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Statistical physics models of aggregation phenomena

T Huillet†

LIMHP-CNRS, Université Paris XIII, Institut Galilée, 93430 Villetaneuse, France

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Abstract. Aggregation phenomena of elementary particles into clusters is one of the most fascinating and challenging problems of statistical physics. Here we adopt a stochastic approach for the modelling of these phenomena. More precisely, we formulate the problem as follows (which we shall refer to as the 'cavity' method): given a population of N atoms partitioned into p groups, how does a new atom eventually connect to any of these p groups forming a new partition of $N+1$ atoms into a certain number of groups? Depending on this local 'logic' of pattern formation, the asymptotic structure of groups (in the thermodynamic limit $N \to \infty$) can be quite different; also the group size distributions may vary widely.

1. Introduction

The purpose of this work is to study the nucleation–aggregation phenomena of elementary particles into clusters at the statistical physics level. Although there are many alternative approaches to this question, such as mean-field population-balance Schmoluchowski equations (see, e.g., [1, 2]), here we adopt a microscopic approach for the modelling of these phenomena, which avoids the need for certain unknown parameters such as coagulation and fragmentation rates. No attempt will be made to relate these models to their equivalent mean-field level because this study, if possible, deserves a paper in itself.

More precisely, we formulate the problem as follows: nucleation–aggregation phenomena consist of problems where 'elementary' particles (atoms) are given the opportunity of forming 'assemblies' (groups or clusters). Thinking a little bit about this problem amounts to asking for the 'connection politics' of a new atom when it 'sees' a certain previously formed group pattern of N similar atoms. In this approach, nucleation of a cluster occurs when the inserted atom does not connect at all, whereas aggregation takes place when it joins any existing cluster. Depending on this local 'logic' of pattern formation, the asymptotic structure of groups (in the thermodynamic limit $N \to \infty$) can be quite different; also the group size distributions may vary widely. These asymptotic studies are the main purpose of this work. First, we illustrate our ideas on three 'monomer addition' models which, in fact, are three different and basic 'connection logics'. In these simplistic models, the additional atom, if it connects, connects to a single group: clusters grow by the addition of single particles. In section 6 we shall give more general models in the same vein where clusters themselves are allowed to aggregate, which should match with more realistic situations. We shall make use of the notion of generating functions from combinatorics [3–5].

† E-mail address: huillet@limhp.univ-paris13.fr

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2. Three monomer addition models

Assume a population of N atoms is partitioned into p distinct non-empty groups. There can be at least one group of size N, and at most N groups of size one. Let $N_j,\ j = 1, \ldots, N$ denote the number of groups of size j in such a partition. Of course, if all this is to be consistent:

$$\sum_{j=1}^{N} jN_j = N \tag{1}$$

and

$$\sum_{j=1}^{N} N_j = p \tag{2}$$

expressing (respectively) the conservation of the number of atoms (groups).

Next we shall focus our attention on the number of partitions of N atoms into p groups. Let $\sigma_N(p),\ p = 1, \ldots, N$ denote this quantity.

In order to clarify what these numbers really are, we now discuss the fate of an additional atom added to this structure (in the transition $N \to N+1$). This new atom may not 'connect' to any of the p existing groups, thereby forming a new group: it nucleates a new cluster. This new atom connects preferentially to (no more than) one of the p existing groups; the question is which group?

Remark 1. Note that the hypothesis that connection, if established, concerns a single group is very restrictive, although, as we shall see, far from elementary. In this sense, these aggregation models are what one may call monomer addition since clusters grow by the addition of single particles only—there is no aggregation of two (or more) larger clusters together. We shall indicate in section 6 how to include aggregation of clusters which appears to be more realistic in practice.

In order to answer the above question, let us make more precise the state-space of our models' class.

Given a population of N atoms, let P_N denote the number of groups in the partition, and let $(S_1(N), \ldots, S_{P_n}(N))$ be the group size vector. Of course

$$\sum_{p=1}^{P_N} S_p(N) = N\,.$$

Next, in the transition $N \to N+1$, consider the (random) event $C_N = p$ that connection C_N of the additional atom is established with group $p \in \{1, \ldots, P_N\}$: the indicator function $\mathbf{1}_{C_N=p}$ will thus be one if its argument is true and zero otherwise. Lack of connection will be represented by the event $C_N = 0$.

