Statistics modification under monomer diffusion

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The diffusion and coalescence of individual atoms on a nanostructured surface are treated in a purely statistical way. From this, analytical formulas are derived which, from a known initial state, give the final cluster size distribution on a surface after the diffusion of all the individual atoms. Unexpectedly, it turns out that these formulas allow obtaining a statistical law giving the size histogram of the clusters when only homogeneous nucleation occurs with a critical germ equal to 2, and in the situation where nucleation starts once the deposition of the atoms is completed.

1 Introduction

A growing interest in surface science is the study of the properties (optical, chemical...) of metal clusters. These clusters can be synthesized by different methods. First synthesis were done by growing metal particles by condensation of metal vapor under UHV (Ultra High Vacuum) on a metal-oxide single crystal or on a thin film on a metal single crystal [1][2][3][4], but the size dispersion of such preparation were too large to study size effects. In order to correct this imperfection new ways to synthesize metal-clusters, such as the deposition of mass-selected particles [5][6][7], lithography [8], or the use of self-assembled colloidal masks [9], are used. For about twenty years, researchers use new supports allowing the organization of particles in a regular array during growth [10][11][12][13] providing model systems with a much higher density than by size selected clusters deposition and however with a sharp size distribution. These arrays can be precisely characterized by surface science techniques like STM (Scanning Tunneling Microscope) [14][15][11][13], GISAXS (Grazing-Incidence Small-angle Scattering) [16][13]. The high density of clusters ($10^{12}-10^{13}$ clusters per cm^2) reachable by these preparation methods allows studying the physical and the chemical properties of few atoms clusters down to the limit of individual atoms [17][13][15]. The sharp size distribution of particles is generally limited by the Poisson distribution [14][15][18]. Moreover, few years ago, the world of heterogeneous catalysis became interested by catalysis by individual atoms (the so-called Single-Atom Catalysis - SAC) [19][20]. One can legitimately wonder what happens to the initial distribution if during the experiments the individual atoms diffuse, as some authors are suggesting [21][22], by temperature increase or by interaction with reactants gases. Experimental studies need perfectly well-characterized model systems, not only after synthesis but also during reaction where coalescence could occur.

2 Motivations

This study is motivated by the following practical problem (which will serve as an experimental reference when it is not specified otherwise): The deposition of metal atoms to study their catalytic activity (for example, by condensing a flux of atoms coming from an evaporator) on a surface exhibiting nucleation centers distributed on an array. 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 already 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 [23]:$P(x,n) = \frac{x^n}{n!}e^{-x}$. If the particles are stable, there is no reason for these probabilities to change, however, as it is almost always the case, 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. This is the case for some works [15][16], and in particular for the experiments described by Düll [14] for which I will make a small analysis, in the light of the formulas determined in this article, in the section 6. Generally speaking, the smaller the size of a metal cluster, the easier 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. Of course, if conditions become so extreme that all metal particles either diffuse or evaporate, the experiments loose 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.

3 Assumptions of this study

For this work we will make six 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 : $1/N \gg 1$
5. The mean free path of a diffusing atom is large in comparison of the distance of nucleation center.
6. 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, and that condition 5 will be fulfilled.

4 Result

With these assumptions and some tedious calculations shown in Annex 1 - Calculations, it comes the following formula that give the final distribution after all monomers have diffused :

$$\begin{aligned} \underline{P}_{n\neq 0} &= e^{-x_a}\sum_{i=0}^{n}\frac{P_{n-i}\ x_a^i}{i!} - e^{-x_a}\frac{x_a^n}{n!} \\ \underline{P}_0 &= (P_0-1)e^{-x_a}+1 \\ &with \\ x_a &= \frac{P_1}{(1-P_0)} \end{aligned} \tag{1}$$

where P_n is the initial probability to have a cluster of size n atoms and $\underline{P}_n$ is the final probability to have a cluster of n atoms. x_a is the mean number of diffusions per site to clean the surface of all single atoms, as properly explained in Annex 1 - Calculations.

5 Some remarks

5.1 remark 1:

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 number of diffusions per site to get rid of monomers is 1, and this, whatever the value of P_1.

