Nonlinear Dynamics and Systems Theory, **19** (2) (2019) 302–312

Particle Distributions in Nucleation Lattice Models: A Matrix Approach

O. Gutiérrez *

Universidad Autnoma de Barcelona – Campus de Bellaterra – 08193 Spain

Received: June 12, 2018; Revised: April 10, 2019

Abstract: In this paper we use a matrix approach to investigate the distribution of particles in nucleation coalescence models with discrete lattices, both in the irreversible coagulation case and in the reversible one. In the irreversible case ($A + A \to A$), the evolution of the particle distribution is described by means of a simple recursive procedure. In two particular cases the model is analytically solvable: with high density and particles that always fuse into one, and in the case of constant density. In the reversible case ($A + A \rightleftharpoons A$) offspring production is allowed, and the system can reach a stationary distribution, which is jointly calculated with the equilibrium density. The particular case, in which meeting particles react with probability one, admits an exact solution.

Keywords: *coalescence models; Markov chain; exponential matrix; Poisson distribution; phase transition.*

Mathematics Subject Classification (2010): 82Cxx, 15A16, 15A18, 60J10.

1 Introduction

In the last decades, diffusion-controlled coalescence processes have attracted much research interest [1], [2], [3], [4], [5], [6] (see [7] and [8] for literature reviews). The models of these processes are applied to the analysis of phenomena involving particles in a solid, chemical species which randomly hop and react with adjacent ones, or non-equilibrium processes ranging from fluorescence to explosions. This kind of models is increasingly being used in biology, chemistry, genetics, sociology or finance, see [9], [10], [11] and [12], in which variations of the Ising model are used. We apply a simple matrix approach to the analysis of one-dimension coalescence models that usually require sophisticated mathematical tools (or Monte-Carlo simulations) to be solved.

* Corresponding author: mailto:oscar.gutierrez@uab.es

In one-dimension diffusion-limited reactions, the reaction time is much shorter than the diffusion time, so it is often assumed to be instantaneous. The physical system has a high number of particles, which can nucleate, and the distances between particles in a nucleus are negligible if compared to the distances between nuclei, which do not interact. The attractive interaction between particles is small, so the particles can diffuse into neighbor regions. Lastly, the energy of nucleated particles is very small, so reactions among the particles are neglected. Then, it is sensible to model the physical system by means of a discrete lattice where separate cells (sites) contain an integer number of particles. Two different situations can be considered: (i) In the case of irreversible coagulation, $A+A \to A$, the particle input is not allowed and particles diffuse until two of them meet and fuse (or not) into one. The fusion happens with some probability k, which reflects the fact that reactions are not necessarily instantaneous ($k = 1$ means that the reaction occurs instantaneously). (ii) If the back reaction is possible, particles can give birth to another particle (offspring production, $A \to A + A$). In the reversible coalescence process, $A + A \rightleftharpoons A$, the system can reach an equilibrium state, often characterized by the existence of a phase transition. Some well-known results in low-dimension diffusion-limited reaction models are: (i) the mean-field approximation for reaction kinetics breaks down (in the mean-field approximation, the particle density goes with the inverse of time, $\rho \sim t^{-1}$, a dependence derived from the dynamics equation $d\rho/dt \propto \rho^2$); (ii) in the irreversible case (coagulation), the system is temporarily described by the classical limit; but in the long-time regime, when the mean distance between particles is very large, it follows a diffusion limited decay, with $\rho \sim t^{-1/2}$; (iii) the one-dimensional single-species reversible reaction, $A + A \rightleftharpoons A$, is characterized by a second-order phase transition.

In this paper we use a one-dimensional discrete model to derive the particle distribution in two nucleation models: the irreversible coalescence model, and the reversible model with back reaction. J. C. Lin [3] also uses a discrete formalism, but centers his attention on the time-dependent probability that an interval with n sites is empty at time t, and Doering and Ben-Avraham [2] use the same interparticle distribution function in continuous formalism. Instead of analyzing the interparticle distribution as in [2] and [3], we propose a simple matrix approach to calculate the occupation probabilities and the particle density. The method offers a description of the system where the particle distribution can be obtained, valid whenever the particle density is not too low. This is so since we implicitly neglect spatial correlations (so, in particular, the occupation numbers in adjacent sites are uncorrelated). In the irreversible case, in which the number of particles never increases, we describe the occupation dynamics (which represents a non-equilibrium state unless $k = 0$). In the two particular cases of high density with $k = 1$, and non-reacting particles ($k = 0$, the number of particles does not vary) the steady state distribution is given in closed-form. In the reversible case, the particle input is allowed, we describe the stationary distribution. In the particular case, where particles always react ($k = 1$), the model is solved in closed-form. The appearance of a phase transition is predicted.

