

Role and Mechanism of Island Formation in Chemisorption

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Chemisorption on solid surfaces is treated as a combination of a seeding process, whereby molecules adsorb directly onto vacant sites, and an island-growth mechanism initiated by physisorption over occupied sites followed by lateral migration towards vacant sites. It is argued that the islands are compact 2D (Eden) clusters, at marked variance with models which assume random distribution of the chemisorbed molecules. Simple general expressions are derived for the sticking probability and adsorption isotherms. Numerical results are presented for several cases of interest.

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Some thirty years ago, Kisliuk derived a simple expression for the chemisorption (sticking) probability of gas molecules onto solid surfaces, which is still widely used for the analysis and interpretation of adsorption data.¹⁻³ According to his model, chemisorption takes place along two pathways, both involving a mobile physisorbed (precursor) state as an intermediate. In one mechanism the precursor is "intrinsic," whereby the molecule is initially physisorbed above a vacant chemisorption site, while in the second and "extrinsic precursor" is formed, i.e., the molecule is trapped above an occupied site. The intrinsic precursor molecule may desorb, migrate laterally to a neighbor site, or become chemisorbed. An extrinsic precursor molecule (epm) can either desorb or jump to a neighbor site; chemisorption can take place if after one or more random jumps it arrives above an unoccupied site thereby becoming an intrinsic precursor.

A fundamental limitation of Kisliuk's model (and others)^{1,2,4} is the underlying assumption that the lateral distribution of the *chemisorbed* molecules on the surface is *random*. This is justified if their diffusion rates are much faster than the rate of adsorption and their lateral interaction energies negligible. However, this is not generally the case, especially at low temperatures. Thus, positional correlations between the chemisorbed molecules may be induced by, as well as affect, the adsorption process. In particular, it is clear that a molecule initially captured above an occupied site will, most likely, be chemisorbed next to an already chemisorbed molecule. Indeed, recent computer simulations reveal that molecules adsorbed via this (epm mediated) mechanism tend to aggregate into two-dimensional (2D) clusters ("islands").^{5,6} Actually, the existence and importance of lateral positional correlations have already been appreciated by Kisliuk, but neglected because of mathematical difficulties.¹

Today, based on recent studies of aggregation and growth phenomena, we know that the indirect adsorption process is, in fact, equivalent to the process of generating

the so-called Eden clusters, namely, clusters which grow by randomly adding particles to their perimeter⁷ (starting with a single particle or a small group of particles, as a nucleation center). It is known that Eden clusters are compact aggregates with smooth boundaries, i.e., aggregates with no holes and with (for 2D) $L \sim A^{1/2} \sim K^{1/2}$ where L , A , and K are the perimeter length, the area, and the number of particles of the cluster, respectively. (Note that the periodicity of the sublattice of the chemisorbed layer need not be the dense 1×1 , but may well be a more open one—depending on lateral interactions.^{3,5,6}) Thus, as opposed to models assuming random distribution we have here a clear picture of the lateral positional correlations between the chemisorbed molecules.

Motivated by this notion and by the need to better understand the role of aggregation and lateral interactions in adsorption kinetics, we present below a theoretical framework for calculating adsorption isotherms and sticking probabilities in systems where island formation is important. The theory also enables us to calculate detailed properties such as the cluster size distribution and its moments.⁸ Although our examples will concern compact islands, the formulation below is applicable to any cluster growth model (e.g., fractal aggregates, $L \sim A^{1/d_f}$), as may be dictated by specific interactions or by kinetic mechanisms. A comment on Kisliuk's model will be added at the end of the discussion.

