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Statistics modification under coalescence

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Abstract

For a few years, the world of heterogeneous catalysis is focusing on tinier and tinier metal clusters with the aim of reducing the amount of noble metals in catalysts. The sizes are approaching the single atom[3][4], and in the model catalysts used by researchers, even if it's not the purpose, there are often isolated atoms[5] that are very sensitive to the conditions and can easily diffuse. Furthermore, some studies focus now on the catalytic activity of single atoms[1][2]. Experimental studies require fully characterized model systems to disentangle the effect of different parameters on the final reaction. Unfortunately, if diffusion occurs during a catalytic reaction, a well-characterized system before the experiment loses its characteristics as soon as the reaction conditions are set. In this paper, I derive the analytic formula (20) giving the size distribution of clusters in a given system after diffusion and recombination of all single atoms.

Introduction

This study is motivated by the following concrete problem: The deposition of metal atoms to survey their catalytic activity (for example, by condensing a flow of atoms coming from an evaporator) on a surface exhibiting nucleation centers distributed on a network. In this case, because each nucleation site is equivalent, the probability, for a diffusing atom on the surface, to be captured is the same for all the nucleation centers considered. One of the first question that can be asked is : "What is the size distribution of the particles formed as a function of the quantity of atoms deposited? » . In fact, the answer to this question is known: After the deposition of an average of x atoms per nucleation site, the probability of having a cluster of n atoms follows Poisson's law [7] :

$P(x, n) = \frac{x^n}{n!} e^{-x}$. If the particles are stable, there is no reason for these probabilities to change,

however, as it is the case in some experiments, the deposition conditions may be different from the conditions under which the properties of these clusters are studied: The temperature may change, the chemical environment (the gases used for the study) can vary, radiation (laser, UV source...) may be used... all these changes can "destabilize" the arrangement of the particles by initiating diffusion. Generally speaking, the smaller the size of a metal aggregate, the more easily it will diffuse (even if in some cases this may not be true). One can expect that the clusters formed by a single atom (the monomers) will be the first to start moving when environmental conditions change[6]. Obviously, if conditions become so extreme that all metal particles either diffuse or evaporate, the experiments lose their interest. The purpose of this paper is to give the probability law of the size distribution of the clusters in the case where only single atoms can diffuse and all the monomers have finally diffused and settled on other clusters.

Assumptions of this study

For this work we will make five assertions :

1. Initial probabilities are known.
2. Only single atoms can move
3. Single atom (monomer) diffusion can be decomposed in two half steps :
 - a) A monomer is removed from the set of monomers.
 - b) The taken atom is then placed randomly at the surface
4. The number N of nucleation sites is very large : $1/N \ll 1$
5. Finally, the size of an atom is negligible in regard of the distance of nucleation sites. this means that the capture probability for an atom does not depend of the size of the cluster already present on the site.

We will note that the first half step of the diffusion affects only the amount of monomers and empty sites, and the second step will affect all size classes.

Enumeration of size's classes and evolution of probabilities

Let be an initial configuration where there is the probability P_0 to have an empty site, the probability P_1 to have a site with a single atom, P_2 to have a site with a dimer... and P_s to have a site with a cluster of s atoms. After a number a of diffusions, the new probabilities will be noted aP_0 , aP_1 , aP_2 , aP_3 ... Let's see to start, how P_0 transforms during a single diffusion.

P_0 :

Let N_0 be the number of empty sites before the diffusion. $N_0 = NP_0$.

The first half step of the diffusion rises by 1 the number of empty sites : $N_0 \rightarrow N_0' = N_0 + 1$. The new probability P_0' is then in a way that $N_0' = NP_0'$ i.e. $NP_0 + 1 = NP_0'$. It therefore follows that $P_0' = P_0 + 1/N$. Since now we will substitute $1/N$ by ε to simplify the notation.

$$P_0' = P_0 + \varepsilon$$

The second half step will decrease the amount of empty sites according the probability of having an empty site : $N_0' \rightarrow N_0'' = N_0' - (1 \times P_0')$. In the same way we can verify that if $N_0'' = NP_0''$ then $P_0'' = P_0' - \varepsilon P_0' = (1 - \varepsilon)P_0' = (1 - \varepsilon)(P_0 + \varepsilon)$.

