

## Renormalized theory of sticking and desorption for physisorption

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Sticking coefficients calculated conventionally in the distorted-wave Born approximation (DWBA) often become greater than 1 even for particles interacting weakly with surfaces in physisorbed systems. We reexamine the quantum formulation of sticking and desorption within the DWBA to correctly account for processes occurring on time scales of the order of the interaction time of extended states with the surface. We obtain expressions for renormalized monochromatic and total sticking coefficients, which are properly bounded by 1, as well as expressions for renormalized desorption time and time-of-flight (TOF) spectra. Standard relationships between sticking coefficients, desorption times, and TOF spectra imposed by the thermodynamic detailed balance are preserved for the renormalized quantities. We propose a modified master equation for physisorption kinetics containing renormalized transition rates between continuum and bound states. It can be used in a conventional way to calculate properly behaving sticking coefficients, desorption times, and TOF spectra. We also analyze the role of the continuum-continuum inelastic transitions in sticking and desorption. Numerical examples of sticking coefficients illustrating the need for their renormalization are also present.

### I. INTRODUCTION

The kinetics of adsorption and desorption of molecules physisorbed on solid surfaces is the most elementary process serving as a starting point for detailed understanding of more complex processes for chemisorbed species. It has been extensively studied both experimentally<sup>1</sup> and theoretically<sup>2,3</sup> in recent years. (For a recent review see Ref. 4.)

The motivation of our work is the observation that the conventional expression for the momentum-dependent sticking coefficient  $\bar{S}_k$  obtained in the distorted-wave Born approximation (DWBA) may lead to values greater than 1,<sup>5</sup> clearly an unacceptable result. This can be explained by observing that, in the DWBA, when a particle sticks to the surface upon scattering, the flux is not removed from the elastic channel, leading to an overcounting of the trapping events.

Brenig<sup>6</sup> approaches the problem of scattering, desorption, and sticking using a master equation with appropriate transition rates leading in principle to a unitary scattering matrix and correctly normalized sticking coefficients. However, he does not calculate these rates from first principles. Formally, the necessary scattering rates could be obtained in the coupled-channel transition-matrix method.<sup>7,8</sup> The formalism is rather involved and computationally expensive so that a simpler approach such as that presented in this work is more practical.

On the other hand, we argue that the overcounting of scattering events inherent in the DWBA can be remedied without going beyond one-phonon emission-absorption

processes. In order to do this we will consider an individual trapping event as a process lasting  $\tau_L$ . For instance,  $\tau_L$  can be interpreted as a period of time during which the wave packet representing the extended state of a particle in the gas phase interacts with the trapping potential. If the rate of trapping calculated for this wave packet is  $\mathcal{W}$ , one could be tempted to define a sticking probability as  $\tau_L \mathcal{W}$ , clearly obtaining an incorrect result when  $\tau_L$  is comparable with  $1/\mathcal{W}$ . This prescription overcounts the trapping by not excluding the possibility of trapping the particle more than once during the time interval  $\tau_L$ . In this paper we attempt to properly account for the quantum processes taking place during the interaction time  $\tau_L$  and obtain the expressions for sticking coefficients bounded by 1. The result obtained is the simplest one beyond DWBA, and we expect it to be valid in cases in which the interaction of the gas particle with the solid surface is weak enough for the processes in which one phonon is either absorbed or emitted to be the dominant ones. Interaction of rare gases with graphite, alkali-metal halides, and some metallic surfaces belong to this class of systems. Emission and absorption of single phonons has been observed, for example, in helium scattering from silver, copper, and alkali-metal halides.<sup>9</sup>

Phenomenologically, one could obtain a sticking coefficient by considering two scattering channels, one elastic with rate  $\omega_{el}$  and one trapping with rate  $\omega_{tr}$ . The sticking coefficient could then be defined as the ratio  $\omega_{tr}/(\omega_{el} + \omega_{tr})$ . This result is equivalent to the one obtained by Brivio and Grimley.<sup>10</sup> However, this statistical approach does not describe properly the individual quantum scattering events.

It is worth noting that similar difficulties with calculating probabilities per one scattering event using transition rates between continuum and bound states are not unique to physisorption. For instance, the problem of trapping of thermal positrons into surface image states<sup>11</sup> belongs to the same category.

General arguments of the thermodynamical detailed balance require certain relationships between sticking coefficient, desorption time, and time-of-flight spectra for desorption.<sup>12</sup> In particular, for gas in equilibrium with the solid, adsorption and desorption processes must balance each other. We show how the quantities characterizing adsorption and desorption can be independently derived in a manner preserving the relationships required by the detailed balance.

In our approach to adsorption we analyze transition processes from continuum to bound states of the surface potential during one collision of a gas particle with the surface. Such transitions need not be direct ones, e.g., the particle can be inelastically scattered into another continuum state in the initial collision with the surface and then trapped into a bound state. The first process can obviously be replaced by a series of transitions through continuum states. When continuum-continuum transition rates are large such processes should be included in the calculations of sticking. For desorption the order of processes is reversed and the initial detrapping is followed by a series of transitions through continuum states.

We start in Sec. II with reexamination of theory of the sticking coefficient. Section III is devoted to the desorption process. In Sec. IV we propose and discuss the modified master equation for physisorption kinetics, while in Sec. V we show how to include the inelastic continuum-continuum transitions into calculations of sticking and desorption. Numerical results for sticking coefficients are presented in Sec. VI followed by summary and final conclusions in Sec. VII.

## II. STICKING COEFFICIENT

The monochromatic ( $\mathbf{k}$ -dependent) sticking coefficient is defined as the probability that a particle of momentum  $\hbar\mathbf{k}$  hitting a surface of a solid is trapped in the surface potential. It is given by the ratio

$$\tilde{S}_{\mathbf{k}} = \frac{\sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})}{[\mathbf{j}_{\mathbf{k}}^{(\text{in})} \cdot (-\mathbf{n})] A}, \quad (2.1)$$

where the numerator is the probability of adsorption per particle per unit time and the denominator represents the number of particles reaching the entire exposed solid surface per unit time.  $\mathbf{j}_{\mathbf{k}}^{(\text{in})}$  is the incoming current density of particles with momentum  $\hbar\mathbf{k}$ , and  $\mathbf{n}$  is a normal to the solid surface of area  $A$ .  $W(\mathbf{i}, \mathbf{k})$  is the transition rate (e.g., due to the interaction with a phonon system of the solid) from the continuum state  $\mathbf{k}$  to a bound state  $\mathbf{i}$  of the physisorption potential calculated in the distorted-wave Born approximation. The vector  $\mathbf{i}$  represents a set of three quantum numbers identifying the quantum state of the adsorbed particle. For instance, for mobile adsorbate

$\mathbf{i} = (\mathbf{K}_i, i)$ , where  $\mathbf{K}_i$  is a wave vector for the free motion along the surface and  $i$  identifies the bound state of the one-dimensional surface potential.