In line with the picture outlined above we treat chemisorption as a combination of two mechanisms: (i) A *seeding process*, whereby a gas-phase molecule is initially captured (with probability α_i) above a vacant site onto which (or nearby vacant site) it may be chemisorbed (with probability P_i). The net sticking probability is $S_0 = \alpha_i P_i$. A molecule adsorbed by this mechanism serves as a nucleus for island formation. (ii) *Island growth*; islands grow as a result of physisorption of molecules on top of the chemisorbed overlayer (with probability α_e), followed by random lateral diffusion jumps (of length a), until arriving at the island's perimeter where chemisorption can take place (with probability P_e). (For

simplicity, we set $a \equiv 1$.) The effective sticking probability by this process, S_1 , depends on α_e and P_e , as well as on the probability that the epm will not desorb prior to reaching the island's coastline. The latter is a function of island size and of w_l and w_d [which denote respectively, the frequency (rate) of lateral jumps and the rate of desorption of an epm]. Since the arrival and the subsequent chemisorption of the epm at the island boundary is random, process (ii) generates 2D Eden clusters.

Activation barriers for lateral diffusion of chemisorbed molecules are quite high (typically ~ 10 Kcal/mol). Thus diffusion is important at relatively high (at, or above room) temperatures and on long experimental time scales. Throughout this Letter we shall only consider systems where diffusion of chemisorbed molecules is not important and accordingly treat them as stationary. It may be noted though that in systems governed by strong lateral attractive forces, lateral diffusion is another important mechanism of aggregation and formation of (typically highly ramified) islands.⁶

Let $g(t)$ denote the seeding rate (per adsorption site), i.e. $Mg(t)dt$ is the number of molecules chemisorbed by process (i) above, in the time interval $t, t+dt$, with M denoting the number of surface sites. Also, let $K(t-t')$ denote the average size, at time t , of an island which was seeded at time t' , with $K(0) \equiv 1$. With these definitions, the coverage at time t can be expressed as a convolution of the two processes,

$$\theta(t) = \int_0^t g(t')K(t-t')dt'. \quad (1)$$

At low coverages the probability of multiple seeding, i.e., island growth around two (or more) neighboring seeds, is small. (It can be shown that this probability is $\sim \theta^2/\langle K \rangle$, where $\langle K \rangle$ is the average island size.) Consequently, different islands grow independently of each other and the fluctuations in size of islands of age t are small, $\delta K(t) \sim K(t)^{1/2}$. Note also that an island growing around two neighboring seeds will exhibit the usual characteristics of an Eden cluster, provided its diameter is large compared to the distance between the seeds. As θ increases, island coalescence, and correspondingly, the variance in island size and shape, become increasingly important and the calculation of K increasingly more complicated. In this Letter we focus attention on the regime of independent island growth. The effects of island-island coalescence will be treated in an approximate manner, to qualitatively account for the behavior at high θ .

The sticking probability is defined by $S = (1/J)d\theta/dt$, where J (the flux) is the number of molecules impinging in unit time on an area ($\sim a^2$) corresponding to one adsorption site. From Eq. (1) we find

$$\dot{\theta} = JS(t) = g(t) + \int_0^t g(t')\dot{K}(t-t')dt', \quad (2)$$

demonstrating the additive contributions of the two ad-

sorption pathways to the sticking probability. For instance, when the island growth rate is negligible, i.e., $\dot{K} = 0$, only the direct (seeding) mechanism survives. The other (less common) extreme may be realized if adsorption takes place by cluster growth around a fixed number of nucleation centers (e.g., defects), implying $g(t) \propto \delta(t)$ and $S \propto \dot{K}(t)$.

Assuming that the seeding rate is given by the "Langmuirian" form

$$g(t) = JS_0[1 - \theta(t)], \quad (3)$$

Eq. (1) becomes an integral equation which may be solved by standard (e.g., Laplace transform) methods; in some cases analytically and in others numerically, depending on the form of $K(t)$. Let us examine two cases of interest, demonstrating the interplay between physisorption, desorption, diffusion, and chemisorption kinetics. Both examples correspond to a power-law growth rate, $\dot{K} \sim K^a$.