$$P_0'' = P_0' - P_0' \varepsilon$$

At the end of the whole diffusion :

$${}^1P_0 = (P_0 + \varepsilon)(1 - \varepsilon)$$

However it is interesting at this point to raise a little bit the difficulty of the game by assuming that each diffusion can rise from a monomer formerly present on the surface or from an atom coming from outside (gas phase during deposition for example). Then the first half step will not subtract ε from P_1 but β ($0 \leq \beta \leq \varepsilon$). This complication will nevertheless lead to the solution of our initial problem setting $\beta = \varepsilon$ and allow to check if we are totally wrong or not : indeed, by setting $\beta = 0$, one should expect to rediscover the Poisson distribution. We can now rewrite the probability after the diffusion :

$${}^1P_0 = (P_0 + \beta)(1 - \varepsilon)$$

Trivially, the upper formula can be generalized to the recurrence relation :

$${}^{a+1}P_0 = ({}^aP_0 + \beta)(1 - \varepsilon) \quad (1)$$

P₁ :

It's a little bit more complicated to address P₁. Indeed, the successive values of P₁ will not only depend of the value of P₁ at the former stage, but also the former value of P₀. After first half step :

$$P_0' = P_0 + \beta \quad \text{and} \quad P_1' = P_1 - \beta$$

If the moving atom is placed on an empty site (probability P₀') P₁'' = P₁' + ε, and if the moving atom is placed on an site with 1 atom (probability P₁'), P₁'' = P₁' + ε. It follows that :

$${}^1P_1 = (P_1 - \beta)(1 - \varepsilon) + \varepsilon(P_0 + \beta)$$

And again the recurrence relation can be deduced very easily :

$${}^{a+1}P_1 = ({}^aP_1 - \beta)(1 - \varepsilon) + \varepsilon({}^aP_0 + \beta) \quad (2)$$

P₂ :

The value of P₂ is not modified by the first half step, but it is changed if during second stage of the diffusion the atom is deposited on a preexisting monomer, or a preexisting dimer. If the atom is dropped on a site with one monomer P₂'' = P₂ + ε, and if is dropped on a site with a dimer P₂'' = P₂ - ε. Taking into account the probabilities of having a monomer or a dimer it follows the recurrence relation :

$${}^{a+1}P_2 = {}^aP_2(1 - \varepsilon) + \varepsilon({}^aP_1 - \beta) \quad (3)$$

P₃ :

In the same way, there are two means to change the probability of having a trimer : Depositing the diffusing atom on a site with a trimer (-ε), or depositing the atom on a dimer (+ε). The associated recurrent formula raises :

$${}^{a+1}P_3 = {}^aP_3(1 - \varepsilon) + \varepsilon {}^aP_2 \quad (4)$$

P_s :

From P₃ we can notice that the result doesn't any-more depend on the first step of the diffusion and only depend on the former values of P_s and P_{s-1}. So for s ≥ 3 :

$${}^{a+1}P_s = {}^aP_s(1 - \varepsilon) + \varepsilon {}^aP_{s-1} \quad (5)$$

Iterations

To obtain the final statistics of site occupation, one has to iterate the elementary process and get an analytic expression of ${}^a P_s$. The expression of ${}^a P_1$ is of main importance because the diffusion process must stop when ${}^a P_1 = 0$. This will be examined in the section "Interrupting the diffusion".

Now we will concentrate in obtaining the expressions of ${}^a P_s$ depending on α , ε , and of the initial values of P_s . Notice that as the number N of sites is very large, ε and β are tiny. The number α of iterations is proportional to N , as increasing by a factor A the number of sites will automatically increase by the same factor A the number of elementary processes to reach the same situation. The product $\alpha \times \varepsilon$ is in fact the mean number of diffusion per site and I will note x this number when the discrete formulas will be extrapolated to continuous formula.

Second order terms implying ε^2 , $\varepsilon\beta$ or β^2 are negligible compared to 1, except if associated with the number α of steps, and, of course, 1 is negligible compared to α .

