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# Thermal desorption of argon and neon from solid xenon. II. Sticking probabilities

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The practical difficulties associated with full molecular dynamics simulations of thermal desorption processes have necessitated the finding of more efficient ways of studying these phenomena. Transition state theory provides part of the solution, but in order to obtain exact rate constants, one must also calculate dynamical corrections, in this case sticking probabilities. The present work proposes a means for computing sticking probabilities that permits the inclusion of both the thermal motion of the solid atoms and also the interactions among adsorbed species. Using this formalism we have made a study of the effects of changes in temperature and adsorbate coverage on sticking probabilities for Ar, Ne-Xe(111), with the results suggesting that these two effects can be indeed significant but that they are not necessarily independent of one another.

## I. INTRODUCTION

By exploiting the obvious analogy between gas-surface adsorption/desorption phenomena and gas-phase molecular combination/dissociation reactions, several workers have contributed significantly to the theoretical model of kinetics at solid surfaces.<sup>1</sup> One of these approaches has involved adapting the well-known transition state theory (TST) formalism to the study of thermal desorption processes. In particular, Tully and co-workers<sup>2</sup> have employed stochastic classical trajectory techniques that treat gas-surface energy exchange via the inclusion of generalized Langevin friction and fluctuating forces and that yield not only the equilibrium (i.e., TST) desorption rates but also the dynamical corrections to those equilibrium results. We have previously reported an equivalent means for getting at the TST portion of the true thermal desorption rate constant via a Monte Carlo thermally biased random walk.<sup>3,4</sup> Such a pseudodynamical approach to the problem both permits the inclusion of concurrent adsorbate diffusion and thermal deformations of the crystal lattice and also allows the incorporation in a straightforward manner of interactions among adsorbed species. That one may easily investigate the degree to which the calculated kinetic behavior depends upon the adsorbate surface coverage constitutes, in fact, one of the most significant features of this method. The present work seeks to complement these equilibrium results with an evaluation of the dynamical corrections, represented in this case by the sticking probability, and hence to provide a way of determining "exact" theoretical rate constants.

One might initially guess that the calculation of gas-surface sticking probabilities should be an almost trivial exercise—one simply integrates the equations of motion for all the particles in the system and thereby observes the likelihood of a particle incident upon the crystal sticking rather than rebounding. Note, however, that carrying out this procedure would be tantamount to performing a full molecular dynamics simulation. For systems where the characteristic

adsorption lifetime (as given by the inverse of the desorption rate constant) is on the order of microseconds to seconds, this sort of strategy will, in the context of current computational technology, be impossible to implement; it was the need to avoid calculations over time scales such as these that in fact prompted the initial TST formulation! As we have indicated previously,<sup>5</sup> though, this seemingly intractable situation may be avoided through the adoption of a formalism developed by Chandler and co-workers,<sup>6</sup> the appropriate modification of which is described in Sec. II below. Of course, if rate constants for the overall adsorption/desorption processes in a particular system should be quite large, it may indeed be convenient to investigate the kinetics directly via standard molecular dynamics techniques, but for a great many systems the two-step approach, namely TST plus dynamical corrections, represents the only reasonable way of proceeding.

In order to investigate the utility of this method for obtaining sticking probabilities when applied to a real gas-surface system, we have returned to an examination of the relatively simple problem of a rare gas impinging upon a single crystal of a heavier rare gas, specifically neon and argon on solid xenon. The rationale for such a choice again stems from the fact that the potential energy functions for such systems are among the best characterized, since it appears likely that gas phase potentials will provide an adequate description of the interactions even when one of the species is in the solid state. Inasmuch as we are thus not plagued by added uncertainty as to the nature of the relevant forces, we can focus our attention on the efficacy of the formalism itself.

Before passing to the description of the present work, we wish to note a numerical error which has been discovered in the TST results published previously.<sup>3,4</sup> An inadvertent programming mistake led to these results being uniformly too small by a factor of  $(2\pi)^{-1/2}$ , and as a consequence the Arrhenius prefactors reported in those papers should be scaled up by a factor of roughly 2.5. This particular error does not, however, alter the values obtained for the desorp-

<sup>a)</sup> Work supported by the U.S. Department of Energy

tion activation energies. Since the interpretation of the results was based around these activation energies rather than the prefactors, the discussion presented in those papers is therefore unaffected.

