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Conceptual model of coalescence and break-up in the presence of external agitation

F-Javier Almaguer [a], Mónica Alcalá [b], Arturo Berrones [c,*], Óscar L. Chacón-Mondragón [c], Eduardo Soto-Regalado [b]

[a] Universidad Autónoma de Nuevo León, Facultad de Ciencias Físico Matemáticas, División de Posgrado, Av. Universidad S/N Ciudad Universitaria San Nicolás de los Garza Nuevo León CP 66451, Mexico

[b] Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Av. Universidad S/N Ciudad Universitaria San Nicolás de los Garza Nuevo León CP 66451, Mexico

[c] Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica, Posgrado en Ingeniería de Sistemas, Av. Universidad S/N Ciudad Universitaria San Nicolás de los Garza Nuevo León CP 66451, Mexico

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ABSTRACT

A Markovian probabilistic cellular automaton with the capability to capture the essential phenomenology of coalescence and break-up processes in the presence of external agitation is introduced. The existence of homogeneous stationary states of the model which admit large cluster formation for a range of agitation speeds is analytically predicted by mean field calculations. Through mean field analysis it is possible to obtain formulas that link experimental and model parameters on the base of simple measurable quantities. In this way, the experimental conditions for which a desirable stationary particle size distribution should be expected can be derived.

1. Introduction

Aggregation and breaking mechanisms are present in several fields like colloidal chemistry, polymer science, magnetic nanoparticle suspensions and wastewater treatment, among many others [1–5]. The usual framework to deal with these processes is given by the aggregation–fragmentation equation [6,1], which is a particular case of the Smoluchowski rate equation,

$$\frac{\mathrm{d}\rho_n}{\mathrm{d}t} = \frac{1}{2}\sum_{i+j=n}\left[K_{i,j}\rho_i\rho_j - F_{i,j}\rho_{i+j}\right] - \sum_{j=1}^{\infty}\left[K_{n,j}\rho_n\rho_j - F_{n,j}\rho_{n+j}\right]. \tag{1}$$

Eq. (1) describes the evolution of cluster density with size n, ρ_n, in terms of the aggregation kernel $K_{i,j}$ (which gives the aggregation reaction rate of an i-mer with a j-mer) and the fragmentation kernel $F_{i,j}$ (which models the break-up of a $(i+j)$-mer into an i-mer and a j-mer). It should be remarked that Eq. (1) is a mean field description, which gives no information regarding spatial dependencies or fluctuations. The study of the mathematical properties of Eq. (1) is an active research area [7,8]. Due to the lack of general solutions for the aggregation–fragmentation equation, the analysis of cases of particular interest and the development of simulation techniques are valuable [9–11]. In the pure aggregation case ($F = 0$) no stationary solutions of Eq. (1) exist giving rise to a single cluster at infinite times with its statistical properties depending

* Corresponding author.
E-mail addresses: arturo.berrones@gmail.com, arturo@yalma.fime.uanl.mx (A. Berrones).
URL: http://www.pisis.fime.uanl.mx/Faculty/arturo.html (A. Berrones).

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on K. When $F > 0$ stationary states can emerge. We are interested in kernels that are influenced by an external agitation speed. Our motivation is wastewater treatment, where it is common to use chemicals that once mixed with wastewater promote the aggregation of the suspended solids into particles large enough to settle or be removed (flocculation) [12,13]. An agitation may improve the floc formation but also promote instabilities that may fracture the clusters. A fundamental interest in such an application is to find a range of experimental conditions (agitation speeds and times) for which the resulting particle size distribution has some desirable shape. The situation at hand can be modeled in a tractable way by introducing an instability threshold $\bar{h}$. The existence of such a threshold is physically justified by empirical observations and allows the definition of simple, yet meaningful, kernel structures. We show that by recasting the variables ρ with respect to $\bar{h}$, it is possible to obtain a version of the aggregation–fragmentation equation from which a complete analytical description of the stationary states is possible. From this analytical description, relations between the actual experimental parameters and statistical properties of interest can be obtained.

2. The model

Our starting point is a conceptual cellular automaton model which considers the spatial distance between clusters and fluctuations. This model derives a mean field description.

The cellular automaton is defined on a one dimensional lattice with periodic boundary conditions. Associated with any cell j in the lattice is a state variable h_j, that is interpreted as an abstract floc size. The state in a cell can change by any integer value from iteration to iteration following a set of local rules. The integer units are called *particles*. The rules that dictate the particle movement in the lattice depend on the average floc size, defined as follows. At an initial stage, M particles are distributed over the N sites of the lattice, giving an average floc size $\bar{h} = M/N$. The subsequent evolution of the automaton is given by the following rules.

- If $h_j \leq \bar{h}$ then, with probability $1 - v$, the cell remains unchanged, and with probability v receives particles from its neighboring cells (from $j-1$, $j+1$, or both).
- On the other hand, if $h_j > \bar{h}$ then, with probability $f(1 - v)$, the *j-th* cell receives particles from its neighboring cells (from $j-1$, $j+1$, or both), and with probability $1 - f(1 - v)$ transfers the excess particles (above average) to any of the neighboring cells $j-1$ or $j+1$.

The decisions that involve transfer of particles to h_j from its neighbors (which neighbors give particles), are taken at random from uniform distributions. The parameter v represents the degree of instability of large clusters: as $v \to 1$ only the flocs with sizes below or equal to the average are stable. The parameter f, on the other hand, acts like a stabilization factor for large aggregates: depending on f it is more or less probable that a large floc grows in a given site from one time step to the next, at $v < 1$. The stability threshold is chosen like the average $\bar{h}$ on the basis of the following experimental observation. At very large agitation speeds, highly stable clusters of minimal mesoscopic sizes are dominant. Mass conservation is assumed in our model, so the threshold definition in terms of $\bar{h}$ follows from the identification of $v = 1$ with the maximum agitation speed limit.

The cellular automaton represents situations in which the experimental control parameters are fixed, hence its rules are in terms of constant rates (f and v). It should be remarked, however, that the automaton's rules imply local fluctuations on the particle transport, which depends on the relative size of the cluster on any given site j with respect to the stability threshold.

The main interest is the particle size distribution, in the sense of the dimensionless mean field Eq. (1). As a first step we propose in this work the simple 1-d model stated above, expecting to capture essential interactions that give rise to sound mean field equations. Generalizations to larger dimensions are expected to be explored in the future.

It is now shown by a mean field analysis that homogeneous stationary states with a positive probability of floc formation, with sizes larger than $\bar{h}$, can evolve from the proposed evolution rules. The following definitions are required:

- $\Delta h_j = h_j - \bar{h} \equiv$ deviation from the average number of particles at site j,
- state $+$: $\Delta h_j > 0$, state $-$: $\Delta h_j \leq 0$,
- $P_j^+(t) \equiv P_t(\Delta h_j > 0)$, $P_j^-(t) \equiv P_t(\Delta h_j \leq 0)$,
- $v \equiv P(+ \mid -)$: transition probability $- \to +$,
- $b = f(1 - v) \equiv P(+|+)$: transition probability $+ \to +$,

with, respectively, the positivity $P_j^{\pm}(t) > 0$ and normalization conditions $P_j^+(t) + P_j^-(t) = 1$, for any time and site, respectively.

We now consider a coarse grained approach in which the size of each aggregate fluctuates due to a mean field which results from the superposition of external system fields and the electrical mean field from other aggregates in the system,

$$P_j^+(t+1) = bP_j^+(t) + vP_j^-(t), \tag{2}$$
$$P_j^-(t+1) = (1-b)P_j^+(t) + (1-v)P_j^-(t),$$