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. Unexpectedly, it turns out that these formulas make possible to obtain the law\(22\) giving the size histogram of clusters in the case of homogeneous nucleation with a critical germ equal to 2. Law that, to my knowledge, did not exist before this work.

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 for the cluster size distribution in the case where only single atoms can diffuse.
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 (i.e. on a nucleation site)
4. The number N of nucleation sites is very large: $1/N \ll 1$
5. Finally, the size of a cluster is negligible in regard of the distance of nucleation center, this means that the capture probability for an atom does not depend of the size of the cluster already present on the center.

We will note than 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 $P_0$ 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 size $s$ atoms. After a number $\alpha$ of diffusions, the new probabilities will be noted $P_0^\alpha$, $P_1^\alpha$, $P_2^\alpha$, $P_3^\alpha$ ... 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. $N_0 = N P_0$.

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 $N_0' = N P_0'$ i.e. $N P_0 + 1 = N P_0'$. It therefore follows that $P_0' = P_0 + 1/N$. Since now we will substitute $1/N$ by $\varepsilon$ to simplify the notation.

$$P_0' = P_0 + \varepsilon$$

The second half step will decrease the amount of empty sites, and this, according to the probability to find an empty site: $N_0' \rightarrow N_0'' = N_0' - (1 \times P_0')$. In the same way that done just above, we can verify that, if $N_0'' = N P_0''$ 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:

$$P_0^\alpha = (P_0 + \varepsilon)(1 - \varepsilon)$$

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 the deposition for example). Then the first half step will not subtract $\varepsilon$ from $P_1$ but $\beta$ ($0 \leq \beta \leq \varepsilon$). This complication will nevertheless lead to the solution expected for our initial problem when setting $\beta = \varepsilon$, and allow us to check if we are 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:

$$P_0^\alpha = (P_0 + \beta)(1 - \varepsilon)$$
Trivially, the upper formula can be generalized to the recurrence relation:

\[ a+1 P_0 = (aP_0 + \beta)(1 - \epsilon) \]  

(1)

**P_1:**

It’s a little bit more complicated to address \( P_1 \). Indeed, the successive values of \( P_1 \) will not only depend on the value of \( P_1 \) at the former stage, but also on the former value of \( P_0 \). After the first half step, one finds:

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

If the moving atom is placed on an empty site (probability \( P_0' \)), \( P_1'' = P_1' + \epsilon \), and if the moving atom is placed on a site with a single atom (probability \( P_1' \)), \( P_1'' = P_1' + \epsilon \). It follows that:

\[ ^1 P_1 = (P_1 - \beta)(1 - \epsilon) + \epsilon(P_0 + \beta) \]

And again, we can very easily deduce the recurrence relation:

\[ a + 1 P_1 = (aP_1 - \beta)(1 - \epsilon) + \epsilon(aP_0 + \beta) \]  

(2)

**P_2:**

The value of \( P_2 \) is not modified by the first half step but changed if during the 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 \( P_2'' = P_2 + \epsilon \), and if it is dropped on a site with a dimer \( P_2'' = P_2 - \epsilon \). Taking into account the probabilities of having a monomer or a dimer it follows the recurrence relation:

\[ a + 1 P_2 = aP_2(1 - \epsilon) + \epsilon(aP_1 - \beta) \]  

(3)

**P_3:**

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 \((-\epsilon)\), or depositing the atom on a dimer \((+\epsilon)\). The associated recurrent formula raises:

\[ a + 1 P_3 = aP_3(1 - \epsilon) + \epsilon aP_2 \]  

(4)

**P_s:**

From \( s = 3 \), 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 \( s \geq 3 \):
\[ a^{*1}P_s = aP_s (1 - \varepsilon) + \varepsilon \]  
\[ aP_{s-1} \]  

\[ (5) \]

**Iterations**

To obtain the final statistics of site occupation, one has to iterate the elementary process and get an analytic expression of \( aP_s \). The expression of \( aP_1 \) is of main importance because the diffusion process must stop when \( aP_1 = 0 \). This will be examined in the section “Interrupting the diffusion”.

Now we are going to concentrate on obtaining the expressions of \( aP_s \) depending on \( a, \varepsilon, \) and of the initial values of \( P_s \). Notice that as the number \( N \) of sites is very large, \( \varepsilon \) and \( \beta \) are tiny. The number \( a \) 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 \( a\times\varepsilon \) 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 \( \varepsilon^2 \), \( \varepsilon\beta \) or \( \beta^2 \) are negligible compared to 1, except if associated with the number \( a \) of steps, and, of course, 1 is negligible compared to \( a \).

