9}$$

Using Eq. (9) one can define an effective potential governing the motion of the two adatom defects on the surface of a solid by performing an average over the substrate degrees of freedom,[7] which gives

$$\begin{aligned}
V_{\text{eff}}(R_1,R_2) = {} & V_1[\{r_s^0\},R_1] + V_2[\{r_s^0\},R_2] \\
& - k_B T \ln\left\langle \exp\left[\frac{-k_B T}{2} \sum_{\lambda,\mu} B_{\lambda\mu} \bar{u}_\lambda \bar{u}_\mu \right] \right\rangle \\
& - \frac{1}{2} \sum_{\lambda,\mu} [(V'_{1,\lambda} + V'_{2,\lambda}) \\
& \times (B^{-1})_{\lambda\mu}(V'_{1,\mu} + V'_{2,\mu})] .
\end{aligned} \tag{10}$$

In the above equation, k_B is Boltzman's constant and T is temperature. To evaluate Eq. (10) we require

$$\underline{B}^{-1} = (\underline{W}'' + \underline{V}_1'' + \underline{V}_2'')^{-1} . \tag{11}$$

Because our knowledge of V and therefore of V' and V'' is rather limited, we make the approximation $\underline{B}^{-1} \approx (\underline{W''})^{-1}$. This approximation assumes that the presence of the adatom on the surface does not significantly affect the susceptibility of the substrate even in the vicinity of the adatom.

In this case the temperature-dependent term in Eq. (10) becomes a constant independent of the adatom position. The other term can be separated into contributions due to local substrate relaxation about a given adatom $\xi=1,2$ and the indirect substrate-mediated interaction between the adatoms at $\mathbf{R}_1$ and $\mathbf{R}_2$. The substrate relaxation energy about each defect ($\xi=1,2$) is

$$E_{\text{relax},\xi} = -\tfrac{1}{2} \sum_{\lambda,\mu} V'_{\xi,\lambda}[\mathbf{R}_\xi](B^{-1})_{\lambda\mu} V'_{\xi,\mu}[\mathbf{R}_\xi] \ . \tag{12}$$

The adatom-adatom interaction can be written

$$E_{\text{ad}}(\mathbf{R}_1,\mathbf{R}_2) = -\sum_{\lambda,\mu} V'_{1,\lambda}[\mathbf{R}_1](B^{-1})_{\lambda\mu} V'_{2,\mu}[\mathbf{R}_2] \ , \tag{13}$$

where we have used the fact that $\underline{B}=\underline{B}^T$. In Eqs. (12) and (13) the sum over λ represents a sum over all of the sites and Cartesian components (x,y,z) of the substrate atoms with which the adatom at position R_1 interacts, and similarly for the sum over μ.

The lattice Green's function at zero frequency is defined by $\underline{G}^{(0)}=\underline{D}^{-1}$, where $\underline{D}=M^{-1}\underline{W''}$ is the dynamical matrix and M is the mass of a substrate atom. Thus

$$(\underline{W''})^{-1}=M^{-1}\underline{G}^{(0)} \equiv \underline{\chi}^{(0)} \ . \tag{14}$$

The relaxation energy and the adatom-adatom interac-

tion energy then can be written

$$E_{\text{relax},\xi \ (=1,2)} = -\tfrac{1}{2} \sum_{\lambda,\mu} V'_{\xi,\lambda} \chi^{(0)}_{\lambda\mu} V'_{\xi,\mu} \tag{15}$$

and

$$E_{\text{ad}}(\mathbf{R}_1,\mathbf{R}_2) = -\sum_{\lambda,\mu} V'_{1,\lambda} \chi^{(0)}_{\lambda\mu} V'_{2,\mu} \ . \tag{16}$$

Because V_1 and V_2 represent interactions with a small cluster of substrate atoms in the vicinity of the adatom, only a finite number of elements of $\chi^{(0)}$ are required to evaluate Eqs. (15) and (16). Furthermore, from Eqs. (14)–(16) it is seen that the relaxation and the adatom-adatom interactions are static effects and do not depend on the mass of the substrate atoms or adatoms.

Using the fact that $\chi^{(0)}$ has translational invariance parallel to the surface plane, we write

$$\chi^{(0)}_{\alpha,\beta}(\mathbf{r}_s,\mathbf{r}'_s) = \frac{1}{N} \sum_{\bar{q}} e^{-i\bar{q}\cdot(\bar{m}-\bar{m}')} \chi^{(0)}_{\alpha,\beta}(l,l',\bar{q}) \ , \tag{17}$$

where α labels the cartesian components of each of the atoms in the unit cell which is located by $\mathbf{r}_s$; $\bar{q}$ is a two-dimensional wave vector, N is the number of unit cells in the surface plane, and lightface Roman characters with overbars represent two-dimensional surface vectors. Then we denote $\mathbf{r}_s = \bar{m} + la_{\text{layer}}\hat{e}$, where $\bar{m}$ is a position vector lying within a layer characterized by the integer l with interlayer spacing a_{layer} and unit vector $\hat{e}$ normal to the surface plane.