(a) *Short-lived extrinsic precursor.*—Consider first the case in which the average distance traversed by an epm before desorption, D , is short compared to the diameter of a typical island. In this case only those molecules which have been physisorbed within an annulus of width $\sim D$ along the island coastline are likely to become chemisorbed. Thus, since the islands are compact 2D clusters, $\dot{K} = cK^{1/2}$; hence

$$K(t) = (1 + \frac{1}{2}ct)^2, \quad (4)$$

with $c \sim J\alpha_e P_e D$. [$\dot{K} \sim K^a$ with $a \sim 1$ is more appropriate for small t , but this also implies fast initial growth and rapid crossover to $a = \frac{1}{2}$ behavior.] D is a function of w_l and w_d . $D \sim a = 1$ if $w_l/w_d \leq 1$, while if $w_l/w_d \gg 1$, the Gaussian approximation $D \sim (w_l/w_d)^{1/2}$ is valid (recall, however, the condition $D < K^{1/2}$). Specific models can be used to obtain detailed expressions for D .

Substitution of Eqs. (3) and (4) into Eqs. (1) and (2) yield adsorption isotherms and sticking probabilities, as shown in Fig. 1, for several values of c . A reduced time scale $\tilde{t} = JS_0 t \equiv t/\tau$ is used for convenience. The special case, $c = 0$ [$\dot{K}(t) = 0$] is, of course, Langmuir's model. In this case only direct adsorption takes place and $S = S_0(1 - \theta) \equiv S_L$ and $\theta(t) = 1 - \exp(-t/\tau)$, as follows from Eqs. (1)-(4). The addition of a second (island mediated) adsorption mechanism implies $S(\theta) > S_L(\theta)$ for all θ , with S/S_L increasing with c , as is confirmed in Fig. 1. More explicitly, for $\tilde{c}\tilde{t} = ct < 1$, Eqs. (1)-(4) can be shown to give $\theta = \tilde{t} + 0.5(\tilde{c} - 1)\tilde{t}^2 + \dots$ and $S/S_0 = 1 + (\tilde{c} - 1)\theta - 0.25\tilde{c}^2\theta^2 + \dots$, with $\tilde{c} \equiv c\tau = c/JS_0$. (Closed-form expressions are also available for $ct \gg 1$ but are less interesting here.) Note in particular that for all $\tilde{c} > 1$, the initial slope of S vs θ is positive [$dS/d\theta \rightarrow S_0(\tilde{c} - 1)$], i.e., the reduction in direct (Langmuir) adsorption as θ increases is overcompensated through the enhanced indirect process. Alternatively phrased: The effective sticking probability due to an island of size K is

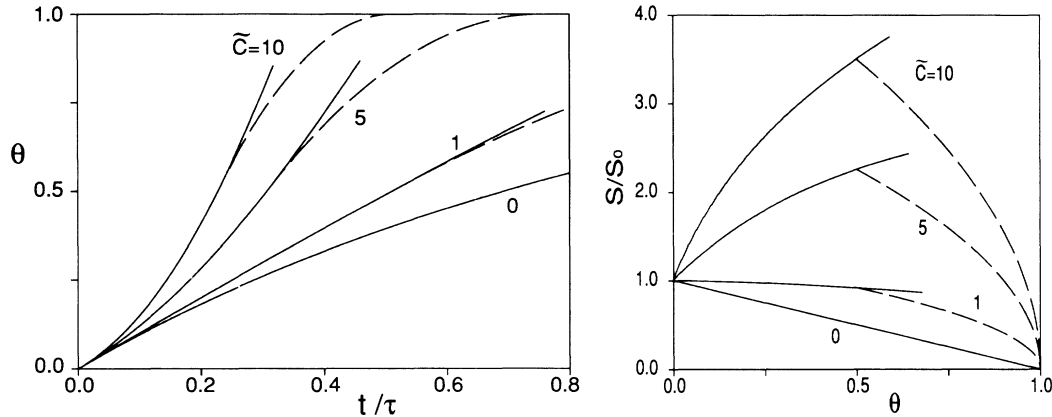


FIG. 1. Adsorption isotherms (left) and sticking probabilities (right), for the island growth model of Eq. (4); for several values of $\tilde{c} = c\tau$. The dashed lines (for $\theta > 0.5$) correspond to the $S'(\theta)$ discussed in the text.