\( P_0 \) :

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

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

(6)

Let us try to find a kind of regularity to the successive expressions of \( aP_0 \):

\[ ^1P_0 = P_0 (1 - \varepsilon) + \beta \]
\[ ^2P_0 = P_0 (1 - \varepsilon)^2 + \beta (1 - \varepsilon) + \beta \]
\[ ^3P_0 = P_0 (1 - \varepsilon)^3 + \beta (1 - \varepsilon)^2 + \beta (1 - \varepsilon) + \beta \]

A form seems to emerge:

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

It is easy to calculate the sum:

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

And then, as \( aP_0 \) is nothing else than \( P_0 \):

\[ aP_0 = (1 - \varepsilon)^a + \beta \left[ 1 - (1 - \varepsilon)^a \right] \]

is to say:
\[ aP_0 = (P_0 - \beta \varepsilon)(1 - \varepsilon)^a + \frac{\beta}{\varepsilon} \quad (7) \]

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 \((1 - \varepsilon)^a = e^{-a\varepsilon}\), when \(\varepsilon \ll 1\) :)

\[ P_0(x) = (P_0 - \frac{\beta}{\varepsilon})e^{-x} + \frac{\beta}{\varepsilon} \quad (8) \]

**P_1 :**

As for \( P_0 \), we will neglect the quadratic terms of \( \varepsilon \) in the recurrent formula (2) for \( P_1 \), Leading to:

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

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

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

Which can be simplified into:

\[ aP_1 = P_1(1 - \varepsilon)^a + (P_0 - \frac{\beta}{\varepsilon})a \varepsilon(1 - \varepsilon)^{a-1} \quad (10) \]

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 :

\[ P_1(x) = (P_1 + x(P_0 - \frac{\beta}{\varepsilon}))e^{-x} \quad (11) \]

**P_2 :**

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

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

and, by the mean already used, the solutions is :

\[ aP_2 = P_2(1 - \varepsilon)^a + \varepsilon \sum_{i=0}^{a-1} [a^{a-1-i}P_0(1 - \varepsilon)^i] \]

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

(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:

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

(14)

\( P_3 \):

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, however, the expressions becomes more and more complicated:

\[ a+1 P_3 = a P_3 (1 - \varepsilon) + \varepsilon^a P_2 \]  

(15)

and so:

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

(16)

To simplify this, we need to sum the square of integers from 0 to \( \alpha - 2 \) [8]. And finally, we get:

\[ a P_3 = P_3 (1 - \varepsilon)^a + P_2 a \varepsilon (1 - \varepsilon)^{a-1} + \frac{1}{2} P_1 a(a-1) \varepsilon^2 (1 - \varepsilon)^{a-2} \]

\[ + \frac{1}{6} (P_0 - \frac{\beta}{\varepsilon}) [(a-1)^2 - 1] \varepsilon^3 (1 - \varepsilon)^{a-3} \]  

(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:

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

(18)

Short discussion

Trying to generalize what is obtained for \( P_3 \), it seems that the beginning of \( P_5 \) is:
forall $P_s = P_s(1-\varepsilon)^a + P_{s-1} a \varepsilon (1-\varepsilon)^{a-1} + \frac{1}{2} P_{s-2} a(a-1) \varepsilon^2 (1-\varepsilon)^{a-2}$

\[ + \frac{1}{6} P_{s-3} (a-1)(a-2) \varepsilon^3 (1-\varepsilon)^{a-3} + \ldots + K \left(P_0 - \frac{\beta}{\varepsilon}\right) \]

\[aP_s = P_s(1-\varepsilon)^a + K_1 P_{s-1} \varepsilon (1-\varepsilon)^{a-1} + K_2 P_{s-2} \varepsilon^2 (1-\varepsilon)^{a-2}
+ K_3 P_{s-3} \varepsilon^3 (1-\varepsilon)^{a-3} + \ldots + K_s \left(P_0 - \frac{\beta}{\varepsilon}\right)\]

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

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

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

Ignoring all that can be neglected, the successive terms for $P_{s-m}$ look like $\alpha(\varepsilon \alpha)^m$. The problem being to determine $\alpha$: 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], which also needs the Bernoulli numbers and is not easiest.