We then have the obvious following state-space evolution equations:

$$\begin{bmatrix} S_1(N+1) \\ \vdots \\ S_p(N) \\ \vdots \\ \vdots \\ S_{P_{N+1}}(N+1) \\ 0 \\ \vdots \end{bmatrix} = \sum_{p=1}^{P_N} \begin{bmatrix} S_1(N) \\ \vdots \\ S_p(N)+1 \\ \vdots \\ S_{P_N}(N) \\ 0 \\ 0 \\ \vdots \end{bmatrix} \mathbf{1}_{C_N=p} + \begin{bmatrix} S_1(N) \\ \vdots \\ S_p(N) \\ \vdots \\ S_{P_N}(N) \\ 1 \\ 0 \\ \vdots \end{bmatrix} \mathbf{1}_{C_N=0} \tag{3}$$

$$P_{N+1} = P_N \, \mathbf{1}_{C_N=p} + (P_N + 1) \, \mathbf{1}_{C_N=0} \, . \tag{4}$$

Equation (3) indicates how to increment the group size vector whenever a connection is established, whereas equation (4) is concerned with the (non-decreasing) number of such groups.

Thus adopting probabilistic language for a while, we consider the following three random self-consistent connection rules of the additional atom giving the probability, say $\boldsymbol{Q}$, that connection is established with group p:

(i) $\boldsymbol{Q}(C_N = 0) = \frac{1}{2}, \ \boldsymbol{Q}(C_N = p) = 1/(2P_N), \ p = 1, \ldots, P_N$

(ii) $\boldsymbol{Q}(C_N = 0) = 1/(P_N + 1), \ \boldsymbol{Q}(C_N = p) = 1/(P_N + 1), \ p = 1, \ldots, P_N$

(iii) $\boldsymbol{Q}(C_N = 0) = 1/(N + 1), \ \boldsymbol{Q}(C_N = p) = S_p(N)/(N + 1), \ p = 1, \ldots, P_N$ for which, respectively,

(i) $\boldsymbol{Q}(C_N = 0) = \frac{1}{2}, \ \boldsymbol{Q}(C_N > 0) = \frac{1}{2}$

(ii) $\boldsymbol{Q}(C_N = 0) = 1/(P_N + 1), \ \boldsymbol{Q}(C_N > 0) = P_N/(P_N + 1)$

(iii) $\boldsymbol{Q}(C_N = 0) = 1/(N + 1), \ \boldsymbol{Q}(C_N > 0) = N/(N + 1)$.

Thus letting $\boldsymbol{Q}(P_N = p) \stackrel{df}{=} \boldsymbol{Q}_N(p)$ denote the probability that the (random) number of groups is p given a population of N atoms, it follows from the state-space equation (4) that

(i) $\boldsymbol{Q}_{N+1}(p) = \frac{1}{2}\boldsymbol{Q}_N(p-1) + \frac{1}{2}\boldsymbol{Q}_N(p)$

(ii) $\boldsymbol{Q}_{N+1}(p) = 1/(p+1)\boldsymbol{Q}_N(p-1) + p/(p+1)\boldsymbol{Q}_N(p)$

(iii) $\boldsymbol{Q}_{N+1}(p) = 1/(N+1)\boldsymbol{Q}_N(p-1) + N/(N+1)\boldsymbol{Q}_N(p)$.

The answer to our question therefore lies in the three recurrences on $\sigma_N(p)$ we shall consider here (omitting normalization constants), skipping from probabilistic language to the one of enumeration

$$\begin{aligned} &\text{(i)} && \sigma_{N+1}(p) = \sigma_N(p-1) + \sigma_N(p) \\ &\text{(ii)} && \sigma_{N+1}(p) = \sigma_N(p-1) + p\sigma_N(p) \\ &\text{(iii)} && \sigma_{N+1}(p) = \sigma_N(p-1) + N\sigma_N(p) \end{aligned} \tag{5}$$

with common boundary conditions

$$\begin{aligned} &\sigma_1(1) = 1 \\ &\sigma_N(0) = 0 \qquad \forall N \geqslant 1 \\ &\sigma_N(p) = 0 \qquad \forall p \geqslant N+1 \qquad \forall N \geqslant 1 \, . \end{aligned} \tag{6}$$

Thus:

In model (i), the additional atom is equally likely to connect or not. If it connects, it forms a new group with all existing p groups with no preference for any of them.

