

Reaction kinetics in confined geometries: Lonely adatoms in space

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There is a close relation between the problems of second-layer nucleation in epitaxial crystal growth and chemical surface reactions, such as hydrogen recombination, on interstellar dust grains. In both cases, standard rate equation analysis has been found to fail because the process takes place in a confined geometry, and under typical conditions the mean number of reactant particles on the surface is small compared to unity (the lonely adatom regime). Using scaling arguments developed in the context of second-layer nucleation, I present a simple derivation of the hydrogen recombination rate for small and large grains. I clarify the reasons for the failure of rate equations for small grains, and point out a logarithmic correction to the reaction rate when the reaction is limited by the desorption of hydrogen atoms (the second-order reaction regime).

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Rate equations are a widely used tool for the mathematical description of kinetic phenomena. Despite successful applications in many different areas of science, however, there are instances where their predictions are known to be qualitatively incorrect. A prominent example is diffusion-controlled reaction in low dimensions [1]. The purpose of this Rapid Communication is to point out the close relation between two kinetic problems, second-layer nucleation in epitaxial crystal growth [2–7] and chemical reactions on dust grain surfaces in interstellar space [8–11], in which deviations from rate equation theory arise because the processes of interest take place in a spatially confined geometry.

In both cases, one is concerned with the rate of a reaction confined to a finite surface region, onto which particles impinge and from which they leave again if no reaction takes place. In the case of second-layer nucleation, the confining region is the top terrace of a two-dimensional island, bounded by a step edge, while in the astrophysical context it is the (closed) surface of a small grain. In the first case, the atoms leave the island by crossing the step, while in the second case they desorb from the grain surface.¹

The two problems also differ in that in second-layer nucleation only the first nucleation event on the island is relevant—all atoms deposited after this event merely contribute to the growth of the second-layer nucleus—whereas in the problem of grain surface reactions the reactants are usually assumed to desorb from the grain once they have formed, so that a steady state with a constant production rate is established. In this sense, second-layer nucleation is a first passage problem [6], while grain surface kinetics deals with stationary processes.

For both problems it has been found that standard rate equation analysis fails when the mean number of particles present on the surface becomes small compared to unity, the *lonely adatom* [3] or *fluctuation-dominated* [4] regime. In this regime, the reaction becomes a rare event which has to be treated statistically. Here, I show how the time scale

analysis developed in the context of second-layer nucleation [3,5] can be applied to the problem of hydrogen recombination, one of the most important grain surface reactions of astrophysical interest. In this reaction, two hydrogen atoms meet to form a H₂ molecule, in analogy to the formation of a second layer nucleus in the case where dimers are stable (irreversible nucleation, critical nucleus size $i^* = 1$). I provide a simple derivation of the recombination rate in all three reaction regimes. I then discuss the reasons for the breakdown of the rate equation theory for small grains, and I point out the existence of a logarithmic correction to the recombination rate in the second-order reaction regime, which was overlooked so far in the astrophysical context.

The notation follows that of Ref. [10]. Atoms impinge on the grain surface at rate f per adsorption site, they hop at rate a and desorb at rate W . The number of adsorption sites on the grain is S , and the quantities $F = fS$ and $A = a/S$ refer to the whole grain. To make contact with the notation of Refs. [3,5], we introduce the lifetime τ of an atom on the grain,

$$\tau = 1/W, \quad (1)$$

the diffusion time τ_D required for an atom to explore the whole grain,

$$\tau_D \approx S/a = 1/A, \quad (2)$$

and the mean time interval Δt between the arrival of two atoms on the grain,

$$\Delta t = 1/F. \quad (3)$$

Estimate (2) ignores a logarithmic correction arising from the distinction between the total number of sites visited by an adatom during its lifetime, $\mathcal{N}_{\text{all}}(\tau)$, and the number $\mathcal{N}_{\text{dis}}(\tau)$ of *distinct* sites visited; we will return to this point towards the end of the paper.