## II. THEORY

In earlier papers<sup>5</sup> we suggested that the same formalism described by Chandler and co-workers<sup>6</sup> as a means for examining isomerization dynamics in classical liquids can be easily extended to the calculation of gas-surface sticking probabilities. The complete details of that work will not be reproduced here—the reader is referred to the original literature. We recognize, however, that these previous derivations apply only to the case of noninteracting species and are thus unsuited *per se* to an application involving adsorbate effects. One clearly must allow for the possibility that even though an impinging atom or molecule may itself become stuck to the surface, it may also stimulate the desorption of like species, the observed result being no *net* sticking. This modification of the formalism is outlined below.

If one defines two states of the system, one being the bound (i.e., adsorbed) state and the other representing free gaseous species, one can write kinetic rate laws for the time-dependent state populations  $N_b$  and  $N_f$ , respectively, in the form

$$\begin{aligned}\dot{N}_b &= k_{f \rightarrow b} N_f - k_{b \rightarrow f} N_b, \\ \dot{N}_f &= -k_{f \rightarrow b} N_f + k_{b \rightarrow f} N_b.\end{aligned}$$

A similar set of rate laws can then be written for the fluctuations in  $N_b$  and  $N_f$  away from their equilibrium values, for example,

$$\delta \dot{N}_b = k_{f \rightarrow b} \delta N_f - k_{b \rightarrow f} \delta N_b,$$

where

$$\begin{aligned}\delta N_b &\equiv N_b - \bar{N}_b, \\ \delta N_f &\equiv N_f - \bar{N}_f.\end{aligned}$$

By then recognizing that if the number of particles in the system is conserved (implying  $\delta N_b + \delta N_f = 0$ ), one finds that

$$\begin{aligned}\delta \dot{N}_b &= -k_{f \rightarrow b} \delta N_b - k_{b \rightarrow f} \delta N_b \\ &= -k_{\text{eff}} \delta N_b,\end{aligned}$$

with the time behavior of the fluctuations in  $N_b$  actually being determined by an effective rate constant,

$$k_{\text{eff}} = k_{f \rightarrow b} + k_{b \rightarrow f}.$$

From these definitions one may easily deduce the general expression for  $k_{\text{eff}}$  in terms of time-correlation functions,

$$k_{\text{eff}} = \frac{\langle \delta \dot{N}_b(0) \delta N_b(t) \rangle}{\langle \delta N_b(0) \delta N_b(t) \rangle}. \quad (2.1)$$

Suppose now that the bound and free regions of space described here are imagined to be separated by a plane parallel to the surface at  $x = q$ , such that a particle is presumed bound if  $x < q$  and free otherwise. The bound state population can therefore be easily expressed as a function of the  $N$  particle positions via the equation

$$N_b(t) = \sum_i^N \theta [q - x_i(t)],$$

where  $\theta$  denotes the standard step function and  $x_i$  is the distance away from the surface of the  $i$ th particle. Using this expression one can write

$$\begin{aligned}\delta N_b(t) &= \sum_i^N \theta [q - x_i(t)] - \left\langle \sum_i^N \theta [q - x_i(0)] \right\rangle \\ &= \sum_i^N \theta [q - x_i(t)] - \bar{N}_b,\end{aligned}$$

and, by substituting into Eq. (2.1), find that

$$k_{\text{eff}} = - \frac{\sum_{i,j}^N \langle \dot{x}_i(0) \delta [q - x_i(0)] \theta [q - x_j(t)] \rangle}{\sum_{i,j}^N \langle \theta [q - x_i(0)] \theta [q - x_j(t)] \rangle - \bar{N}_b^2}. \quad (2.2)$$

