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Collision complex model of molecules scattering from corrugated surfaces

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A collision complex that gives almost quantitative agreement with a large set of data for inelastic scattering of atoms and molecules from surfaces is presented. In the model, a scattering molecule and a small part of the surface form a collision complex, that decomposes in a unimolecular fashion after statistical redistribution of energy. Both molecular translation and rotation are included in the model, and the surface is represented by a small number of harmonic oscillators. The surface is considered as locally flat at the place of impact, and surface corrugation is represented by a Gaussian distribution of local normal directions. Analytical solutions of simple integrals clearly illustrate the functional dependence on the principal parameters: translational energy, scattering angle, surface temperature, the relative size of the surface directly interacting with a scattering molecule, and the active degrees of freedom. Angular distributions for atoms, diatomic and polyatomic molecules scattering from metals, graphite and liquid surfaces are shown to be in good agreement with experimental results at thermal translational energies, and at least up to 0.5 eV. The model provides a simple and useful way to interpret and inter-relate experimental results, and makes it possible to evaluate the total information content in experimental data. © 1995 American Institute of Physics.

I. INTRODUCTION

Scattering of molecular beams from surfaces is a well-known technique for studies of energy transfer in gas-surface interactions.^{1,2} For atom collisions with surfaces, angular distributions, and velocity distributions for the scattered species are the primary sources of information on the surface interaction. For molecules, measurements of internal energy distributions can also contribute to the understanding of the scattering dynamics. Light species as helium or hydrogen are likely to scatter elastically, and measured distributions can be used to deduce information about the gas-surface interaction potential. In particular, helium scattering has during recent years developed into a powerful surface sensitive technique. Heavier species have a small probability to scatter elastically from surfaces and the outcome is instead dominated by inelastic processes, which leads to either scattering or trapping. Scattering data still contain information about the gas-surface interaction potential but the information is mixed with effects due to energy transfer.

A large body of data¹ on inelastic surface scattering of atoms and molecules indicate that in general energy exchange in the normal direction is far more efficient than in the tangential direction. The energy transfer efficiency is influenced by the phonon spectrum of the surface, and the possibility of multiple collisions. In case of molecules, energy transfer involves not only surface phonons and molecular translation, but also internal degrees of freedom. Energy transfer in the tangential direction does, however, take place and is a direct indication of corrugation of the gas-surface interaction potential. This corrugation can originate in the inherent surface structure, but may also be caused by system dynamics. The incident energy will determine how far a particle penetrates into the surface plane, and the corrugation will therefore be energy dependent. Thermal motion of the surface atoms leads to increased corrugation, and a particle may also disturb the surface structure at impact and itself

“induce” corrugation. Experimental data from inelastic surface scattering are nontrivial to interpret since these different contributions are not easily separated. We will in this study address the question what can be learned from the experimental observation of inelastic collisions, and to what extent the different contributions can be separated.

Several theoretical approaches have been used to model the interaction between gas species and surfaces in the inelastic regime.³ Classical trajectory calculations are often able to give semiquantitative agreement with experimental data, and the technique is an important tool for increasing the understanding of the dynamics for a particular scattering system. Muhlhausen *et al.*⁴ experimentally investigated argon and nitrogen scattering from Ag[100] and compared with stochastic trajectory calculations. Three different gas-surface interaction potentials were applied, and reasonable agreement with experimental angular distributions were obtained with one of the potentials. Muhlhausen *et al.*⁵ were also able to find a potential that gave good agreement with both experimental angular distributions and rotational energy distributions for the NO/Ag[111] system. In a recent study, Barker and Rettner⁶ have also determined an empirical potential energy function for Xe/Pt[111], which is consistent with a wide range of experimental data. It is, however, difficult to determine how much information about the potential that may be extracted even from a successful comparison with experimental data. The approach is also complicated by the need to evaluate a large number of potentials, which may be difficult due to the complexity of the calculations.

In general, much simpler descriptions of the dynamics are at least qualitatively successful. One important model is the hard cube model,⁷ in which a surface interaction is treated as an impulsive collision with momentum transfer taking place in the surface normal direction. The model has been extended to include exchange of parallel momentum, which improve the agreement with experimental data consid-

erably. Corrugation has been introduced by using a sinusoidal formed surface⁸ and also by assuming the surface to be composed of overlapping spheres.^{9,10}

In this study, we show that another simplified model, the collision complex model, can give almost quantitative agreement with a large set of experimental data. In the model, a surface scattering event is treated as the formation of a collision complex between a gas species and a small part of the surface, followed by a unimolecular decomposition. The model has already been shown to give good agreement with experimental rotational energy distributions. We used the model to simulate “rotational rainbows” in NO/Ag[111] scattering,¹¹ and the limitation of the rotational temperature when the surface temperature is increased in NO/graphite scattering.¹² In particular, the model explains the appearance of both “rotational rainbows” and the dependence of rotational temperature on surface temperature as due to angular momentum restrictions. The surface was treated as perfectly flat in these previous studies, and the model then is sufficiently simple that closed-form analytical solutions can be obtained. These solutions clearly illustrates the functional dependence on the principal parameters; the incident translational energy, incident scattering angle, surface temperature, the relative size of the surface directly interacting with the scattering species, and the number of active degrees of freedom.

The flat surface approximation is not valid when angular distributions are considered since the distributions are sensitively depending on the surface corrugation. We show in this study that good or almost quantitative agreement with experimental data is obtainable when we include surface corrugation into the collision complex model. We use a new approach where the surface corrugation is represented by a Gaussian distribution of local normal directions. We also make a comparison between the Gaussian corrugation model and the “sinus-shaped” and “capped sphere”-type corrugations previously used as extensions of the hard-cube model.^{8–10}

We apply the model to angular distributions for atoms, diatomic molecules, and polyatomic molecules scattering from surfaces. We consider metal surfaces, graphite, and liquid surfaces, and investigate the problem of extracting information on the interaction potential from experimental results. We only consider data without indications of rainbow scattering, i.e., surface structure is less important compared to other factors given corrugation. We show that effects of energy transfer and interaction potential are partly separable and that important but limited information can be extracted from well-resolved experimental angular distributions. The study indicates that the model may provide a simple and useful way to interpret and inter-relate experimental results for seemingly different systems. The model rationalizes experimental results into quantitative information, and it also makes it possible to evaluate the total information content in the experimental data.

The article is organized in the following way. The collision complex model is described in the next section, and corrugation models are introduced in Sec. III. In Sec. IV, the model is applied to experimental angular distributions for a

few systems, followed by a discussion in Sec. V. The main conclusions from this study are finally given in Sec. VI.

II. THE COLLISION COMPLEX MODEL

The model has been presented and applied to rotational energy distributions elsewhere.^{11,12} The basic idea of the model is to consider an incoming molecule and a small surface domain as a closed system that interacts strongly during a collision. Energy is statistically redistributed among the accessible degrees of freedom within the system, while no energy is exchanged with the surrounding surface. A scattering molecule and a small part of the solid surface thus form a collision complex and the departure from the surface is treated as a unimolecular decomposition of this complex.^{13,14} The final energy and angular distribution functions are derived from the classical densities of states of the active degrees of freedom. This makes the calculations very simple, and atoms and molecules scattering from surfaces are easily treated as will be seen in the following.

We represent the surface by a small set of harmonic oscillators. The number of oscillators can be thought to correspond to the relative number of surface atoms directly participating in an interaction. For a set of S harmonic oscillators, the density of states is

$$\rho(E_{\text{osc}}) = \frac{E_{\text{osc}}^{S-1}}{(S-1)! \prod_{k=1}^S h \nu_k}, \quad (1)$$

where E_{osc} is the total energy of the oscillators, h Planck's constant and ν_k the frequency of the k th oscillator.