Following Ref. [10], we introduce the dimensionless quantities

$$s_{\text{visit}} = a/W = S(\tau/\tau_D) \quad (4)$$

and

¹At high temperatures, desorption plays a role also in epitaxial growth; see Ref. [12] for an analysis of two-dimensional nucleation in the presence of desorption.

$$s_{\text{vacant}} = W/f = S(\Delta t/\tau). \quad (5)$$

For large grains ($S > s_{\text{visit}}$ and $S > s_{\text{vacant}}$, respectively), s_{visit} is the number of sites visited by an atom during its lifetime, and s_{vacant} is the number of vacant sites surrounding a site occupied by an atom. If $\tau > \tau_D$ the atom has time to explore the whole grain, so that the number of sites visited becomes equal to S , while for $\tau < \Delta t$ the grain is typically occupied by zero or one atom, so that an atom is surrounded by S vacant sites; note that the mean number of atoms on the grain is equal to

$$\bar{n} = \tau/\Delta t = F/W. \quad (6)$$

The relative ordering of the three dimensionless numbers S , s_{visit} , and s_{vacant} defines six different regimes. It turns out, however, that the behavior of the reaction rate in a given regime depends only on which of the three numbers is the smallest. Thus we are left with three different regimes, which will be discussed in the following.

The fluctuation-dominated (lonely adatom) regime is characterized by the condition [10]

$$S \ll \min[s_{\text{visit}}, s_{\text{vacant}}]. \quad (7)$$

According to Eqs. (4) and (5) this is equivalent to (i) $\tau \ll \Delta t$ and (ii) $\tau \gg \tau_D$. The first condition simply implies that the mean number (6) of atoms on the grain is small compared to unity. In this limit, the probability that a freshly deposited atom participates in a recombination event is equal to the probability P_1 that a second atom is already present on the grain, times the *encounter probability* p_{enc} that the two atoms, once both present on the grain, will meet before one of them redesorbs. The first probability is given by [3] $P_1 = \tau/(\tau + \Delta t) \approx \tau/\Delta t = F/W$. Multiplying this with the number of atoms $F = 1/\Delta t$ arriving on the grain per unit time, we find that the total recombination rate (the number of molecules produced by the grain per unit time) is given by

$$R = \frac{\tau}{(\Delta t)^2} p_{\text{enc}} \quad (8)$$

whenever $\bar{n} \ll 1$. The second condition $\tau \gg \tau_D$ implied by Eq. (7) means that, if two atoms are present simultaneously on the grain, they will meet with unit probability, because each atom spends enough time on the grain to visit all sites many times. Thus we have $p_{\text{enc}} = 1$ and

$$R = R_{\text{lonely}} = \tau/(\Delta t)^2 = F^2/W. \quad (9)$$

In the small grain limit where Eq. (7) is satisfied, this expression is *exact*. The recombination efficiency defined by $\eta = R/(F/2)$ is then equal to $2F/W$, in agreement with the result obtained in Ref. [10] from the full solution of the master equation. In second-layer nucleation, the lonely adatom regime is realized under typical experimental conditions when $i^* = 1$ [3].

In the remaining two regimes, the finite grain size is irrelevant. These regimes, therefore, appear also in the standard rate equation treatment [13]. According to the scaling of the

reaction rate with hydrogen flux, these two regimes will be referred to as the *first-* and *second-order* regimes [note that the lonely adatom regime is also of second order in this sense, see Eq. (9)].

The first-order regime is characterized by the condition

$$s_{\text{vacant}} \ll \min[S, s_{\text{visit}}]. \quad (10)$$

In this regime, the mean number of atoms on the grain is large compared to unity ($\tau \gg \Delta t$), and the number of sites visited by an atom during its lifetime ($= \min[S, s_{\text{visit}}]$) is large compared to the number of vacant sites surrounding each atom. Hence, each freshly deposited atom will certainly find a partner. In this case, the recombination rate is

$$R = R_1 = F/2 \quad (11)$$

and the recombination efficiency is equal to unity; the factor 1/2 appears in Eq. (11) because two hydrogen atoms are needed to form one H_2 molecule. In the context of second-layer nucleation, this regime corresponds to the nonstationary scaling regime I of Refs. [4,5], where the energy barriers at the step edges are so strong that $\tau \gg \Delta t$, and nucleation occurs as soon as a second atom is deposited onto the island.