Let us now examine the numerator and denominator terms in Eq. (2.2) separately. The numerator is a sum of correlation functions involving the velocity of the  $i$ th particle, which at time zero is located at  $x = q$ , and a step function that is unity if the  $i$ th particle is adsorbed but vanishes otherwise. Since in the present case we are interested in a single particle impinging on the surface, the expression can be reduced to a single summation, namely

$$\begin{aligned}& \sum_{i,j}^N \langle \dot{x}_i(0) \delta [q - x_i(0)] \theta [q - x_j(t)] \rangle \\ &= N \sum_j^N \langle \dot{x}_1(0) \delta [q - x_1(0)] \theta [q - x_j(t)] \rangle \\ &= N \langle \dot{x}_1(0) \delta [q - x_1(0)] \theta [q - x_1(t)] \rangle \\ &+ N \sum_{j=2}^N \langle \dot{x}_1(0) \delta [q - x_1(0)] \theta [q - x_j(t)] \rangle, \quad (2.3)\end{aligned}$$

where the index 1 refers to the incident particle. The first of these two terms is essentially just the result which would be obtained if the incoming projectile were unable to stimulate the desorption of adsorbed species, with the case  $N = 1$  representing the clean surface limit. Induced desorption effects are, however, accounted for in the second term, the inclusion of these contributions constituting the primary correction to the formalism described previously.

We shall furthermore assume that  $q$  can be taken sufficiently far away from the surface that any particles located initially at  $q$  with velocities which direct them away from the surface have a negligible probability of becoming adsorbed at some later time. There is, then, no longer any contribution to the correlation function appearing in the first term of Eq. (2.3) deriving from those particle trajectories satisfying  $\dot{x}(0) > 0$ , inasmuch as the step function will vanish for all  $t$ . In addition, since particle 1 will be unable to induce desorption of any of the adsorbed species, the correlation functions involving particles 2 through  $N$  reduce to a product of averages. Specifically, Eq. (2.3) becomes

$$\begin{aligned}
& N \langle \dot{x}_1^{(+)}(0) \delta[q - x_1(0)] \theta[q - x_1(t)] \rangle \\
& + N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_1(t)] \rangle \\
& + N \sum_{j=2}^N \langle \dot{x}_1^{(+)}(0) \delta[q - x_1(0)] \theta[q - x_j(t)] \rangle \\
& + N \sum_{j=2}^N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_j(t)] \rangle \\
& = N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_1(t)] \rangle \\
& + N \langle \dot{x}_1^{(+)}(0) \delta[q - x_1(0)] \left\langle \sum_{j=2}^N \theta[q - x_j(t)] \right\rangle \rangle \\
& + N \sum_{j=2}^N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_j(t)] \rangle \\
& \simeq N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_1(t)] \rangle \\
& + N(N-1) \langle \dot{x}_1^{(+)}(0) \delta[q - x_1(0)] \rangle \\
& + N \sum_{j=2}^N \langle \dot{x}_1^{(-)}(0) \delta[q - x_1(0)] \theta[q - x_j(t)] \rangle, \quad (2.4)
\end{aligned}$$

if the thermal desorption time scale is long compared with that of the initial fast system relaxation. Here  $\dot{x}^{(+)}$  and  $\dot{x}^{(-)}$  denote velocities which direct particles, respectively, away from or toward the surface. [While we note that a somewhat better approximation to the average number of bound species would be, instead of simply  $(N-1)$ ,

$$(N-1)e^{-k^{\text{TST}}\tau},$$

where  $k^{\text{TST}}$  is the transition state theory equilibrium thermal desorption rate constant calculated in Ref. 4, for many cases this additional correction appears to be unnecessary.] We expect a plot of Eq. (2.4) vs time to display much the same plateau behavior<sup>6</sup> as that which is observed using the unmodified formalism due to this separation of time scales. Again, the only independent "slow" variable in the system is  $N_b(t)$ . Consequently, the extraction of sticking probabilities should be possible from the results of trajectories that are run for times comparable to the fast relaxation time rather than for times corresponding to the longer desorption time.