Throughout this study we will always treat the surface as flat, or “locally flat” when surface corrugation is introduced as described in the next section. The translational degrees of freedom perpendicular to the normal direction are therefore conserved during a collision. The density of states for the active one-dimensional translation is

$$\rho_{\text{trz}}(E_{\text{trz}}) = \frac{(2m)^{1/2}}{h E_{\text{trz}}^{1/2}}, \quad (2)$$

where E_{trz} is the translational energy in the surface normal direction and m is the mass of the scattering particle. We consider a flux across a transition state surface, f_{TS} , and the translational motion therefore has to be weighted with the velocity. The positive flux out from the surface then simply becomes,

$$f_{\text{TS}} = \frac{1}{h}. \quad (3)$$

For atom scattering from a flat surface, only one translational degree of freedom and the densities of states for the surface oscillators have to be considered. We place the transition state far away from the surface so that the interaction potential can be approximated to zero, which simplifies the following derivations. The general form of the distribution function for a final energy ϵ is obtained from the following expression:

$$P_A(\epsilon) = \frac{\rho_A(\epsilon)\rho_B(E-\epsilon)}{\int_0^E d\epsilon \rho_A(\epsilon)\rho_B(E-\epsilon)}. \quad (4)$$

In case of atom scattering, the distribution function for the translational energy in the surface normal direction, E_{trz} , is then given by

$$F(E_{\text{trz}}) = \frac{f_{\text{TS}}\rho_{\text{osc}}(E-E_{\text{trz}})}{\int_0^E f_{\text{TS}}\rho_{\text{osc}}(E-E_{\text{trz}})dE_{\text{trz}}} = \frac{S}{E^S}(E-E_{\text{trz}})^{S-1}, \quad (5)$$

where E is the total energy of the collision complex.

To treat a molecule scattering from a flat surface, we have to introduce the density of states for internal degrees of freedom. In this study, vibrational and electronic states are conserved in the calculations. This is well motivated when we deal with thermal energies where experimental data indicate that coupling to these degrees of freedom is small or negligible. We represent the molecule by a rigid rotor. In case of linear molecules, only one rotational degree of freedom is active since the flat surface makes the angular momentum along the surface normal become conserved. The density of states for a one-dimensional rotation is

$$\rho_{\text{rot}}(E_{\text{rot}}) = \left(\frac{2I}{\hbar^2 E_{\text{rot}}} \right)^{1/2}, \quad (6)$$

where I is the moment of inertia and $\hbar = h/2\pi$. For a nonlinear molecule, one rotational degree of freedom is added and we instead use the density of states for a two-dimensional rotation

$$\rho_{\text{rot}}(E_{\text{rot}}) = \frac{2I}{\hbar^2}. \quad (7)$$

Since more than two densities of states corresponding to active degrees of freedom are involved, we need to obtain combined densities of states of different degrees of freedom. For any system which can be separated into two independent subsystems of densities of states ρ_A and ρ_B , the total density of states is given by

$$\rho_{A+B}(E) = \int_0^E \rho_A(\epsilon)\rho_B(E-\epsilon)d\epsilon, \quad (8)$$

where E is the total energy available. We combine the density of states for rotation and the surface oscillators,

$$\begin{aligned} \rho_{\text{rot+osc}}(E_{\text{rot}}+E_{\text{osc}}) \\ = \int_0^{E_{\text{rot}}+E_{\text{osc}}} \rho_{\text{rot}}(\epsilon)\rho_{\text{osc}}(E_{\text{rot}}+E_{\text{osc}}-\epsilon)d\epsilon. \end{aligned} \quad (9)$$

The distribution function for E_{trz} is then obtained as

$$\begin{aligned} F(E_{\text{trz}}) &= \frac{f_{\text{TS}}\rho_{\text{rot+osc}}(E-E_{\text{trz}})}{\int_0^E f_{\text{TS}}\rho_{\text{rot+osc}}(E-E_{\text{trz}})dE_{\text{trz}}} \\ &= \frac{S+A}{E^{S+A}}(E-E_{\text{trz}})^{S+A-1}, \end{aligned} \quad (10)$$

where

$$A = \frac{1}{2} \quad \text{linear molecule,}$$

$$A = 1 \quad \text{nonlinear molecule.}$$

The obtained equation also holds for atom scattering when $A=0$ [compare with Eq. (5)]. The final angular distribution is found from the combination of E_{trz} with the conserved momentum parallel to the surface plane. The angular distribution $F(\theta_f)$ is found from

$$F(\theta_f)d\theta_f = F(E_{\text{trz}})\frac{dE_{\text{trz}}}{d\theta_f}d\theta_f. \quad (11)$$

The scattering geometry gives

$$E_{\text{trz}} = E_{\text{tri}} \frac{\sin^2 \theta_i}{\tan^2 \theta_f}, \quad (12)$$

where E_{tri} is the total initial translational energy and θ_i is the incident angle. From the last three expressions we derive the following expression for the final angular distribution:

$$F(\theta_f) \propto \frac{\sin^2 \theta_i}{E^{S+A} \cos^2 \theta_f \tan^3 \theta_f} \left[E - E_{\text{tri}} \frac{\sin^2 \theta_i}{\tan^2 \theta_f} \right]^{S+A-1}, \quad (13)$$

where

$$A = 0 \quad \text{atom,}$$

$$A = \frac{1}{2} \quad \text{linear molecule,}$$

$$A = 1 \quad \text{nonlinear molecule.}$$

Before we investigate the behavior of this function we need to specify the total energy E available for the collision complex. We will in this study give each surface oscillator an energy $k_B T_S$. This approximation was seen to be sufficient in our previous studies of rotational energy distributions.^{11,12} The incident translational energy is given a fixed value and the rotational temperature is set to 0 K. The total energy then becomes

$$E = S k_B T_S + E_{\text{tri}} \cos^2 \theta_i. \quad (14)$$

The approximation of 0 K translational and rotational temperature is justified when dealing with supersonic molecular beams where these temperatures in general are below 50 K. The validity of the approximations is easily tested by integration over appropriate energy distributions.

The only adjustable parameter in Eq. (13) is the number of harmonic oscillators, S , describing the surface. Figure 1 shows the effect of S on angular distributions for scattering of atoms with an incident angle of 45° . The S value is varied between 1–5 oscillators, which is the relevant range used in this study. For one surface oscillator, the angular distribution is cut off at an angle corresponding to the total energy available for the complex, while a higher S value results in a continuous function through the distribution maximum. At a surface temperature of 0 K the distribution is shifted towards the tangential direction when the number of oscillators increases, as shown in Fig. 1(a). The reason is that more energy on the average is transferred from translational energy in the surface normal direction to the initially cold surface oscillators. The shift of the distribution is much smaller in