$S_1 = \dot{K}/JK = \tilde{c}S_0/K^{1/2}$; thus, $\tilde{c} > 1$ implies that $S_1 > S_0/K^{1/2}$, which for small islands [low θ ; hence $K \rightarrow K(0) = 1$] reads $S_1 > S_0$. (S_1 decreases with K , because only the $\sim DK^{1/2}$ perimeter sites support chemisorption.)

In most experimental systems $S(\theta)$ is a monotonically decreasing function of θ , as shown by some curves in Figs. 1 and 2. Increasing $S(\theta)$ vs θ curves as shown in Fig. 1 for $\tilde{c} > 1$, though much less common, have been observed in experiments⁹ and computer simulations,⁵ e.g., for the $N_2/\text{Ru}(001)$ system. [The results of Ref. 9(a) which show a pronounced maximum in S at $\theta_{\text{max}} \sim 0.5$, may be well fitted to a curve as in Fig. 1(b), similarly so for the CO/W ^{9(b)} and the $\text{CO}/\text{Re}(0001)$ ^{9(c)} systems.] The simulations reveal that attractive interactions between extrinsic precursor molecules and neighboring chemisorbed molecules are responsible for this behavior.⁵ Similarly, in our terminology, the effect of such interactions is to increase α_e and P_e (compared to α_i and

P_i), as well as to reduce w_d ; all contributing to increase \tilde{c} .

Equation (4) describes the growth of a single island, and is therefore applicable insofar as island-island coalescence is not appreciable. The value of θ above, where this is no longer the case, depends on the island size distribution (which in the present case emphasizes the large islands⁸), but $\theta \sim 0.5$ is a sound estimate. ($\theta \approx 0.55$ is the so-called "jamming limit" in the "random sequential addition" problem of disks on a surface,^{10,11} the coverage above which further addition of disks implies overlap. Also, $\theta \approx 0.5-0.6$ is the threshold region of site percolation on different 2D lattices.) A detailed treatment of island merging is beyond the scope of this Letter.⁸ Nevertheless, as a qualitative guideline for the behavior at high θ , we have used in Fig. 1 the phenomenological (decreasing) function $S'(\theta) = S_0(1 - \theta) + \gamma(1 - \theta)^{1/2}$ for $\theta \geq 0.5$. The constant γ is determined by the condition $S(\theta = 0.5) = S'(\theta = 0.5)$. The corresponding correction for $\theta(t)$ is obtained by integration. The first term in S' is the direct adsorption, the second—which represents the indirect process—was chosen in this form because $(1 - \theta)^{1/2}$ is proportional to the total coastline length of the lakes of vacant sites characterizing the ("percolated") adlayer at high θ . (This form is exact for equal size islands whose centers form a periodic 2D lattice.)

(b) *Exponential island growth.*— Consider now a system where w_d is so much smaller than w_l that all molecules physisorbed on top of an island survive long enough to reach its boundary [i.e., $D \sim (w_l/w_d)^{1/2} > K^{1/2}$], and become chemisorbed there upon first or subsequent arrival. If w_d and w_e are Arrhenius type, i.e., $w_d = v_d \times \exp(-\epsilon_d/kT)$, etc., this condition will be realized at sufficiently low T , provided $\epsilon_d > \epsilon_l$, which is typically the case (see, e.g., Ref. 5). Since the rate of physisorption on an island of size K is $J\alpha_e K$, we have $\dot{K} = J\alpha_e K = JS_1 K$; hence $K = \exp(JS_1 t)$. (Here $S_1 \equiv \dot{K}/JK = \alpha_e$ is independent of K .) With the aid of