Substituting Eq. (17) into Eq. (16) we find

$$E_{\text{ad}}(\mathbf{R}_1,\mathbf{R}_2) = -\frac{1}{N} \sum_{\substack{\alpha,\beta \\ l,l'}} \sum_{\bar{\sigma}_1,\bar{\sigma}_2} V'_{1,\bar{\sigma}_1 l\alpha}(\mathbf{R}_1) V'_{2,\bar{\sigma}_2 l'\beta}(\mathbf{R}_2) \sum_{\bar{q}} e^{-i\bar{q}\cdot(\mathbf{R}^{\|}_1-\mathbf{R}^{\|}_2+\bar{\sigma}_1-\bar{\sigma}_2)} \chi^{(0)}_{\alpha,\beta}(l,l',\bar{q}) \ . \tag{18}$$

For convenience we have written $\bar{m}=\mathbf{R}^{\|}_1+\bar{\sigma}_1$ and $\bar{m}'=\mathbf{R}^{\|}_2+\bar{\sigma}_2$, where $\bar{\sigma}_1$ and $\bar{\sigma}_2$ are two-dimensional position vectors measured from origins at $\mathbf{R}^{\|}_1$ and $\mathbf{R}^{\|}_2$, which indicate the positions of the substrate atoms with which the adatoms at $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, interact. Then we define

$$V'_{\xi,l\alpha}(\bar{q}) = \sum_{\bar{\sigma}} e^{i\bar{q}\cdot\bar{\sigma}} V'_{\xi,\bar{\sigma}l\alpha}(\mathbf{R}_\xi) \tag{19}$$

as the Fourier-transformed force vector, and we obtain

$$E_{\text{ad}}(\mathbf{R}_1,\mathbf{R}_2) = -\frac{1}{N} \sum_{\bar{q}} \sum_{\substack{l,l' \\ \alpha,\beta}} V^{*\prime}_{1,l\alpha}(\bar{q}) \chi^{(0)}_{\alpha\beta}(l,l',\bar{q}) V'_{2,l'\beta}(\bar{q}) e^{-i\bar{q}\cdot(\mathbf{R}^{\|}_1-\mathbf{R}^{\|}_2)} \tag{20}$$

where $*$ stands for complex conjugation.

Equation (20) for $E_{\text{ad}}(\mathbf{R}_1,\mathbf{R}_2)$ clearly shows the dependence of E_{ad} on the separation $\mathbf{R}^{\|}_1-\mathbf{R}^{\|}_2$ between the two adatom defects. A similar expression is obtained for the relaxation energy

$$E_{\text{relax}, \xi \ (=1,2)} = -\frac{1}{2N} \sum_{\bar{q}} \sum_{\substack{l,l' \\ \alpha,\beta}} V'^{*}_{\xi,l\alpha}(\bar{q}) \chi^{(0)}_{\alpha\beta}(l,l',\bar{q}) V'_{\xi,l'\beta}(\bar{q}) \ . \tag{21}$$

Equations (20) and (21) are the main results of this paper.

It is useful to compare the present lattice-dynamics approach for the adatom-adatom interaction on surfaces with that from continuum elasticity theory, which is valid only in the limit of large adatom-adatom separations.

From elasticity theory $\chi(q) \propto f(\phi)/q$, where (q,ϕ) are the polar coordinates of the two-dimensional wave vector. $f(\phi)$ includes any effects due to anisotropy which may have been introduced into the vibrational properties of the substrate, and for isotropic continuum theory

$f(\phi) \rightarrow$ const. For short-ranged forces the Fourier transform of the force $V'(q) \propto q$ in the long-wavelength approximation. Then,

$$E_{ad}(\mathbf{R}_\parallel) = \int d\bar{q}\, e^{i\bar{q}\cdot\mathbf{R}_\parallel} f(\phi)q = \frac{C(\theta)}{R_\parallel^3} , \qquad (22)$$

where $\mathbf{R}_\parallel = (R_\parallel, \theta)$, and θ is the angle between $\mathbf{R}_\parallel$ and the crystallographic axes of the substrate. For an isotropic solid $C(\theta) \rightarrow$ const. From Eq. (22) it is seen that for a given direction of $\mathbf{R}_\parallel$ the interaction remains attractive or repulsive and changes monotonically as $R_\parallel$ increases. The present lattice-dynamics approach, on the other hand, is valid for all adatom-adatom separations including the small distances which are of particular physical interest.

In the next two sections, we shall apply Eqs. (20) and (21) in order to evaluate the adatom interaction energy and the relaxation energy for two model systems: pairs of As-As dimers absorbed on the unreconstructed Si(100) surface, and H adatoms on the reconstructed W(100) surface. We shall demonstrate that the results of the present approach differ qualitatively from those of elasticity theory. In particular, it will be seen that the interactions depend on the direction of the adatom separation along the surface and that they often have an oscillatory dependence on the magnitude of the separation.