The asymptotic form of the wave function representing a particle in the gas phase is given by

$$\begin{aligned} \Psi_{\mathbf{k}}^{(\infty)}(z, \mathbf{R}) &= \frac{1}{\sqrt{A}} \exp(i\mathbf{K} \cdot \mathbf{R}) \left[ \frac{2}{L} \right]^{1/2} \sin(kz + \delta) \\ &= \Psi_{\mathbf{k}}^{\text{in}}(\mathbf{r}) - \Psi_{\mathbf{k}}^{\text{out}}(\mathbf{r}). \end{aligned} \quad (2.2)$$

We use a convention according to which  $\mathbf{r} = (\mathbf{R}, z)$  and  $\mathbf{k} = (\mathbf{K}, k)$  with  $k > 0$ .  $L$  is the normalization box length in the direction perpendicular to the surface. The term  $\Psi_{\mathbf{k}}^{\text{in}}$  representing the particle moving towards the surface gives

$$A \mathbf{j}_{\mathbf{k}}^{(\text{in})} \cdot (-\mathbf{n}) = \frac{\hbar k}{2mL} \quad (2.3)$$

and thus

$$\tilde{S}_{\mathbf{k}} = \frac{2L}{\hbar k / m} \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}). \quad (2.4)$$

As pointed out in the Introduction  $\tilde{S}_{\mathbf{k}}$  can become greater than 1. This happens when the quantum time  $\tau_L = 2Lm / \hbar k$  of the duration of the interaction of the incoming particle with the surface per one elastic scattering is longer than the inverse of the rate of sticking  $[\sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})]^{-1}$ . In such a case we must take into account the possibility that the particle can be adsorbed before the interaction time  $\tau_L$  has elapsed. To avoid any misunderstanding we point out that although  $\tau_L$  depends on  $L$  no *experimentally accessible* physical quantity contains  $L$ . Heuristically,  $2L$  can be interpreted as the length of the wave packet whose time of interaction with the surface is  $\tau_L$ . This length can be chosen arbitrarily within the limits imposed by Eq. (2.7) since in the final expressions for the sticking coefficient  $\tau_L$  is always multiplied by  $W(\mathbf{i}, \mathbf{k})$  [cf. Eqs. (2.4) and (2.12)] and  $L$  cancels out in such a product.

Firstly we consider the relationships between  $\tau_L$  and other time scales characterizing adsorption. Kinetic description of the adsorption processes is valid provided the macroscopic relaxation time  $\tau_d$  is long in comparison with a typical time  $\tau_s$  over which the quasistationary occupation distribution in the adsorbate is established. It implies that for  $t \gg \tau_s$  we have

$$n_{\mathbf{i}}(t) = n_{\mathbf{i}}^{\text{stat}} f(t), \quad (2.5)$$

where

$$f(t) = \begin{cases} 1 - \exp(-t/\tau_d), \\ \exp(-t/\tau_d) \end{cases} \quad (2.6)$$

for adsorption and desorption, respectively. We can then choose the interaction time  $\tau_L$  of the extended states with the surface in such a way that

$$\tau_s \ll \tau_L \ll \tau_d. \quad (2.7)$$

This condition can easily be satisfied in the experimental-

ly interesting temperature regime because  $\tau_s$  is typically of the order of the inverse Debye frequency ( $\approx 10^{-13}$  s) while  $\tau_d$  is, e.g., for He on nichrome, of the order of  $10^{-4}$  s at  $T \approx 4$  K.

The probability that a particle with momentum  $\hbar\mathbf{k}$  is adsorbed during one encounter with the surface lasting from  $t$  until  $t + \tau_L$  can be written in the following form:

$$S_{\mathbf{k}}(t, \tau_L) = \int_0^{\tau_L} \omega_{\mathbf{k}}^{\text{ads}}(t, \tau) d\tau. \quad (2.8)$$

Here  $\omega_{\mathbf{k}}^{\text{ads}} d\tau$  is the probability that the particle is captured between  $t + \tau$  and  $t + \tau + d\tau$  provided it survived in the  $\mathbf{k}$  state during the time interval  $[t, t + \tau]$ . We have

$$\omega_{\mathbf{k}}^{\text{ads}}(t, \tau) d\tau = \left[ \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}) d\tau \right] \exp \left[ - \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}) \tau \right]. \quad (2.9)$$

Equation (2.8) can now be integrated over  $\tau$  after using Eq. (2.9). The result does not depend on  $t$  and  $\tau_L$  and therefore we obtain the renormalized sticking coefficient

$$S_{\mathbf{k}} = 1 - \exp(-\tilde{S}_{\mathbf{k}}), \quad (2.10)$$

where  $\tilde{S}_{\mathbf{k}}$  is given by Eq. (2.4). This is the central result of our approach. It is worth noting that if  $\tilde{S}_{\mathbf{k}} \ll 1$  then

$$\begin{aligned} \dot{n}_{\mathbf{k}}(t) &\equiv -n_{\mathbf{k}}(t) \frac{1}{\tau_L} S_{\mathbf{k}}(t, \tau_L) = -n_{\mathbf{k}}(t) \frac{2Lm}{\hbar k} [1 - \exp(-\tilde{S}_{\mathbf{k}})] \\ &= -n_{\mathbf{k}}(t) \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}) \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} \xrightarrow{\tilde{S}_{\mathbf{k}} \ll 1} -n_{\mathbf{k}}(t) \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}). \end{aligned} \quad (2.14)$$

Clearly, in the limit of small  $\tilde{S}_{\mathbf{k}}$  we again recover the well-known result.

### III. DESORPTION

Let us consider now the isothermal desorption process triggered at  $t=0$ , e.g., by a sudden removal of the gas phase. The time-dependent total numbers of particles in the gas and in the adsorbed phase are, respectively,

$$N_g(t) = N_a^0 \sum_{\mathbf{k}} n_{\mathbf{k}}(t), \quad N_a(t) = N_a^0 \sum_{\mathbf{i}} n_{\mathbf{i}}(t), \quad (3.1)$$

where  $N_a^0$  is the total number of initially adsorbed particles. We must have  $\sum_{\mathbf{i}} n_{\mathbf{i}}(t) + \sum_{\mathbf{k}} n_{\mathbf{k}}(t) = 1$ , and the initial condition is

$$n_{\mathbf{i}}(0) = \frac{\exp(-E_{\mathbf{i}}/k_B T)}{\sum_{\mathbf{j}} \exp(-E_{\mathbf{j}}/k_B T)}, \quad n_{\mathbf{k}}(0) = 0 \quad (3.2)$$

where  $T$  is the temperature of the solid.