P_0 :

After neglecting what has to be neglected in formula (1) we have :

$${}^{a+1}P_0 = {}^aP_0(1-\varepsilon) + \beta \quad (6)$$

Let us try to find a kind of regularity to the successive expressions of ${}^a P_0$:

$$\begin{aligned} {}^1P_0 &= P_0(1-\varepsilon) + \beta \\ {}^2P_0 &= P_0(1-\varepsilon)^2 + \beta(1-\varepsilon) + \beta \\ {}^3P_0 &= P_0(1-\varepsilon)^3 + \beta(1-\varepsilon)^2 + \beta(1-\varepsilon) + \beta \end{aligned}$$

A form seems to emerge :

$${}^aP_0 = {}^0P_0(1-\varepsilon)^a + \beta \sum_{i=0}^{a-1} (1-\varepsilon)^i$$

It is easy to calculate the sum :

$$\sum_{i=0}^{a-1} (1-\varepsilon)^i = \frac{(1-\varepsilon)^a - 1}{(1-\varepsilon) - 1} = -\frac{1}{\varepsilon} [(1-\varepsilon)^a - 1]$$

And then, as 0P_0 is nothing else than P_0 :

$${}^aP_0 = P_0(1-\varepsilon)^a + \frac{\beta}{\varepsilon} [1 - (1-\varepsilon)^a]$$

is to say :

$${}^aP_0 = (P_0 - \frac{\beta}{\varepsilon})(1-\varepsilon)^a + \frac{\beta}{\varepsilon} \quad (7)$$

The proof of this formula can be found in the annex subsection “Proof of the formula for P_0 :”
This discrete formula (7) can be expressed in a continuous formula (knowing that $(1-\varepsilon)^a = e^{-\varepsilon a}$
when $\varepsilon \ll 1$) :

$$P_0(x) = \left(P_0 - \frac{\beta}{\varepsilon}\right)e^{-x} + \frac{\beta}{\varepsilon} \quad (8)$$

P₁ :

As for P_0 , we will neglect the quadratic terms of ε in the recurrent formula (2) for P_1 . This leads to :

$${}^{a+1}P_1 = {}^aP_1(1-\varepsilon) + \varepsilon {}^aP_0 - \beta \quad (9)$$

After iterations and search for regularities, it turns out that :

$${}^aP_1 = P_1(1-\varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [{}^{a-1-i}P_0(1-\varepsilon)^i] - \beta \sum_{i=0}^{a-1} (1-\varepsilon)^i$$

That can be simplified into :

$${}^aP_1 = P_1(1-\varepsilon)^a + \left(P_0 - \frac{\beta}{\varepsilon}\right)a\varepsilon(1-\varepsilon)^{a-1} \quad (10)$$

The proof of this formula can be found in the annex subsection “Proof of the formula for P_1 :”
As for P_0 , we can express a continuous form of this formula :

$$P_1(x) = \left(P_1 + x\left(P_0 - \frac{\beta}{\varepsilon}\right)\right)e^{-x} \quad (11)$$

P₂ :

Once the quadratic terms of formula (3) removed we have :

$${}^{a+1}P_2 = {}^aP_2(1-\varepsilon) + \varepsilon {}^aP_1 \quad (12)$$

and, by the way already used the solutions is :

$${}^aP_2 = P_2(1-\varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [{}^{a-1-i}P_1(1-\varepsilon)^i]$$

Leading to :

$${}^aP_2 = P_2(1-\varepsilon)^a + P_1 a \varepsilon (1-\varepsilon)^{a-1} + \left(P_0 - \frac{\beta}{\varepsilon}\right) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-2} \quad (13)$$

The proof of this formula can be found in the annex subsection “Proof of the formula for P_2 :” and the associated continuous formula takes the form :

$$P_2(x) = \left[P_2 + P_1 x + \left(P_0 - \frac{\beta}{\varepsilon} \right) \frac{x^2}{2} \right] e^{-x} \quad (14)$$

P₃ :

The recurrence relation for P_3 is the same as for P_2 , and one could expect that all can be deduced easily from here, nevertheless, the expressions becomes more and more complicated :

$${}^{a+1}P_3 = {}^aP_3(1-\varepsilon) + \varepsilon^a P_2 \quad (15)$$

and so :

$${}^aP_3 = P_3(1-\varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [{}^{a-1-i}P_2(1-\varepsilon)^i] \quad (16)$$

To simplify this we need to sum the square of integers from 0 to $a-2$ [8] and finally we get :

$$\begin{aligned} {}^aP_3 = & P_3(1-\varepsilon)^a + P_2 a \varepsilon (1-\varepsilon)^{a-1} + \frac{1}{2} P_1 a(a-1) \varepsilon^2 (1-\varepsilon)^{a-2} \\ & + \frac{1}{6} \left(P_0 - \frac{\beta}{\varepsilon} \right) (a-1) [(a-1)^2 - 1] \varepsilon^3 (1-\varepsilon)^{a-3} \end{aligned} \quad (17)$$