In model (ii), all existing p groups are equally likely to form a new group (or not) with the additional atom, independently of the sizes of these p groups. 'Randomness' is maximal.

In model (iii), the connection is more likely to occur with a group of large size: the additional atom behaves gregariously and moves preferentially towards larger groups.

In models (ii) and (iii), connection is very likely to occur compared to model (i). The number of distinct groups is thus intuitively expected to be much smaller than in situation (i) as the number of atoms goes to infinity. One of the problems is to quantify this observation.

Recurrences (5) identify the number sequences under investigation, namely

(i) $\sigma_N(p) = \binom{N-1}{p-1}$ the binomial coefficients,

(ii) $\sigma_N(p) = S_N(p)$, the second kind of Stirling numbers,

(iii) $\sigma_N(p) = |s_N(p)|$, the absolute values of the first kind of Stirling numbers.

Let us also introduce the numbers $\sigma_N = \sum_{p=1}^{N} \sigma_N(p)$, giving the total number of partitions of N atoms, which are, respectively,

(i) $\sigma_N = 2^{N-1}$

(ii) $\sigma_N = B_N$, the Bell numbers

(iii) $\sigma_N = N!$

Also observe that

$$\sigma_N(p) \stackrel{df}{=} \#\{q \in \{1, \ldots, \sigma_N\} : P_N(q) = p\} \qquad p = 1, \ldots, N \tag{7}$$

where $\#\{\cdots\}$ is to be read as 'the cardinal of the set...'.

Remark 2. Let us show how to generate such sequences $\sigma_N(p)$, $p = 1, \ldots, N$, which follows from the recurrences (5) in a straightforward way.

(i) The sequence: $\sigma_N(p) = \binom{N-1}{p-1}$, $p = 1, \ldots, N$, can be obtained from the Nth iterate (power) of the operator

$$A : (x_1, x_{2,}, \ldots, x_p, \ldots) \to (x_1, x_1 + x_2, \ldots, x_{p-1} + x_p, \ldots)$$

acting on the initial condition: $X_0 \stackrel{df}{=} (1, 0, \ldots, 0, \ldots)$. This operator is bounded in ℓ_1 (the set of summable series with non-negative entries), with $\|A\|_1 = 2$. Its spectrum is purely continuous and identified with the unit disc of the complex plane, centred at $(1, 0)$. Therefore, its spectral radius is 2.

(ii) The sequence $\sigma_N(p) = S_N(p)$, $p = 1, \ldots, N$, can be obtained from the Nth iterate of the operator

$$A : (x_1, x_{2,}, \ldots, x_p, \ldots) \to (x_1, x_1 + 2x_2, \ldots, x_{p-1} + px_p, \ldots)$$

acting on the initial condition X_0. This operator is unbounded in ℓ_1. Its spectrum is purely discrete and identified with the set of natural numbers $\mathbb{N}$.

(iii) Concerning the third sequence $\sigma_N(p) = |s_N(p)|$, $p = 1, \ldots, N$, it can be reached from the action on X_0 of the ordered left-product operator $A_N \stackrel{df}{=} \prod_{p=1}^{N} B_p$, with

$$B_p : (x_1, x_{2,}, \ldots, x_q, \ldots) \to (px_1, px_1 + x_2, \ldots, px_{q-1} + x_q, \ldots).$$

Clearly, for this operator sequence $\lim_{N\to\infty} \|A_N\|_1^{1/N} = \infty$.