In order to calculate  $\dot{n}_{\mathbf{k}}(t)$  we observe that in analogy to Eqs. (2.14) and (2.8)

$$\dot{n}_{\mathbf{k}}(t) = \frac{1}{\tau_L} \int_0^{\tau_L} \omega_{\mathbf{k}}^{\text{des}}(t, \tau) d\tau, \quad (3.3)$$

where  $\omega_{\mathbf{k}}^{\text{des}}(t, \tau) d\tau$  is the probability that the particle

$S_{\mathbf{k}} \approx \tilde{S}_{\mathbf{k}}$ .

The total sticking coefficient  $S$  is defined as the average of  $S_{\mathbf{k}}$  over the spectrum of the incoming flux

$$S = \frac{\sum_{\mathbf{k}} S_{\mathbf{k}} [\mathbf{j}_{\mathbf{k}}^{(\text{in})} \cdot (-\mathbf{n})] n_{\mathbf{k}} A}{\sum_{\mathbf{k}} [\mathbf{j}_{\mathbf{k}}^{(\text{in})} \cdot (-\mathbf{n})] n_{\mathbf{k}} A}. \quad (2.11)$$

For the thermal flux of incoming particle we get the renormalized total sticking coefficient

$$S = \left[ \frac{\pi \hbar^2}{2mk_B T} \right]^{1/2} \sum_{\mathbf{k}} kn_{\mathbf{k}}^{\text{eq}} [1 - \exp(-\tilde{S}_{\mathbf{k}})], \quad (2.12)$$

where

$$n_{\mathbf{k}}^{\text{eq}} = \exp(-E_{\mathbf{k}}/k_B T) / \sum_{\mathbf{k}'} \exp(-E_{\mathbf{k}'}/k_B T)$$

with  $E_{\mathbf{k}} = \hbar^2 \mathbf{k}^2 / 2m$ . Equation (2.12) should be compared with the conventional result

$$\tilde{S} = \left[ \frac{\pi \hbar^2}{2mk_B T} \right]^{1/2} \sum_{\mathbf{k}} kn_{\mathbf{k}}^{\text{eq}} \tilde{S}_{\mathbf{k}}. \quad (2.13)$$

Using (2.8) and (2.10) we can obtain the rate with which the occupation number of the  $\mathbf{k}$  state decreases:

desorbs into the  $\mathbf{k}$  state between  $t + \tau$  and  $t + \tau + d\tau$  provided it was not recaptured into any of the bound states in the time interval  $[t + \tau + d\tau, t + \tau_L]$ . It is given by

$$\begin{aligned} \omega_{\mathbf{k}}^{\text{des}}(t, \tau) d\tau &= \left[ \sum_{\mathbf{i}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}(t) d\tau \right] \\ &\times \exp \left[ - \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k}) (\tau_L - \tau) \right], \end{aligned} \quad (3.4)$$

provided condition (2.7) holds.  $n_{\mathbf{i}}(t)$  is the occupation probability for the state  $\mathbf{i}$  at time  $t$ . We have used the fact that due to condition (2.7)  $n_{\mathbf{i}}(t)$  can be treated as a constant during the interaction time  $\tau_L$ . Inserting (3.4) into (3.3) and integrating over  $\tau$  we get

$$\begin{aligned} \dot{n}_{\mathbf{k}}(t) &= \sum_{\mathbf{i}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}(t) \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} \\ &\xrightarrow{\tilde{S}_{\mathbf{k}} \ll 1} \sum_{\mathbf{i}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}(t). \end{aligned} \quad (3.5)$$

Note the similarity between the results (3.5) and (2.14). In the regime (2.7) we have from Eqs. (2.5) and (2.6) for desorption

$$n_{\mathbf{i}}(t) = n_{\mathbf{i}}^{\text{stat}} \exp(-t/\tau_d). \quad (3.6)$$

In the Appendix we have derived the expression for the

TOF spectrum, Eq. (A10). Using definition (A2) of the density of particles in the velocity space  $\Gamma(\mathbf{v}, t)$  we have

$$\frac{\partial \Gamma(\mathbf{v}, t)}{\partial t} = \left[ \frac{m}{2\pi\hbar} \right]^3 V_g N_a^0 \dot{n}_{\mathbf{k}=m\mathbf{v}/\hbar}(t), \quad (3.7)$$

since  $N_a^0 \dot{n}_{\mathbf{k}}$  is the rate of creation of particles in the  $\mathbf{k}$  state. Here  $V_g = AL$  is the volume of the gas phase.

Using (3.5), (3.7), and (A10) we get the TOF signal in the following form:

$$\frac{dN_{\text{reg}}}{d\Omega dt} = N_a^0 V_g \left[ \frac{m}{2\pi\hbar} \right]^3 \left[ \frac{\mathcal{R}}{t} \right]^3 \frac{\tau_d}{t} \times \left[ \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} \sum_{\mathbf{i}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}^{\text{stat}} \right]_{\mathbf{k}=m\mathcal{R}/\hbar t}, \quad (3.8)$$

where  $\mathcal{R}$  is the position of the detector window with respect to the desorbing surface.

In order to obtain the desorption time  $\tau_d$  we note that since all particles will eventually have desorbed after long time we have the condition

$$\sum_{\mathbf{k}} \int_0^{\infty} \dot{n}_{\mathbf{k}}(t) dt = 1. \quad (3.9)$$

Using Eqs. (3.5), (3.6), and (3.9) we obtain the renormalized desorption time:

$$\tau_d^{-1} = \sum_{\mathbf{k}\mathbf{i}} \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}^{\text{stat}}, \quad (3.10)$$

which should be inserted into Eq. (3.8). This result can be compared with the conventional expression

$$\tilde{\tau}_d^{-1} = \sum_{\mathbf{k}\mathbf{i}} W(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}^{\text{stat}}. \quad (3.11)$$

Further simplification is obtained if the quasistationary distribution  $n_{\mathbf{i}}^{\text{stat}}$  is replaced by the equilibrium distribution  $n_{\mathbf{i}}(0)$ . This is known to be a very good approximation for the isothermal desorption in the experimentally interesting regime of temperatures.<sup>4,13</sup> We can then use the detailed balance condition satisfied by the transition rates

$$W(\mathbf{i}, \mathbf{k}) \exp(-E_{\mathbf{k}}/k_B T) = W(\mathbf{k}, \mathbf{i}) \exp(-E_{\mathbf{i}}/k_B T). \quad (3.12)$$