It is easy to derive an interpolation formula connecting Eqs. (9) and (11) under the assumption that the diffusion of the reactants, as well as the desorption of the hydrogen molecule, is very fast. Then the only possible value for the number of atoms on the grain is 0 or 1, since recombination occurs instantaneously as soon as a second atom is deposited. The probability P_1 for having one atom on the grain satisfies the master equation²

$$dP_1/dt = FP_0 - (F+W)P_1 = F(1-P_1) - (F+W)P_1 \quad (12)$$

with the stationary solution $P_1 = F/(W+2F)$. Since $p_{\text{enc}} = 1$, the recombination rate is

$$R = FP_1 = \frac{F^2}{W+2F}, \quad (13)$$

which includes Eqs. (9) and (11) as limiting cases.

The remaining second-order regime is characterized by the condition

$$s_{\text{visit}} \ll \min[S, s_{\text{vacant}}]. \quad (14)$$

The condition $s_{\text{visit}} \ll S$ (i.e., $\tau \ll \tau_D$) has no clear analog in the context of second-layer nucleation, because there the lifetime of the atom is always at least as large as the diffusion time (the atom has to reach the island edge before it can leave the island). It is useful to distinguish the cases $S \gg s_{\text{vacant}}$ (large grains) and $S \ll s_{\text{vacant}}$ (small grains). In the first case, many atoms are present on the grain simultaneously. The encounter probability for a freshly deposited

²This is a simple case of the master equations considered in Refs. [4,8–10].

atom to find a partner during its lifetime is equal to $p_{\text{enc}} = s_{\text{visit}}/s_{\text{vacant}}$. Thus the recombination rate can be estimated as

$$R = R_2 = F p_{\text{enc}} = F \frac{\tau^2}{\tau_D \Delta t} = \frac{f^2 S a}{W^2} \quad (15)$$

and the recombination efficiency is $\eta = 2af/W^2$. For small grains, the probability that a freshly deposited atom will undergo a reaction is the product of the probability $P_1 = F/W$ that a second atom is present on the grain when it arrives, and the encounter probability, which now reads $p_{\text{enc}} = s_{\text{visit}}/S$ (note that the second atom occupies any site of the grain with equal probability). The recombination rate then becomes

$$R = \frac{F^2}{W} p_{\text{enc}} = \frac{f^2 S a}{W^2}, \quad (16)$$

which is *identical* to Eq. (15). Thus the second-order result holds irrespective of whether the number of atoms on the grain is large compared to unity or not. This is similar to certain regimes of second-layer nucleation with critical nucleus size $i^* > 1$ [5].

The last observation shows that the failure of rate equation theory cannot generally be attributed to the fact that the number of reactants on the grain is small compared to unity. To clarify this issue, it is instructive to consider the amount by which the reaction rate is overestimated by the rate equation expressions when condition (7) is satisfied. Two cases have to be distinguished. For $s_{\text{vacant}} \ll s_{\text{visit}}$, we have to compare Eq. (9) to R_1 , which yields

$$R_{\text{lonely}}/R_1 = 2F/W = 2\tau/\Delta t. \quad (17)$$

The ratio $\tau/\Delta t$ is precisely the mean number of atoms \bar{n} on the grain. Thus in this case, it is justified to say that the rate equations fail because $\bar{n} \ll 1$. On the other hand, for $s_{\text{visit}} \ll s_{\text{vacant}}$ we have

$$R_{\text{lonely}}/R_2 = SW/a = S/s_{\text{visit}}. \quad (18)$$

This ratio is not related to the mean number of atoms on the grain. Instead, it is equal to the ratio between the number of distinct sites visited by an adatom during its lifetime ($\mathcal{N}_{\text{dis}} = S$) and the number of all sites visited ($\mathcal{N}_{\text{all}} = a/W = s_{\text{visit}}$). Politi and Castellano have emphasized that it is the distinction between \mathcal{N}_{dis} and \mathcal{N}_{all} which is responsible for the failure of rate equation theory in the case of second-layer nucleation [6]. Here we see that this mechanism is responsible for the breakdown of rate equations in the second-order regime, but not in the first-order regime, where the mean number of atoms on the grain is decisive.