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

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

"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 the discrete one (13).
On one hand, we have:

\[ a^i P_3 = a P_3 (1 - \varepsilon) + \varepsilon^a P_2 \]

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 on the other hand:

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

Replacing \( x \) by \( \alpha \varepsilon \), this formula transforms to:

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

that is, in fact, the discrete formula (13):

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

free from all negligible terms.

Let’s focus on the sum:

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

Inverting the order of the terms will simplify the understanding of the meaning of this kind of sum.

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

I keep inside the sum \( \varepsilon \), because this will have its importance.

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

\[ = \left[ P_2 + P_1 \varepsilon j + \frac{1}{2} \left( P_0 - \frac{\beta}{\varepsilon} \right) \varepsilon^2 j^2 \right] (1 - \varepsilon)^{(a-1)} \]
when ε tends towards 0: \((1 - ε)^{a-1} = (1 - ε)^a\) and finally:

\[jP_2(1 - ε)^{a-1-j} = \left[ P_2 + P_1 ε + \frac{1}{2} \left( \frac{P_0 - β}{ε} \right) ε^2 j^2 \right] e^{-εa}\]

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

\[
\sum_{j=0}^{a-1} \left[ P_2 + P_1 ε + \frac{1}{2} \left( \frac{P_0 - β}{ε} \right) ε^2 j^2 \right] e^{-εa} × ε = \int_0^x \left[ P_2 + P_1 α + \frac{1}{2} \left( \frac{P_0 - β}{ε} \right) α^2 \right] e^{-α} dα
\]

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

And the continuous form for \(P_3\) is directly deduced, avoiding the tedious calculus of the discrete form:

\[P_3(x) = P_3 e^{-x} + \int_0^x \left[ P_2 + P_1 α + \frac{1}{2} \left( \frac{P_0 - β}{ε} \right) α^2 \right] e^{-α} dα\]

\[= P_3 e^{-x} + \int_0^x P_2(α) dα\]

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

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 \( x_0 \) 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 \( x_0 \) exists, it is such that \( P_1 + x_0(P_0 - \frac{\beta}{\varepsilon}) = 0 \) is to say \( x_0 = \frac{P_1}{(\frac{\beta}{\varepsilon} - P_0)} \)

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:

\[
P_s^{x_0} = P_s^{x_0}(x_0) = \left[ \sum_{i=0}^{s-1} \frac{P_{s-i}x_0^i}{i!} + \frac{1}{s!}(P_0-1)x_0^s \right]e^{-x_0}.
\]

\[
P_0 = P_0(x_0) = (P_0 - 1)e^{-x_0} + 1
\]

with

\[
x_0 = \frac{P_1}{(1 - P_0)}
\]

Where I note \( P_s \), the value of \( P_s \) once the amount of initial monomers have been consumed, to distinguish the initial probabilities from the final ones.

Some verifications and remarks

remark 1:
If only monomers are found at the beginning of the diffusion process, then \( P_0 = 1 - P_1 \) implying that \( x_0 = 1 \). The mean number of diffusions per site to get rid of monomers is 1, and this, whatever the value of \( P_1 \)!

Remark 2:
Of course, one expects that the statistic will not change much when the number of monomers and the number of unoccupied sites are small. In these conditions, according to the formula giving \( x_a \):

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

we expect only a few numbers of steps before the disappearance of all the
monomers. What happens for the probability \( P_0 \) is particularly interesting since \( P_0 \) is easily measurable experimentally, using an STM for example, (which is not necessarily true for other size classes). With \( P_1 \) and \( P_0 \) small, \( x_0 \) is small, and one can make a Taylor expansion of the exponential term in the formula giving the probability of having an empty site: 
\[
e^{-x_0} = 1 - x_0 + \frac{1}{2} x_0^2 + \ldots
\]
Replacing \( x_0 \) with its expression depending on \( P_0 \) and \( P_1 \), one gets:
\[
e^{-x_0} \approx 1 + \frac{P_1}{P_0} - \frac{1}{2} \frac{P_1^2}{(P_0 - 1)^2}
\]
, and finally:
\[
P_0 \approx P_0 + P_1 - \frac{1}{2} P_1^2
\]
In the case of a deposit of more than 2 atoms per site, the Poisson distribution is such that \( P_0 \) is very little different from \( P_0 + P_1 \). It’s only for very small deposits that this statistic will clearly distinguish itself from the trivial situation in which one simply removes the monomers without caring about anything else.