5.2 remark 2:

One expects that the statistic will not change much when the number of monomers and the number of vacant 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_a is small, and one can make a Taylor expansion of the exponential term in the formula giving the probability of having an empty site: $e^{-x_a} = 1 - x_a + \frac{1}{2}x_a^2 + ...$ Replacing x_a with its expression depending on P_0 and P_1, one gets:

$$e^{-x_a} \approx 1 + \frac{P_1}{P_0 - 1} + \frac{1}{2}\frac{P_1^2}{(P_0-1)^2}$$

and finally :

$$\underline{P}_0 \approx P_0 + P_1 - \frac{1}{2}P_1^2$$

In the case of a deposit of more than 3 atoms per site, the Poisson distribution is such that $\underline{P}_0$ will be very little different from $P_0 + P_1$. It's only for deposits lower than 3 atoms per site that this statistic will clearly distinguish itself from the trivial situation in which one simply removes the monomers without caring about anything else.

5.3 remark 3 - Size histogram before coalescence:

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

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

$$= \left[P_1 \frac{x_a^{n-1}}{(n-1)!} + \frac{1}{n!}(P_0 - 1)x_a^n\right] e^{-x_a}$$

as $x_a = 1$ and $P_0 - 1 = -P_1$,

$$\underline{P}_{n\geq 2} = \left[\sum_{i=0}^{n-1} \frac{P_{n-i}x_a^i}{i!} + \frac{1}{n!}(P_0 - 1)x_a^n\right] e^{-x_a}$$

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

$$= \frac{1}{e}\frac{n-1}{n!}P_1$$

$$\underline{P}_{n\geq 2} = \frac{1}{e}\frac{(n-1)}{n!}P_1 \tag{2}$$

The probability of presence for sizes $n \geq 2$ is strictly proportional to P_1. Whatever the value of P_1. Considering the sizes n and n' the ratio $\underline{P}_n/\underline{P}'_n$ is a constant. The limit where P_1 tends towards 0 is interesting and deserves to be interpreted physically: First, for $P_1 \ll 1$, the atoms arranged on the surface are totally random and do not show any particular order: the underlying lattice of nucleation sites appears continuous in the same way 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 $\underline{P}_n$ give, ignoring a multiplier factor, the quantity of cluster of size s just after nucleation and before a possible coalescence.

$\underline{P}_n$ can be amplified by a factor α to ensure that $\sum_{n=2}^{\infty}(\alpha\underline{P}_n) = 1$. This factor is easy to calculate, indeed :

$$\sum_{n=2}^{\infty}\underline{P}_n + \underline{P}_0 = 1 \Leftrightarrow \sum_{n=2}^{\infty}\underline{P}_n = 1 - \underline{P}_0 = \frac{1}{\alpha}$$

as

$$\underline{P}_0 = (P_0 - 1)e^{-x_a} + 1 = 1 - \frac{1}{e}P_1$$

one gets

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

by including α in formula (2), we finally get :

$$\Pi_{n\geq 2} = \frac{(n-1)}{n!} \tag{3}$$

Π_n being the probabilities after normalization. It is shown in Annex 2 - Supplementary material in the section 10.5 that, as expected, $\sum_{n=2}^{\infty}\Pi_n = 1$ Formula (3) 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, deposit at low temperature followed by annealing to allow the monomers to move, 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, to ensure a large average free path and a capture probability independent of the size of growing clusters.
The average size of the clusters thus formed is easily calculated (see 10.6 in Annex 2 - Supplementary material) :

$$\overline{n} = \sum_{n=2}^{\infty} s\Pi_n = e \tag{4}$$

This makes it easy to test formula (3): Indeed, if N atoms have been deposited on a given surface, one should expect to be able to observe only N/e clusters, i.e. approximately 2.7 times less than the number of atoms present. It should be quite easy to verify this prediction by choosing a suitable atom-substrate pair. The only constraint is that, since we are dealing with homogeneous nucleation, the substrate must be free of defects.

6 Confronting experience

The work described in reference [14] shows the interest that can have the knowledge of these formulas to characterize a studied system. In this paper, Düll et al. make a platinum deposit on an h-BN/Rh(111) moiré. It is said that a Mono Layer (ML) of platinum corresponds to 144 atoms per cell. They show a result obtained at 295K by STM imaging, after a deposit of 0.005 ML at 295K. As written in the article: « ∼27% of the h-BN pores are filled with Pt clusters,... ». They write also that, given the small size of the clusters, some of the Pt clusters are expected to consist of just one single atom.