3. Elementary arithmetic: partition functions

Inspecting equations (1) and (2), and asking for the number of ways, say $q_N(p)$, one may partition N atoms into p groups under the constraints (1) and (2) yielding

$$q_N(p) \stackrel{df}{=} \#\left\{N_j \geqslant 0,\, j = 1, \ldots, N : \sum_{j=1}^{N} jN_j = N, \sum_{j=1}^{N} N_j = p\right\}. \tag{8}$$

It is part of standard theory [4] that this sequence can be reached from the infinite product representation of the partition function, in the formal variables θ and γ

$$1 + \sum_{N\geqslant 1} \theta^N \sum_{p=1}^{N} q_N(p)\gamma^p = \prod_{n\geqslant 1} \left(1 - \gamma\theta^n\right)^{-1}.$$

Let us now form the generating function $\Phi_N(\gamma)$ of the sequence $\sigma_N(p)$, $p = 1, \ldots, N$, namely

$$\Phi_N(\gamma) \stackrel{df}{=} \sum_{p=1}^{N} \sigma_N(p)\gamma^p$$

and the partition function

$$\Phi(\gamma, \theta) \stackrel{df}{=} 1 + \sum_{N\geqslant 1} \frac{\theta^N}{N!} \Phi_N(\gamma). \tag{9}$$

Particularizing to the three models of interest yields, respectively, for models (i), (ii), (iii)

$$\Phi(\gamma, \theta) = 1 + \frac{\gamma}{\gamma + 1}\left(\mathrm{e}^{\theta(1+\gamma)} - 1\right) \tag{10}$$

$$\Phi(\gamma, \theta) = \mathrm{e}^{\gamma(\mathrm{e}^{\theta}-1)} \tag{11}$$

$$\Phi(\gamma, \theta) = (1 - \theta)^{-\gamma} = \mathrm{e}^{-\gamma \log(1-\theta)}. \tag{12}$$

A closer inspection of the sequence $\sigma_N(p)$ shows that it may be written as

$$\sigma_N(p) = \sum\nolimits^{*}_{N,p} \Omega(N_1, \ldots, N_N) \tag{13}$$

where the complex numbers $\Omega(N_1, \ldots, N_N)$, are to be understood as the degeneracy of the aggregation systems, that is, the total number of ways one can partition N atoms into p groups, with N_j being the number of groups of size j, $j = 1, \ldots, N$.

In identity (13), the 'star-sum' is a notational convenience for

$$\sum_{N,p}^{*} \Omega(N_1, \ldots, N_N) \stackrel{df}{=} \sum_{\substack{N_1,\ldots,N_N\geqslant 0 \\ \sum_j N_j = p,\ \sum_j jN_j = N}} \Omega(N_1, \ldots, N_N)$$

(there are $q_N(p)$ terms in this sum).

Now let $(c_N)_{N\geqslant 1}$ be a non-decreasing sequence of integral numbers, to be interpreted later as the number of micro-states for N particles occupying the same single-particle state. Define the double sequence of real numbers

$$w_{l,N} \stackrel{df}{=} \frac{1}{l!}\left(\frac{c_N}{N!}\right)^l \qquad l \geqslant 1 \qquad N \geqslant 1.$$

Next introduce

$$\tilde{\Omega}(N_1, \ldots, N_N) \stackrel{df}{=} \prod_{j=1}^{N} w_{N_j,j} = \prod_{j=1}^{N} \frac{c_j^{N_j}}{N_j!(j!)^{N_j}} \stackrel{df}{=} \frac{1}{N!}\Omega_B(N_1, \ldots, N_N) \prod_{j=1}^{N} c_j^{N_j}$$

where $\Omega_B(N_1, \ldots, N_N)$ is the Boltzmann degeneracy.

It is easy to see that $\Omega(N_1, \ldots, N_N)$ can be expressed in terms of $\tilde{\Omega}(N_1, \ldots, N_N)$ and for a particular choice of $(c_N)_{N\geqslant 1}$ in our three models, namely

(i) $c_N = N!$ and $\Omega(N_1, \ldots, N_N) = p!$, $\tilde{\Omega}(N_1, \ldots, N_N) = p!/\prod_{j=1}^{N} N_j!$

(ii) $c_N = 1$ and $\Omega(N_1, \ldots, N_N) = N!,\ \tilde{\Omega}(N_1, \ldots, N_N) = N!/\prod_{j=1}^{N} N_j!(j!)^{N_j}$

(iii) $c_N = (N-1)!$ and $\Omega(N_1, \ldots, N_N) = N!,\ \tilde{\Omega}(N_1, \ldots, N_N) = N!/\prod_{j=1}^{N} N_j! j^{N_j}$.