The denominator of Eq. (2.2) presents special difficulties in that it cannot be calculated via the same method as that indicated for the numerator. In particular, it does not describe a system in which one of the particles is initially located at  $x = q$ . Some progress can be made by assuming that the correlations involved are slowly decaying, but in order to reduce the term to one not requiring independent evaluation one must presume the adsorbed species to be non-interacting. Fortunately, however, it is really not necessary for us to evaluate the weakly time-dependent denominator at all. As was noted in previous work, the sticking probability (which in the present context is the dynamical correction to the TST thermal desorption rate constant) is found from the plateau behavior of the time-evolved quantity

$$\kappa(t) = k_{\text{eff}}(t)/k_{\text{eff}}^{\text{TST}},$$

which at  $t = 0$  necessarily takes on a value of unity. So by dividing  $k_{\text{eff}}(t)$  by its value at  $t = 0$ , we easily obtain the ratio of interest. A linear fit to the plateau region of a plot of  $\kappa$  vs  $t$  can then be extrapolated to zero time to give a value of the

sticking probability  $p_s$ , the assignment of which is not confused by the long-time decay of  $\kappa$  due to thermal desorption. One thus obviates the need for performing two independent molecular dynamics calculations in order to obtain sticking probability values.

### III. RESULTS

Sticking probabilities were calculated for gaseous neon and argon impinging on the close-packed crystal face of solid xenon. The single crystal itself is modeled by a rectangular slab, the surface of which contains 24 primitive lattice cells of (111) symmetry. By imposing periodic boundary conditions we can consider this slab to be characteristic of the entire "infinite" surface even though we are actually working with a relatively small number of xenon atoms (24 atoms per layer). The slab's thickness is taken to be three atomic layers in the present calculations, and only those atoms in the topmost layer are allowed to move (the atoms in the second and third layers being held fixed in their equilibrium lattice positions). Trial calculations in which additional layers of mobile solid atoms were included yielded results which were statistically indistinguishable from those obtained when a single layer was used. Clearly, one might not expect this same model to apply in the case where a high Miller index crystal face is being studied, simply because there the second layer would be more exposed and hence would interact more directly with the adsorbed and impinging species. Present evidence suggests, however, that a single layer of moving atoms is indeed sufficient to describe the thermal deformations of the close-packed face.

The potential functions used in this work are identical with those adopted previously, namely Lennard-Jones 6-12 potentials, the relevant parameters being tabulated in Ref. 4. Total potentials are then computed via direct summation of two-body interactions, with the range cutoffs occurring at twice the lattice spacing of the solid (8.68 Å for fcc xenon). We note in retrospect that perhaps a more efficient way of summing the potential would involve the same direct summation of interactions between moving particles (either adatoms or the atoms of the top solid layer) but would use Steele's Fourier expansion method<sup>7</sup> in calculating interactions between mobile atoms and the static atoms of the second and third solid layers. Such a strategy might prove advantageous due to the fact that evaluation of the potential energy represents a slow step in the trajectory calculations for these systems.

Equation (2.4) gives us only a little direction in setting up the initial conditions for the trajectories, namely that the particle incident upon the surface (the particle labeled 1) is located at a distance above the surface  $q$  (as in our previous work,  $q$  is taken to be 7.8 Å) at time zero with an initial momentum which is directed towards the surface. [Note that the second term on the right-hand side of Eq. (2.4) may be evaluated without recourse to trajectories at all. In practice one may either obtain this term analytically or may assume that for each value of  $\dot{x}_1^{(-)}$  chosen for the trajectory calculations, there will be another value  $\dot{x}_1^{(+)}$  which is equal in magnitude but which is directed away from the surface. Averaging over these outward directed velocities then yields

the required term.] We have chosen to generate the requisite initial system configurations via the same sort of thermally biased random walk used in the Monte Carlo evaluation of the TST desorption rate constants.<sup>3,4</sup> In this procedure trial displacements of the adatoms and the atoms in the uppermost solid layer are accepted or rejected with certain probabilities, these probabilities being functions of both the system temperature and the change in the total potential resulting from the displacements. Recall, of course, that displacements of particle 1 must be constrained somewhat in the random walk so that this atom will remain at distance  $q$  from the surface. Our initial positions for the trajectories, which represent instantaneous snapshots of the system, may then be easily obtained by storing the atomic positions at fixed intervals in the random walk (say, every 5000 single-particle steps, roughly half of which constitute accepted displacements). By selecting one of these configuration snapshots and assigning initial particle momenta on the basis of a random choice from the appropriate thermal distributions, we thus determine completely the time zero conditions of the system.