First, just after deposition, we would expect to obtain a Poisson distribution as all cells are equivalent. 0.005 ML corresponds to an average occupancy of 0.72 atoms per site, and the expected Poisson distribution is :

$P_0 = 0.4867$
$P_1 = 0.3504$
$P_2 = 0.1261$
$P_3 = 0.0302$
$P_4 = 0.0054$
$P_5 = 0.0008$

meaning that the number of occupied sites should be $1 - P_0 = 1 - 0.4867 = 0.51331$, that means 51%, far from the 27% observed in the paper.

Considering monomer diffusion and time enough between deposition and STM observations, we can apply the formulas given in the present work: these probabilities become (after 0.6828 movements per site on average):

$P_0 : 0.4867 \rightarrow 0.7407$
$P_1 : 0.3504 \rightarrow 0.0$
$P_2 : 0.1261 \rightarrow 0.1241$
$P_3 : 0.0302 \rightarrow 0.0863$
$P_4 : 0.0054 \rightarrow 0.0351$
$P_5 : 0.0007 \rightarrow 0.0105$

The occupancy rate is now only $1 - 0.7407 = 0.2593$, or 26%, which corresponds well to the experimental observation. We can add that, when STM images have been recorded, none of the cell was occupied by a single atom.

7 Conclusion

The size distribution exact law (1) after the monomer diffusion is deduced rigorously by assuming some assumptions (germination centers on an array, 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 (3), which is a fundamental result that could be useful in many fields of physics: laser ablation, very short duration deposits of atoms, nucleation of droplets in cloud chambers, etc.

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9 Annex 1 - Calculations

From Assumptions of this study we can calculate exactly, diffusion by diffusion, the modification of the size histogram.

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.

9.1 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_n to have a site with a cluster of size n 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.

9.1.1 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, 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 $N_0'' = NP_0''$ 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 the 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 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 :

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

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

$${}^{a+1}P_0 = ({}^aP_0 + \beta)(1 - \varepsilon) \tag{5}$$

9.1.2 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:

$$P'_0 = P_0 + \beta \quad and \quad P'_1 = P_1 - \beta$$

If the moving atom is placed on an empty site (with probability P'_0) $P''_1 = P'_1 + \varepsilon$, and if the moving atom is placed on a site with a single atom (with probability P'_0), $P''_1 = P'_1 - \varepsilon$. It follows that :

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

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

$$^{a+1}P_1 = (^aP_1 - \beta)(1 - \varepsilon) + \varepsilon(^aP_0 + \beta) \tag{6}$$

9.1.3 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 $P''_2 = P_2 + \varepsilon$, and if it is dropped on a site with a dimer $P''_2 = P_2 - \varepsilon$. Taking into account the probabilities of having a monomer or a dimer it follows the recurrence relation:

$$^{a+1}P_2 = {}^aP_2(1 - \varepsilon) + \varepsilon(^aP_1 - \beta) \tag{7}$$

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

$$^{a+1}P_3 = {}^aP_3(1 - \varepsilon) + \varepsilon {}^aP_2 \tag{8}$$

9.1.5 P_n

From s=3, we can notice that the result doesn't any-more depend on the first step of the diffusion but only on the former values of P_n and P_{n-1}. So for $s \geq 3$:

$$^{a+1}P_n \;=\; {}^aP_n(1 - \varepsilon) + \;\varepsilon\; {}^aP_{n-1} \tag{9}$$

9.2 Iterations

To obtain the final statistics of site occupation, one has to iterate the elementary process and get an analytic expression of ^aP_n . 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_n depending on a, ε, β, and of the initial values of P_n . Notice that as the number N of sites is very large, ε and β 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 ε^2 , $\varepsilon\beta$ or β^2 are negligible compared to 1, except if associated with the number a of steps, and, of course, 1 is negligible compared to a.