The proof of this formula can be found in the annex subsection “Proof of the formula for P_3 :” The discrete formula (17) leads to the following continuous formula :

$$P_3(x) = \left[P_3 + P_2 x + \frac{1}{2} P_1 x^2 + \frac{1}{6} \left(P_0 - \frac{\beta}{\varepsilon} \right) x^3 \right] e^{-x} \quad (18)$$

Short discussion

Trying to generalize what is obtained for P_3 , it seems that the beginning of P_s is :

$$\begin{aligned} {}^aP_s = & P_s(1-\varepsilon)^a + P_{s-1} a \varepsilon (1-\varepsilon)^{a-1} + \frac{1}{2} P_{s-2} a(a-1) \varepsilon^2 (1-\varepsilon)^{a-2} \\ & + \frac{1}{6} P_{s-3} (a-1) [(a-1)^2 - 1] \varepsilon^3 (1-\varepsilon)^{a-3} + \dots + K \left(P_0 - \frac{\beta}{\varepsilon} \right) \end{aligned}$$

$${}^a P_s = P_s(1-\varepsilon)^a + K_1 P_{s-1} \varepsilon (1-\varepsilon)^{a-1} + K_2 P_{s-2} \varepsilon^2 (1-\varepsilon)^{a-2} \\ + K_3 P_{s-3} \varepsilon^3 (1-\varepsilon)^{a-3} + \dots + K_s (P_0 - \frac{\beta}{\varepsilon})$$

Every coefficient K_m associated with P_{s-m} are coming from the sums found in the generic recurrence formula for P_{s-m-1} :

$${}^a P_s = P_s(1-\varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [{}^{a-1-i} P_{s-1} (1-\varepsilon)^i]$$

This means that, to calculate K_m , we have to compute the sum of the sum of the sum... m times of something depending of P_0 leading to calculate the sum of powers of a every steep higher.

Ignoring all what can be neglected, the successive terms for P_{s-m} look like $\alpha(\varepsilon a)^m$. The problem being to determine α : Indeed, it does not exist a simple formula for the sum of powers $\sum_{i=0}^N i^k$, We

can use the Von Staudt formula [9] $\sum_{i=0}^N i^k = N^k + \sum_{i=0}^k \left[\frac{B_i k!}{i!(k-i+1)!} N^{k-i+1} \right]$, B_i being the Bernoulli numbers : $B_0 = 1$; $B_1 = -1/2$; $B_2 = 1/6$; $B_3 = 0$; $B_4 = -1/30$ or the Faulhaber formula [10] that also needs the Bernoulli numbers and is not easiest.

However, the limit where $\beta=0$ suggests that α should be equal to $m!$, and we would have the following continuous version for the sizes different from 0 :

$$P_{s \neq 0}(x) = \left[\sum_{i=1}^{s-1} \frac{P_{s-i} x^i}{i!} + \frac{1}{s!} (P_0 - \frac{\beta}{\varepsilon}) x^s \right] e^{-x} \quad (19)$$

"Hybrid" proof of formula (19)

By "hybrid" I mean that instead of making iterations of the recurrence formula injecting the discrete and complicated probability expression for the previous size, I will use the continuous form obtained. Let us return to the procedure that allowed us to deduce P_3 , and use the continuous formula (14) instead of discrete formula (13).

In one hand we have :

$${}^{a+1} P_3 = {}^a P_3 (1-\varepsilon) + \varepsilon^a P_2$$

that leads to :

$${}^a P_3 = P_3(1-\varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [{}^{a-1-i} P_2(1-\varepsilon)^i]$$

and in other hand :

$$P_2(x) = \left[P_2 + P_1 x + (P_0 - \frac{\beta}{\varepsilon}) \frac{x^2}{2} \right] e^{-x}$$

Replacing x by εa this formula transforms to :

$${}^a P_2 = \left[P_2 + P_1 \varepsilon a + \frac{1}{2} (P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 a^2 \right] (1-\varepsilon)^a$$

that is in fact the discrete formula (13) :

$${}^a P_2 = P_2(1-\varepsilon)^a + P_1 a \varepsilon (1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon}) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-2}$$

free from all negligible terms.