A matrix approach to systems of interacting particles with random dynamics is already used in [13], but applied to different phenomena (the authors analyze the one-dimensional fully asymmetric exclusion model, where the particles hop in a preferred direction with hard core interactions). J.M. Cushing [14] also applies a matrix approach to analyze a bifurcation phenomenon for a class of nonlinear matrix models, describing the evolutionary dynamics of a structured population.

Section 2 presents a simple coalescence model where the particle input is forbidden, so

the number of particles cannot increase. We analytically show some results derived in [15] by means of Monte-Carlo simulations. In Section 3, the particle input is allowed. The equilibrium distribution is obtained, and the appearance of a dynamic phase transition is analyzed. Section 4 summarizes the paper results and concludes.

2 Irreversible Coagulation: $A + A \to A$

Consider a system with N identical particles located in a lattice containing L identical sites. The initial distribution can be approximated by a Poisson one with the parameter $\rho = N/L$. The choice is natural: if each particle initially occupies a site chosen at random, the occupation number (the random number of particles in an arbitrary site) follows a binomial distribution, which tends to the Poisson one as N and L tend to $+\infty$. Particles leap from one site to an adjacent one. Then, the reaction can take place (with probability k) or not, which reflects that reactions are not instantaneous. If the reaction takes place, the number of particles in the system decreases by one unity; the occupation number in the former site of the leaping particle is one unit less; and the site, where the particle leaps, has the same occupation number since the reaction takes place and one particle disappears. If the reaction does not take place, the particle just changes its location, so the number of particles in the system remains the same. The model is more complex than the hard-core model, where sites can be occupied by only one particle, see [15]. [8] offers a simple explanation of why a particle in a many-particle quantum system can behave as a classical object that occasionally hops from one lattice cell to another.

The interval of time between two leaps is assumed to be the inverse of the number of particles: $\delta t = 1/N(t)$. We center our attention on the number of particles in a representative site, and calculate the transition probabilities associated to the representative site. The transition probabilities are put in an infinite matrix that resembles a Markov chain matrix (see the matrix below). However, probabilities depend on time since N varies with time, so we must notice that, strictly speaking, it is not a Markov chain unless $k = 0$ (N remains then constant). In spite of this limitation, we use the Markov chain formalism to describe the particle distributions in discrete one-dimensional coagulation systems. The transition matrix at time t is

$$M \equiv (M_i^j)_{i,j=0,1,2,\ldots,N} = (I_i^j)_{i,j=0,1,2,\ldots,N} + (A_i^j)_{i,j=0,1,2,\ldots,N} \tag{1}$$

with $(I_i^j)_{i,j=0,1,2,\ldots,N}$ being the identity matrix and $(A_i^j)_{i,j=0,1,2,\ldots,N}=$

$$= \begin{pmatrix} -\frac{1}{L} & \frac{1}{L} & 0 & 0 & 0 & \ldots \\ \frac{1}{N} & -\frac{1}{N} - \frac{1}{L}(1-k) & \frac{1}{L}(1-k) & 0 & 0 & \ldots \\ 0 & \frac{2}{N} & -\frac{2}{N} - \frac{1}{L}(1-k) & \frac{1}{L}(1-k) & 0 & \ldots \\ 0 & 0 & \frac{3}{N} & -\frac{3}{N} - \frac{1}{L}(1-k) & \frac{1}{L}(1-k) & \ldots \\ 0 & 0 & 0 & \frac{4}{N} & -\frac{4}{N} - \frac{1}{L}(1-k) & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}.$$

Stricto sensu, matrix M has finite dimension. However, given that the number of particles is very large, matrix M can be thought of as defined in $\mathbb{R}^N$ with $N \to +\infty$, a vector space of infinite dimension, and the particle distribution can be taken as a Poisson one. The master equation of the system can be obtained from the transition matrix (1).

As in any stochastic matrix, the sum of elements in a row is equal to one. We observe that transitions can only occur to adjacent sites; the transition matrix is then *systolic*, like all the transition matrices in the paper. The probability that a site with $j(\geq 1)$ particles turns to be occupied by $j+1$ particles when the system contains $N(t)$ particles is equal to $P_{j\to j+1} \equiv M_j^{j+1} = (1/L)(1-k)$, independently of N, while the probability of remaining with j particles is $P_{j\to j} \equiv M_j^j = 1 - j/N - (1/L)(1-k)$. Next, we explain how the diagonal element (j,j) in matrix M (with $j \geq 1$) is obtained. Let us look at the adjacent elements: on the one hand, if the representative site has j particles at time t, the element $(j, j-1)$ in matrix M, denoted by M_j^{j-1}, which represents the probability associated to the event "the site will have $j-1$ particles at $t+\delta t$", is equal to j/N; this means that one of the j particles in the site is the one which hops between t and $t+\delta t$. On the other hand, the site can be occupied by $j+1$ particles after the next hop. Taking into account that a particle can hop from any adjacent site, and that a particular particle hops with probability $1/N$, the probability that an additional particle will occupy the site considered is $M_j^{j+1} = \frac{1-k}{N}[0.5\sum_{j=1}^{N} jP(j) + 0.5\sum_{j=1}^{N} jP(j)] = \frac{1-k}{N}\rho = \frac{1-k}{L}$. Consequently, for $j \geq 1$, the element (j,j) in M must be $M_j^j = 1 - j/N - (1/L)(1-k)$.