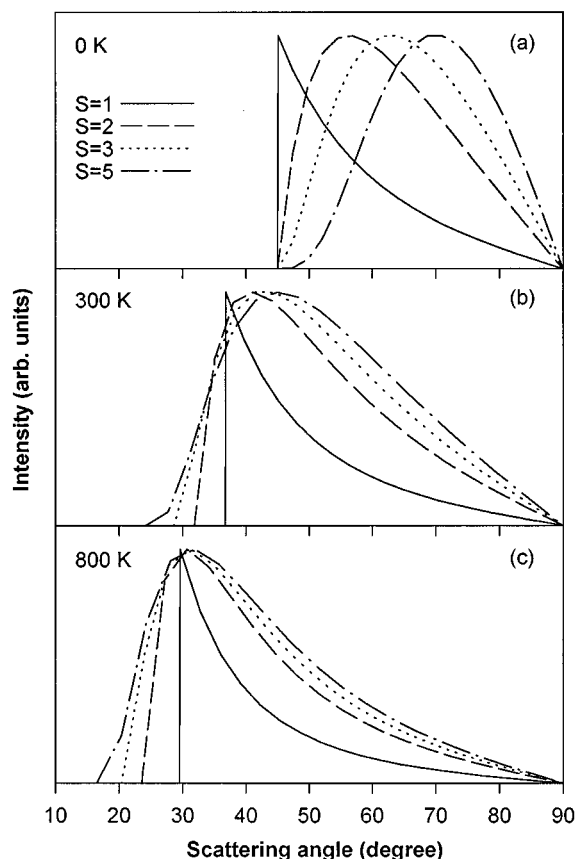


FIG. 1. Angular distributions for atom scattering from a flat surface simulated with the collision complex model. The effect of the number of surface oscillators, S , in the model is shown at the surface temperatures 0, 300, and 800 K. The S value corresponding to each curve is indicated in the top panel. The incident angle, θ_i , was 45° and the translational energy, E_{tr} , was 65 meV. The specular direction is indicated in the lowest panel.

Fig. 1(b), where the surface oscillators initially have an energy corresponding to 300 K. At high surface temperature, the distributions are all shifted towards the normal direction as illustrated in Fig. 1(c). A net transfer of energy from the surface to the atom thus takes place in this case. It is also seen that the S value influences the width of the distribution. The change of the width with S is largest when going from one to two oscillators and become less pronounced at higher S values.

Figure 2 illustrates the importance of rotational degrees of freedom for the angular distributions. In Fig. 2(a), atom scattering is compared with linear and nonlinear molecules scattering from a surface with one oscillator. We see that introduction of the initially cold rotational degrees of freedom have the same effect as adding cold surface oscillators. In both cases energy is transferred from normal translation into the cold degrees of freedom, resulting in a shift of the distribution towards the tangential direction. The effect is largest at small S values and becomes less apparent when the number of oscillators is increased, as illustrated in Figs. 2(b) and 2(c). The difference between the distributions is rather small in Fig. 2(c) where $S=3$. Addition of more degrees of freedom influences the result less in this case, just as we concluded when adding more surface oscillators in Fig. 1(c).

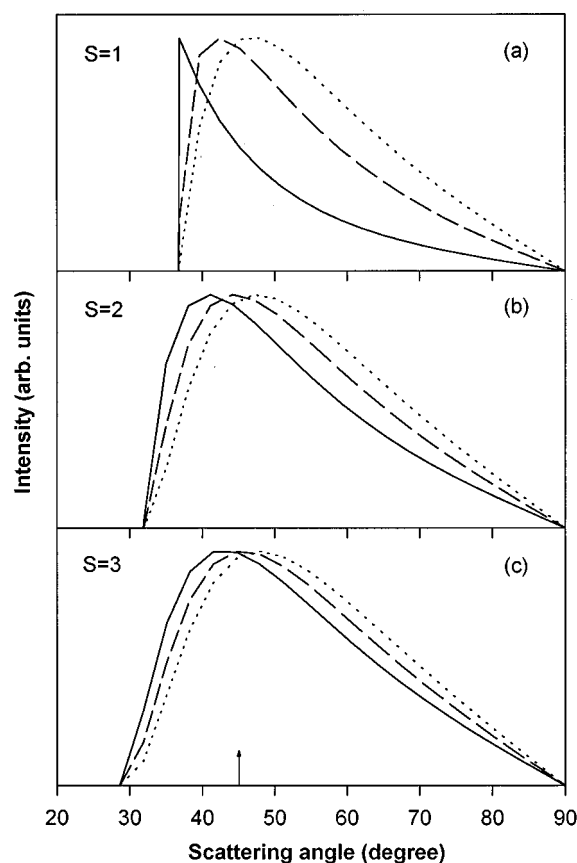


FIG. 2. Importance of internal degrees of freedom on angular distributions: scattering of atoms (—), linear molecules (---), and nonlinear molecules (····). The S value used in the model is indicated in each panel. The scattering conditions were $\theta_i=45^\circ$, $E_{\text{tr}}=65$ meV, $T_s=300$ K.

The model indicates that experimental distributions should be shifted towards the tangential direction when internal degrees of freedom are excited in surface scattering. We may also expect that the effect of rotational degrees of freedom is larger for small molecules that interacts with a small surface region.

The collision complex model in the form given above is useful for qualitative comparison with experimental data. The model, however, fails to quantitatively simulate angular distributions and angle-resolved velocity distributions, and this is at least partly due to lack of surface corrugation. Even for surfaces as graphite or Ag[111], which are often referred to as flat, do angular distributions show considerable effects of corrugation. The flat surface approximation normally fails completely for scattering angles smaller than the specular direction, and an infinite final translational energy is needed for a molecule with an incidence angle larger than 0° to be scattered into the surface normal direction. To improve the comparison with experimental results, we will therefore introduce corrugation in the following.

III. SCATTERING FROM CORRUGATED SURFACES

In the collision complex model, the interaction in the surface normal direction is treated as a strong collision. When we consider parallel momentum one approach could

be to model the interaction parallel to the surface as a “weak collision,” i.e., the parallel momentum partly participates in the statistical energy redistribution. Weak collisions have been discussed in gas-phase kinetics.¹⁵ The detailed shape of the energy transfer probability function for a gas-phase collision is generally not known, and several types of functions have been tested. Exponential functions and shifted Gaussian functions have been shown to be useful approximations. For high velocities and low surface temperatures, this is in case of surface scattering similar to a friction force parallel to the surface since only energy loss transitions have to be considered. The cause of parallel momentum exchange is, however, surface corrugation, and we therefore want to find another approach where parallel momentum exchange is directly connected to the corrugation of the gas–surface interaction potential. We decide to introduce corrugation into the collision complex model in the same way as has previously been done for the hard cube model.^{8–10} The main extension of the collision complex model then is to treat the surface as *locally* flat, instead of macroscopically flat. This means that the direction of the local normal at the place of impact may change depending on the position on the surface, but the derivations for the flat surface hold for each individual scattering event. We first make general derivations for corrugated surfaces in the following. We will thereafter introduce local normal distributions corresponding to different surface structures or dynamical behavior. We introduce a new “Gaussian” corrugation model, and compare with previously used models.

A. General derivations for collision complex model with corrugation

We assume that the surface is locally flat, i.e., the local point of impact is felt as flat by the incoming species. This makes it possible to use all equations derived in Sec. II. We introduce a deviation angle α , which is the angle between the local normal at the point of impact and the macroscopic surface normal. The α value is taken to be positive if the local normal is directed away from the incoming direction. The only changes introduced in the previously given formulas are then to replace θ_i by $(\theta_i + \alpha)$, and θ_f by $(\theta_f - \alpha)$ and the angular distribution becomes

$$F(\theta_f, \alpha) \propto \frac{\sin^2(\theta_i + \alpha)}{E^{(S+A)} \cos^2(\theta_f - \alpha) \tan^3(\theta_f - \alpha)} \times \left[E - E_{\text{tr}} \frac{\sin^2(\theta_i + \alpha)}{\tan^2(\theta_f - \alpha)} \right]^{S+A-1}, \quad (15)$$

where

$A=0$ atom,

$A=\frac{1}{2}$ linear molecule,

$A=1$ nonlinear molecule.