9.2.1 P_0

After neglecting what has to be neglected in formula (5), we have :

$$ {}^{a+1}P_0 \;=\; {}^{a}P_0(1-\varepsilon) + \;\beta \tag{10}$$

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

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

A form seems to emerge:

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

It is easy to calculate the sum:

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

And then, as ${}^{0}P_0$ is nothing else than P_0:

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

$$ {}^{a}P_0 \;=\; (P_0-\frac{\beta}{\varepsilon})(1-\varepsilon)^a \;+\; \frac{\beta}{\varepsilon} \tag{11}$$

The proof of this formula can be found in Annex 2 - Supplementary material - Proof of the formula for P_0:. This discrete formula (11) can be expressed in a continuous formula (knowing that $(1-\varepsilon)^a = e^{-a\varepsilon}$, when $-\varepsilon \ll 1$) :

$$ P_0(x) \;=\; (P_0-\frac{\beta}{\varepsilon})e^{-x} \;+\; \frac{\beta}{\varepsilon} \tag{12}$$

9.2.2 P_1

As for P_0, we will neglect the quadratic terms of ε in the recurrent formula (6) for P_1, Leading to:

$$ {}^{a+1}P_1 \;=\; {}^{a}P_1(1-\varepsilon) \;+\; \varepsilon\;{}^{a}P_0 \;-\; \beta \tag{13}$$

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

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

Witch can be simplified into:

$$ {}^{a}P_1 \;=\; P_1(1-\varepsilon)^a \;+\; (P_0-\frac{\beta}{\varepsilon})a\varepsilon(1-\varepsilon)^{a-1} \tag{14}$$

The proof of this formula can be found in Annex 2 - Supplementary material subsection Proof of the formula for P_1:
As for P_0, we can express a continuous form of this formula :

$$P_1(x) \;=\; (P_1 \;+\; x(P_0 - \frac{\beta}{\varepsilon}))e^{-x} \tag{15}$$

9.2.3 P_2

Once the quadratic terms of formula (7) removed we have :

$$^{a+1}P_2 \;=\; {}^{a}P_2(1-\varepsilon) \;+\; \varepsilon\, {}^{a}P_1 \tag{16}$$

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

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

Leading to :

$$^{a}P_2 = P_2(1-\varepsilon)^a + P_1 a\varepsilon(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\frac{a(a-1)}{2}\varepsilon^2(1-\varepsilon)^{a-2} \tag{17}$$

The proof of this formula can be found in Annex 2 - Supplementary material subsection Proof of the formula for P_2:.
and the associated continuous formula takes the form:

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

9.2.4 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 :

$$^{a+1}P_3 = {}^{a}P_3(1-\varepsilon) + \varepsilon {}^{a}P_2 \tag{19}$$

and so :

$$^{a}P_3 = P_3(1-\varepsilon)^a + \varepsilon\sum_{i=0}^{a-1}[^{a-1-i}P_2(1-\varepsilon)^i] \tag{20}$$

To solve this, we need to sum the square of integers from 0 to $(a-2)$ [24]. And finally, we get :

$$^{a}P_3 = P_3(1-\varepsilon)^a + P_2 a\varepsilon(1-\varepsilon)^{a-1} + \frac{1}{2}P_1 a(a-1)\varepsilon^2(1-\varepsilon)^{a-2} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-3} \tag{21}$$

The proof of this formula can be found in Annex 2 - Supplementary material subsection Proof of the formula for P_3:.
The discrete formula (17) leads to the following continuous formula:

$$P_3(x) = \left[P_3 + P_2 x + \frac{1}{2}P_1 x^2 + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})x^3\right] e^{-x} \tag{22}$$

9.3 Short discussion

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

$$
\begin{aligned}
{}^{a}P_n = P_n(1-\varepsilon)^a + P_{n-1}a\varepsilon(1-\varepsilon)^{a-1} + \frac{1}{2}P_{n-2}a(a-1)\varepsilon^2(1-\varepsilon)^{a-2} \\
+\frac{1}{6}P_{n-3}(a-1)[(a-1)^2-1]\varepsilon^3(1-\varepsilon)^{a-3} + ... + K(P_0 - \frac{\beta}{\varepsilon}) \\
{}^{a}P_n = P_n(1-\varepsilon)^a + K_1P_{n-1}\varepsilon(1-\varepsilon)^{a-1} + K_2P_{n-2}\varepsilon^2(1-\varepsilon)^{a-2} \\
+K_3P_{n-3}\varepsilon^3(1-\varepsilon)^{a-3} + ... + K_n(P_0 - \frac{\beta}{\varepsilon})
\end{aligned}
$$