**Remark 3 - Size histogram just after nucleation**

Let’s go back to the case where only monomers are present: \( P_0 = 1 - P_1 \). As we have seen \( x_0 = 1 \). Since only \( P_0 \) and \( P_1 \) are different from 0, the sum in formula (20) is simplified and we obtain:

\[
P_{s \geq 0} = \left[ \sum_{i=0}^{s-1} \frac{P_{s-1} x_a^i}{i!} + \frac{1}{s!} (P_0 - 1) x_a^s \right] e^{-x_0}
\]

\[
= \left[ P_1 \frac{x_a^{s-1}}{(s-1)!} + \frac{1}{s!} (P_0 - 1) x_a^s \right] e^{-x_0}
\]
as \( x_0 = 1 \) and \( P_0 - 1 = -P_1 \),

\[
P_{s \geq 2} = \left[ \sum_{i=0}^{s-1} \frac{P_{s-1} x_a^i}{i!} + \frac{1}{s!} (P_0 - 1) x_a^s \right] e^{-x_0}
\]

\[
= \left[ \frac{P_1}{(s-1)!} - \frac{P_1}{s!} \frac{1}{e} \right] e^{1 - \frac{(s-1)}{s!} P_1}
\]

\[
P_{s \geq 2} = \frac{1}{e} \frac{(s-1)}{s!} P_1
\]

(21)
The probability of presence for sizes $s \geq 2$ is strictly proportional to $P_1$. Whatever the value of $P_1$. Considering the size $s$ and $s'$ the ratio $P_s / P_{s'}$ is a constant. The limit where $P_1$ tends towards 0 is interesting and deserves to be interpreted physically: First, for $P_1 << 1$, the atoms arranged on the surface are totally random and do not show any particular order, the underlying lattice of nucleation sites appears continuous, as the granular structure of the atoms fades away when considering a macroscopic object. Secondly, the successive diffusions will randomly impact different monomers, and although the procedure described here starts from a sequential process, it is in parallel that the individual atoms will diffuse and meet each other. The meeting place is absolutely random and in fact, describes homogeneous nucleation with a critical germ equal to 2. The different probabilities $P_s$ give, ignoring a multiplicator factor, the quantity of cluster of size $s$ just after nucleation and before a possible coalescence. $P_s$ can be amplified by a factor $\alpha$ to ensure that $\sum_{s=2}^{\infty} (\alpha P_s) = 1$.

This factor is easy to calculate, indeed:

$$\sum_{s=2}^{\infty} P_s + P_0 = 1 \iff \sum_{s=2}^{\infty} P_s = 1 - P_0 = \frac{1}{\alpha}$$

as

$$P_0 = (P_0 - 1)e^{-x_0} + 1 = 1 - \frac{1}{e}P_1$$

one gets $\alpha = \frac{e}{P_1}$

by including $\alpha$ in formula (21), we finally get:

$$\Pi_{s \geq 2} = \frac{(s-1)}{s!}$$

(22)

$\Pi_s$ being the probabilities after normalization.

It is shown in the appendix in the section "Proof of the convergence" that, as expected, $\sum_{s=2}^{\infty} \Pi_s = 1$.

Formula (22) gives the size histogram in a system where only homogeneous nucleation operates, with a critical germ equal to 2, and before a possible coalescence or eventual growth in case monomers are injected (by evaporation-condensation for example) after the primordial nucleation process. To reach such a statistic experimentally, it will be necessary, either to make an evaporation of very short duration so that the nucleation has no time to really start before the end of the evaporation process, or then in the gas phase, a very brutal cooling (i.e. in a supersonic jet after laser ablation). It is also necessary, that the cluster sizes are negligible compared to the characteristic distances in the system, which ensures a large average free path and a capture probability independent of the size of growing clusters.
**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 \( \beta/\varepsilon \) with \( \gamma \).