This equation again holds for active translation and rotation while vibrational and electronic excitations are not allowed. The surface corrugation can be described by a distribution of local normal directions $F(\alpha)$. When a type of surface corrugation has been chosen, $F(\theta_f, \alpha)$ is integrated over $F(\alpha)$ to obtain the resulting angular distribution

$$F(\theta_f) = \int F(\alpha) F(\theta_f, \alpha) d\alpha. \quad (16)$$

We neglect integration over initial energy terms, as previously done for flat surfaces in Eq. (14), and the total energy E available for redistribution then is

$$E = S k_B T_S + E_{\text{tr}} \cos^2(\theta_i + \alpha). \quad (17)$$

The active translational energy, and the total energy, will now vary in the calculations depending on the α value at the place of surface impact. The momentum parallel to the macroscopic surface therefore partly participate in the energy redistribution, and the degree of participation depends on α . The model thus includes effects of parallel momentum transfer, which was not the case in the flat surface approximation. The angular momentum component along the macroscopic surface normal is not conserved either, which may influence rotational energy distributions.

B. Gaussian corrugation model

Our next step is to introduce the local normal distribution $F(\alpha)$. In this study, we propose a new treatment of the corrugation where the distribution of local normal directions is given by a Gaussian function

$$F(\alpha) = \exp \left[-\frac{(\alpha - \alpha_m)^2}{2\sigma^2} \right], \quad (18)$$

with α_m being the most probable α , and σ the width of the distribution. The use of a Gaussian function is an empirical approach, which can be justified by comparison with experimental data. That good comparison is obtained for a large number of systems will be shown in Sec. IV. In this study, we will only treat systems with weak or moderate corrugation and we therefore neglect effects due to final scattering angles below the surface plane, leading to multiple collisions.

Figure 3(a) illustrates the effect of sigma on angular distributions. The sharp peak shown for a perfectly flat surface ($\sigma=0$) becomes broader when σ is increased, and the distribution is extended towards the surface normal direction. The sigma value is not completely separable from the S value since they both influence the width of the distribution. However, a flux in the normal direction is easily obtained by increasing the σ value, while the same effect can not be obtained by changing the number of surface oscillators. The effect of the model parameter α_m is mainly to shift the distribution by a given angle, as shown in Fig. 3(b).

Final translational energy distributions gives additional information about the surface interaction. Figure 4 shows the mean translational energy as a function of scattering angle using the same parameter values as in Fig. 3. The effect of introducing corrugation is clearly seen in Fig. 4(a) when different σ values are used. The translational energy increases towards the normal direction for a flat surface ($\sigma=0$), and goes to infinity at $\theta_f=0^\circ$. The distributions for the corrugated surfaces instead level out at scattering angles smaller than the specular direction. On the other hand, the distributions for the flat and corrugated surfaces are very similar at scattering angles larger than the specular. The model thus predict

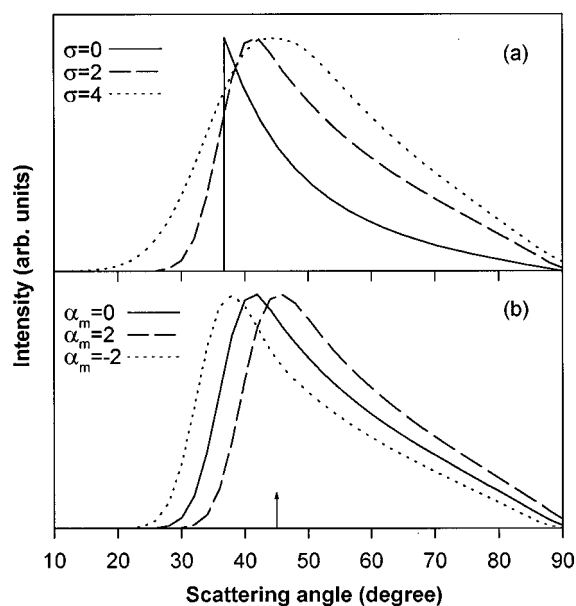


FIG. 3. Angular distributions for atom scattering from a corrugated surface described by the Gaussian model. Effect of Gaussian parameters: (a) distribution width σ (with $\alpha_m=0$), (b) most probable alpha value α_m (with $\sigma=2$). The parameter values used are indicated in each panel. The model parameter $S=1$, and the scattering conditions $\theta_i=45^\circ$, $E_{in}=65$ meV, and $T_s=300$ K.

that most information about the gas-surface interaction potential is to be found at scattering angles smaller than specular, just as is the case with angular distributions. When comparing with experimental data, the flat surface model often works well for final scattering angles larger than the angle with maximum intensity. This is also the part where experi-

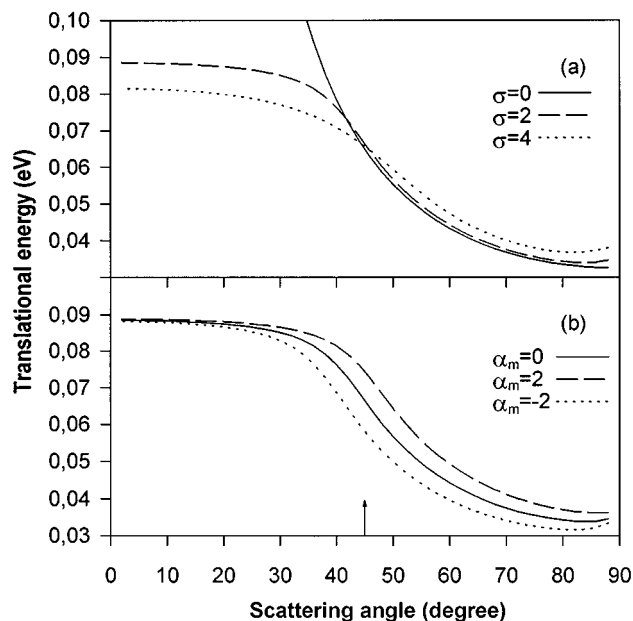


FIG. 4. Angle-resolved mean final translational energy for atom scattering from a surface described by the Gaussian model. Effect of Gaussian parameters: (a) σ (b) α_m . The parameter values are indicated in each panel, and the conditions are the same as in Fig. 3.

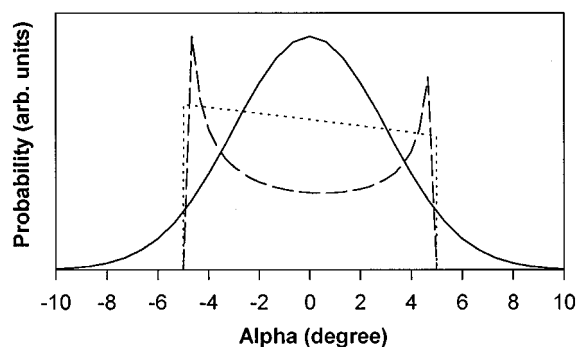


FIG. 5. Typical distribution of local normal directions $F(\alpha)$ for the Gaussian model, $\alpha_m=3$, (—) compared to distributions for two other corrugation models: sinus-shaped surface, $\alpha_m=5$, (---), and capped sphere surface, $\alpha_m=5$, (···). The incident angle, $\theta_i=45^\circ$.

mental velocity distributions indicate that a flat surface is a good approximation. At scattering angles closer to the surface normal, the intensity is dominated by species that have partly lost parallel momentum. In Fig. 4(b), we also show that the effect of α_m is a shift of the translational energy distribution, just as for the angular distribution in Fig. 3(b). The maximum energy reached at small scattering angles is mainly influenced by σ , and not by α_m .