The trajectories themselves were constructed by numerical integration of Hamilton's equations via the fourth-order Runge-Kutta-Gill algorithm.<sup>8</sup> An example of the results obtained for Eq. (2.4) using 200 of such trajectories is shown in Fig. 1 for the case of three neon adatoms, one being the impinging particle, at a temperature of 50 K. In this case we have plotted  $\kappa(t)$  (as defined in Sec. II,  $k_{\text{eff}}(t)/k_{\text{eff}}(0)$ ) vs time, and we note that indeed the plateau behavior expected on the basis of Chandler's arguments concerning separation of time scales is evident.<sup>6</sup> The appearance of such behavior signals the dominance of the long-time relaxation processes (in this case, at times beyond about 6 ps), which may be identified with the equilibrium thermal desorption of the remaining adspecies. (The negative slope seen in the linear region reflects the contribution from a few desorption events even on this short time scale. Note that a characteristic adsorption lifetime for neon on xenon at this temperature is roughly 100 ps<sup>45</sup>; even for the relatively rapid desorption that we see here, the present formalism provides an order of magnitude

savings in computer time over that which would be required for a full molecular dynamics simulation for this system.) Extrapolation to zero time, by subtracting out both thermal desorption effects and the short-time system relaxation processes, then yields the sticking probability  $p_s$ , which is found to be about 0.85 at 50 K.

### A. Neon-xenon

As a first step in characterizing neon atom sticking on the (111) face of a xenon single crystal, we calculated  $p_s$  values at various equilibrium system temperatures for the case of a perfectly clean surface. The results of these calculations are displayed in Fig. 2, with each point representing a determination of  $p_s$  based on 200–300 individual trajectories. Note in particular that the general shape of the curve matches that seen by Tully<sup>2</sup> in the Xe–Pt(111) system, namely that its slope is negative and that the absolute value of the slope decreases with increasing temperature, even though we have adopted a quite different definition of sticking. As described in the previous section, our criterion for deciding whether or not an impinging species sticks is one based on proximity to the surface. Tully, on the other hand, uses an energy criterion, that a species must be trapped by  $3kT$  of energy in order for it to be judged stuck.

Using these sticking probabilities we then constructed the exact rate constants,

$$k(T) = k^{\text{TST}}(T)p_s(T),$$

again in the limit of a clean surface. The first step in the process involved obtaining the TST rate constants in this same limit, since in the earlier paper<sup>4</sup> only finite surface coverages were investigated. The reader should refer to that paper for a description of the calculation, this time for a neon concentration of one adatom per surface slab. We give the results of those calculations, as well as the values obtained by scaling the equilibrium values by the corresponding sticking probabilities, in the Arrhenius plot shown in Fig. 3. One should first notice that the temperature behavior of the TST rate constants exhibits the same transition from high to low temperature limits that we observed when partially covered surfaces were examined, but that this transition is smoothed

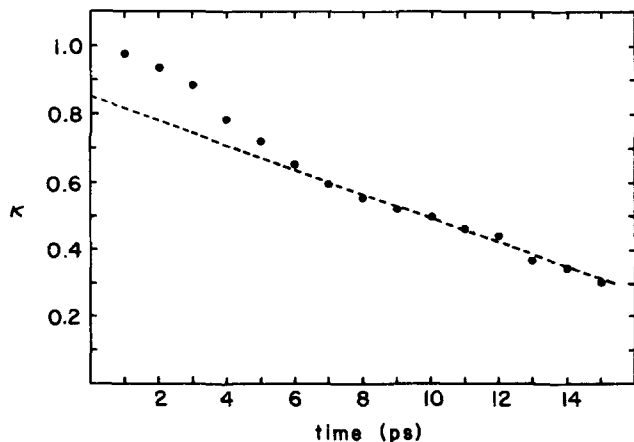


FIG. 1. Time decay of  $\kappa$  (defined in Sec. II) for Ne on a clean Xe(111) surface at  $T = 50$  K. The broken line represents the extrapolation to zero time, which yields the sticking probability.