III. AS-AS DIMERS ON THE SI(100) SURFACE

In this section we shall evaluate the relaxation energy and the adatom-adatom interaction energy for the system consisting of two isolated arsenic-arsenic dimer defects adsorbed on the unreconstructed Si(100) surface. In order to evaluate Eqs. (20) and (21), we must generate expressions for the forces, $-\partial V_\xi / \partial r_s$, $\xi = 1, 2$, acting on the substrate atoms in the vicinity of the dimer defects as well as determine the appropriate substrate response functions $\chi^{(0)}$.

Recently, Uhrberg et al.[8] studied the problem of a periodic overlayer of arsenic dimers adsorbed on unreconstructed Si(100). Their method of analysis involved a comparison between angle-resolved photoemission data and ab initio pseudopotential calculations. They concluded that the observed 2×1 pattern on Si(100)-As is caused by the formation of symmetric As-As dimers on the unreconstructed Si(100) surface.

In the symmetric As-As dimer model each arsenic atom bonds to two silicon atoms and to the other arsenic atom forming the dimer pair. This leaves all arsenic atoms threefold coordinated and all Silicon atoms fourfold coordinated as in the bulk of each material. The minimum energy structure from the calculations of Urberg et al. for the full periodic overlayer of arsenic dimers on the unreconstructed Si(100) surface is shown in Fig. 1 along with the subsurface relaxation displacements of the silicon substrate atoms from their bulk equilibrium positions. As noted by Uhrberg et al., although these displacements are fairly large, they are understandable in terms of elastic energy considerations and are qualitatively similar to the subsurface displacements calculated by Appelbaum and Hamann[9] for the symmetric dimerized
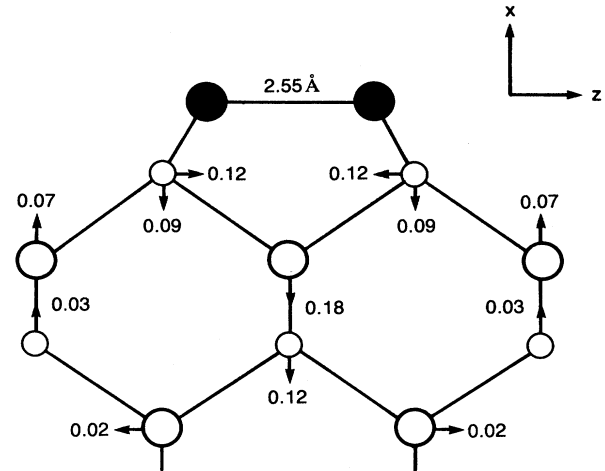
FIG. 1. Side view of As-As dimer model of the Si(100)-As 2×1 surface with the As atoms shaded (from Ref. 8). The bond lengths between the As atoms and also the subsurface displacements are given in Å. The distance between the top layer Si atoms before the adsorption of As atoms is $a/\sqrt{2}$, where $a = 5.43$ Å is the lattice constant of the Si fcc lattice.

Si(100) 2×1 surface with the use of the Keating lattice-dynamics model. A top view of the symmetry of the As overlayer with respect to the Si substrate is shown in Fig. 2.

First, we must obtain the forces exerted by the adatoms on the atoms of the clean substrate which are required to produce the displacements given in Ref. 8. This can be done through Eq. (7), which relates the adatom-substrate interaction to the displacements of the substrate $\{p_v\}$. It is not possible, however, to determine uniquely the forces on the substrate due to an isolated As-As dimer from the displacement pattern $\{p_v\}$ in Ref. 8, which is for a uniform overlayer of As dimers. For the present purposes we assume that the forces on a given Si substrate atom are due to equal additive contributions from all nearest-neighbor As-As dimers. This specifies all of
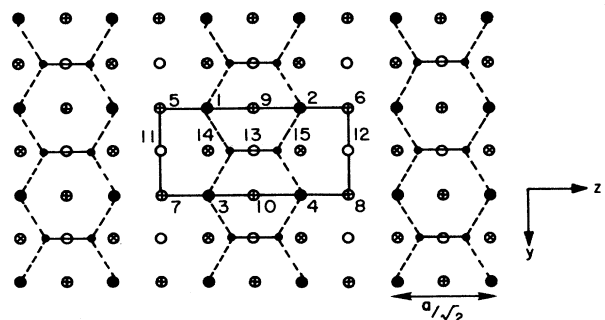
FIG. 2. Top view of the Si(100)-As 2×1 surface. ●, As; ●, first-layer Si; ⊕, second-layer Si; ○, third-layer Si; and ⊗, fourth-layer Si. In the present treatment the atoms labeled $1, 2, \ldots, 15$ surrounding an isolated As-As defect have nonvanishing forces arising from the As-As dimer. The y axis corresponds to the $[01\bar{1}]$ crystallographic direction and the z axis to the $[011]$ direction.

the forces on the substrate except for the forces in the [01$\bar{1}$] crystallographic direction on the Si atoms in the top layer (in the direction of the y axis in Fig. 2). For these atoms we assume that the magnitude of the force in the [01$\bar{1}$] direction is equal to that on the same atom in the [011] direction. This is, of course, somewhat arbitrary, but the results are not too sensitive to the magnitude of the force along this direction.