Let's focus on the sum : $\sum_{i=0}^{a-1} [{}^{a-1-i} P_2(1-\varepsilon)^i \varepsilon]$

This sum can be arranged inverting the order of the terms : this will simplify the understanding of the meaning of a such sum.

$$\sum_{i=0}^{a-1} [{}^{a-1-i} P_2(1-\varepsilon)^i \varepsilon] = \sum_{i=a-1}^0 [{}^{a-1-i} P_2(1-\varepsilon)^i \varepsilon] = \sum_{j=0}^{a-1} [{}^j P_2(1-\varepsilon)^{a-1-j} \varepsilon]$$

I keep inside the sum ε , because this will have its importance.

$$\begin{aligned} {}^j P_2(1-\varepsilon)^i &= \left[P_2 + P_1 \varepsilon j + \frac{1}{2} (P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 j^2 \right] (1-\varepsilon)^j \times (1-\varepsilon)^{(a-1-j)} \\ &= \left[P_2 + P_1 \varepsilon j + \frac{1}{2} (P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 j^2 \right] (1-\varepsilon)^{(a-1)} \end{aligned}$$

when ε tends towards 0 : $(1-\varepsilon)^{a-1} = (1-\varepsilon)^a$ and finally :

$${}^j P_2(1-\varepsilon)^{a-1-j} = \left[P_2 + P_1 \varepsilon j + \frac{1}{2}(P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 j^2 \right] e^{-\varepsilon a}$$

And we will notice, once again when ε tends towards 0 that :

$$\sum_{j=0}^{a-1} \left[\left[P_2 + P_1 \varepsilon j + \frac{1}{2}(P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 j^2 \right] e^{-\varepsilon a} \times \varepsilon \right] = \int_0^x \left[P_2 + P_1 \alpha + \frac{1}{2}(P_0 - \frac{\beta}{\varepsilon}) \alpha^2 \right] e^{-x} d\alpha$$

$$P_2(x) = \left[P_2 + P_1 x + (P_0 - \frac{\beta}{\varepsilon}) \frac{x^2}{2} \right] e^{-x}$$

And the continuous form for P_3 is directly deduced avoiding the tedious calculus of the discrete form. :

$$\begin{aligned} P_3(x) &= P_3 e^{-x} + \int_0^x \left[P_2 + P_1 \alpha + \frac{1}{2}(P_0 - \frac{\beta}{\varepsilon}) \alpha^2 \right] e^{-x} d\alpha \\ &= P_3 e^{-x} + \int_0^x P_2(\alpha) d\alpha \\ &= \left[P_3 + P_2 x + \frac{1}{2} P_1 x^2 + \frac{1}{6} (P_0 - \frac{\beta}{\varepsilon}) x^3 \right] e^{-x} \\ P_3(x) &= P_3 e^{-x} + \int_0^x \left[P_2 e^{-x} + \int_0^x \left[P_1 e^{-x} + \int_0^x \left[(P_0 - \frac{\beta}{\varepsilon}) e^{-x} \right] d\alpha \right] d\alpha \right] d\alpha \end{aligned}$$

Considering the probability P_s for the size s requires an integration that raises the power of x and brings out, as expected, the factorial of the number of successive integrations.

Interrupting the diffusion

As explained at the beginning of this article, the diffusion will stop after x_i movements per site, when no more monomers are present. One has to solve the following equation :

$$P_1(x) = (P_1 + x(P_0 - \frac{\beta}{\varepsilon}))e^{-x} = 0$$

If x_i exists, it is such that $P_1 + x_i(P_0 - \frac{\beta}{\varepsilon}) = 0$ is to say $x_i = \frac{P_1}{(\frac{\beta}{\varepsilon} - P_0)}$

Let us remember that here, we are interested by the particular case where $\beta = \varepsilon$, and finally, the new distribution after the monomer diffusion process is expressed in the following concise form :

$$P_{s \neq 0}(x_a) = \left[\sum_{i=1}^{s-1} \frac{P_{s-i} x_a^i}{i!} + \frac{1}{s!} (P_0 - 1) x_a^s \right] e^{-x}$$

$$P_0(x_a) = (P_0 - 1)e^{-x_a} + 1 \tag{20}$$

with

$$x_a = \frac{P_1}{(1 - P_0)}$$

Some verifications and remarks

remark :

If only monomers are found at the beginning of the diffusion process, then $P_0 = 1 - P_1$ implying that $x_a = 1$. The mean numbers of diffusions per site to get rid of monomers is 1, and this, whatever the value of P_1 !