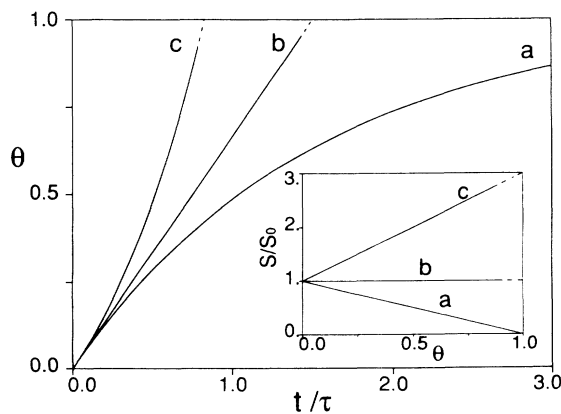


FIG. 2. Inset: Adsorption isotherms and sticking probabilities for the exponential island growth model, Eqs. (5) and (6). Curves a, b, and c correspond to $S_1/S_0 = 0$ (Langmuir), 1, and 3, respectively.

Eqs. (1)–(3) we then find

$$\theta(t) = [S_0/(S_1 - S_0)] \{ \exp[J(S_1 - S_0)t] - 1 \}, \quad (5)$$

from which it follows that the sticking probability is a simple weighted sum of the direct and indirect adsorption pathways,

$$S(\theta) = S_0(1 - \theta) + S_1\theta. \quad (6)$$

We see again that if the indirect, island-mediated, adsorption pathway is preferential ($S_1 > S_0$), $S(\theta)$ increases with θ ; see Fig. 2. Note, however, that the expressions for $\theta(t)$ and $S(\theta)$ do not depend on the sizes or the shapes of the islands. This is because if all extrinsic precursor molecules are eventually chemisorbed, the structure of the adlayer is irrelevant. Thus, although the indirect adsorption mechanism generates 2D Eden clusters, this will not be reflected in $\theta(t)$ or $S(\theta)$. [Indeed, Eq. (6) has been derived by another approach in Ref. 6.] Furthermore, as long as extrinsic precursors do not desorb, Eqs. (5) and (6) are valid for all t and θ . Thus, unlike in Fig. 1, we have not attempted here any correction to account for island coalescence (although the assumption of negligible desorption must fail at very high θ).

We close with a comment on the relation between our approach and Kisliuk's model.¹ Since Eqs. (5) and (6) do not depend on adlayer structure, they are valid as well for a random distribution of the chemisorbed molecules, as in Kisliuk's model. In this case the probability that an epm will execute n lateral diffusion steps without desorbing is $(\alpha\theta)^n$, where $\alpha = w_l/(w_l + w_d)$. Multiplying by $S_0(1 - \theta)$ [the probability of arrival and chemisorption onto a vacant site upon the $(n+1)$ jump], and summing over all n ($n=0$ is the seeding process) yields Kisliuk's well-known expression $S(\theta) = S_0(1 - \theta)/(1 - \alpha\theta)$. Indeed, for $w_d/w_l \ll 1$, $\alpha \rightarrow 1$, and $S(\theta) = S_0$ which coincides with Eq. (6), provided $S_1 = S_0$, as is tacitly assumed in Kisliuk's model (for $\alpha = 1$). Finally, we note that although casual island growth is not a part of that model, clusters do exist even for random distributions. Actually, these are the familiar percolation clusters. For chemisorption problems this notion is primarily relevant when $S_1 \ll S_0$, i.e., when only direct adsorption takes place, or when lateral diffusion of the chemisorbed molecules is very fast.

The above discussion has demonstrated how the growth function $K(t)$ affects the adsorption process. In principle, the theory can also be applied in the reverse direction, namely, to derive $K(t)$ from experimental adsorption isotherm. Formally, with Eq. (3) for $g(t)$, one

can use Laplace transform methods to invert Eq. (1) and obtain $K(t)$ as a function of $\theta(t)$. We are currently pursuing this direction for real and model systems.⁸ Additional work is called for in several other directions, including a better and more general treatment of island merger, alternative island-growth models, and analysis of the effects of adsorbate lateral interactions, mainly in systems with adlayer periodicities (higher than 1×1) where grain boundaries are important.

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