The resulting forces from an isolated As-As dimer on the substrate are shown in Fig. 3. We note that the sum of the forces on all of the atoms of the substrate is zero; this is a useful test of the procedure for obtaining the forces on the substrate, which follows from the condition that the net force on the adatom must be zero.

In previous work[7,10] we have studied the vibrational properties of the ideal unreconstructed Si(100) surface and the clean reconstructed Si(100) 2×1 surface using a Keating model[11] with the choice of force constant parameters α and β given in Ref. 12. The reconstructed Si(100) 2×1 surface is characterized by dimer bonds, similar to those in the bulk, between alternate pairs of surface atoms along the [01$\bar{1}$] direction (the "dimer-bond direction"). The spectral density of the ideal unreconstructed surface for vibrations along the dimer-bond direction has a large weight at low frequencies, which is associated with the softness of this surface for vibrations in the direction in which the dimer bonds are formed upon reconstruction. This softness is not present on the reconstructed surface due to the dimer bonds.

We must consider how best to represent the vibrational properties Si(100) surface for the present purposes. In the immediate vicinity of the As-As dimer it is seen from the results of Ref. 8 that the Si surface does not have the dimer bonds of the reconstructed surface. On the other hand, we expect that for the region between the As-As dimers the surface correlation functions $\chi^{(0)}$ will behave more like those for the reconstructed case. In particular,

FIG. 3. Force field acting on the Si substrate atoms due to an isolated As-As dimer defect. Note that the top-layer Si atoms have nonvanishing forces in the y direction, which are indicated in the figure. The forces are calculated in the text. The units for the forces are eV/Å.

we expect that the soft response in the direction of the Si dimers will be absent. We have studied a dynamical matrix for the Si(100) surface in which the unreconstructed geometry is maintained, but the Si dimer atoms have a central force constant α_d between them. For values of $\alpha_d(r_d)^2/\alpha(r_b)^2 \gtrsim \frac{4}{9}$ the vibrational spectral densities are qualitatively similar to those for the reconstructed Si(100) 2×1 surface, and therefore we will use this model of the surface to calculate $\chi^{(0)}$. We use the fact that the Keating energy scales as the product of the force-constant parameter α times the square of the relevant bond length. $r_d = a/\sqrt{2}$ is the distance between top-layer Si atoms on the (100) surface, and $r_b = a\sqrt{3}/4$ is the bulk bond length. For the results given here we have used $\alpha_d = \frac{1}{6}\alpha$.

We have evaluated the relaxation energy in Eq. (21) for an As-As dimer on the Si(100) surface and the interaction energy between pairs of As-As dimers in Eq. (20). The force field in Fig. 3 and the model of the Si surface dynamical matrix described above have been used. The method described in Ref. 10 has been employed to evaluate the $\bar{q}$-space matrix $\chi^{(0)}$ for the Si(100) surface. Here Fourier transforms of the dynamical matrix parallel to the surface are used, and recursion calculations perpendicular to the surface have been made. The convergence of the results for the adatom interactions with respect to the levels used in the recursion calculation and also for the density of points in $\bar{q}$ space needed for the summations in Eq. (21) have been checked. We find that recursions employing more than 50 levels and q-space meshes having 16×16 points in the first quadrant of the square Brillouin zone give well-converged results for the separations studied here.

We find that the relaxation energy per As-As dimer is −146 meV. As expected, the energy corresponding to the local relaxation near the dimer is negative and gives an attractive contribution to the total energy of the system. The interaction energy between two dimers is given as a function of their separation in Figs. 4(a)–4(c) for separations along the [01$\bar{1}$] direction, the [011] direction, and the [010] direction, respectively. In Fig. 4(a) it is seen that at the closest separation along the [01$\bar{1}$] direction ($a/\sqrt{2}$) the interaction energy is large and negative. This behavior can be understood qualitatively by noting in Fig. 2 that for this geometry the dominant effect on the substrate atoms arises from the forces on the first-layer Si atoms located between the As dimers. For these atoms the forces in the [011] direction are parallel and give rise to substrate relaxation; the forces in the [01$\bar{1}$] direction, on the other hand, are antiparallel and tend to cancel one another. For increasing separation the interaction energy rises to a positive maximum and then decreases to zero. The large decrease of the interaction energy by an order of magnitude with increasing separation from the nearest-neighbor distance is typical of all directions. The change of sign of the interaction and the accompanying large decrease in its magnitude within a few lattice constants are quite interesting.