C. Comparison with other corrugation models

Before we apply the Gaussian model to experimental data, we compare the general features of the model with results from a sinus-shaped surface⁸ and a capped sphere surface.^{9,10} The distribution functions for these models are

$$F(\alpha) = \cos(\theta_i + \alpha) \quad \text{capped sphere surface,} \quad (19)$$

$$F(\alpha) = \frac{(1 - \tan \alpha \tan \theta_i)}{\pi \cos^2 \alpha (\tan^2 \alpha_m - \tan^2 \alpha)^{1/2}} \quad \text{sinus-shaped surface.} \quad (20)$$

These models are related to the possible structure of the surface plane, and we have therefore considered the probability of hitting slopes with different directions. For a given incidence angle, the probability of hitting a surface section directed into the scattering flux is larger than for one directed away from it. The distribution functions have therefore been weighted with a factor $\cos(\theta_i + \alpha)$. In the Gaussian model, this factor has not been introduced since the corrugation treated with this model is not obviously related to surface structure, but rather to the collective response of the surface to a scattering particle. We thus make a qualitative distinction between corrugation due to static and dynamic effects, and we think that the Gaussian model may reproduce corrugation caused by system dynamics better than the structure-related corrugation models.

Typical distribution functions $F(\alpha)$ for the three models, with an incident angle of 45° , are plotted in Fig. 5. The sinus-shaped surface model peaks at α -values corresponding to the inflection points of the sinus curve. These maxima give rise to rainbow scattering, sometimes seen as two distinctive peaks in the angular distribution. The features of the

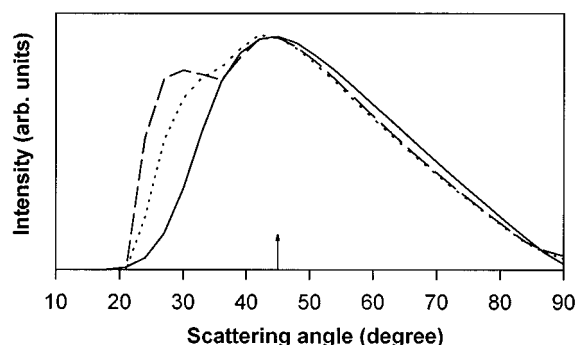


FIG. 6. Typical angular distributions for atom scattering using three different surface corrugation models: Gaussian model (—), sinus-shaped surface (---), and capped sphere surface (···). The model distributions $F(\alpha)$ used are shown in Fig. 5. The model parameter $S=1$, and the scattering conditions $\theta_i=45^\circ$, $E_{\text{in}}=65$ meV, and $T_S=300$ K.

capped sphere model is less pronounced, and is likely to give results intermediate between the two other models. The collision complex model was used with the three different corrugation models, and typical angular distributions are shown in Fig. 6, where the $F(\alpha)$ distributions from Fig. 5 were used. The different corrugation models give similar results at large scattering angles. The two structure related $F(\alpha)$ distributions result in a higher intensity closer to the surface normal compared to the Gaussian model. The sinus-shaped surface gives rise to yet another peak in this region, while the capped sphere surface results in a slower decay than for the Gaussian model.

IV. APPLICATIONS

We will in this study exemplify the use of the Gaussian corrugation model on molecules scattering from weakly or moderately corrugated surfaces. We choose experimental inelastic scattering results that show no direct sign of structure-induced corrugation, such as rainbow scattering. A combination of structure-induced and dynamics-induced corrugation factors may in some cases give better agreement with the experimental results we have chosen. Since the form of such a distribution function is at present unknown, we will make no attempts in that direction.

Factors like the geometry of the experimental setup, the detector function, and beam characteristics should be carefully considered when simulating experimental data. All these factors can in principle be included in our model, however, some of the necessary data are normally not published. In this study, we neglect effects due to beam width at the surface, beam divergence, geometry and size of detector parts, and angular acceptance of the detector. We also neglect the width of the incident velocity distributions and initial internal molecular temperature, as previously described. The effect of all these factors is to add averaging to the calculations, and the importance of them can be tested by integrating over appropriate distributions. It should be emphasized that the influence of these factors is not large enough to explain the experimental data discussed in the following. We apply the model to a few systems from the literature for

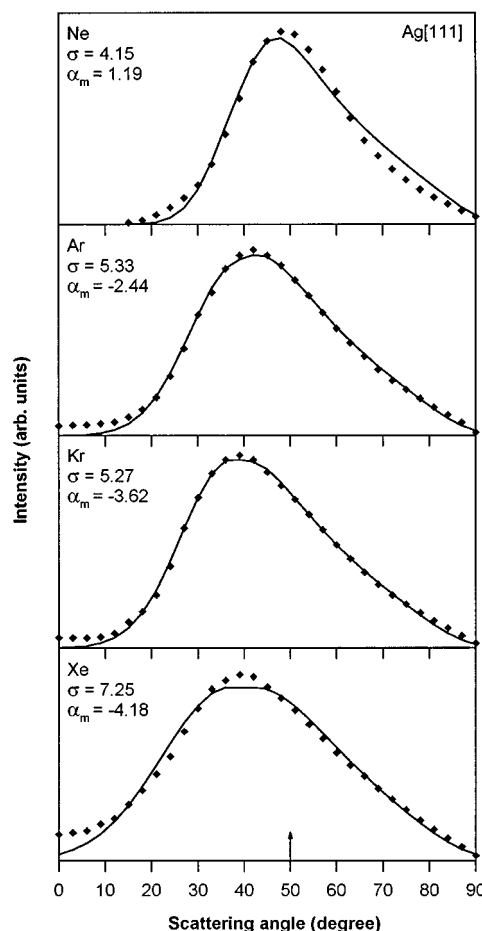


FIG. 7. Scattering of noble gas atoms from Ag[111]. Experimental data from Ref. 16 (♦), and calculated fits (—) using the Gaussian corrugation model with $S=1$. The sigma and alpha values of the best fits are indicated in each panel. The scattering conditions were $\theta_i=50^\circ$, $E_{\text{in}}=65$ meV, and $T_S=500$ K. The specular direction is indicated in the lowest panel.

which well-resolved data are available. A mass spectrometer with electron-impact ionization was used in all experiments here discussed and we therefore treat the detector as density sensitive, unless otherwise stated.

We begin by applying the collision complex model with Gaussian corrugation to scattering from the Ag[111] surface. Asada investigated scattering of noble gas atoms¹⁶ and molecules¹⁷ from Ag[111] using supersonic beams expanded from a room temperature beam source. Figure 7 shows experimental angular distributions for Ne, Ar, Kr, and Xe and fits to the distributions using one surface oscillator. One oscillator in all cases gave the best result, but fits for $S=2$ and 3 were also satisfactory. When the S value was further increased, the agreement gradually became worse. The obtained values for σ and α are indicated in each panel. The agreement is overall good and almost quantitative agreement is found in case of Ar and Kr. A contribution from a cosine distribution influences the results but has not been removed here, which in particular influences the fit of the Xe distribution that becomes too broad. The Ne distribution can not be quantitatively reproduced. We believe that the interaction is more elastic than assumed in the calculation, which may be

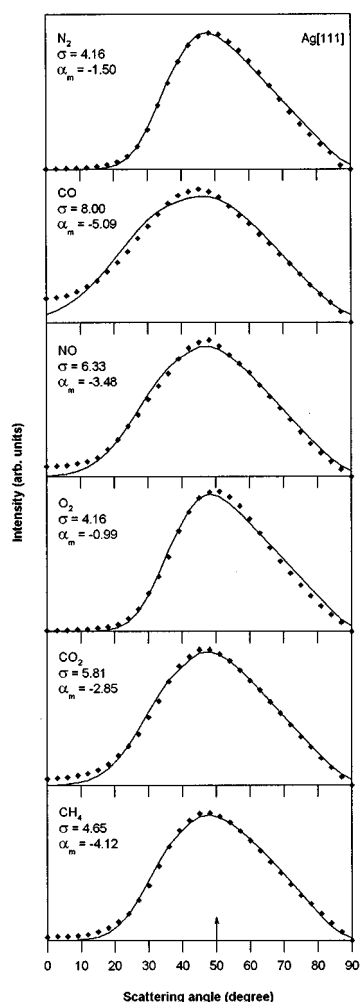


FIG. 8. Scattering of molecules from Ag[111]. Experimental data from Ref. 17, otherwise the same as Fig. 7.

expected for this rather light atom. The σ values indicate that the surface corrugation felt by the different species is of the same order. The α_m values found are low and normally negative, i.e., the angular distribution is shifted towards the surface normal. This could be a corrugation effect related to a single surface collision, but it is likely that multiple collisions with the surface also have influenced the data, in particular for the heavier species.