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

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

This means that to obtain K_m, we have to calculate the sum of the sum of the sum... m times of something depending on P_0 , leading to calculate the sum of powers of a at every steep higher. Ignoring all that can be neglected, the successive terms for P_{n-m} look like $\alpha(a\varepsilon)^m$. 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 [25] $\sum_{i=0}^{N} i^k = N^k + \sum_{i=0}^{k}\left[\frac{B_i k!}{i!(k-i+1)!}N^{k-i+1}\right]$, 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 [26], which also needs the Bernoulli numbers and is not simpler.
However, the case 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 :

$$
P_{n\neq 0}(x) = \left[\sum_{i=1}^{n-1}\frac{P_{n-i}x^i}{i!} + \frac{1}{n!}(P_0 - \frac{\beta}{\varepsilon})x^n\right]e^{-x} \tag{23}
$$

9.4 "Hybrid" proof of formula (23)

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 (18) instead of the discrete one ((17).

On 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 on the other hand:

$$
P_2(x) = \left[P_2 + P_1x + (P_0 - \frac{\beta}{\varepsilon})\frac{x^2}{2}\right]e^{-x}
$$

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 (17) 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 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 leave ε inside the sum because it will have its importance.

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

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

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

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

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

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

And the continuous form for Py_3 is directly deduced, avoiding the tedious calculus of the discrete formulas:

$$ \begin{aligned} P_3(x) &= P_3e^{-x} + \int_0^x \left[P_2 + P_1\alpha + \frac{1}{2}(P_0 - \frac{\beta}{\varepsilon})\alpha^2\right]e^{-x}d\alpha \\ &= P_3e^{-x} + e^{-x}\int_0^x P_2(\alpha)d\alpha \\ &= \left[P_3 + P_2x + \frac{1}{2}P_1x^2 + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})x^3\right]e^{-x} \end{aligned} $$

and we can even write that :

$$ P_3(x) = P_3e^{-x} + e^{-x}\int_0^x \left[P_2 + \int_0^\gamma \left[P_1 + \int_0^\delta \left[(P_0 - \frac{\beta}{\varepsilon})\right]d\alpha\right]d\delta\right]d\gamma $$

Considering the probability P_n 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.

9.5 Interrupting the diffusion

As explained at the beginning of Iterations, the diffusion will stop after x_a 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 xa exists, it is such that $P_1 + x_i(P_0 - \frac{\beta}{\varepsilon}) = 0$ is to say :

$$x_a = \frac{P_1}{\frac{\beta}{\varepsilon} - P_0}$$

Let us remember that here, we are interested by the particular case where $\beta = \varepsilon$. Finally the new distribution, after the monomer diffusion process compleeted, is expressed in the following concise form [equation (1)]:

$$\begin{aligned} \underline{P}_{n\neq 0} = P_{n\neq 0}(x_a) &= \left[\sum_{i=0}^{n-1} \frac{P_{n-i}\ x_a^i}{i!} + \frac{1}{n!}(P_0 - 1)x_a^n\right] e^{-x_a} \\ \underline{P}_0 = P_0(x_a) &= (P_0 - 1)e^{-x_a} + 1 \\ & with \\ x_a &= \frac{P_1}{(1 - P_0)} \end{aligned} \tag{24}$$

9.6 Some verifications

9.6.1 Sum of probabilities

We have to check, at least in specific cases, that the sum of the probabilities (1) 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 with γ.

$$\begin{aligned} P_0(x)e^x &= \gamma e^x - \gamma \\ P_1(x)e^x &= 1 - \gamma x \\ P_2(x)e^x &= x - \frac{1}{2}\gamma x^2 \\ P_3(x)e^x &= \frac{1}{2}x^2 - \frac{1}{6}\gamma x^3 \\ P_4(x)e^x &= \frac{1}{6}x^3 - \frac{1}{24}\gamma x^4 \\ P_{n-1}(x)e^x &= \frac{1}{n-2)!}x^{n-2} - \frac{1}{n-1)!}\gamma x^{n-1} \\ P_n(x)e^x &= \frac{1}{n-1)!}x^{n-1} - \frac{1}{n!}\gamma x^n \end{aligned}$$