For large grains, the distinction between \mathcal{N}_{dis} and \mathcal{N}_{all} implies a logarithmic correction to the reaction rate (15) in the second-order regime. The number of distinct sites visited by a two-dimensional random walk during time τ is given by $\mathcal{N}_{\text{dis}}(\tau) \approx \pi a \tau / \ln(a\tau)$ [14]. The diffusion time should, therefore, be determined more accurately by $\mathcal{N}_{\text{dis}}(\tau_D) = S$, and

expression (4) has to be replaced by $s_{\text{visit}} = \mathcal{N}_{\text{dis}}(\tau)$. Using this in the derivation of the reaction rate in the second-order regime, we find

$$R_2 = \frac{f^2 S}{W} s_{\text{visit}} \approx \frac{\pi f^2 S a}{W^2 \ln(a/W)}, \quad (19)$$

which replaces Eq. (15). The experimental estimates for the activation energies for H diffusion and desorption on amorphous carbon surfaces quoted in Ref. [10] show that the logarithmic factor in Eq. (19) is $\ln(a/W) \approx 15$ at a temperature of 10 K.

To go beyond the order-of-magnitude estimate (19) would require a detailed analysis of the random walk problem on the grain surface along the lines of Ref. [6]. The master equation analysis of Refs. [8–10] is not sufficient for this purpose, because it keeps track only of the total number of atoms on the grain, thus ignoring the spatial aspects of the encounters between the atoms. As a first step in this direction, I present here a simple model calculation of the encounter probability p_{enc} for the case of small grains (in the sense of $\bar{n} \ll 1$), which allows to interpolate between expressions (9) and (19); a similar approach has previously been applied in the context of second-layer nucleation [15] (see also [7]).

We take the grain surface to be a circular disk of radius L . One of the reacting atoms is assumed to be immobile, and is placed at the center of the large disk in the form of a small disk of radius l . In this way, the problem becomes radially symmetric. The deposition, diffusion, and desorption of the second atom are described by the stationary diffusion equation

$$D \left(\frac{\partial^2}{\partial r^2} + \frac{\partial}{\partial r} \right) n + \tilde{f} - Wn = 0, \quad (20)$$

where $n(r)$ is the probability density for the second atom in polar coordinates, \tilde{f} is the impingement flux per unit area, and the diffusion coefficient is $D = al^2$. The boundary conditions for Eq. (20) are reflecting at the outer boundary, $\partial n / \partial r = 0$ at $r = L$, and absorbing at the inner boundary, $n(r=l) = 0$. The encounter probability is then obtained as the ratio of the diffusion flux incident onto the inner boundary to the total deposition flux incident onto the surface,

$$p_{\text{enc}} = \frac{2\pi l D \partial n / \partial r|_{r=l}}{\tilde{f} \pi L^2}. \quad (21)$$

The solution to this diffusion problem can be found in the thin film growth literature [16]. In the limit where the atom radius l becomes the smallest length in the problem, the encounter probability takes the form

$$p_{\text{enc}} = \frac{4a}{SW} [\ln(a/W) + 2K_1(\sqrt{SW/a})/I_1(\sqrt{SW/a})]^{-1}, \quad (22)$$

where I_1 and K_1 are incomplete Bessel functions. For small arguments, $K_1(x)/I_1(x) \approx 2/x^2$ and $p_{\text{enc}} \rightarrow 1$, while for large

arguments, $K_1(x)/I_1(x) \rightarrow 0$ and Eq. (22) reduces to $p_{\text{enc}} \approx 4a/[SW \ln(a/W)]$. Inserting the second result into Eq. (8) we obtain an expression identical to Eq. (19), apart from the factor π which is replaced by a factor 4.

To summarize, I have shown in this paper how recent results from the theory of second-layer nucleation can be applied to the closely related problem of hydrogen recombination on dust grain surfaces. Expressions (9), (11), and (15) for the recombination rate have been obtained before in Ref. [10], but the present derivation seems more straightforward. The analysis shows that the failure of the rate equation ap-

proach is not always related to the fact that the mean number of atoms \bar{n} on the grain is small compared to unity. Important consequences are the logarithmic factor in the second-order regime, Eq. (19), and the interpolation formulas (13) and (22). The derivation of the encounter probability for realistic grain geometries using the methods of Ref. [6] seems like a promising problem for future studies.

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