By means of the transition matrix M in (1) we obtain the evolution of the particle distribution, from which we calculate the particle density: the product of the initial distribution (a vector) by the time-dependent matrices (written in terms of $N(t)$) gives us the particle distribution across time (a vector), and its scalar product with vector (0,1,2,3,...) gives us the particle density $\rho(t) = \sum_{j=1}^{N} jP(j)$, which changes with time. The distributions are written in terms of N (or, alternatively, ρ), and are readily obtained by a simple recursive procedure. The evolution of the density and particle distribution can be explicitly written in terms of time by using the fact that $\delta N(t) = -k((1-P(0))$ and $\delta t = 1/N(t)$. The method works when the particle density is not very low. In the long-time regime, however, the mean distance between particles is very large, so the occupation numbers are low and not independent of the occupation numbers of adjacent sites. So, correlations between the number of particles in adjacent sites are not negligible, which is confirmed by the well-known dynamics corresponding to the long-term regime, see [15], [16]. Consequently, the method proposed does not work in the long-run and in general with very low densities.

The numerical experiments performed by implementing the recursive method based on matrix M show that the time-dependent particle distribution quickly departs from the initial Poisson distribution (unless the reaction constant k is very low). In particular, the proportion of empty sites, $P(0)$, is well below the Poisson probability, while $P(j \geq 1)$ can be greater or lower than its Poisson counterpart, depending on the particular values of k, ρ and j. Let us check it for the two first probabilities. Recall that the first three probabilities of a Poisson distribution are: $P_{POI}(0) = e^{-\rho}$, $P_{POI}(1) = \rho e^{-\rho}$, $P_{POI}(2) = \rho^2 e^{-\rho}/2!$. Let us denote by $P(j|X)$ the probability that the representative cell has j particles when the system has X particles. If the system initially contains N particles, after the first iteration the probability of null occupation remains unchanged, $P(0|N-\delta N) = P_{POI}(0|N)$. However, in expectation the number of particles has decreased (from N to $N-\delta N$), so the density has also decreased (in expectation). This implies that the Poisson distribution overestimates the true probability of null occupation (so, there are more occupied cells actually than the Poisson pattern establishes). For $P(1)$, however, we obtain $P(1|N-\delta N) = P_{POI}(1|N) + k\rho e^{-\rho}/L$, so in this case the true probability $P(1|N-\delta N)$ can be above or below the Poisson one, $P_{POI}(1|N-\delta N)$ (observe that $\rho e^{-\rho}$ is not a monotone function of ρ). In general, the deviation of $P(j \geq 1)$

from the Poisson case has not a definite sign. For a typical parameter configuration, k=0.5, $L = 10^5$ and $N(0) = 3L$, for $\rho = 1.5$ we obtain $P(0)$=0.179, $P(1)$=0.391 and $P_{POI}(0)$=0.223, $P_{POI}(1)$=0.335, in concordance with the explanation above. These results are in excellent agreement with the Monte-Carlo simulations of Figs. 1 and 2 in [15].

In two particular cases the particle distribution admits a closed-form solution.

Case 1: $\rho \gg 1$ and $k = 1$: density is high and particles always react fusing into one. Next, we show that the particle distribution obeys a Poisson distribution as long as density remains high (say, above 5). Obviously, in the distant future, inequality $\rho \gg 1$ will not hold since the number of particles decreases with time, and the approximation then fails. The proof resembles that in [17], where in a different context the authors first calculate the infinitesimal generator of the transition, and then derive the equilibrium condition of the system and the steady-state probability distribution. Condition $\rho \gg 1$ implies $P(0) \approx 0$, so N diminishes in one unity every time step with probability close to one (recall that $k = 1$), and the transition probability $P_{0\to 1}$ can be neglected. Then, the transition matrix M reduces to

$$M = (I_i^j) + \frac{1}{N}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & ... \\ 1 & -1 & 0 & 0 & 0 & ... \\ 0 & 2 & -2 & 0 & 0 & ... \\ 0 & 0 & 3 & -3 & 0 & ... \\ 0 & 0 & 0 & 4 & -4 & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}, \text{ so the transition matrix can be ex-}$$