Some verifications

Sum of probabilities

We have to check, at least in specific cases, that the sum of the probabilities is equal to 1. Let's check what happens if all stating probabilities are equal to zero except $P_1 = 1$:

To lighten the notation let's replace β/ε by γ .

$$P_0(x)e^x = \gamma e^x - \gamma$$

$$P_1(x)e^x = 1 - \gamma x$$

$$P_2(x)e^x = x - \frac{1}{2}\gamma x^2$$

$$P_3(x)e^x = \frac{1}{2}x^2 - \frac{1}{6}\gamma x^3$$

$$P_4(x)e^x = \frac{1}{6}x^3 - \frac{1}{24}\gamma x^4$$

$$P_{s-1}(x)e^x = \frac{1}{(s-2)!}x^{s-2} - \frac{1}{s-1!}\gamma x^{s-1}$$

$$P_s(x)e^x = \frac{1}{(s-1)!}x^{s-1} - \frac{1}{s!}\gamma x^s$$

$$\sum_{s=0}^{\infty} P_s(x)e^x = \gamma e^x + (1-\gamma) + x(1-\gamma) + \frac{1}{2}x^2(1-\gamma) + \frac{1}{3!}x^3(1-\gamma) + \dots + \frac{1}{s!}x^s(1-\gamma) + \dots$$

$$= \gamma e^x + (1-\gamma) \sum_{s=0}^{\infty} \left(\frac{x^s}{s!} \right)$$

$$= \gamma e^x + (1-\gamma)e^x = e^x$$

$$\sum_{s=0}^{\infty} P_s(x)e^x = e^x \Leftrightarrow \sum_{s=0}^{\infty} P_s(x) = 1$$

Poisson distribution

By taking $\beta = 0$, $P_0 = 1$, and of course all $P_{i \neq 0} = 0$, we expect to find the values given by the Poisson Distribution.

$$\begin{aligned} P_{s \neq 0}(x) &= \left[\sum_{i=1}^{s-1} \frac{P_{s-i}}{i!} x^i + \frac{1}{s!} (P_0 - \frac{\beta}{\varepsilon}) x^s \right] e^{-x} \\ &= \left[\sum_{i=1}^{s-1} \frac{0 \times x^i}{i!} + \frac{1}{s!} 1 \times x^s \right] e^{-x} \\ &= \frac{x^s}{s!} e^{-x} \end{aligned}$$

$$P_0(x) = (P_0 - \frac{\beta}{\varepsilon}) e^{-x} + \frac{\beta}{\varepsilon} = e^{-x}$$

which matches exactly the Poisson distribution : $P(x, n) = \frac{x^n}{n!} e^{-x}$

evolution of Poisson distribution

again with $\beta = 0$, we can as starting point have a Poisson distribution with the corresponding probabilities P_0, P_1, P_2, \dots and check how transforms these probabilities during a deposit of atoms. As an example I will focus on the evolution of P_3 :

$$P_3(x) = \left[P_3 + P_2 x + \frac{1}{2} P_1 x^2 + \frac{1}{6} P_0 x^3 \right] e^{-x}$$

The Poisson distribution for a mean number y of atoms per site is :

$$\begin{aligned} P_0 &= e^{-y} \\ P_1 &= y e^{-y} \\ P_2 &= \frac{1}{2} y^2 e^{-y} \\ P_3 &= \frac{1}{6} y^3 e^{-y} \end{aligned}$$

After having deposited a mean number x of atoms per site P_3 becomes :

$$\begin{aligned} P_3(x) &= \left[\frac{1}{6} y^3 e^{-y} + \frac{1}{2} y^2 e^{-y} x + \frac{1}{2} y e^{-y} x^2 + \frac{1}{6} e^{-y} x^3 \right] e^{-x} \\ &= \left[\frac{1}{6} y^3 + \frac{1}{2} y^2 x + \frac{1}{2} y x^2 + \frac{1}{6} x^3 \right] e^{-x} e^{-y} \\ &= \frac{1}{6} [y^3 + 3y^2 x + 3y x^2 + x^3] e^{-(x+y)} \\ &= \frac{1}{6} (x+y)^3 e^{-(x+y)} \end{aligned}$$

that matches the expected probability for trimers with a mean number $x+y$ atoms per site.

Conclusion

The exact size distribution law (20) after the diffusion of the monomers is deduced rigorously under some hypotheses (germination centers on a network, mobility of the monomers). This law should be useful to all experimenters working on surfaces with very small deposits of atoms or molecules wishing to characterize as well as possible their studied samples. As an exact law, one can easily imagine that it could also be useful in other fields for which I have no particular skills.