\[
\begin{align*}
P_0(x)e^x &= \gamma e^x - \gamma \\
P_1(x)e^x &= 1 - \gamma x \\
P_2(x)e^x &= x - \frac{1}{2} \gamma x^2 \\
P_3(x)e^x &= \frac{1}{2} x^2 - \frac{1}{6} \gamma x^3 \\
P_4(x)e^x &= \frac{1}{6} x^3 - \frac{1}{24} \gamma x^4 \\
P_{s-1}(x)e^x &= \frac{1}{(s-2)!} x^{s-2} - \frac{1}{s-1!} \gamma x^{s-1} \\
P_s(x)e^x &= \frac{1}{(s-1)!} x^{s-1} - \frac{1}{s!} \gamma x^s \\
\sum_{s=0}^{\infty} P_s(x)e^x &= \gamma e^x + (1 - \gamma) + x(1-\gamma) + \frac{1}{2} x^2(1-\gamma) + \frac{1}{3!} x^3(1-\gamma) + \ldots + \frac{1}{s!} x^s(1-\gamma) + \ldots \\
&= \gamma e^x + (1 - \gamma) \sum_{s=0}^{\infty} \left( \frac{x^s}{s!} \right) \\
&= \gamma e^x + (1 - \gamma) e^x = e^x \\
\sum_{s=0}^{\infty} P_s(x)e^x &= e^x \iff \sum_{s=0}^{\infty} P_s(x)=1
\end{align*}
\]

**Poisson distribution**

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

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

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 have a Poisson distribution with the corresponding probabilities $P_0$, $P_1$, $P_2$ as the starting point,… and check how transforms these probabilities during an extra 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:

$$P_0 = e^{-y}$$

$$P_1 = y e^{-y}$$

$$P_2 = \frac{1}{2} y^2 e^{-y}$$

$$P_3 = \frac{1}{6} y^3 e^{-y}$$

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

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

$$= \left[ \frac{1}{6} y^3 + \frac{1}{2} y^2 x + \frac{1}{2} y x^2 + \frac{1}{6} x^3 \right] e^{-y} e^{-x}$$

$$= \frac{1}{6} (x+y)^3 e^{-(x+y)}$$

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

Conclusion

The size distribution exact law (20) after the monomer diffusion is deduced rigorously by assuming some hypotheses (germination centers on a network, mobility of the monomers). This formula predicting the size statistic modification should be useful to all experimenters working with very small deposits of atoms or molecules on surfaces, wishing to best characterize 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 expertise. For example, I am thinking about the diffusion and coalescence of atoms on powders, or about the nucleation in gel solutions. A consequence of this law is that it allows predicting the size distribution after homogeneous nucleation by a simple and concise formula (22), which is a fundamental result that can be useful in many fields of physics: laser ablation, very short duration deposits of atoms of, nucleation of droplets in cloud chambers, etc.
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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:

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

and we know the following recursive expression:

$$^aP_0 = ^aP_0(1-\epsilon) + \beta$$

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

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

and obviously:

$$0P_0 = (P_0-1)(1-\epsilon)^0+1 = P_0 - 1+1 = P_0$$

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:

$$^aP_1 = P_1(1-\epsilon)^a + (P_0 - \frac{\beta}{\epsilon}) a \epsilon(1-\epsilon)^{a-1}$$

and we know that (formula (9)): 

$$^aP_1 = ^aP_1(1-\epsilon) + \epsilon ^aP_0 - \beta$$

and also:

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

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

$$^aP_1(1-\epsilon) + \epsilon ^aP_0 - \beta$$

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

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

$$= P_1(1-\epsilon)^{a+1} + (P_0 - \frac{\beta}{\epsilon})(a+1) \epsilon(1-\epsilon)^a = ^aP_1$$

and we can check easily that:
\[ {}^0 P_1 = P_1(1-\varepsilon)^0 + (P_0 - \frac{\beta}{\tau}) \times 0 \times (1-\varepsilon)^{-1} = P_1 \]

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

**Proof of the formula for \(P_2\):**

In one hand we have \({}^{a+1} P_2 = P_2 {}^a (1-\varepsilon) + \varepsilon {}^a P_1\) and

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

and we have to demonstrate that

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

Let's calculate a little bit :

\[ {}^a P_2(1-\varepsilon) + \varepsilon {}^a P_1 \]

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

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

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

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

since

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

hence :

\[ {}^a P_2(1-\varepsilon) + \varepsilon {}^a P_1 = {}^{a+1} P_2 \]

And finally the particular case \(a=0\) leads \(0^0 P_2 = P_2\) that demonstrates the correctness of the formula.
Proof of the formula for P₃:

We start with \( ^aP₃ = ^aP₃(1-\epsilon) + \epsilon \cdot ^aP₂ \) and \( ^aP₂ = P₂(1-\epsilon)^a + P₁a\epsilon(1-\epsilon)^{a-1} + \left(P₀-\frac{β}{\epsilon}\right)\frac{a(a-1)}{2}\epsilon²(1-\epsilon)^{a-2} \), and we have to check that the following formula is correct:

\[ ^aP₃ = P₃(1-\epsilon)^a + P₂a\epsilon(1-\epsilon)^{a-1} + \frac{1}{2} P₁a(a-1)\epsilon²(1-\epsilon)^{a-2} + \frac{1}{6}(P₀-\frac{β}{\epsilon})(a-1)[(a-1)^2-1]\epsilon³(1-\epsilon)^{a-3} \]

\[ ^aP₃(1-\epsilon) + \epsilon \cdot ^aP₂ = \left[P₃(1-\epsilon)^a + P₂a\epsilon(1-\epsilon)^{a-1} + \frac{1}{2} P₁a(a-1)\epsilon²(1-\epsilon)^{a-2} + \frac{1}{6}(P₀-\frac{β}{\epsilon})(a-1)[(a-1)^2-1]\epsilon³(1-\epsilon)^{a-2}
+ \epsilon \left[P₂(1-\epsilon)^a + P₁a\epsilon(1-\epsilon)^{a-1} + \left(P₀-\frac{β}{\epsilon}\right)\frac{a(a-1)}{2}\epsilon²(1-\epsilon)^{a-2}\right]\right](1-\epsilon) + \epsilon \cdot ^aP₂ \]

\[ = P₃(1-\epsilon)^{a+1} + P₂a\epsilon(1-\epsilon)^a + \frac{1}{2} P₁a(a-1)\epsilon²(1-\epsilon)^{a-1} + \frac{1}{6}(P₀-\frac{β}{\epsilon})(a-1)[(a-1)^2-1]\epsilon³(1-\epsilon)^{a-2}
+ P₂\epsilon(1-\epsilon)^a + P₁a\epsilon²(1-\epsilon)^{a-1} + \left(P₀-\frac{β}{\epsilon}\right)\frac{a(a-1)}{2}\epsilon³(1-\epsilon)^{a-2}\]

\[ = P₃(1-\epsilon)^{a+1} + P₂(a+1)\epsilon(1-\epsilon)^a + \frac{1}{2} P₁(a+1)a\epsilon²(1-\epsilon)^{a-1} + (P₀-\frac{β}{\epsilon})\epsilon³(1-\epsilon)^{a-2}\left[\frac{(a-1)[(a-1)^2-1]}{6} + \frac{a(a-1)}{2}\right]\]

Simplifying the expression in the square brackets:
\[
\frac{(a-1)[(a-1)^2-1]}{6} + \frac{a(a-1)}{2} = \frac{1}{6} \left[ (a-1)[(a-1)^2-1] + 3a(a-1) \right] = \frac{1}{6} \left( a-1)(a^2-2a+1+3a) \right) \\
= \frac{1}{6}[(a-1)(a^2+a)] = \frac{1}{6}[ a^3-a^2+a^2-a] = \frac{1}{6}(a(a^2-1))
\]

leads to:

\[
^aP_3(1-\varepsilon) + \varepsilon^a P_2 = P_3(1-\varepsilon)^{a+1} + P_2(a+1)\varepsilon(1-\varepsilon)^a + \frac{1}{2} P_3(a+1) a \varepsilon^2(1-\varepsilon)^{a-1} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon}) \varepsilon^3(1-\varepsilon)^{a-2} a(a^2-1) = \ ^{a+1}P_3
\]

And in a trivial way, when \( a=0 \) leads to \(^6P_3 = P_3\). The formula (17) is then demonstrated.

**Proof of the convergence of** \( \sum_{n=2}^{\infty} \frac{n-1}{n!} \):

\[
\sum_{n=2}^{\infty} \frac{n-1}{n!} = \sum_{n=2}^{\infty} \frac{n}{n!} - \sum_{n=2}^{\infty} \frac{1}{n!} \\
= \sum_{n=2}^{\infty} \frac{1}{(n-1)!} - \sum_{n=2}^{\infty} \frac{1}{n!} \\
= \sum_{n=1}^{\infty} \frac{1}{n!} - \sum_{n=2}^{\infty} \frac{1}{n!} \\
= \frac{1}{0!} + \sum_{n=2}^{\infty} \frac{1}{n!} - \sum_{n=2}^{\infty} \frac{1}{n!} = 1
\]