pressed as $M = I + G\delta t$, with I being the identity matrix, G being the infinitesimal generator of the transition, and $1/N$=δt being the time step. Next, we calculate the exponential matrix $\exp(GT)$. It corresponds to the finite transformation corresponding to the time interval T, and gives the solution to the Kolmogorov forward equation when applied to the initial distribution vector. Time T is the sum of incremental time intervals: T=$\sum \delta t$=$\sum_{N=N(0)}^{N(T)} 1/N \approx \int_{N(0)}^{N(T)} (1/x)dx$=$\ln(N(0)/N(T))$. The matrix $\exp(GT)$ is calculated by diagonalizing G, which can be expressed as $G = PDP^{-1}$, where D represents the diagonal matrix constructed with the eigenvalues of G, D=diag $(0, -1, -2, -3, ...)$, and P is constructed with the eigenvectors of G. The eigenvectors form a basis under which G becomes diagonal and are obtained (up to constants) by solving a system of linear equations, whose solution gives us a possible choice for matrix P. We choose the basis written in terms of the binomial coefficients, $(P)_i^j = \binom{i}{j} \equiv \frac{i!}{j!(i-j)!}$. The inverse matrix is given by $(P^{-1})_i^j = (-1)^{i+j}\binom{i}{j}$. The exponential matrix is then written as

$\exp(GT) = P\exp(DT)P^{-1}$ with

$$P = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & ... \\ 1 & 1 & 0 & 0 & 0 & ... \\ 1 & 2 & 1 & 0 & 0 & ... \\ 1 & 3 & 3 & 1 & 0 & ... \\ 1 & 4 & 6 & 4 & 1 & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}, P^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & ... \\ -1 & 1 & 0 & 0 & 0 & ... \\ 1 & -2 & 1 & 0 & 0 & ... \\ -1 & 3 & -3 & 1 & 0 & ... \\ 1 & -4 & 6 & -4 & 1 & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix},$$

$$\exp(DT)=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & ... \\ 0 & \alpha & 0 & 0 & 0 & ... \\ 0 & 0 & \alpha^2 & 0 & 0 & ... \\ 0 & 0 & 0 & \alpha^3 & 0 & ... \\ 0 & 0 & 0 & 0 & \alpha^4 & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}, \text{ where } \alpha := \exp(-T).$$

Finally, performing the product of the three matrices above we obtain

$$\exp(GT)=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & ... \\ 1-\alpha & \alpha & 0 & 0 & 0 & ... \\ 1-2\alpha+\alpha^2 & 2\alpha-2\alpha^2 & \alpha^2 & 0 & 0 & ... \\ 1-3\alpha+3\alpha^2-\alpha^3 & 3\alpha-6\alpha^2+3\alpha^3 & 3\alpha^2-3\alpha^3 & \alpha^3 & 0 & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}.$$

The element j of the first column in $\exp(GT)$ obeys the form $\sum_{i=0}^{j}\binom{j}{i}(-1)^i\alpha^i$, with $j \geq 0$. The element j in the second column obeys the form $\sum_{i=1}^{j} j\binom{j-1}{i-1}(-1)^{i+1}\alpha^i$, with $j \geq 1$, et cetera. The (matrix) product of the initial distribution vector and $\exp(GT)$ gives the particle distribution at T, valid whenever k=1 and ρ is high. We can show that if the initial distribution follows a Poisson distribution with parameter $\rho(0)$, the time-dependent distribution of particles follows a Poisson distribution with parameter $\rho(t)$. Let us check it for the two first probabilities of the distribution. Consistently with the Poisson assumption, we take $N \to +\infty$:

$$P(0) = \sum_{j=0}^{\infty} P_{POI}(j) \sum_{i=0}^{j} \binom{j}{i}(-1)^i\alpha^i \qquad [\text{making } -\alpha \equiv \beta]$$

$$=\sum_{j=0}^{\infty} e^{-\rho_0}({\rho_0}^j/j!) \sum_{i=0}^{j} \binom{j}{i}\beta^i = \sum_{i=0}^{\infty} \beta^i e^{-\rho_0} \sum_{j=i}^{\infty}({\rho_0}^j/j!)\binom{j}{i}$$

$$=e^{-\rho_0}\sum_{i=0}^{\infty}(\beta^i/i!) \sum_{j=i}^{\infty} \frac{\rho_0^j}{(j-i)!} =e^{-\rho_0}\sum_{i=0}^{\infty} (\beta^i/i!)\rho_0^i e^{\rho_0}$$

$$=\sum_{i=0}^{\infty} (\beta^i/i!)\rho_0^i = e^{\rho_0\beta}.$$

Recalling that $\beta := -\alpha = -\exp(-T) = -N(T)/N(0)$, we finally obtain $P(0) = \exp(-\rho(t))$. Similarly we obtain $P(1)$:

$$P(1) = \sum_{j=0}^{\infty} P_{POI}(j)\sum_{i=1}^{j} j\binom{j-1}{i-1}(-1)^{i+1}\alpha^i = (-1)\sum_{j=1}^{\infty} \frac{je^{-\rho_0}{\rho_0}^j}{j!}\sum_{i=1}^{j}\beta^i \frac{(j-1)!}{(i-1)!(j-i)!}$$

$$=-e^{-\rho_0}\sum_{i=1}^{\infty}\frac{\rho_0^i\beta^i}{(i-1)!}\sum_{j=i}^{\infty}\frac{\rho_0^{j-i}}{(j-i)!} =-\sum_{i=1}^{\infty}\frac{\rho_0^i\beta^i}{(i-1)!} = -\rho_0\beta e^{\rho_0\beta} = \rho(t)e^{-\rho(t)}.$$

The rest of probabilities, $P(j \geq 2)$, are similarly obtained and correspond to a Poisson distribution of parameter ρ. In [15], the authors use Monte-Carlo simulations to show that the particle distribution is sensibly described by means of a Poisson distribution (of parameter equal to the system density) when densities are high. We have shown this result analytically.

Case 2: k=0 (particles never react, so $N(t)$=N). Now the transition matrix (1) is

$$(M_i^j) = (I_i^j) + \begin{pmatrix} -\frac{1}{L} & \frac{1}{L} & 0 & 0 & 0 & \dots \\ \frac{1}{N} & -\frac{1}{N} - \frac{1}{L} & \frac{1}{L} & 0 & 0 & \dots \\ 0 & \frac{2}{N} & -\frac{2}{N} - \frac{1}{L} & \frac{1}{L} & 0 & \dots \\ 0 & 0 & \frac{3}{N} & -\frac{3}{N} - \frac{1}{L} & \frac{1}{L} & \dots \\ 0 & 0 & 0 & \frac{4}{N} & -\frac{4}{N} - \frac{1}{L} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}.$$

The stationary distribution corresponds to the eigenvector with eigenvalue 1. Solving the system of equations $xM = x$ we obtain: $\delta_1 = \rho\delta_0$, $\delta_2 = \rho\delta_1/2$, $\delta_3 = \rho\delta_2/3$, ..., $\delta_j = \rho\delta_{j-1}/j$ and so on. Then, $\delta_j = \rho^j\delta_0/j!$. Condition $\sum P(j) = 1$ implies that $\delta_0 \sum_{j=0}^{\infty} \rho^j/j! = 1$, so δ_0=exp$(-\rho)$: the stationary distribution is a Poisson one with parameter $\rho = N/L$, the constant density. The result is independent of the initial distribution. So, if the system initially follows a Poisson distribution, particles merely diffuse, and the particle distribution remains; otherwise, the particle distribution evolves over time towards the Poisson one.

3 Reversible Coalescence: $A + A \rightleftharpoons A$

In this section we consider that particles can give birth to another particle at rate λ: in the time interval between t and $t + \delta t$ any particle will give birth to a new particle with probability $\lambda\delta t$. Then both the offspring production ($A \to A + A$) and the coagulation processes ($A + A \to A$) coexist. We assume that the new particle stays in the same site as the generating one, in contrast with [3], where the new particle appears in an adjacent site (an assumption made for the sake of tractability in order to make the model solvable). We also assume that the particle born does not react (this is assumed without lost of generality, as parameter λ can be redefined to account for the situation where the new particle can react). We impose that inequality $\lambda < k$ must hold; otherwise, the number of particles would increase without boundary. As the time step is inversely related to the current number of particles in the system, $\delta t = 1/N$, the probability that a given particle gives birth to a new particle between t and $t + \delta t$ is λ/N. The disappearance of one particle between t and $t+\delta t$ occurs if a particle hops in such time interval and reacts. So, the probability associated to the disappearance of an arbitrary given particle in the interval δt is k/N if it jumps to a non-empty site, and 0 otherwise. In the stationary state, $P_{eq}(0)$ is calculated by imposing that the number of particles in the system does not change in expectation: $E(\delta N)$=$\lambda N\delta t - (1 - P_{eq}(0))k$=$\lambda - (1 - P_{eq}(0))k = 0$, where the minuend represents the probability of birth of a new particle in the interval $(t, t+\delta t)$, and the subtrahend represents the probability of disappearance of some particle in the same interval (a hopping particle arrives at a non-empty site and reacts). Then, at equilibrium, the probability associated to an empty site is $P(0) = 1 - \lambda/k$ with $\lambda < k$. The transition matrix is now