$$\begin{aligned} \sum_{n=0}^{\infty} P_n(x)e^x &= \gamma e^x + (1-\gamma) + x(1-\gamma) + \frac{1}{2}x^2(1-\gamma) + \frac{1}{3!}x^3(1-\gamma) + ... + \frac{1}{n!}x^n(1-\gamma) + ... \\ &= \gamma e^x + (1-\gamma)\sum_{n=0}^{\infty}\left(\frac{x^n}{n!}\right) \\ &= \gamma e^x + (1-\gamma)e^x = e^x \end{aligned}$$

$$\sum_{n=0}^{\infty} P_n(x)e^x = e^x \Leftrightarrow \sum_{n=0}^{\infty} P_n(x) = 1$$

9.6.2 Poisson distribution

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

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

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

which matches exactly the Poisson distribution:

$$P(x,n) = \frac{x^n}{n!} e^{-x}$$

9.6.3 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:

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

After an extra deposition of a mean number of x atoms per site is P_3 becomes :

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

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

10 Annex 2 - Supplementary material

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

10.1 Proof of the formula for P_0:

The expression (11) 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 recurrence expression:

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

Few lines allows us to calculate ${}^{a+1}P_0$ and check that the result is consistent with the formula (11) :

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

and obviously :

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

The accuracy of the formula (11) is then proved

10.2 Proof of the formula for P_1:

We have to check that the formula (14) 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 (13)):

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

The formula follows correctly the recurrence law 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 :

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

that definitively proofs the accuracy of the formula for(14) P_1.

10.3 Proof of the formula for P_2:

In one hand we have ${}^{a+1}P_2 = P_2{}^aP_1(1-\varepsilon) + \varepsilon^a P_1$ 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 the following formula is correct :

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

Let's calculate a little bit :

$$ {}^aP_2(1-\varepsilon) + \varepsilon^a P_1 = \left[P_2(1-\varepsilon)^a + P_1 a\varepsilon(1-\varepsilon)^{a-1} + (P_0 - \frac{\beta}{\varepsilon})\frac{a(a-1)}{2}\varepsilon^2(1-\varepsilon)^{a-2}\right](1-\varepsilon) + \varepsilon\ {}^aP_1 $$

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

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

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

since

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

hence:

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

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

10.4 Proof of the formula for P_3:

We start with

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

and

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

, and we have to check that the following formula is correct :

$$ {}^aP_3 = P_3(1-\varepsilon)^a + P_2 a\varepsilon(1-\varepsilon)^{a-1} + \frac{1}{2}P_1 a(a-1)\varepsilon^2(1-\varepsilon)^{a-2} + \frac{1}{6}(P_0 - \frac{\beta}{\varepsilon})(a-1)[(a-1)^2 - 1]\varepsilon^3(1-\varepsilon)^{a-3} $$

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

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

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

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

Simplifying the expression in the square brackets :

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

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 ${}^{0}P_3=P_3$. The formula (21) is then demonstrated.

10.5 Proof of the convergence of $\sum_{n=2}^{\infty}\frac{n-1}{n!}$:

$$
\begin{aligned}
\sum_{n=2}^{\infty}\frac{n-1}{n!}&=\sum_{n=2}^{\infty}\frac{n}{n!}-\sum_{n=2}^{\infty}\frac{1}{n!}\\
&=\sum_{n=2}^{\infty}\frac{1}{(n-1)!}-\sum_{n=2}^{\infty}\frac{1}{n!}\\
&=\sum_{n=1}^{\infty}\frac{1}{n!}-\sum_{n=2}^{\infty}\frac{1}{n!}\\
&=\frac{1}{0!}+\sum_{n=2}^{\infty}\frac{1}{n!}-\sum_{n=2}^{\infty}\frac{1}{n!}=1
\end{aligned}
$$

10.6 Number of clusters after «homogeneous nucleation»:

$$\begin{aligned}\overline{n} = \sum_{n=2}^{\infty} s\Pi_n &= \sum_{n=2}^{\infty} \frac{n(n-1)}{n!} \\ &= \sum_{n=2}^{\infty} \frac{(n-1)}{(n-1)!} \\ &= \sum_{n=2}^{\infty} \frac{1}{(n-2)!} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} = e\end{aligned}$$