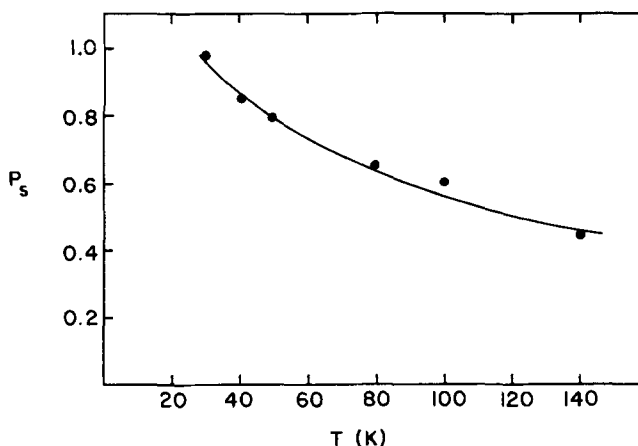


FIG. 2. Temperature dependence of the sticking probability for Ne on a clean Xe(111) surface.

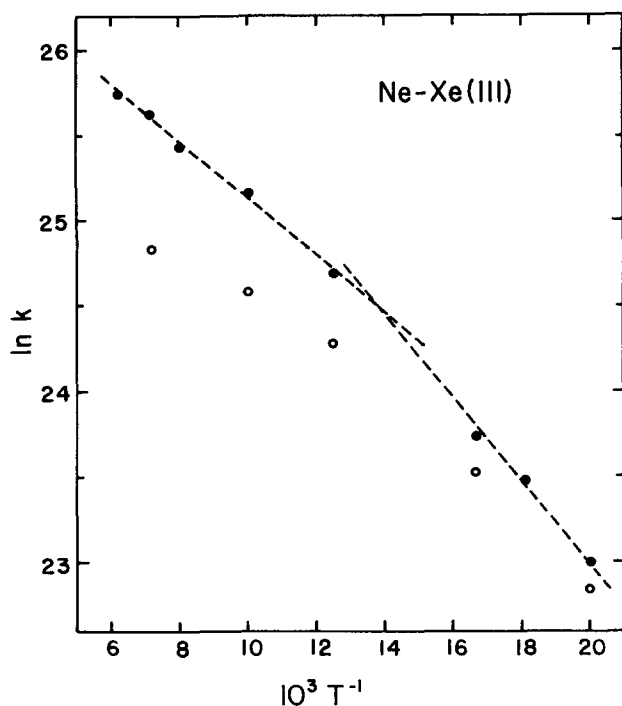


FIG. 3. Arrhenius plot for Ne-Xe(111) thermal desorption. The closed circles represent results obtained using the TST methods of Refs. 3 and 4, while the open circles represent the exact theoretical values. (All calculations refer to the clean surface limit.)

out when temperature-dependent dynamical corrections are introduced. It also appears that the sticking factors increase the curvature evident in the Arrhenius plot, with the principal change occurring at the higher temperatures. Whereas in the low temperature regime the dynamical effects manifest themselves in the preexponential factor, a substantial decrease in the activation energy can be found as the system is warmed. This result is not particularly surprising, however, since Tully<sup>2(b)</sup> has in fact attributed nearly all the high-temperature curvature seen in the analogous plots for Xe, Ar-Pt(111) to dynamical contributions.

Of even more interest, though, is the adsorbate coverage dependence of  $p_s$ , inasmuch as the formalism of Sec. II provides the only convenient means of characterizing this effect. Figure 4 shows the values calculated at two different temperatures for a range of coverages from the perfectly clean surface ( $N_a = 0$ ) to nine adatoms per surface slab ( $N_a = 9$ ; this coverage corresponds to  $[\text{Ne}] = 2.3 \times 10^{14} \text{ cm}^{-2}$ —roughly half of a monolayer—prior to the tenth neon atom impinging on the slab). One is immediately struck by the degree to which the system temperature affects the coverage dependence. At the lower temperature ( $T = 50 \text{ K}$ ) we find no significant variation in  $p_s$  over the coverage range examined here, whereas by raising the temperature to 100 K, not only do we obtain a sharp decrease in the probability of sticking as the coverage is increased but the calculated values become negative beyond about a tenth of a monolayer of adsorbed neon. Of course, at that point  $p_s$  should no longer be interpreted in terms of a probability *per se*, but even so the negative values are not without meaning. Consider first the case when  $p_s = 0$ : if there are no adsorbed species present,