Equations (3.10) and (3.11) then read, respectively,

$$\begin{aligned} \tau_d^{-1} &= \frac{\hbar}{2Lm} \Xi(T) \sum_{\mathbf{k}} k n_{\mathbf{k}}^{\text{eq}} [1 - \exp(-\tilde{S}_{\mathbf{k}})] \\ &= \frac{1}{L} \left[ \frac{k_B T}{2\pi m} \right]^{1/2} \Xi(T) S \end{aligned} \quad (3.13)$$

and

$$\tilde{\tau}_d^{-1} = \frac{\hbar}{2Lm} \Xi(T) \sum_{\mathbf{k}} k n_{\mathbf{k}}^{\text{eq}} \tilde{S}_{\mathbf{k}} = \frac{1}{L} \left[ \frac{k_B T}{2\pi m} \right]^{1/2} \Xi(T) \tilde{S}, \quad (3.14)$$

where

$$\Xi(T) = \sum_{\mathbf{k}} \exp(-E_{\mathbf{k}}/k_B T) / \sum_{\mathbf{i}} \exp(-E_{\mathbf{i}}/k_B T).$$

Similarly, with (3.12) the TOF spectrum becomes

$$\begin{aligned} \frac{dN_{\text{reg}}}{d\Omega dt} &= \frac{N_a^0 V_g \cos\theta}{(2\pi)^3} \frac{1}{t} \left[ \frac{m\mathcal{R}}{\hbar t} \right]^4 \\ &\times \frac{\{ [1 - \exp(-\tilde{S}_{\mathbf{k}})] n_{\mathbf{k}}^{\text{eq}} \}_{\mathbf{k}=m\mathcal{R}/\hbar t}}{\sum_{\mathbf{k}} k [1 - \exp(-\tilde{S}_{\mathbf{k}})] n_{\mathbf{k}}^{\text{eq}}}, \end{aligned} \quad (3.15)$$

where  $\theta$  is the angle between the normal to the surface and  $\mathcal{R}$ . Equation (3.15), expressing the TOF spectrum in terms of the renormalized sticking coefficient, satisfies the requirements of the thermodynamical detailed balance.<sup>10</sup> The conventional result for the TOF spectrum is obtained by replacing  $1 - \exp(-\tilde{S}_{\mathbf{k}})$  with  $\tilde{S}_{\mathbf{k}}$  in (3.15).

#### IV. RENORMALIZATION OF TRANSITION RATES AND THE MASTER EQUATION

The rate equations (2.14) and (3.5) describe adsorption and desorption processes, respectively. In situations when both adsorption and desorption are present we should add (2.14) and (3.5) to get

$$\dot{n}_{\mathbf{k}}(t) = \sum_{\mathbf{i}} W^{\text{ren}}(\mathbf{k}, \mathbf{i}) n_{\mathbf{i}}(t) - \sum_{\mathbf{i}} W^{\text{ren}}(\mathbf{i}, \mathbf{k}) n_{\mathbf{k}}(t), \quad (4.1)$$

where we have introduced the renormalized transition rates between bound and continuum states:

$$W^{\text{ren}}(\mathbf{i}, \mathbf{k}) = \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} W(\mathbf{i}, \mathbf{k}) = \mathcal{R}(\tilde{S}_{\mathbf{k}}) W(\mathbf{i}, \mathbf{k}), \quad (4.2a)$$

$$W^{\text{ren}}(\mathbf{k}, \mathbf{i}) = \frac{1 - \exp(-\tilde{S}_{\mathbf{k}})}{\tilde{S}_{\mathbf{k}}} W(\mathbf{k}, \mathbf{i}) = \mathcal{R}(\tilde{S}_{\mathbf{k}}) W(\mathbf{k}, \mathbf{i}), \quad (4.2b)$$

with

$$\mathcal{R}(x) = \frac{1 - \exp(-x)}{x}. \quad (4.3)$$

Equation (4.2a) lends itself to the following interpretation. Assume that the transition from  $\mathbf{k}$  to  $\mathbf{i}$  takes place at an instant  $\tau$  between  $\tau=0$  and  $\tau_L$ . In order for the process to take place the particle must have survived until  $\tau$ , the probability of survival being  $\exp[-\tau \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})]$ . Averaging this probability over all possible transition instances produces the factor  $\mathcal{R}(\tilde{S}_{\mathbf{k}})$  since

$$\frac{1}{\tau_L} \int_0^{\tau_L} \exp\left[-\tau \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})\right] d\tau = \mathcal{R}(\tilde{S}_{\mathbf{k}}). \quad (4.4a)$$

In case of a transition from  $\mathbf{i}$  to  $\mathbf{k}$  [Eq. (4.2b)] the survival probability  $\exp[-(\tau_L - \tau) \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})]$  of the particle in the state  $\mathbf{k}$  from  $\tau$  until  $\tau_L$  must be averaged giving the same factor  $\mathcal{R}(\tilde{S}_{\mathbf{k}})$  since

$$\frac{1}{\tau_L} \int_0^{\tau_L} \exp\left[-(\tau_L - \tau) \sum_{\mathbf{i}} W(\mathbf{i}, \mathbf{k})\right] d\tau = \mathcal{R}(\tilde{S}_{\mathbf{k}}). \quad (4.4b)$$

It is obvious that the renormalized rates  $W^{\text{ren}}$  satisfy the detailed balance (3.12). It is important to note that (4.1) is valid only when  $n_i(t)$  and  $n_k(t)$  remain constant on the time scale of  $\tau_L$ . The role of the fast transients (time scale  $\tau_s$ ) is to establish a quasistationary distribution (2.5) varying appreciably only on the time scale determined by  $\tau_d \gg \tau_L$ . To close the system of the master equations we should supplement (4.1) with an equation for  $n_i(t)$ . We write it as

$$\dot{n}_i = \sum_j W(\mathbf{i}, \mathbf{j}) n_j(t) - \sum_j W(\mathbf{j}, \mathbf{i}) n_i(t) + \sum_k W^{\text{ren}}(\mathbf{i}, \mathbf{k}) n_k(t) - \sum_k W^{\text{ren}}(\mathbf{k}, \mathbf{i}) n_i(t). \quad (4.5)$$

The presence of the renormalized rate in the third term on the rhs of (4.5) is justified because  $n_k(t)$  varies slowly. However, its presence in the last term can only be treated as a postulate. We can argue, however, that such a form of the master equation [(4.1) and (4.5)] guarantees conservation of particles, and thermal equilibrium occupations are its stationary solutions. It is a challenging task to derive (4.1) and (4.5) starting from the microscopic Liouville equation.

In this paper we have restricted our attention to the prompt<sup>5</sup> sticking coefficient and desorption times. The prompt sticking coefficient accounts for the trapping process occurring on the time scale  $\tau_L$ . However, the particle is effectively adsorbed if it stays trapped for times of the order of  $\tau_d$ . To get the nonprompt sticking coefficient one must solve the master equation (4.5). The solution of (4.5), averaged over time scale  $\tau_L$ , provides a quasistationary solution (2.5) which can be used in (4.1). If  $n_i^{\text{stat}}$  differs from the equilibrium distribution (3.2), one obtains the nonprompt sticking coefficient and the nonprompt desorption time.