The interaction energies for separations along the [011] direction are shown in Fig. 4(b). For the closest separation of the dimers along this direction the electronic cores of the As atoms overlap and give rise to a large
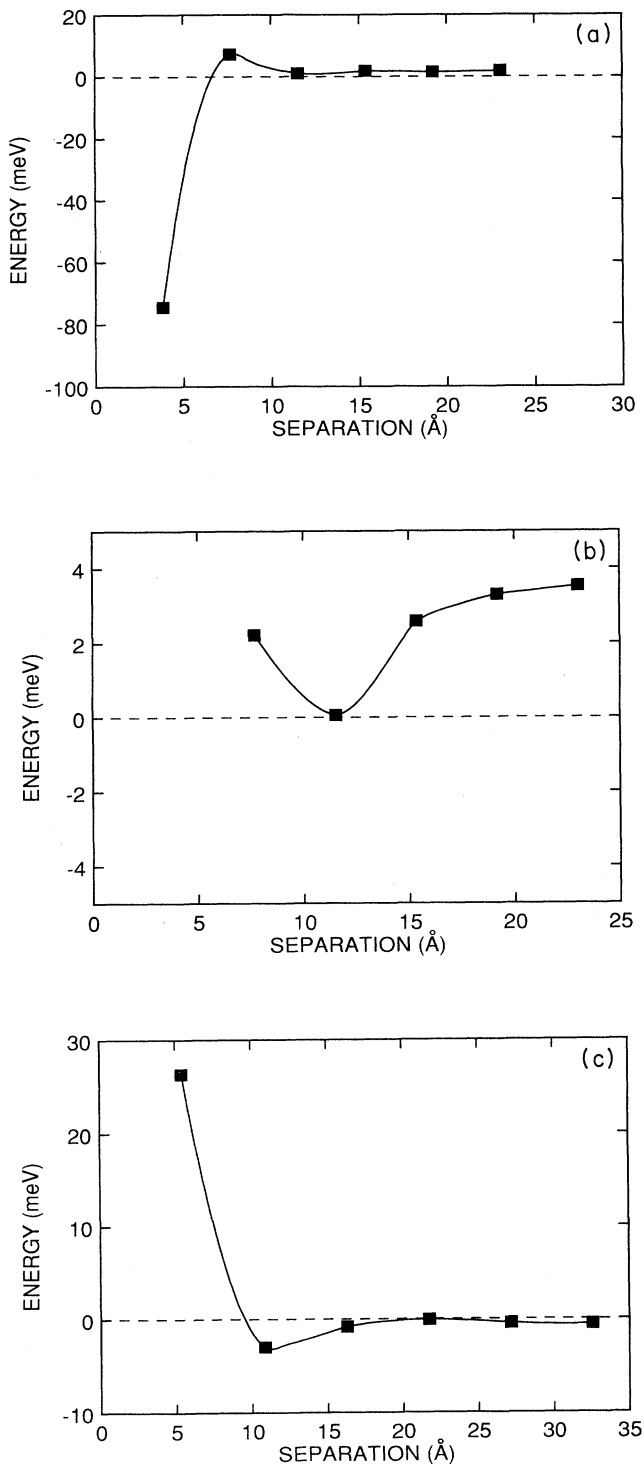
FIG. 4. Energy of indirect interaction between pairs of As-As dimers vs separation between dimer pairs. (a) Adatom separation parallel to the y axis, (b) adatom separation parallel to the z axis, and (c) adatom separation parallel to the $y = z$ axis. The square symbols represent the discrete positions of the dimer defects for which the calculations have been made. The solid lines are meant as guides for the eye.

repulsion, which dominates the indirect interaction, and therefore the indirect interaction is not shown for this separations. For increasing separations the interaction is repulsive and then tends to zero for large separations. For separations along the [010] direction the interaction for the nearest-neighbor separation is repulsive, and for increasing separations it becomes attractive and then tends to zero.

We also have examined the sensitivity of the present results to the value used here for α_d, the strength of the bond between the Si dimer atoms and to the value of the force due to the As-As dimer in the [01$\bar{1}$] direction on the atoms of the Si surface layer ($F_{[01\bar{1}]}$). We find that the relaxation energy increases with decreasing values of α_d and with increasing values of $F_{[01\bar{1}]}$. These trends are understandable, because the relaxation increases with increasing softness of the surface; in addition, the relaxation should increase with increasing $F_{[01\bar{1}]}$ because this force acts along the direction of the surface dimer. For nonzero values of α_d ($\gtrsim 0.1\alpha$) and nonzero $F_{[01\bar{1}]}$ the qualitative features of the spatial dependence of the interaction energies do not depend on the choices of these parameters. The magnitudes of the interaction energies increase with decreasing α_d and with increasing $F_{[01\bar{1}]}$ in a manner similar to that found for the relaxation energy. The results for the case in which α_d is zero and $F_{[01\bar{1}]}$ is nonzero are qualitatively different from those described above (e.g., nearest-neighbor repulsion becomes an attraction). We feel that these parameters do not provide an appropriate description of the present system because for them the force $F_{[01\bar{1}]}$ acts in the direction in which the response of the surface is unphysically soft. We feel that the parameters used in the calculations presented here provide a physically reasonable picture and qualitatively correct results for the system of As-As dimers on the Si(100) surface. In this context we would like to point out that in an early version of this work[13] we presented results for As-As dimers on the ideal unreconstructed Si(100) surface using a nonzero $F_{[01\bar{1}]}$; we now believe this to be an inappropriate description of the system.