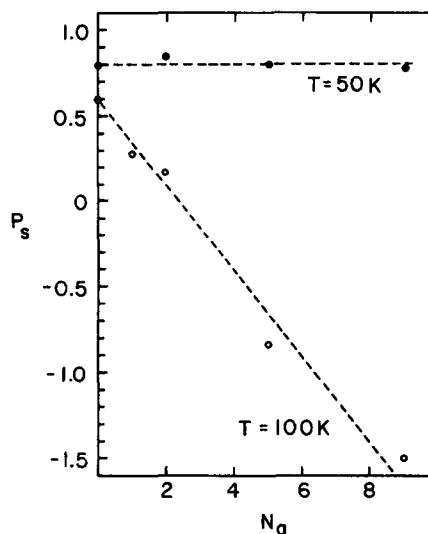


FIG. 4. Coverage dependence of the Ne-Xe(111) sticking probability at two different temperatures.  $N_a$  is the number of adsorbed adatoms present on the surface slab prior to particle 1 striking the surface. The broken lines shown are meant "to guide the eye" and not necessarily to imply strictly linear dependences.

then when the sticking probability vanishes, we conclude that an incident atom will always rebound and never stick. If, however, identical adsorbed species are present, then  $p_s = 0$  really implies that no net sticking occurs, either because the impinging atom never adheres or because adsorption is always accompanied by the ejection of one of the other adatoms. Consequently, we are led to identify a negative value of  $p_s$  with net stimulated desorption. At the given temperature those adsorbate coverages beyond that at which  $p_s$  vanishes (the equilibrium surface coverage) may thus only be attained through pressurization of the system. Note that this information cannot be extracted from the TST formalism; one implicitly assumes an equilibrium system pressure when the adsorbate coverage is specified.

The very different coverage dependences derived for temperatures 50 and 100 K may be understood when one recalls that the neon-xenon potential function used herein<sup>4</sup> has a well depth  $\epsilon k^{-1}$  of 75.0 K. Consequently, at temperatures below 75.0 K, most of the adatoms will be bound in definite surface sites, more or less isolated from one another, and relatively immobile. Unless the impinging atom should happen to strike one of these adsorbed species, the presence of the adsorbate will prove insignificant, at least at relatively low coverages where the probability of a direct collision with an adatom is minimal. Quite a different situation exists in the high temperature regime, though; here the adatoms diffuse readily, with the concept of a specific binding site being rather poorly defined. Accompanying this increased mobility comes the increased probability of collisions with incident atoms and of subsequent desorption, since the desorption activation energy has been found to decrease upon passing into this limit. One should therefore expect to see a decrease in the equilibrium surface coverage (i.e., an increase in the equilibrium adsorbate vapor pressure) upon raising the temperature of the system.

## B. Argon-xenon

In order to test the validity of our conclusions indicated above, we now shift our attention to the consideration of an argon adsorbate. Note first that the depth of the Ar-Xe potential well,<sup>4</sup> the quantity that, we have suggested, demarcates the high and low temperature limits of the sticking behavior, is taken to have a value of 171 K. Thus, if we confine our discussion to the same temperature interval described in the TST rate constant calculations, specifically 125–160 K, we find ourselves working entirely within the low temperature regime. The analogous neon results suggest that the clean-surface argon sticking probabilities will change significantly over a narrow temperature range (for neon the change is as much as 0.1 for an increase of 10 K). Calculations of  $p_s$  for this system in fact confirm this supposition; at 125 K we obtain  $p_s = 0.91$ , with a temperature increase of 15 to 140 K being accompanied by a decrease of 0.13 in the sticking probability. (Our attempts to extend these calculations to higher temperatures have proved, however, somewhat unsuccessful. As the system temperature, and hence the gas-surface average collision energy, is further increased, we begin to find a number of trajectories involving surface damage.)

The effect of changing the surface coverage may also be estimated by analogy with the neon-xenon system. In that case we found, again referring to Fig. 4, that increasing the concentration of adsorbed species does not alter the sticking probability as long as the temperature remains low relative to the adatom-solid atom potential well depth. A calculation of  $p_s$  for argon-xenon at 140 K and with  $N_a = 2$  yields the value 0.78, which is, in fact, practically identical with the clean-surface result of 0.77. We should reiterate our earlier statement that these conclusions dealing with coverage dependences really only apply to those adsorbate concentrations in which we have been particularly interested, namely those corresponding to fractions of a monolayer. Since the ratio of the adatom-adatom well depth to the corresponding adatom-solid atom energy is larger for the argon adsorbate than it is for the neon adsorbate (respectively, 0.70 and 0.56) and since the range of the argon-argon interaction is substantially greater than that of the neon-neon interaction (the respective Lennard-Jones  $\sigma$  values<sup>4</sup> are 3.405 and 2.74 Å), one would expect differences in the adsorbate dynamics to appear at higher coverages.