## V. ROLE OF CONTINUUM-CONTINUUM TRANSITIONS

In the development presented so far we have ignored the transitions between the continuum states of the surface potential. In order to show how they can change our results we first focus our attention on adsorption.

We begin with derivation of the expression for the rate of direct transition from  $\mathbf{i}$  to  $\mathbf{k}$ ,  $W^{\text{ren}}(\mathbf{i}, \mathbf{k})$ . In analogy with Eqs. (4.2a) we have

$$\begin{aligned} W^{\text{ren}}(\mathbf{i}, \mathbf{k}) &= \frac{1}{\tau_L(k)} \int_0^{\tau_L(k)} d\tau W(\mathbf{i}, \mathbf{k}) \\ &\quad \times \exp[-(\tilde{S}_k + \tilde{C}_k)\tau/\tau_L(k)] \\ &= W(\mathbf{i}, \mathbf{k}) \frac{1 - \exp[-(\tilde{S}_k + \tilde{C}_k)]}{\tilde{S}_k + \tilde{C}_k} \equiv W(\mathbf{i}, \mathbf{k}) \mathcal{R}_k, \end{aligned} \quad (5.1)$$

where

$$\mathcal{R}_k = \mathcal{R}(\tilde{S}_k + \tilde{C}_k), \quad (5.2)$$

with  $\mathcal{R}(x)$  defined in Eq. (4.3).  $\tilde{S}_k$  is given by (2.4) and

$$\tilde{C}_k = \sum_{\mathbf{k}'} W(\mathbf{k}', \mathbf{k}) \tau_L(k). \quad (5.3)$$

For clarity of further discussion, from now on we indicate explicitly the dependence of  $\tau_L$  on  $k$ . The result (5.1) differs from Eq. (4.2a) since now we have taken into account the possibility of particle escaping from the  $\mathbf{k}$  state to any  $\mathbf{k}'$  state before time  $t + \tau$ . This introduces additional terms involving  $\tilde{C}_k$  in Eq. (5.1). If we drop  $\tilde{C}_k$  from Eq. (5.1), sum it over  $\mathbf{i}$ , and multiply by  $\tau_L(k)$  we recover the result (2.10) for  $S_k$ .

Equation (5.1) underestimates the trapping rate since we have left out the possibility that a particle that escaped into state  $\mathbf{k}'$  can still be trapped; it may even be trapped after transition through a series of continuum states. In order to include such processes we have to calculate continuum-continuum transition rates.

The rate  $W^{\text{ren}}(\mathbf{k}', \mathbf{k})$  of direct transition from  $\mathbf{k}$  to  $\mathbf{k}'$  can be derived in analogy to Eq. (5.1). We get

$$\begin{aligned} W^{\text{ren}}(\mathbf{k}', \mathbf{k}) &= \frac{1 - \exp[-(\tilde{S}_{\mathbf{k}'} + \tilde{C}_{\mathbf{k}'})]}{\tilde{S}_{\mathbf{k}'} + \tilde{C}_{\mathbf{k}'}} \\ &\quad \times W(\mathbf{k}', \mathbf{k}) \frac{1 - \exp[-(\tilde{S}_k + \tilde{C}_k)]}{\tilde{S}_k + \tilde{C}_k} \\ &\equiv \mathcal{R}_{\mathbf{k}'} W(\mathbf{k}', \mathbf{k}) \mathcal{R}_k. \end{aligned} \quad (5.4)$$

Here the factor  $\mathcal{R}_{\mathbf{k}'}$  results from averaging over the creation time of the state  $\mathbf{k}'$  [cf. Eq. (4.4b)] while the factor  $\mathcal{R}_k$  arises from averaging over the destruction time of the state  $\mathbf{k}$  [cf. Eq. (4.4a)].

From Eq. (5.4) we obtain the probability of scattering  $\mathbf{k}$  to  $\mathbf{k}'$  per one encounter with the surface by multiplying it by  $\tau_L(k)$ . In order to calculate the probability of the second-order process in which the particle scatters through the intermediate state  $\mathbf{k}_1$  we write

$$\begin{aligned} \sum_{\mathbf{k}_1} [W^{\text{ren}}(\mathbf{k}', \mathbf{k}_1) \tau_L(k_1)] [W^{\text{ren}}(\mathbf{k}_1, \mathbf{k}) \tau_L(k)] \\ = \sum_{\mathbf{k}_1} \mathcal{R}_{\mathbf{k}'} W(\mathbf{k}', \mathbf{k}_1) \tau_L(k_1) \mathcal{R}_{\mathbf{k}_1}^2 W(\mathbf{k}_1, \mathbf{k}) \mathcal{R}_k \tau_L(k). \end{aligned} \quad (5.5)$$

The factor  $\mathcal{R}_{\mathbf{k}_1}^2$  arises from the *independent* averages over the creation time  $\tau_c$  and the destruction time  $\tau_d$  of the particle in the state  $\mathbf{k}_1$ . However, for this process we should average instead the probability of survival of the wave packet from time  $\tau_c$  to  $\tau_d$  subject to the condition  $\tau_c < \tau_d$ . Therefore, the factor  $\tau_L(k_1) \mathcal{R}_{\mathbf{k}_1}^2$  should be replaced in Eq. (5.5) by

$$\mathcal{T}(\mathbf{k}_1) = \frac{1}{\tau_L(k_1)} \int_0^{\tau_L(k_1)} d\tau_c \int_{\tau_c}^{\tau_L(k_1)} d\tau_d \exp\left[-(\tilde{S}_{\mathbf{k}_1} + \tilde{C}_{\mathbf{k}_1}) \frac{\tau_d - \tau_c}{\tau_L(k_1)}\right] = \tau_L(k_1) \frac{1 - \mathcal{R}(\tilde{S}_{\mathbf{k}_1} + \tilde{C}_{\mathbf{k}_1})}{\tilde{S}_{\mathbf{k}_1} + \tilde{C}_{\mathbf{k}_1}} \xrightarrow{(\tilde{S}_{\mathbf{k}_1} + \tilde{C}_{\mathbf{k}_1}) \ll 1} \frac{1}{2} \tau_L(k_1). \quad (5.6)$$