IV. INTERACTIONS BETWEEN H ADATOMS ON THE RECONSTRUCTED W(100) SURFACE

The system composed of H adatoms on the W(100) surface is perhaps the most widely and intensively studied of all surface systems.[14] It exhibits an interesting variety of phases as functions of temperature and H coverage. At low temperature the clean W(100) surface undergoes a phase transition as shown in Fig. 5 in which alternate rows of W atoms displace along the ⟨011⟩ direction giving rise to a ($\sqrt{2} \times \sqrt{2}$)$R45°$ structure. H adatoms are located at the bridge-site positions, and at low coverage they tend to stabilize the low-temperature phase. Knowledge of the interactions between the H adatoms would give insight into surface phase transitions, vibrational linewidths for H atoms, and the adsorption and desorption processes, which are of particular interest for this system. The possibility of a repulsive interaction be-
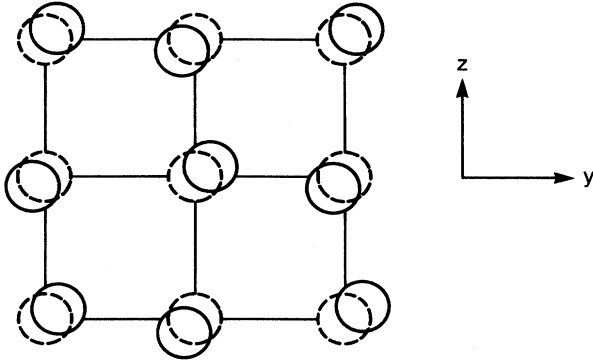
FIG. 5. The W(100) surface showing the $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction. Dashed circles indicate ideal unreconstructed atomic sites and solid circles give the reconstructed positions.

tween adatoms has been suggested[15] in order to explain the infrared data for H-adatom vibrations. To date, however, there is little microscopic information concerning the interactions between H adatoms on this surface.

In the present study we use a force-constant model with nearest-neighbor and next-nearest-neighbor central-force interactions. Such a model has been used previously as a basis to study surface stability[16] and surface phase transitions.[17] The interatomic potential when expanded to harmonic order is written

$$V = \sum_{i\neq j} [\alpha_{ij}(dR_{ij})+\tfrac{1}{2}\beta_{ij}(dR_{ij})^2] , \qquad (23)$$

where the α_{ij} and β_{ij} are the first and second derivatives, respectively, of the W-W pair potential, and dR_{ij} are the deviations from the equilibrium separation R_{ij}^0 between atoms i and j. The values of the force constants[18] which give a good fit to the bulk dispersion relations are $\alpha_1/R_1^0 = (-0.04 \text{ THz}^2)M$, $\beta_1=(6.11 \text{ THz}^2)M$, $\beta_2=(4.37 \text{ THz}^2)M$, and $\alpha_1/R_1^0 = -\alpha_2/R_2^0$, where $n=1,2$ represent the first and second neighbors which have separations R_1^0 and R_2^0, respectively. Here M is the mass of the W atom, and 1 THz$=4.132$ meV.

We have introduced[19] a model for the surface force constants of the clean reconstructed W(100) surface at low temperature by fitting recent accurate total-energy calculations[20] for this surface. The changes in the electronic energy accompanying the surface reconstruction and relaxation are found to involve mainly the first few layers. In our treatment the central potentials between the two surface atoms $[u(r)]$, atoms in the first and second layers $[v(r)]$, and those in the first and third layers $[w(r)]$ are changed from their bulk values. Then the dynamical matrix is given in terms of the reconstructed geometry and the first and second derivatives of these potentials (u', u'', etc.).

Total-energy calculations have been made for several high-symmetry distortions in which surface atoms only are displaced from their equilibrium positions. These distortions include a uniform displacement of the surface layer perpendicular to the surface, a distortion of the sur-

face atoms along [011] in which the two atoms in the unit cell move out of phase, and a motion in which the displacements of the surface atoms are rotated from the [011] direction to the [010] direction. The force constants are determined by equating the energies obtained from the total-energy calculations with the corresponding expressions obtained from the dynamical matrix. Although there is not yet enough information available from the total-energy calculations to determine a unique set of surface force constants, we find that the qualitative features of the surface vibrational modes and the surface vibrational correlation functions are not significantly affected by modest variations of the force constants which satisfy the constants imposed by the total-energy results.