The agreement with experimental data¹⁷ for molecules scattering from Ag[111] is equally good as shown in Fig. 8. One oscillator was used also in this case. All diatomic molecules and CO₂ were simulated with one rotational degree of freedom, and CH₄ with two rotational degrees of freedom. Again, the fits are almost quantitatively correct, except in cases where a cosine contribution influences the data. Sigma values between 4 and 8 are found, which is in the same range as found for the noble gases. The weakest interactions like for N₂ and O₂ give small σ values, no indication of a cosine component from trapping-desorption, and α_m values close to 0°. All these factors are changed simultaneously for the other systems where stronger interaction can be expected. There is thus a clear connection between the appearance of a cosine

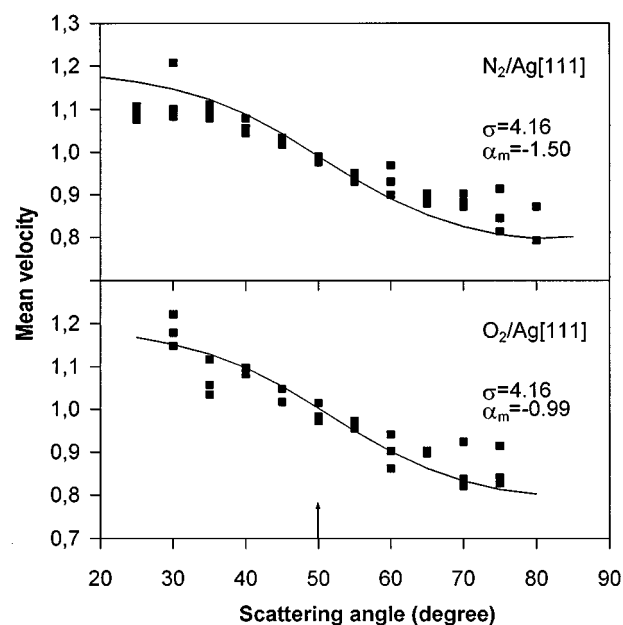


FIG. 9. Angle-resolved mean speed for N₂ and O₂ scattering from Ag[111]. Experimental data from Ref. 18 (■), where also the mean velocity is defined. Calculated distributions (—) using the Gaussian corrugation model with $S=1$, and σ and α_m values from the best fits in Fig. 8. The scattering conditions were the same as in Fig. 7.

component and the size of σ , and the distributions are simultaneously shifted towards the surface normal as shown by the α_m values. We conclude that adsorption and the strength of the gas-surface interaction potential is closely connected to the degree of corrugation for these systems.

A second independent test of the model is to simulate angle-resolved final velocity distributions. We show in Fig. 9 experimental data from Asada¹⁸ for the mean final velocity as a function of scattering angle for N₂ and O₂. The parameter values chosen are the same as found from the fits shown in Fig. 8. The distributions are well represented by the model, which shows that the model can give simultaneous agreement with both velocity and angular distributions. To summarize, we conclude that experimental data for several species scattering from Ag[111] is well reproduced with the Gaussian model. The only exception is scattering of Ne that we may identify as too elastic to be represented by a strong surface collision.

We show in Fig. 10 fits to experimental data⁴ on nitrogen and argon scattering from Ag[001]. Excellent agreement is obtained in case of thermal incident energies, and the parameter values are comparable to data for Ag[111]. At hyperthermal velocities, the model fails at large scattering angles. This may indicate that the strong collision assumption is not valid, and that too much energy is transferred to the surface in the model calculations. Another explanation may be that surface structure effects start to become more important than dynamic effects. The sigma and alpha values are also low when the incident energy is high.

The behavior of xenon scattering from the Ag[100] is illustrated in Fig. 11 where experimental data measured by Amirav *et al.*¹⁹ are compared with the model calculations.

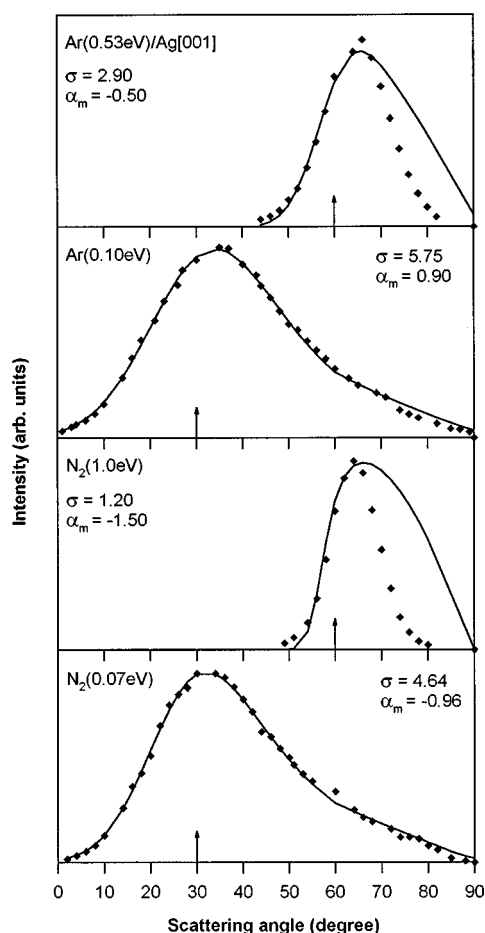


FIG. 10. Angular distributions for N_2 and Ar scattering from Ag[001]. Experimental data from Ref. 4 (\blacklozenge), and calculated fits (—) using the Gaussian corrugation model with $S=1$. The sigma and alpha values of the best fits are indicated. The translational energy and the specular direction are indicated in each panel, and $T_s=300$ K.

Xenon scattering with 2.0 eV from the surface with three different incident angles. The agreement with experimental results is good for an incident angle of 75° . When going to 60° and 45° , the agreement is not as good and the distributions resembles what was found for Ar and N_2 scattering from Ag[001] with high translational energy. In case of xenon, the data indicate that experiments with a too high translational energy in the macroscopic surface normal direction can not be quantitatively simulated. The conclusions found for the last two systems also hold for oxygen scattering from W[110]. Figure 12 shows experimental angular distributions at 0.06 and 1.36 eV translational energy.²⁰

In Fig. 13 it is shown that the collision complex model works well even for nonmetal surfaces, i.e., NO scattering from graphite.^{21,22} The graphite system is somewhat different to the metal systems that we have just discussed since the individual surface atoms are much lighter, and more than one collision with a surface atom often is necessary to reverse the momentum in the normal direction. This may contribute to the large σ values, needed to reproduce the experimental data.