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Annex

Proof of the discrete formulas. All the formulas are proved by induction.

Proof of the formula for P_0 :

The expression (7) is easily proven. We want to check that:

$${}^a P_0 = P_0(1-\varepsilon)^a - \frac{\beta}{\varepsilon}(1-\varepsilon)^a + \frac{\beta}{\varepsilon}$$

and we know the following recursive expression:

$${}^{a+1}P_0 = {}^a P_0(1-\varepsilon) + \beta$$

Few lines allows us to calculate ${}^{a+1}P$ and check that the result is consistent with the formula (7) :

$$\begin{aligned} {}^a P_0(1-\varepsilon) + \beta &= \left[P_0(1-\varepsilon)^a - \frac{\beta}{\varepsilon}(1-\varepsilon)^a + \frac{\beta}{\varepsilon} \right] (1-\varepsilon) + \beta \\ &= P_0(1-\varepsilon)^{a+1} - \frac{\beta}{\varepsilon}(1-\varepsilon)^{a+1} + \frac{\beta}{\varepsilon}(1-\varepsilon) + \beta \\ &= P_0(1-\varepsilon)^{a+1} - \frac{\beta}{\varepsilon}(1-\varepsilon)^{a+1} + \frac{\beta}{\varepsilon} - \beta + \beta \\ &= P_0(1-\varepsilon)^{a+1} - \frac{\beta}{\varepsilon}(1-\varepsilon)^{a+1} + \frac{\beta}{\varepsilon} = {}^{a+1}P_0 \end{aligned}$$

and obviously :

$${}^0 P_0 = (P_0 - 1)(1-\varepsilon)^0 + 1 = P_0 - 1 + 1 = P_0$$

The accuracy of the formula (7) is then proved

Proof of the formula for P_1 :

We have to check that the formula (10) is correct. I remind this formula here :

$${}^a P_1 = P_1(1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^{a-1}$$

and we know that (formula (9)):

$${}^{a+1}P_1 = {}^a P_1(1-\varepsilon) + \varepsilon {}^a P_0 - \beta$$

and also :

$${}^a P_0 = (P_0 - \frac{\beta}{\varepsilon})(1-\varepsilon)^a + \frac{\beta}{\varepsilon}$$

The recursive formula is correct as we can check in the following calculus :

$$\begin{aligned} &{}^a P_1(1-\varepsilon) + \varepsilon {}^a P_0 - \beta \\ &= P_1(1-\varepsilon)^{a+1} + (P_0 - \frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^a + \varepsilon {}^a P_0 - \beta \\ &= P_1(1-\varepsilon)^{a+1} + (P_0 - \frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^a + \varepsilon \left[(P_0 - \frac{\beta}{\varepsilon})(1-\varepsilon)^a + \frac{\beta}{\varepsilon} \right] - \beta \\ &= P_1(1-\varepsilon)^{a+1} + (P_0 - \frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^a + \varepsilon(P_0 - \frac{\beta}{\varepsilon})(1-\varepsilon)^a \\ &= P_1(1-\varepsilon)^{a+1} + (P_0 - \frac{\beta}{\varepsilon})(a+1)\varepsilon(1-\varepsilon)^a = {}^{a+1}P_1 \end{aligned}$$

and we can check easily that :

$${}^0P_1 = P_1(1-\varepsilon)^0 + (P_0 - \frac{\beta}{\varepsilon}) \times 0 \times \varepsilon(1-\varepsilon)^{-1} = P_1$$

that definitively proves the accuracy of the formula (10) for P_1 .

Proof of the formula for P_2 :

In one hand we have ${}^{a+1}P_2 = {}^aP_2(1-\varepsilon) + \varepsilon^a P_1$ and ${}^aP_1 = P_1(1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^{a-1}$ and we have to demonstrate that

$${}^aP_2 = P_2(1-\varepsilon)^a + P_1 a \varepsilon (1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon}) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-2} .$$