A detailed discussion of the fitting of the force constants will be given elsewhere. The force constants used in the present calculations[21] are $u''=(-0.14 \text{ THz}^2)M$, $v_1''=(11.7 \text{ THz}^2)M$, $v_2''=4.75 \text{ THz}^2 M$, $w''=7.5 \text{ THz}^2 M$, and the atomic displacements from the ideal unreconstructed positions are taken to be 0.18 Å from recent experimental[14] and theoretical[20] studies. Here v_2'' is the force constant for the nearest neighbors which in the unreconstructed positions are located perpendicular to the direction of the reconstruction, and v_1'' is for the other nearest neighbors. We have found that the inclusion of the strain parameters u', v', and w' does not have significant effects on the correlation functions. This set of parameters satisfies the constraints given by the total-energy results and is in overall agreement with available experimental data. Among the important features of the force constants which are given by the total-energy conditions are that the interlayer force constants corresponding to vibrations perpendicular to the surface are stiffened and that those for vibrations in the surface plane perpendicular to the [011] direction are softened as compared to the bulk values.

The interaction of the H adatom with the substrate W atoms has been estimated by Roelofs and Ying,[23] who compared the results of numerical studies of a lattice-gas Hamiltonian representing the H/W(100) system with experimental data for the phase diagram as a function of temperature and coverage. For the reconstructed surface they estimated that the projection onto the surface plane of the force of the H atom on the two W atoms being bridged is ≈ 0.2 eV/Å and that the projection of the force is directed between the atoms. They estimated that the force on the W atoms perpendicular to the surface and also the forces on other W atoms are small. In the present work we take the force of the H atom on the W atoms to be in the surface plane and to be 0.2 eV/Å, and we neglect the other smaller forces. The relaxation energy in Eq. (21) and the interaction energy in Eq. (20) have been calculated using the methods discussed above.

The relaxation energy for a H adatom in the bridge site for which the two W atoms being bridged are pinched together in the reconstruction (see Fig. 5) is -10.9 meV, and that for which the two W atoms are moved apart from their unreconstructed positions is -10.4 meV. Thus in both cases the relaxation energy tends to increase the binding of the H in the bridge site as expected, and

the relaxation energy is approximately 5% larger for the site with pinched W atoms. The displacement of the W atoms from their equilibrium positions as a result of the relaxation is found to be ~0.05 Å, which indicates that the harmonic approximation is adequate in the present treatment.

The interaction energy between H adatoms separated along the [010] direction is shown in Fig. 6. Note that the interaction for adatoms in nearest-neighbor bridge sites is repulsive and is about 11 meV in magnitude. In this nearest-neighbor geometry the relaxations of the W surface atom caused by each of the two neighboring H adatoms oppose one another, and this results in a strong nearest-neighbor repulsion between the adatoms. The H adatom on the bridge site switches the reconstruction of the neighboring W atoms from the [011] direction back to the [010] directions by pinching the two nearest-neighbor W atoms toward it. The W atom which is shared by two nearest-neighbor H adatoms thus is in a frustrated state, which leads to the strong nearest-neighbor repulsion between the H adatoms. The local transformations of the W atoms around H adatoms which are next nearest neighbors are both along the [010] direction and thus enhance one another leading to an attractive interaction for this separation.

Other interesting adatom separations are shown in Fig. 7, and the corresponding interaction energies are given in Table I. There the interaction energy between a H atom at site 1 with a H adatom at other sites (2, 2', etc.) is given. The interaction between a H at site 1 with that at site 2 is repulsive and about one-third of the magnitude as that for nearest neighbors along the [010] direction. For greater separations (2', 2'', etc.) the magnitude of the interaction falls off. The interaction between H atoms at sites 1 and 3 is attractive and becomes repulsive as atom 3 is moved along the [010] axis to positions 3', 3'', etc.

Although all of the qualitative features of the interaction between H adatoms on W(100) surfaces are given by
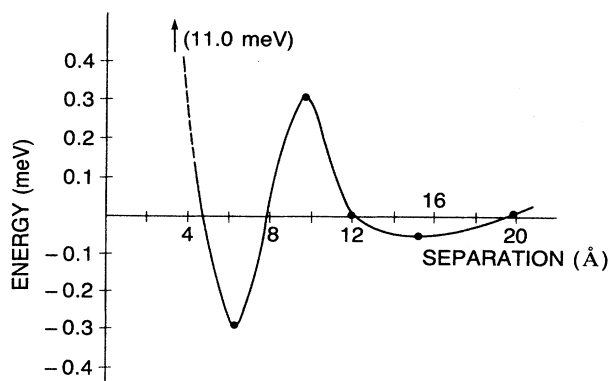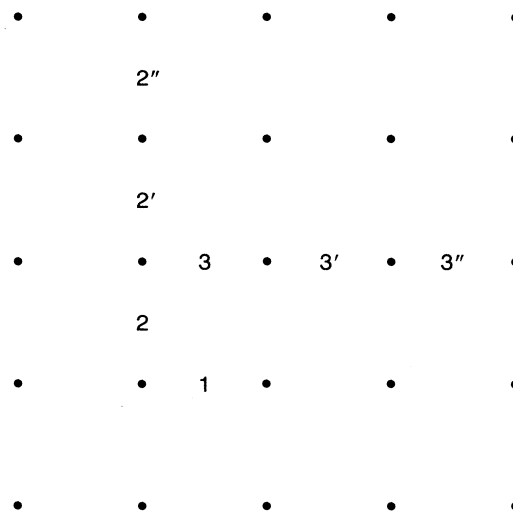