Thus, for the second-order process we have

$$W_2^{\text{ren}}(\mathbf{k}', \mathbf{k}) = \mathcal{R}_{\mathbf{k}'} \left[ \sum_{\mathbf{k}_1} W(\mathbf{k}', \mathbf{k}_1) \mathcal{T}(\mathbf{k}_1) W(\mathbf{k}_1, \mathbf{k}) \right] \mathcal{R}_{\mathbf{k}}, \quad (5.7)$$

and the all-order sum can be immediately written as

$$W_\infty^{\text{ren}}(\mathbf{k}', \mathbf{k}) = \mathcal{R}_{\mathbf{k}'} W_\infty(\mathbf{k}', \mathbf{k}) \mathcal{R}_{\mathbf{k}}, \quad (5.8)$$

where  $W_\infty(\mathbf{k}', \mathbf{k})$  satisfies either of the integral equations

$$W_\infty(\mathbf{k}', \mathbf{k}) = W(\mathbf{k}', \mathbf{k}) + \sum_{\mathbf{k}_1} W(\mathbf{k}', \mathbf{k}_1) \mathcal{T}(\mathbf{k}_1) W_\infty(\mathbf{k}_1, \mathbf{k}) \quad (5.9a)$$

or

$$W_\infty(\mathbf{k}', \mathbf{k}) = W(\mathbf{k}', \mathbf{k}) + \sum_{\mathbf{k}_1} W_\infty(\mathbf{k}', \mathbf{k}_1) \mathcal{T}(\mathbf{k}_1) W(\mathbf{k}_1, \mathbf{k}). \quad (5.9b)$$

Now we can return to Eq. (5.1). It describes the process of direct transition from  $\mathbf{k}$  to  $\mathbf{i}$ . As we have already mentioned a different process is also possible in which a particle scatters from  $\mathbf{k}$  into another continuum state (or goes through a sequence of them) before getting trapped into the bound state  $\mathbf{i}$ . The transition through a sequence of continuum states is described by the rate given in Eqs. (5.8) and (5.9). Therefore, the total transition rate from the continuum state  $\mathbf{k}$  into the bound state  $\mathbf{i}$  is given by

$$W_\infty^{\text{ren}}(\mathbf{i}, \mathbf{k}) = W_\infty(\mathbf{i}, \mathbf{k}) \mathcal{R}_{\mathbf{k}}, \quad (5.10)$$

where

$$W_\infty(\mathbf{i}, \mathbf{k}) = W(\mathbf{i}, \mathbf{k}) + \sum_{\mathbf{k}_1} W(\mathbf{i}, \mathbf{k}_1) \mathcal{T}(\mathbf{k}_1) W_\infty(\mathbf{k}_1, \mathbf{k}). \quad (5.11)$$

$W_\infty(\mathbf{k}_1, \mathbf{k})$  is the total rate of continuum-continuum transition given by Eq. (5.9). The monochromatic sticking coefficient is then obtained using Eq. (5.10):

$$S_{\mathbf{k}} \equiv \sum_{\mathbf{i}} W_\infty^{\text{ren}}(\mathbf{i}, \mathbf{k}) \tau_L(k) = \left[ \tilde{S}_{\mathbf{k}} + \sum_{\mathbf{k}_1} \tilde{S}_{\mathbf{k}_1} \frac{\mathcal{T}(\mathbf{k}_1)}{\tau_L(k_1)} W_\infty(\mathbf{k}_1, \mathbf{k}) \tau_L(k) \right] \mathcal{R}_{\mathbf{k}}, \quad (5.12)$$

where  $\tilde{S}_{\mathbf{k}}$  is given in Eq. (2.4) and  $W_\infty(\mathbf{k}_1, \mathbf{k})$  is the solution of the integral equation (5.9). Equation (5.12) reduces back to (2.10) when  $W(\mathbf{k}', \mathbf{k}) \equiv 0$ .

Analysis of the desorption process, similar to that for adsorption leading to Eq. (5.1), gives the rate of direct transitions between  $\mathbf{i}$  and  $\mathbf{k}$  in the following form:

$$W^{\text{ren}}(\mathbf{k}, \mathbf{i}) = \mathcal{R}_{\mathbf{k}} W(\mathbf{k}, \mathbf{i}). \quad (5.13)$$

Consequently, when the scattering to the  $\mathbf{k}$  state is preceded by a series of transitions to other continuum states, the total transition rate from  $\mathbf{i}$  to  $\mathbf{k}$  is given by the expressions analogous to Eqs. (5.10) and (5.11):

$$W_\infty^{\text{ren}}(\mathbf{k}, \mathbf{i}) = \mathcal{R}_{\mathbf{k}} W_\infty(\mathbf{k}, \mathbf{i}), \quad (5.14)$$

where

$$W_\infty(\mathbf{k}, \mathbf{i}) = W(\mathbf{k}, \mathbf{i}) + \sum_{\mathbf{k}_1} W_\infty(\mathbf{k}, \mathbf{k}_1) \mathcal{T}(\mathbf{k}_1) W(\mathbf{k}_1, \mathbf{i}). \quad (5.15)$$

The direct transition rates  $W^{\text{ren}}$  [Eqs. (5.1), (5.4), and (5.13)] satisfy the condition of detailed balance since the rates  $W$  do. It is easy to show that also the total transition rates  $W_\infty^{\text{ren}}$  [Eqs. (5.8), (5.10), and (5.14)] satisfy the same conditions:

$$W_\infty^{\text{ren}}(\mathbf{k}, \mathbf{k}') \exp(-E_{\mathbf{k}'} / k_B T) = W_\infty^{\text{ren}}(\mathbf{k}', \mathbf{k}) \exp(-E_{\mathbf{k}} / k_B T), \quad (5.16)$$

$$W_\infty^{\text{ren}}(\mathbf{k}, \mathbf{i}) \exp(-E_{\mathbf{i}} / k_B T) = W_\infty^{\text{ren}}(\mathbf{i}, \mathbf{k}) \exp(-E_{\mathbf{k}} / k_B T). \quad (5.17)$$

In Sec. IV we have shown that the adsorption-desorption kinetics can be described by the conventional master equations (4.1) and (4.5) provided the transition rates are renormalized according to Eq. (4.2). We have demonstrated in this section that when the continuum-continuum transitions are important, the rates  $W_\infty^{\text{ren}}$  [(5.10) and (5.14)] should replace those given by Eq. (4.2) in the master equations (4.1) and (4.5). Obviously the rates  $W_\infty^{\text{ren}}$  reduce to  $W^{\text{ren}}$  given by (4.2) when the continuum-continuum transitions are absent.

## VI. PHONON-INDUCED STICKING AND DESORPTION

The approach developed in the preceding four sections is general since it does not depend on particular microscopic mechanisms of sticking or desorption. For physisorbed species the microscopic energy exchange process between the solid and the adsorbate is dominated by emission and absorption of phonons. The phonon-cascade approach to sticking and desorption was developed with the kinetics described by a master equation in which the transition rates were calculated for one-phonon processes. Desorption times<sup>2</sup> and TOF spectra<sup>3</sup> were analyzed in detail; however, the problem of sticking was left out because the approach did not guarantee the proper normalization of sticking coefficients.