We finally apply the model to scattering from liquid sur-

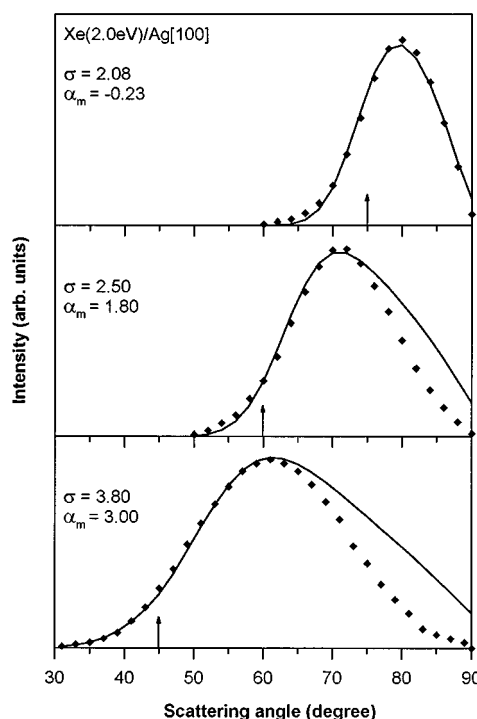


FIG. 11. Angular distributions for Xe scattering from Ag[100] with three different incident angles. Experimental data from Ref. 19 (\blacklozenge), and calculated fits (—) using the Gaussian corrugation model with $S=1$. The incident translational energy was 2.0 eV in all cases and $T_s=300$ K.

faces. Figure 14 illustrates the result for scattering of Xe from squalane (2,6,10,15,19,23 hexamethyltetracosane), experimentally investigated by King *et al.*²³ A cosine distribution was subtracted from the data. Five surface oscillators gave better agreement with experimental data compared to one oscillator, which was used for all other systems here

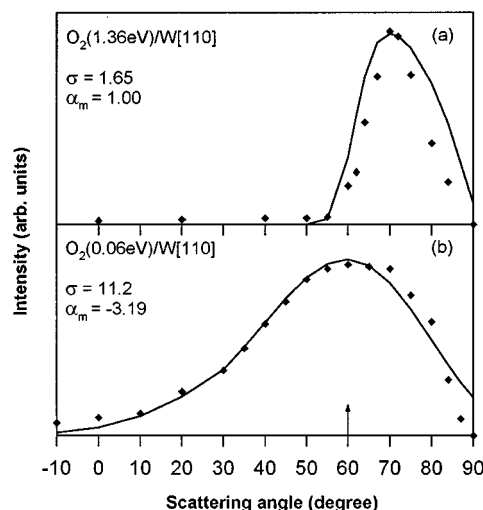


FIG. 12. Angular distributions for O_2 scattering from W[110]. Experimental data from Ref. 20 (\blacklozenge), and calculated fits (—) using the Gaussian corrugation model with $S=1$. The translational energy and the specular direction are indicated in each panel. The surface temperature was (a) 800 K, and (b) 400 K.

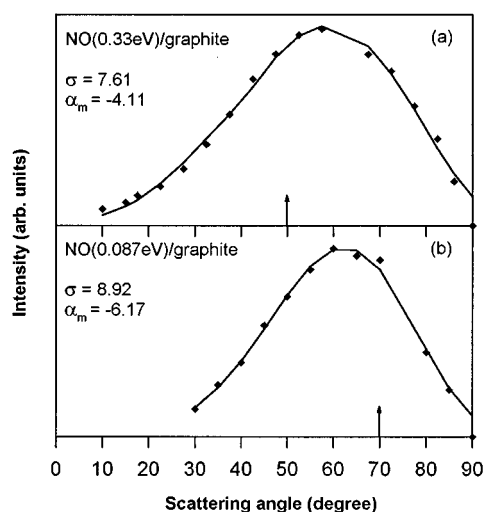


FIG. 13. Angular distributions for NO scattering from graphite. Experimental data (\blacklozenge) from (a) Ref. 22, and (b) Ref. 21. Calculated fits (—) using the Gaussian corrugation model with $S=1$. The translational energy and the specular direction are indicated in each panel. The surface temperature was (a) 600 K, and (b) 360 K.

discussed. The Gaussian model parameter values are also larger compared to the results for solid surfaces, and indicates a stronger corrugation.

V. DISCUSSION

The results indicate that the collision complex model with Gaussian corrugation may be generally applicable to molecule scattering at thermal velocities from moderately corrugated surfaces. The model give good agreement with a large set of experimental angular distributions, and makes it possible to compare seemingly different systems. The information content of the angular distributions considered here is limited, as illustrated by the fact that the simplified model is sufficient to explain the experimental data, and the information available is contained in the three parameters used to fit the distributions.

The number of oscillators, S , is related to the size of the impact region that couples strongly to the impacting gas mol-

ecule. The S value is thus a relative measure of the size of the local spot on the surface being directly involved in a collision between a gas molecule and the surface. The number of surface oscillators giving good agreement with experimental data in this study is always 1–5 oscillators. This fact illustrates that the active region always is very small. The modeling of a surface interaction as a localized event has been used to interpret experiments with impact of fast particles on surfaces, where a localized area with a higher temperature, a hot spot, is formed at impact. Recently, Danon *et al.*²⁴ studied the high degree of surface ionization of Hg impacting with energies of 4–10 eV at a Pt[111] surface, and interpreted the high degree of ionization found as being due to the formation of hot spots on the surface. Lim *et al.*²⁵ carried out trajectory calculations on Xe scattering from GaAs[110] with incident energies of 1–8 eV. They concluded that energy stays very localized during the course of an interaction also at these high energies. The collective response of the surface usually involved the impacted surface atom and only a half-dozen or so of its neighbors. Zeiri and Lucchese²⁶ also came to the conclusion that xenon scattering from W[111] interacts with a limited small number of surface atoms and forms a hot spot at high incident energy, from which energy is dissipated during a period of a few picoseconds. When we compare with the thermal conditions treated in this study, we conclude that the interaction time at low incident velocities may be longer but still on the same time scale, and it is also reasonable to believe that the energy dissipation rate is of the same order at thermal collision energies.

Except for the number of oscillators, two parameters are in general necessary to quantitatively simulate experimental angular distributions. The sigma parameter describes the average corrugation felt by the species. It is not completely decoupled from the S value. The effect is, however, not large in the relevant range $S=1$ –5 found in this study, and we therefore conclude that the σ value can be used to characterize the degree of corrugation in experimental data. We thus also conclude that the two factors corrugation and energy transfer can be at least partly separated. This decoupling between energy transfer and corrugation makes it possible to study the effect of surface temperature, incident angle, and incident velocity on the degree of corrugation. It also makes comparison between different gas/surface systems possible. The parameter describing the shift of the most probable alpha value, α_m , does not always have to be included to obtain agreement with experimental data. For systems with weak surface interactions, good agreement is found with α_m set to zero. However, in many cases the distribution is shifted towards the macroscopic surface normal direction. The reason for the shift of α_m can be a real effect of the corrugation induced by the incoming molecule. In other cases the data are certainly influenced by multiple collisions with the surface.