Now let us discuss how one skips from the formal variables (γ, θ) to the thermodynamic ones which are identified as the chemical potential and inverse of the temperature (μ, β).

Let the level-N partition function be

$$Z_N(\lambda) \stackrel{df}{=} \sum_{p=1}^{N} \sigma_N(p) \mathrm{e}^{-\lambda p} = \Phi_N\left(\mathrm{e}^{-\lambda}\right)$$

with $\lambda \stackrel{df}{=} \beta\mu$. Here β stands for the inverse of the 'temperature', μ for the 'chemical potential', so that $\gamma \stackrel{df}{=} \mathrm{e}^{-\beta\mu}$ is the thermodynamic 'fugacity'.

Also, the correspondence between the formal variable θ and β is $\theta \stackrel{df}{=} \mathrm{e}^{-\beta}$. Therefore, in physics, one works with the grand canonical partition functions

$$Z(\lambda, \beta) \stackrel{df}{=} \Phi\left(\mathrm{e}^{-\lambda}, \mathrm{e}^{-\beta}\right).$$

Equation (9) can therefore be reformulated in an equivalent manner as

$$Z(\lambda, \beta) = 1 + \sum_{N \geqslant 1} \frac{\mathrm{e}^{-\beta N}}{N!} Z_N(\lambda). \tag{14}$$

4. Group number asymptote

We now discuss in some detail the group number variables in the thermodynamic limit $N \to \infty$.

Define the probabilities that the number of groups is p by

$$\boldsymbol{P}(P_N = p) \stackrel{df}{=} \boldsymbol{P}_N(p) \stackrel{df}{=} \frac{\sigma_N(p)}{\sigma_N}.$$

Also define the $\boldsymbol{P}$ means and variances by $\boldsymbol{E}(P_N)$ and $\boldsymbol{D}^2(P_N)$.

4.1. Central limit results

It follows from standard results [6–8], that the following central limit theorem holds:

$$\lim_{N\to\infty} \boldsymbol{P}\left(\frac{P_N - \boldsymbol{E}(P_N)}{\boldsymbol{D}(P_N)} < \alpha\right) = \mathrm{Erf}(\alpha). \tag{15}$$

Some details on this are now recalled in three different situations:

(i) The sequence $\sigma_N(p),\ p = 1, \ldots, N$ presents only one mode and constitutes the Pascal's triangle for which it is well known that

$$\boldsymbol{E}(P_N) = 1 + \frac{N-1}{2} \qquad \boldsymbol{D}^2(P_N) = \frac{N-1}{4}.$$

Thus

$$\frac{1}{N}\boldsymbol{E}(P_N) \stackrel{N\to\infty}{\to} \frac{1}{2} \stackrel{df}{=} \alpha_0.$$

Also recall that $\sigma_N = 2^{N-1}$ which thus grows exponentially fast.

(ii) Concerning the sequence $\sigma_N(p)$, $p = 1, \ldots, N$, it can be shown [7] that $\boldsymbol{E}(P_N) = B_{N+1}/B_N - 1$ and that $\boldsymbol{D}^2(P_N) = B_{N+2}/B_N - (B_{N+1}/B_N)^2$, so that the asymptotic evaluation

of these quantities amounts to the asymptotic evaluation of the Bell number behaviour for which a saddle-point method [9] gives

$$\frac{1}{N}\log B_N = \log N - \log\log N - 1 + \mathrm{O}(\log\log N/\log N).$$

Thus $B_N \sim (N/\log N)^N$ which grows faster than exponentially with N (compare with (i)).

This provides the evaluation $\boldsymbol{E}(P_N) \sim N/\mathrm{e}\log N$.

Also, it has been shown that the sequence $\sigma_N(p),\ p = 1,\ldots,N$ presents only one mode, with

$$p^*(N) \stackrel{df}{=} \operatorname*{Arg\,max}_p \sigma_N(p) \sim \frac{N}{\mathrm{e}\log N}$$

(the mean), so that

$$\alpha(N) \stackrel{df}{=} \frac{p^*(N)}{N} \stackrel{N\to\infty}{\longrightarrow} 0 \stackrel{df}{=} \alpha_0\,.$$

The most probable group density in model (ii) is thus zero, corroborating an earlier observation of section 2.