We present here numerical examples of sticking coefficients for He-graphite and He-solid argon. The necessary rates  $W(\mathbf{i}, \mathbf{k})$  were calculated by Gortel and Kreuzer<sup>2</sup> for a model of a mobile adsorbate, in which the adsorbed particle can move freely along the surface (the surface potential depends on  $z$  only) and the particle momentum parallel to the surface is conserved in any elementary phonon emission or absorption process. In this case

$$W(\mathbf{k}, \mathbf{i}) = W(k, i) \delta_{\mathbf{k}, \mathbf{k}_i}, \quad (6.1)$$

where  $\delta_{\mathbf{k}, \mathbf{k}_i}$  is the Kronecker delta. The rates  $W(k, i)$  were calculated for the Morse surface potential of depth  $V_0$  and the range parameter  $\gamma$  with the derivative coupling used to represent the particle-phonon interaction;<sup>14</sup> the Debye model characterized by the Debye frequency  $\omega_D$  was used to describe the phonon spectrum. The result for the transition rate can be written in the form

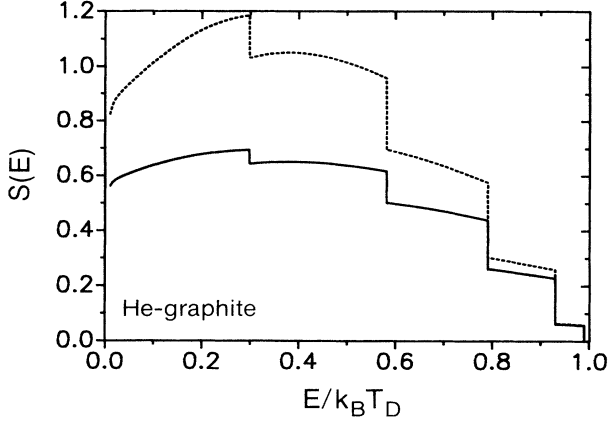


FIG. 1. Monochromatic prompt sticking coefficient for He-graphite system vs energy of He atoms for  $T=30$  K. Dotted line: conventional result [Eq. (2.4)]; solid line: renormalized result [Eq. (2.10)]. Parameters:  $\sigma_0=4.88$ ,  $r=27.46$ ,  $T_D=185$  K.

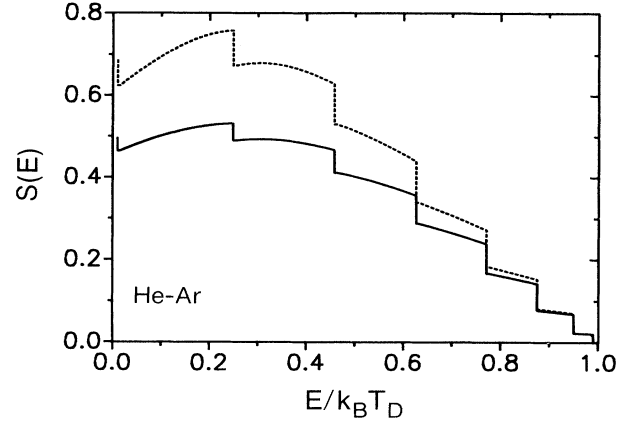


FIG. 2. Same as Fig. 1, but for He-solid argon at  $T=3$  K.  $\sigma_0=10.2$ ,  $r=60$ ,  $T_D=92$  K.

$$W(k, j) = \omega_D \frac{3\pi^2 m}{2\gamma L r^4 M_s} \frac{2\sigma_0 - 2j - 1}{j! \Gamma(2\sigma_0 - j)} \frac{\eta \sinh(2\pi\eta)}{\cos^2(\pi\sigma_0) + \sinh^2(\pi\eta)} |\Gamma(\frac{1}{2} + \sigma_0 + i\eta)|^2 \frac{[(\sigma_0 - j - \frac{1}{2})^2 + \eta^2]^3}{\exp\{[(\sigma_0 - j - \frac{1}{2})^2 + \eta^2]\delta/r\} - 1} \times \Theta(r - (\sigma_0 - j - \frac{1}{2})^2 - \eta^2), \quad (6.2)$$

where

$$\sigma_0^2 = \frac{2mV_0}{\hbar^2 \gamma^2}, \quad r = \frac{2m\omega_D}{\hbar \gamma^2}, \quad \delta = \frac{\hbar\omega_D}{k_B T}, \quad \eta = \frac{k}{\gamma}, \quad (6.3)$$

$m$  is the mass of the particle, and  $M_S$  is the mass of the unit cell of the solid.

Inserting (6.1) and (6.2) into (2.4) we obtain  $\tilde{S}_k$ , and from (2.10) we get the renormalized sticking coefficient  $S_k$ . In Figs. 1 and 2 we plot  $S_k$  and  $\tilde{S}_k$  for two model systems: He-graphite and He-solid argon, respectively. We have checked numerically that for lower energies  $\tilde{C}_k \ll \tilde{S}_k$  [cf. Eqs. (5.1) and (2.10)] and thus we can ignore the effects of the continuum-continuum transitions. At higher energies, when the sticking probability gets smaller the continuum-continuum scattering will be more important. Each discontinuity in Figs. 1 and 2 appears at the energy for which one of the bound states of the surface potential becomes inaccessible by one phonon transition. Clearly, even for these weakly interacting systems, for which the one-phonon approximation is expected to be valid, renormalization (2.10) of the sticking coefficient proves necessary.

Temperature dependence of the isothermal total sticking coefficient  $S$  and  $\tilde{S}$  is plotted in Figs. 3 and 4. Note that for He-graphite  $\tilde{S}$  becomes greater than 1 at higher temperatures.

In order to obtain the renormalized desorption time we note that using Eqs. (3.13) and (3.14) we have

$$\frac{\tau_d}{\tilde{\tau}_d} = \frac{\tilde{S}}{S}. \quad (6.4)$$

The renormalized desorption time  $\tau_d$  may differ from  $\tilde{\tau}_d$  by a factor of up to 2 for He-graphite. However, this renormalization affects only the preexponential factor in the Frenkel-Arrhenius parametrization of the desorption time and its effect is hardly seen on the usual Arrhenius plot of  $\log_{10}(\tau_d)$  vs  $1/T$ .

## VII. CONCLUSIONS

In this paper we have reexamined the problem of sticking and desorption to account for quantum processes tak-

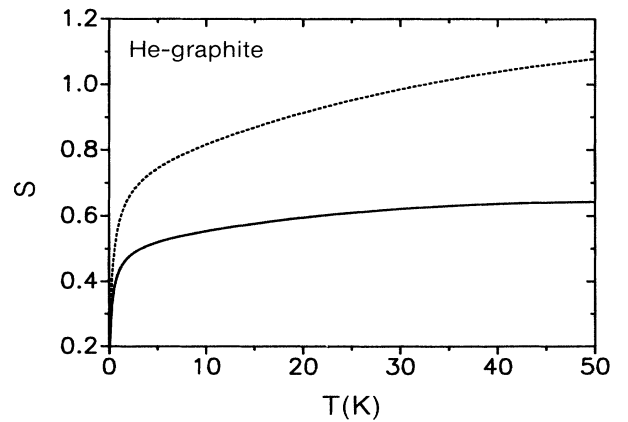


FIG. 3. Total isothermal prompt sticking coefficient for He-graphite vs temperature. Dotted line: conventional result [Eq. (2.13)]; solid line: renormalized result [Eq. (2.12)]. Parameters as in Fig. 1.