The assumption of statistical redistribution of energy taking place during the short interaction time with the surface does not have to be unrealistic. In gas phase collisions, statistical redistribution in a three-atomic system is often achieved if the collision complex lives for more than half a

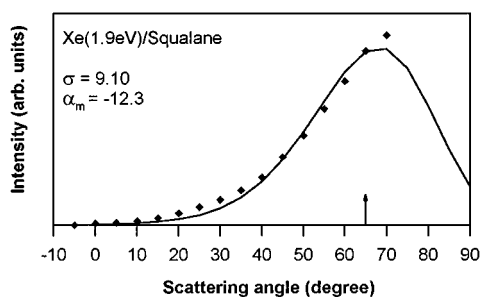


FIG. 14. Scattering of Xe from liquid squalane (2,6,10,15,19,23 hexamethyltetracosane). Experimental angular distribution (\blacklozenge) from Ref. 23 and calculated fits (—) using the Gaussian corrugation model with $S=5$. The translational energy and the specular direction are indicated, and the surface temperature was 298 K.

rotation.²⁷ In case of surface collisions, our previous studies^{11,12} show that single collision conditions are sufficient for statistical energy redistribution for NO scattering with translational energies up to 1 eV. This was also supported by trajectory calculations using a one-dimensional model with one harmonic oscillator representing the surface.²⁸ In this study, we have seen that the model can not always reproduce scattering data with translational energies of 0.5–1 eV, which may indicate incomplete energy redistribution. Also the assumption of the surface as locally flat needs some further comment. This could be understood as the potential felt by a molecule interacting with a single surface atom, but an alternative interpretation is at least important in case of scattering from graphite. This surface consists of light and relatively small surface atoms that normally have time for several vibration periods during particle impact. The direction of the local normal could therefore instead be interpreted as the resulting force vector acting on the scattering species, due to the collective response of the surface.

It is also interesting to relate the collision complex model to the cube models.⁷ In the cube model, a surface interaction is treated as a single impulsive collision with an isolated surface atom. Multiple interactions with the surface atoms are thus normally neglected. The assumption that the scattering species rebound instantaneously is definitely not valid for all systems. Certainly, impulsive scattering from a single independent surface atom may not even be sufficient to reverse the momentum of the incoming molecule. This is often solved by increasing the mass of the surface atom. The collision complex model instead rely on that the interaction time is long enough for statistical redistribution of energy to take place in the very localized region of the surface interaction, and thus relates to a collective surface response to the incoming molecule. This may be looked at as another extreme compared to an impulsive collision. It is reasonable to believe that the hard-cube model should do best at high incident energy and for systems where light species scatter from heavy surface atoms, as was stated already by Logan and Stickney.⁷ The collision complex model instead treats the opposite situation, heavy species scattering at not too high translation energies. The present study indicates that scattering of species heavier than neon and with translational energies below 0.5 eV, can be successfully treated with the model. The model is thus useful for the waste majority of relevant systems under thermal conditions. The range of systems of course overlaps a large part of the range covered by the hard cube model.

VI. CONCLUSIONS

A collision complex model that treats atom and molecule scattering from surfaces is presented. The model includes surface corrugation in the form of a Gaussian distribution of local normal directions, and almost quantitative agreement with experimental angular distributions for a large number of systems is found. Velocity distributions and angular distributions become substantially better in accordance with experimental data when a Gaussian corrugation model is used compared to the use of a flat surface approximation. Calculated angular distributions for atoms, diatomic and polyatomic

molecules scattering from metals, graphite, and liquid surfaces are shown to be in agreement with experimental results at thermal translational energies. The results demonstrate that effects of energy transfer and surface corrugation can be partly separated in angular distributions from gas–surface scattering experiments. The model is applicable for systems with a translational energy up to 0.5 eV. Above this energy dynamic effects and the formation of shock waves in the material may become important. We conclude that the model may be generally applicable for atoms and molecules scattering from surfaces with low to moderate incident energies.

Important factors favors the use of the collision complex model. The idea that statistical redistribution takes place is consistent with the dynamics for many systems at thermal energies. The model can treat internal degrees of freedom without difficulty, e.g., to simulate polyatomic molecules scattering from surfaces. It is also easy to include different experimental conditions, i.e., incident energy distributions and angular acceptance of the detector. The model may therefore provide a simple and useful way to interpret and inter-relate experimental results. The model is also easy to extend to other surface processes, such as adsorption and desorption, including dissociative chemisorption²⁹ and recombinative desorption.³⁰ We have only considered inplane scattering in this study. This is, however, no limitation of the model and also three-dimensional corrugation can be included to study out-of-plane scattering. The model should be useful for calculating joint distributions, e.g., final velocity distributions for specific rotational states, where the computer facilities often sets the limit for other methods.

ACKNOWLEDGMENT

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- ¹J. A. Barker and D. J. Auerbach, *Surf. Sci. Rep.* **1/2**, 4 (1984).
- ²M. C. Lin and G. Ertl, *Annu. Rev. Phys. Chem.* **37**, 587 (1986).
- ³R. B. Gerber, *Chem. Rev.* **87**, 29 (1987).
- ⁴C. W. Muhlhausen, J. A. Serri, J. C. Tully, G. E. Becker, and M. J. Cardillo, *Isr. J. Chem.* **22**, 315 (1982).
- ⁵C. W. Muhlhausen, L. R. Williams, and J. C. Tully, *J. Chem. Phys.* **83**, 2594 (1985).
- ⁶J. A. Barker and C. T. Rettner, *J. Chem. Phys.* **97**, 5844 (1992).
- ⁷R. M. Logan and R. E. Stickney, *J. Chem. Phys.* **44**, 195 (1966).
- ⁸J. C. Tully, *J. Chem. Phys.* **92**, 680 (1990).
- ⁹C. Steinbruchel, *Chem. Phys. Lett.* **76**, 58 (1980).
- ¹⁰C. Steinbruchel, *Surf. Sci.* **115**, 247 (1982).
- ¹¹J. B. C. Pettersson, *J. Chem. Phys.* **100**, 2359 (1994).
- ¹²G. Nyman, L. Holmlid, and J. B. C. Pettersson, *J. Chem. Phys.* **93**, 845 (1990).
- ¹³P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, New York, 1972).
- ¹⁴W. Forst, *Theory of Unimolecular Reactions* (Academic, New York, 1973).
- ¹⁵R. Arakawa and B. S. Rabinovitch, *J. Phys. Chem.* **86**, 4772 (1982).
- ¹⁶H. Asada, *Jpn. J. Appl. Phys.* **19**, 2055 (1980).
- ¹⁷H. Asada, *Jpn. J. Appl. Phys.* **20**, 527 (1981).
- ¹⁸H. Asada, *Jpn. J. Appl. Phys.* **21**, 259 (1982).
- ¹⁹A. Amirav, M. J. Cardillo, P. L. Trevor, C. Lim, and J. C. Tully, *J. Chem. Phys.* **87**, 1796 (1987).
- ²⁰C. T. Rettner, L. A. DeLouise, and D. J. Auerbach, *J. Chem. Phys.* **85**, 1131 (1986).
- ²¹J. Häger and H. Walther, *J. Vac. Sci. Technol. B* **3**, 1490 (1985).
- ²²H. Kuze, J. Häger, and H. Walther, *Chem. Phys. Lett.* **153**, 569 (1988).

- ²³M. E. King, G. M. Nathanson, M. A. Hanning-Lee, and T. K. Minton, Phys. Rev. Lett. **70**, 1026 (1993).
- ²⁴A. Danon, A. Vardi, and A. Amirav, Phys. Rev. Lett. **65**, 2038 (1990).
- ²⁵C. Lim, J. C. Tully, A. Amirav, P. Trevor, and M. J. Cardillo, J. Phys. Chem. **87**, 1808 (1982).
- ²⁶Y. Zeiri and R. R. Lucchese, J. Chem. Phys. **94**, 4055 (1991).
- ²⁷J. B. C. Pettersson, G. Nyman, and L. Holmlid, J. Chem. Phys. **89**, 6963 (1988).
- ²⁸R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University, New York, 1987),
- ²⁹J. B. C. Pettersson and G. Nyman (unpublished).
- ³⁰B. Halpern and M. Kori, Chem. Phys. Lett. **138**, 261 (1987).