(iii) Concerning the sequence $\sigma_N(p),\ p = 1,\ldots,N$, one can show [8] that $\boldsymbol{E}(P_N) \sim \log N$ and that $\boldsymbol{D}^2(P_N) \sim \log N$.

Whereas $\sigma_N = N! \sim N^N\mathrm{e}^{-N}\sqrt{2\pi N}$ grows much faster than exponentially with N, by Stirling's formula, and also faster than in model (ii).

The sequence $\sigma_N(p), p = 1,\ldots,N$ has only one mode [8], with $p^*(N) \stackrel{df}{=} \operatorname*{Arg\,max}_p \sigma_N(p) \sim \log N$, so that

$$\alpha(N) \stackrel{df}{=} \frac{p^*(N)}{N} \stackrel{N\to\infty}{\longrightarrow} 0 \stackrel{df}{=} \alpha_0\,.$$

The most probable group density in model (iii) also goes to zero, but slower than in situation (ii).

4.2. Very large deviation result

Concerning large deviation to the central limit theorem, we have the 'very' large deviation result, strongly reminiscent of multifractal theory,

$\forall\alpha > \alpha_0 \in [0,1]$:

$$\lim_{N\to\infty} \#\left\{q \in \{1,\ldots,\sigma_N\} : \frac{P_N(q)}{N} > \alpha\right\}^{1/\log\sigma_N} = \mathrm{e}^{f(\alpha)+1} \tag{16}$$

or

$$\lim_{N\to\infty} \boldsymbol{P}\left\{\frac{P_N}{N} > \alpha\right\}^{1/\log\sigma_N} = \mathrm{e}^{f(\alpha)} \tag{17}$$

where it remains to interpret the rate functions $-1 \leqslant f(\alpha) \leqslant 0$ which will be shown to be concave on the unit interval. They attain their maximum, zero, at α_0. Moreover $f(1) = -1$.

Remark 3. In equation (17) the scaling factor $1/N$ of the random variable P_N is not of the same order of magnitude as $1/\log\sigma_N$, at least in situations (ii) and (iii). Deviation from normality is thus extremely unlikely to occur, which justifies the term 'very' large deviation.

We now come to the proof of this assertion.

If this result is to hold true, one must indeed show the standard large deviation result [10],

$$\lim_{N\to\infty} \boldsymbol{P}\left\{\frac{\tilde{P}_N}{\log\sigma_N} > \alpha\right\}^{1/\log\sigma_N} = \mathrm{e}^{f(\alpha)}$$

for the new scaled variable $\tilde{P}_N \stackrel{df}{=} P_N \log\sigma_N/N$.

Then define the Laplace transform

$$\alpha_N(\lambda) \stackrel{df}{=} \boldsymbol{E}\mathrm{e}^{-\lambda\tilde{P}_N}.$$

Let $P_{N,\lambda}(q) \stackrel{df}{=} \mathrm{e}^{-\lambda\tilde{P}_N(q)}/(\sigma_N\alpha_N(\lambda)),\ q = 1,\ldots,\sigma_N$ to be an exponential family of probability measures, with $P_{N,0}(q) = 1/\sigma_N,\ q = 1,\ldots,\sigma_N$.

Here $\tilde{P}_N(q) \stackrel{df}{=} P_N(q)\log\sigma_N/N,\ q = 1,\ldots,\sigma_N$.

Next, introduce the Kullback–Leibler information functions

$$\tilde{f}_N(\lambda) \stackrel{df}{=} -\sum_{q=1}^{\sigma_N} P_{N,\lambda}(q)\log_{\sigma_N}\left(\frac{P_{N,\lambda}(q)}{P_{N,0}(q)}\right).$$

Clearly, the $\tilde{f}_N(\lambda) \stackrel{df}{=} f_N(F_N'(\lambda))$ are concave functions and $\tilde{f}_N(\lambda) = \lambda F_N'(\lambda) - F_N(\lambda)$, with

$$F_N(\lambda) \stackrel{df}{=} -\log_{\sigma_N}\alpha_N(\lambda)$$

so that $\tilde{f}_N(\lambda)$ and $F_N(\lambda)$ are dual functions in the Legendre sense.