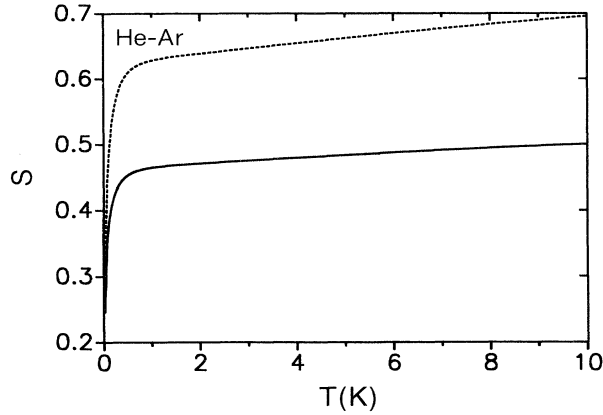


FIG. 4. Same as in Fig. 3 but for He–solid argon. Parameters as in Fig. 2.

ing place on the time scale  $\tau_L$ , the quantum oscillation period of the extended states. We have derived the expression for the sticking coefficient substantially different from the conventional one. In contrast to the latter our result for the sticking coefficient is appropriately bounded by 1. We have demonstrated that the renormalized TOF spectrum is related to the renormalized sticking coefficient, satisfying the requirements of the thermodynamical detailed balance. We have also shown how to modify the calculations of sticking and desorption for the case when the rates of inelastic continuum-continuum transitions are comparable with the rates of transitions between continuum and bound states of the surface potential.

The renormalized sticking coefficients, TOF spectra, and desorption times can be obtained in the conventional manner from the master equation if we modify the transition rates between continuum and bound states according to Eqs. (4.2) [or Eqs. (5.10) and (5.14) when the inelastic continuum-continuum transitions are important]. The renormalized master equation can be used to obtain nonprompt<sup>5</sup> quantities characterizing sticking and desorption. It might be possible to derive the modified master equations (4.1) and (4.5) from the Liouville equation using, e.g., methods employed by Tsukada and Gortel,<sup>15</sup> who have incorporated into the master equation a competition between processes occurring at various competing time scales.

We have demonstrated on a particular example of relatively weakly physisorbed systems (He-graphite and He–solid argon) that the renormalization of the sticking coefficient can reduce it by a factor of 2 or more. For He–solid argon our calculated sticking coefficient at  $T = 3$  K agrees with the experimental value of 0.48.<sup>16</sup>

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#### APPENDIX

In this Appendix we outline a derivation of the expression for the angular resolved time-of-flight spectrum in desorption. This derivation is based on the one presented in Ref. 4 and is given here in order to establish appropriate normalization.

Let  $f(\mathbf{r}, \mathbf{v}, t)$  be the configuration-space particle number density of particles in the gas phase. The particle density,  $\mathbf{v}$ -space particle density, and the total number of particles in the gas phase, respectively, are given by

$$\rho(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d^3v, \quad (\text{A1})$$

$$\Gamma(\mathbf{v}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d^3r, \quad (\text{A2})$$

$$N_g(t) = \int \int f(\mathbf{r}, \mathbf{v}, t) d^3v d^3r. \quad (\text{A3})$$

The function  $f(\mathbf{r}, \mathbf{v}, t)$  satisfies the Boltzmann equation

$$\left[ \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \right] f(\mathbf{r}, \mathbf{v}, t) = \sigma(\mathbf{r}, \mathbf{v}, t), \quad (\text{A4})$$

where  $\sigma(\mathbf{r}, \mathbf{v}, t)$  is the source term due to the desorption process. Integrating (A4) over  $\mathbf{r}$  and using (A2) we obtain

$$\int \sigma(\mathbf{r}, \mathbf{v}, t) d^3r = \frac{\partial \Gamma(\mathbf{v}, t)}{\partial t}. \quad (\text{A5})$$

For the TOF spectra we approximate the solid surface by a point source at  $\mathbf{r}_s$ , obtaining

$$\sigma(\mathbf{r}, \mathbf{v}, t) = \delta(\mathbf{r} - \mathbf{r}_s) \frac{\partial \Gamma(\mathbf{v}, t)}{\partial t}. \quad (\text{A6})$$

For the desorption process triggered at  $t = 0$  the solution of the equation (A4) is

$$\begin{aligned} f(\mathbf{r}, \mathbf{v}, t) &= \int_0^t \sigma(\mathbf{r} - \mathbf{v}(t - \tau), \mathbf{v}, \tau) d\tau \\ &= \int_0^t \delta(\mathbf{r} - \mathbf{r}_s - \mathbf{v}(t - \tau)) \frac{\partial \Gamma(\mathbf{v}, \tau)}{\partial \tau} d\tau. \end{aligned} \quad (\text{A7})$$

The rate at which particles are registered by a small detector at  $\mathbf{r}_D$  is given by

$$\frac{dN_{\text{reg}}}{dt} = \mathbf{j}(\mathcal{R}, t) \cdot d\mathbf{S} = \left[ \mathbf{j}(\mathcal{R}, t) \cdot \frac{\mathcal{R}}{\mathcal{R}} \right] \mathcal{R}^2 d\Omega, \quad (\text{A8})$$

where  $\mathcal{R} = \mathbf{r}_D - \mathbf{r}_s$ , and  $d\Omega$  is the solid angle subtended by the detector window of area  $dS$  assumed to be normal to  $\mathcal{R}$ . Since the current density  $\mathbf{j}(\mathbf{r}, t)$  is given by

$$\mathbf{j}(\mathbf{r}, t) = \int d^3v \mathbf{v} f(\mathbf{r}, \mathbf{v}, t), \quad (\text{A9})$$

we get, using (A7) and (A8),

$$\frac{dN_{\text{reg}}}{d\Omega dt} = \int_0^t \frac{d\tau}{\tau} \left[ \frac{\mathcal{R}}{\tau} \right]^3 \frac{\partial \Gamma(\mathcal{R}/\tau, t - \tau)}{\partial t}. \quad (\text{A10})$$

The above result can be easily generalized to the case of the extended source by integrating (A10) over  $\mathbf{r}_s$  over the desorbing surface and dividing by the area of the surface.



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