$$M \equiv (I_i^j) + (B_i^j) \tag{2}$$

with (I_i^j) being the identity matrix and $(B_i^j) =$

$$= \begin{pmatrix} -\frac{1}{L} & \frac{1}{L} & 0 & 0 & ... \\ \frac{1}{N} & -\frac{1}{N} - \frac{1}{L}(1-k+\lambda/\rho) & \frac{1}{L}(1-k+\lambda/\rho) & 0 & ... \\ 0 & \frac{2}{N} & -\frac{2}{N} - \frac{1}{L}(1-k+2\lambda/\rho) & \frac{1}{L}(1-k+2\lambda/\rho) & ... \\ 0 & 0 & \frac{3}{N} & -\frac{3}{N} - \frac{1}{L}(1-k+3\lambda/\rho) & ... \\ 0 & 0 & 0 & \frac{4}{N} & ... \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}.$$

The stationary particle distribution corresponds to the eigenvector with eigenvalue 1. By solving the system of equations $xM = x$, with M being the matrix given in (2), we obtain the following recursive relation: $P(1) = \rho P(0), P(2) = (\rho/2)(1 - k + \lambda/\rho)P(1), ..., P(j) = (\rho/j)[1-k+(j-1)\lambda/\rho]P(j-1)$, with $P(n)$ denoting the probabilities of the stationary distribution; the equilibrium density, ρ_{eq}, is still to be determined. Disentangling the recursive relation, the general term of the succession can be written as $P(j \geq 2) = P(0)(\rho^j/j!)\prod_{n=1}^{j-1}(1 - k + n\lambda/\rho)$.

Finally, ρ_{eq} is obtained by imposing that the sum of probabilities is one. We must observe that the system can reach an arbitrarily high population even though the birth rate is below the nucleation rate ($\lambda < k$).

A particular case deserves attention. If $k = 1$ (meeting particles always react and fuse into one), we obtain an exact solution. Let us see it. The computation of $P(j \geq 2)$ reduces to

$$P(j \geq 2) = P(0)(\rho^j/j!)\prod_{n=1}^{j-1}(n\lambda/\rho) = \rho P(0)\lambda^{j-1}/j.$$

The equilibrium density is calculated as follows:

$$1 = \sum_{j=0}^{\infty} P(j) = 1 - \lambda + \rho(1-\lambda) + \sum_{j=2}^{\infty} P(j) =$$

$$= (1+\rho)(1-\lambda) + (P(1)/\lambda)(\sum_{j=1}^{\infty} \lambda^j/j - \lambda) =$$

$$= (1+\rho)(1-\lambda) + (P(1)/\lambda)\sum_{j=1}^{\infty} \lambda^j/j - P(1).$$

Taking into account the fact that $P(1) = \rho P(0) = \rho(1-\lambda)$ and that

$\sum_{j=1}^{\infty} \lambda^j/j = \lambda + \lambda^2/2 + \lambda^3/3 + ... = -ln(1-\lambda)$ if $\lambda < 1$, we finally obtain:

$$\rho_{eq} = \frac{\lambda^2}{(1-\lambda)[-ln(1-\lambda)]}. \tag{3}$$

This equilibrium density is a positive number that can be above 1 (if $\lambda > 0.606$) or below 1 (if $\lambda < 0.606$). The quantity $-ln(1-\lambda)$, denoted by ρ^* henceforth, is necessarily smaller than ρ_{eq} (inequality $\rho^* < \rho_{eq}$ is easily shown using the fact that $-ln(1-\lambda) = \lambda + \lambda^2/2 + \lambda^3/3 + ...$). This inequality is relevant later on.

The particular case $k = 1$ (which leads to (3)) is not as restrictive as it may seem, since the condition $k < 1$ represents that reactions are not instantaneous, so time can be re-scaled to kt. Then we can also re-scale the birth rate λ (changing it to λ/k) to have a model similar to the previous one. After re-scaling, the simpler model ($k = 1$) gives a good

approximation to ρ_{eq} when $k < 1$. Both models are not mathematically identical, but qualitatively similar. The approximation $\rho_{eq} = \dfrac{(\lambda/k)^2}{(1-(\lambda/k))[-ln(1-(\lambda/k))]}$ obtained from (3) is very good if the ratio λ/k is small.

An apparent paradox arises: both $\rho(t)$ and $P_t(0)$ can be increasing functions of time. Consider, for example, $L = 10^5$, $N = 0.7 \times 10^4$, $k = 1$ and $\lambda = 0.5$; then $\rho(t)$ increases from $\rho(0) = 0.7$ to $\rho_{eq} = 0.7213$ and $P(0)$ increases from $P_0(0)$=$e^{-\rho(0)} = 0.4966$ to $P_{eq}(0) = 1 - \lambda = 0.5$. Can both the density and the number of empty sites simultaneously increase? The answer is affirmative. The paradox is not such since the particle distribution follows a Poisson one only at $t = 0$, but in equilibrium the system has more empty sites than in the Poisson case (oppositely to the irreversible model, $A + A \to A$). A distinguishing feature of the model is that the particle density does not necessarily evolve monotonically towards the equilibrium. This fact is related to the existence of a kinetic phase transition. Let us see it.