Let's calculate a little bit :

$$\begin{aligned} & {}^aP_2(1-\varepsilon) + \varepsilon^a P_1 \\ = & \left[P_2(1-\varepsilon)^a + P_1 a \varepsilon (1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon}) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-2} \right] (1-\varepsilon) + \varepsilon^a P_1 \\ = & P_2(1-\varepsilon)^{a+1} + P_1 a \varepsilon (1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon}) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-1} \\ & + \varepsilon \left[P_1(1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon}) a \varepsilon (1-\varepsilon)^{a-1} \right] \\ = & P_2(1-\varepsilon)^{a+1} + P_1 a \varepsilon (1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon}) \frac{a(a-1)}{2} \varepsilon^2 (1-\varepsilon)^{a-1} \\ & + P_1 \varepsilon (1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon}) a \varepsilon^2 (1-\varepsilon)^{a-1} \\ = & P_2(1-\varepsilon)^{a+1} + P_1(a+1) \varepsilon (1-\varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon}) \varepsilon^2 (1-\varepsilon)^{a-1} \left[\frac{a(a-1)}{2} + a \right] \end{aligned}$$

since

$$\frac{a(a-1)}{2} + a = (a+1)a$$

hence :

$${}^aP_2(1-\varepsilon) + \varepsilon^a P_1 = {}^{a+1}P_2$$

And finally the particular case $a=0$ leads ${}^0P_2 = P_2$ that demonstrates the correctness of the formula.

Proof of the formula for P_3 :

We start with ${}^{a+1}P_3 = {}^aP_3(1-\varepsilon) + \varepsilon {}^aP_2$ and ${}^aP_2 = P_2(1-\varepsilon)^a + P_1a\varepsilon(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\frac{a(a-1)}{2}\varepsilon^2(1-\varepsilon)^{a-2}$, and we have to check that

the following formula is correct : ${}^aP_3 = P_3(1-\varepsilon)^a + P_2a\varepsilon(1-\varepsilon)^{a-1} + \frac{1}{2}P_1a(a-1)\varepsilon^2(1-\varepsilon)^{a-2} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-3}$.

$$\begin{aligned}
{}^aP_3(1-\varepsilon) + \varepsilon {}^aP_2 &= \left[P_3(1-\varepsilon)^a + P_2a\varepsilon(1-\varepsilon)^{a-1} + \frac{1}{2}P_1a(a-1)\varepsilon^2(1-\varepsilon)^{a-2} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-3} \right] (1-\varepsilon) + \varepsilon {}^aP_2 \\
&= P_3(1-\varepsilon)^{a+1} + P_2a\varepsilon(1-\varepsilon)^a + \frac{1}{2}P_1a(a-1)\varepsilon^2(1-\varepsilon)^{a-1} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-2} \\
&\quad + \varepsilon \left[P_2(1-\varepsilon)^a + P_1a\varepsilon(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\frac{a(a-1)}{2}\varepsilon^2(1-\varepsilon)^{a-2} \right] \\
&= P_3(1-\varepsilon)^{a+1} + P_2a\varepsilon(1-\varepsilon)^a + \frac{1}{2}P_1a(a-1)\varepsilon^2(1-\varepsilon)^{a-1} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-2} \\
&\quad + P_2\varepsilon(1-\varepsilon)^a + P_1a\varepsilon^2(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\frac{a(a-1)}{2}\varepsilon^3(1-\varepsilon)^{a-2} \\
&= P_3(1-\varepsilon)^{a+1} + P_2(a+1)\varepsilon(1-\varepsilon)^a + \frac{1}{2}P_1(a+1)a\varepsilon^2(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\varepsilon^3(1-\varepsilon)^{a-2} \left[\frac{(a-1)[(a-1)^2-1]}{6} + \frac{a(a-1)}{2} \right]
\end{aligned}$$

Simplifying the expression in the square brackets :

$$\begin{aligned} \frac{(a-1)[(a-1)^2-1]}{6} + \frac{a(a-1)}{2} &= \frac{1}{6} [(a-1)[(a-1)^2-1] + 3a(a-1)] = \frac{1}{6} [(a-1)(a^2-2a+1-1+3a)] \\ &= \frac{1}{6} [(a-1)(a^2+a)] = \frac{1}{6} [a^3 - a^2 + a^2 - a] = \frac{1}{6} (a(a^2-1)) \end{aligned}$$

leads to :

$${}^a P_3(1-\varepsilon) + \varepsilon {}^a P_2 = P_3(1-\varepsilon)^{a+1} + P_2(a+1)\varepsilon(1-\varepsilon)^a + \frac{1}{2}P_1(a+1)a\varepsilon^2(1-\varepsilon)^{a-1} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})\varepsilon^3(1-\varepsilon)^{a-2}a(a^2-1) = {}^{a+1}P_3$$

And in a trivial way, when $a=0$ leads to ${}^0P_3 = P_3$. The formula (17) is then demonstrated.