FIG. 7. Sketch indicating numbered positions of sites of H adatoms discussed in the text. The solid dots give the positions of the W surface atoms in the unreconstructed geometry.

the present treatment, some quantitative details may be affected by the approximations used here. The feature of the dynamical matrix to which the interactions are most sensitive is the energy for in-plane vibrations perpendicular to the [011] direction because this determines the softness of the surface in a direction which has a component along both the $\hat{y}$ and $\hat{z}$ directions. At present we can only estimate this curvature from total-energy results.[22] Analysis of experimental data[23] suggests the possibility of a lower barrier for this rotation. We find that by lowering this barrier the magnitude of the adatom-adatom interactions increases but that the spatial dependence remains unchanged; thus, for example, the oscillatory dependence on separation given in Fig. 6 is unchanged. A related issue is that if the small vertical component of the force of the H adatoms on the W atoms is included or if the small interactions of the H with W atoms other than those being bridged are included, then the strength of the adatom-adatom interaction also is increased.

We have seen that the phonon-mediated interactions between H adatoms on the reconstructed W(100) surface

FIG. 6. Interaction energy between two H adatoms on the reconstructed W(100) surface as a function of separation between the adatoms along the $\hat{y}$ direction. Solid dots show calculated energies at bridge sites, and the curve is given as a guide for the eye. The lattice constant of the unreconstructed surface is 3.16 Å. Note that the point at nearest separation is off scale as indicated in the figure.

TABLE I. Interaction energies corresponding to the atomic locations shown in Fig. 7. The interaction energy is that between the atom numbered 1 and the second atom (2, 2', etc.) shown in the first column of the table.

H position	Interaction energy (meV)
2	+3.3
2'	−0.3
2''	~0
3	−2.9
3'	+1.1
3''	+0.3

are appreciable in magnitude, that they can be both attractive or repulsive depending on the adatom-adatom separation, and that they differ along different directions on the surface. The dominant feature of the interactions is a relatively strong repulsion for nearest-neighbor sites. This interaction is sufficiently great (≈ 100 K) that it should influence surface phase transitions, H vibrational linewidths, and adsorption and desorption processes. We note that the repulsion between atoms 1 and 2 in Fig. 7, which is given in Table I, is consistent with a repulsion which Woods et al.[24] have found to be necessary to fit the optical mode of asymmetrical stretch vibration of H on W(100) in recent electron-energy-loss spectroscopy experiments.

Recently Sugibayashi et al.[25] have used Monte Carlo techniques to obtain results for the interactions between H adatoms adsorbed on the low-temperature reconstructed W(100) surface based on a phenomenological model of the substrate combined with a lattice-gas approach for the H adatoms. On a qualitative level they also find a strong nearest-neighbor repulsion, changes of sign of the interaction with separation, and a dependence of the interaction on direction of the adatom-adatom separation with respect to the surface. Our work, on the other hand, is based on a detailed quantitative treatment of the lattice dynamics of the reconstructed surface, and therefore the results of the two treatments for the H-H interactions to differ on a quantitative level.

V. DISCUSSION

We have presented a formalism in which the phonon-mediated interactions between adatoms on surfaces are given in terms of the detailed lattice dynamics of the surface and the interaction potential of the adatom with the rigid substrate. Unlike approaches based on elasticity theory, the present approach is valid for all adatom-adatom separations including the close separations which are of particular physical interest.

In order to demonstrate the applicability of this formalism and the dramatic deviations from continuum elasticity theory, we have applied this approach to calculate the adatom-adatom interactions for two model systems: the interactions between pairs of As-As dimers on the Si(100) surface, and the interactions between pairs of H adatoms on the reconstructed W(100) surface. We find a number of significant features which are qualitatively different than those of elasticity theory. These include the facts that the interaction depends on the direction of the adatom separation with respect to the surface, and that for a given direction along the surface the interaction can change sign or oscillate as a function of the magnitude of the separation. These properties are a result of the inclusion of local features in the lattice dynamics. As discussed in the previous sections, the sign of the interaction at close separations often can be understood in terms of the dominant forces on the substrate atoms or the constructive or destructive interference of the relaxation around each adatom and thus does not depend on the details of the model used.

Because of the rather large uncertainty in extracting the adatom-substrate interactions used in the present calculations and also because of possible anharmonic corrections in the lattice dynamics, one must be cautious in using the results for the two systems we have studied in a quantitative fashion. Nevertheless, we have found that the magnitudes of the substrate-mediated adatom-adatom interactions are significant. These interactions must be included in studying such issues as surface phase transitions, the clustering and geometry of adatoms, and surface kinetic processes such as adsorption, desorption, and diffusion.

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