## IV. DISCUSSION

In this paper we have presented a method for computing gas-surface sticking probabilities that, when coupled with a TST determination of equilibrium rate constants, permits one to describe kinetic processes occurring on time scales beyond those accessible to conventional molecular dynamics simulations. The unique feature of the present prescription lies in its ability to encompass a wide range of dynamical influences, an important example being adsorbate coverage effects. These particular effects have been shown to be quite significant in certain temperature ranges for simple rare gas-rare gas systems; however, one cannot make general statements concerning the effect of adatom interactions without having first defined this temperature regime of in-

terest. It appears that one *can* correlate variations in sticking probabilities with changes in adsorbate mobility, with this observation suggesting that comparisons between sticking probabilities and surface diffusion constants<sup>9</sup> might prove useful.

The sticking probability values calculated herein depend, of course, upon the choice made for  $q$ , the distance away from the surface of the plane which separates bound and free adsorbate states. If, in fact,  $q$  is taken to be sufficiently large that the potential energy of a particle located at  $q$  is negligibly small, then one need not worry much about the value of  $q$  chosen. The construction of exact rate constants does require, however, that this dividing surface be placed at the same position in both TST and  $p_s$  calculations. This requirement is a fairly obvious one—since  $p_s$  is interpreted as being the dynamical correction factor for the equilibrium results (which are also inherently  $q$  dependent), any errors introduced into the TST calculations due to a less than optimal choice for  $q$  should be completely accounted for when this same position is adopted for the sticking probability work. Hence, one will find that the exact rate constants will not show a dependence on the somewhat arbitrarily chosen  $q$ . (This lack of  $q$  dependence was recognized by Chandler<sup>6</sup> in his original work.)

The fact that our definition of the sticking probability is ultimately tied to the manner in which we carry out the TST calculations eliminates the need for us to adopt an arbitrary criterion for deciding whether or not a species is stuck. Not only do we thus avoid the problems alluded to by Tully<sup>2</sup> that arise upon deciding whether or not an impinging species has actually adsorbed and thermally equilibrated, but also we eschew the use of Tully's adsorption energy criterion for defining sticking. That one need not introduce additional assumptions in order to characterize unambiguously the overall rate processes thus represents an added advantage associated with this particular formulation of the exact rate constant calculation.

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<sup>1</sup>For reviews of recent work see J. C. Tully, *Annu. Rev. Phys. Chem.* **31**, 319 (1980); T. F. George, K. Lee, W. C. Murphy, M. Hutchinson, and H. Lee, in *The Theory of Chemical Reaction Dynamics*, edited by M. Baer (to be published).

<sup>2</sup>(a) E. K. Grimmelmann, J. C. Tully, and E. Helfand, *J. Chem. Phys.* **74**, 5300 (1981); (b) J. C. Tully, *Surf. Sci.* **111**, 461 (1981).

<sup>3</sup>J. E. Adams and J. D. Doll, *J. Chem. Phys.* **74**, 1467 (1981).

<sup>4</sup>J. E. Adams and J. D. Doll, *J. Chem. Phys.* **77**, 2964 (1982).

<sup>5</sup>J. E. Adams and J. D. Doll, *Surf. Sci.* **103**, 472 (1981); **111**, 492 (1981).

<sup>6</sup>D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978); J. A. Montgomery, Jr., D. Chandler, and B. J. Berne, *ibid.* **70**, 4056 (1979).

<sup>7</sup>W. A. Steele, *Surf. Sci.* **36**, 317 (1973).

<sup>8</sup>See, for example, B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods* (Wiley, New York, 1969), p. 363.

<sup>9</sup>See, for example, J. D. Doll and H. K. McDowell, *J. Chem. Phys.* **77**, 479 (1982).