At any time t, the system density decreases if the birth rate λ is smaller than the disappearance rate $kC(t)$, with $C(t) \equiv 1 - P(0)$ being the system concentration. Take $k = 1$ and assume $\rho_0 = \rho_{eq}$ for simplicity, with ρ_{eq} given in (3). At $t = 0$, the density decreases if $\lambda < kC(t) = 1 - e^{-\rho_0}$; recall that $k = 1$ and the initial distribution is a Poisson one. Inequality $\lambda < 1 - e^{-\rho^*}$ is equivalent to $-ln(1-\lambda) < \rho^*$, which necessarily holds because $\rho^* \equiv -ln(1-\lambda)$ is smaller than ρ_{eq} (see above). So, starting at $\rho_0 = \rho_{eq}$, the density initially decreases and then increases (towards ρ_{eq}). In the case where ρ_0 is below ρ^*, the density initially increases instead, since $\lambda > kC(t)$ necessarily holds. In sum: ρ^* is lower than ρ_{eq}, as in [3] and [18], and for initial densities lying between ρ^* and ρ_{eq}, $\rho(t)$ first decreases and then increases. If, for example, $\lambda = 0.2$, the equilibrium density is $\rho_{eq} = 0.2241$; if the initial density is between 0.2231 and 0.2241, equal to $-ln(1-\lambda)$ and ρ_{eq} respectively, the system density initially decreases and then increases towards ρ_{eq}. The concentration evolves from $C(0) = 1 - e^{-\rho_0} = 0.2007$ to $\lambda = 0.2$.

Then, the system evolution depends on the initial conditions. In particular, the time until equilibrium behaves differently depending on whether the initial density is above or below ρ^*: if T denotes the time elapsed until the density first reaches ρ_{eq}, it is easy to show that in the neighborhood of ρ^*, $\partial T/\partial\rho_0 < 0$ if $\rho_0 < \rho^*$ but $\partial T/\partial\rho_0 > 0$ if $\rho_0 > \rho^*$. The discontinuity in the derivative suggests the existence of a dynamic phase transition at $\rho_0 = \rho^*$, which confirms a result in [3]: the lattice effect is not important qualitatively in predicting the transition. Equivalently, the dynamic phase transition corresponds to an initial concentration $C(0) = \lambda$. In fact, the system concentration (rather than the density) is the key to explain the system behavior, which shows a manifestation of the lattice effect. The order of the phase transition requires the calculation of the relaxation time, which is not available from the transition matrix; see [3] or [18] for its computation in a different formulation.

If we assume instead that the particle input occurs in an adjacent site to the site of the mother particle, the transition matrix is slightly different from the previous case (in which the particle input occurs in the cell of the mother particle). The matrix elements are now: $M_0^0 = 1 - (1/L)(1+\lambda)$, $M_j^j = 1 - j/N - (1/L)(1+\lambda)(1-k)$ and $M_j^{j+1} = (1/L)(1+\lambda)(1-k)$ for $j \geq 1$, and the rest of elements are obtained by taking into account the fact that the matrix is stochastic.

If $k < 1$, from the new matrix we obtain $P(0) = 1 - \frac{\lambda}{k(\lambda+1)}$, $P(1) = \rho(1+\lambda)P(0)$, and the recursive relation $P(j) = (\rho/j)(1+\lambda)(1-k)P(j-1)$, which leads to $P(j) = \frac{[\rho(1+\lambda)(1-k)]^{j-1}}{j!}P(1)$. By imposing that the sum of probabilities is one, we obtain an

equation from which the equilibrium density ρ_{eq} can be computed. The density obtained is below the equilibrium density obtained in the previous case, because now the new particle is born in an adjacent site and can react, which is neglected by assumption in the previous model (in which the particle remains in the site of the mother particle without reacting).

If $k = 1$, then $P(j \geq 2) = 0$, and the equilibrium density reduces to $\rho_{eq} = \lambda/(1 + \lambda)$. In equilibrium, sites are either empty or occupied by one particle, so, asymptotically, the model resembles the hard-core model.

4 Concluding Remarks

In this paper we use a matrix method to analyze the particle distribution in nucleation diffusion-limited models, both in the irreversible case ($A + A \to A$) and in the reversible one ($A + A \rightleftharpoons A$). In the irreversible case, the number of particles in the system cannot increase with time. We focus our attention on the situation where the system density is not too low and decays with $\rho \sim t^{-1}$. In the long-time regime, however, the decay goes with $\rho \sim t^{-1/2}$, which remains out of our scope. In the reversible case particles give birth to other particles, and the density reaches an equilibrium level for some parameter configurations. According to the method proposed, the particle distribution can be calculated by using a simple recursive procedure based on Markov chains, with the density being part of the solution.

In some particular cases, exact solutions are obtained. In particular, in the irreversible coagulation case, if density is high and particles react with probability 1 (i.e., $\rho \gg 1$ and $k = 1$), then the time-dependent distribution is Poisson with parameter equal to the time-dependent density. Also, if offspring production is not allowed and particles do not react ($k = 0$, so the number of particles remains constant), the stationary distribution also follows a Poisson one, in this case independently of the initial distribution. In the reversible case, in which offspring production is allowed, an equilibrium stationary state is reached if $\lambda < k$. The model admits an exact solution when particles always react, $k = 1$. This simple model predicts a dynamic phase transition.

The matrix approach presented can be used in many other contexts. For example, it can be used to analyze situations in which the porosity of a medium depends on the particle distribution of its cells, which relates to percolation problems. It can also be used to analyze other problems from physics, chemistry, biology or social sciences.

Acknowledgment

The author gratefully thanks the financial support from the research project ECO2017-86305-C4-3-R MINECO (Ministerio de Economia y Competitividad - Fondos FEDER).

References

[1] C. R. Doering and D. Ben-Avraham. Interparticle distribution functions and rate equations for diffusion-limited reactions. *Physical Review A* **38** (6) (1988) 3035–3042.

[2] C. R. Doering and D. Ben-Avraham. Diffusion-limited coagulation in the presence of particle input: Exact results in one dimension. *Physical Review Letters* **62** (21) (1989) 2563–2566.

[3] J.C. Lin. Exact results for one-dimensional reversible coagulation in discrete spatial formalism. *Physical Review A* **45** (6) (1992) 3892–3895.

[4] V. Privman. Exact results for diffusion-limited reactions with synchronous dynamics. *Physical Review E* **50** (1) (1994) 50–53.

[5] D. J. Aldous. Deterministic and stochastic models for coalescence (aggregation and coagulation): a review of the mean-field theory for probabilists. *Bernoulli* **5** (1) (1999) 3–48.

[6] G. Odor. Universality classes in nonequilibrium lattice systems. *Reviews of Modern Physics* **76** (3) (2004) 663–724.

[7] D.C. Mattis and M.L. Glasser. The uses of quantum field theory in diffusion-limited reactions. *Reviews of Modern Physics* **70** (3) (1998) 979–1001.

[8] H. Hinrichsen. Non-equilibrium phase transitions. *Physica A: Statistical Mechanics and its Applications* **369** (1) (2006) 1–28.

[9] Y. W. Teh, C. Blundell, and L. Elliott. Modelling genetic variations using fragmentation-coagulation processes. In *Advances in neural information processing systems*, 2011, 819–827.

[10] S. Biswas, S. Sinha, and P. Sen. Opinion dynamics model with weighted influence: Exit probability and dynamics. *Physical Review E* **88** (2) (2013) 022152.

[11] P. Roy, S. Biswas, and P. Sen. Universal features of exit probability in opinion dynamics models with domain size dependent dynamics. *Journal of Physics A: Mathematical and Theoretical* **47** (49) (2014) 495001

[12] F. Bagnoli and R. Rechtman. Stochastic bifurcations in the nonlinear parallel Ising model. *Physical Review E* **94** (5) (2016) 052111.

[13] B. Derrida, M.R. Evans, V. Hakim, and V. Pasquier. Exact solution of a 1D asymmetric exclusion model using a matrix formulation. *Journal of Physics A: Mathematical and General* **26** (7) (1993) 1493–1517.

[14] J. M. Cushing. On the dynamics of a class of Darwinian matrix models. *Nonlinear Dynamics and Systems Theory* **10** (2)(2010) 103-116.

[15] L. A. Braunstein and R.C Buceta. Nucleation model for diffusion-limited coalescence with finite reaction rates in one dimension. *Physical Review E* **53** (4) (1996) 3414–3419.

[16] V. Privman, C.R. Doering, and H.L. Frisch. Crossover from rate-equation to diffusion-controlled kinetics in two-particle coagulation. *Physical Review E* **48** (2) (1993) 846–851.

[17] D. Yue, C. Li, and W. Yue. The matrix-geometric solution of the M/Ek/1 queue with balking and state-dependent service. *Nonlinear Dynamics and Systems Theory* **6** (3) (2006) 295–308.

[18] E. Abad, T. Masser, and D. Ben-Avraham. Lattice kinetics of diffusion-limited coalescence and annihilation with sources. *Journal of Physics A: Mathematical and General* **35** (7) (2002) 1483–1500.