It follows from [10] that $f(\alpha)$ is the Legendre transform of

$$F(\lambda) = \lim_{N\to\infty} F_N(\lambda)$$

if such a limit exists.

Now observe that $\alpha_N(\lambda) \stackrel{df}{=} \boldsymbol{E}\mathrm{e}^{-\lambda\tilde{P}_N} = \sum_{p=1}^{N}(\sigma_N(p)/\sigma_N)\sigma_N^{-\lambda p/N}$ is a linear convex combination of exponentials, so that $F_N(\lambda)$ is a sequence of analytic concave functions. Moreover,

$$F_N(\lambda) \underset{\lambda\to-\infty}{\sim} \lambda + 1 \qquad \text{and} \qquad F_N(\lambda) \underset{\lambda\to+\infty}{\sim} \lambda/N + (1 - \log_{\sigma_N}\sigma_N(1)).$$

The convergence $F(\lambda) = \lim_{N\to\infty} F_N(\lambda)$ is now straightforward; indeed, for any $\lambda < 0$, $F_N(\lambda) \leqslant F_{N+1}(\lambda) \leqslant \lambda+1$ and for any $\lambda > 0,\ 0 \geqslant F_N(\lambda) \geqslant F_{N+1}(\lambda)$. As a result, $F_N(\lambda)$ is a bounded from above (below) non-increasing (non-decreasing) sequence for $\lambda < 0$ ($\lambda > 0$). Therefore, it converges, pointwise, to a concave function of λ. Moreover, it follows from the concavity of $F_N(\lambda)$ that $F_N(\lambda) = \sup_{\lambda'\leqslant\lambda} F_N(\lambda')$. Therefore convergence is uniform, which guarantees that the limit $F(\lambda)$ is continuous, possibly not differentiable in most interesting cases. Phase transitions certainly may occur [11]. The concave rate functions of the large deviation result (16) meet the Legendre equation

$$f(\alpha) = \inf_{\lambda}(\lambda\alpha - F(\lambda)).$$

This completes the proof.

Some details on the three models are available, namely

(i) In this situation,

$$F_N(\lambda) \stackrel{df}{=} -\log_{2^{N-1}}\alpha_N(\lambda) = -\log_{2^{N-1}}\left(2^{-\lambda}\left(\frac{1+2^{-\lambda}}{2}\right)^{N-1}\right).$$

So that $F(\lambda) = \lim_{N\to\infty} F_N(\lambda) = -\log_2((1+2^{-\lambda})/2)$. We therefore have the usual bell-shape ($\cap$) for the (symmetric) and concave Legendre transform of $F(\lambda)$, which is explicitly checked to be $f(\alpha) = \log_2((1-\alpha)^{\alpha-1}/2\alpha^{\alpha})$.

It can be noticed that $f(0) = f(1) = -1$ and $f\left(\frac{1}{2}\right) = 0$.

(ii) and (iii), in these cases, no such explicit computation exists, but the limit rate functions are right-sided [12], in the sense that one only exhibits the 'right-hand side of the previous bell'; this is because $\alpha(N) \stackrel{df}{=} p^*(N)/N \stackrel{N\to\infty}{\longrightarrow} 0 = \alpha_0$, in both cases (ii) and (iii). It can be checked that $f(0) = 0$ and $f(1) = -1$ in both cases. Here we have the signature of a phase transition.

5. Most probable cluster size distributions

This section relies upon standard work in statistical physics, see for example [13, 14]. It addresses the important practical problem of determining the group size distributions of the aggregates.

Looking at equations (9), (16), (18), in the thermodynamic variables (β, μ) yields

$$Z(\beta\mu, \beta) = 1 + \sum_{N\geqslant 1} \frac{1}{N!} \sum_{p=1}^{N} \sum_{N,p}^{*} \Omega_{\beta,\mu}(N_1, \ldots, N_N)$$

with

$$\Omega_{\beta,\mu}(N_1, \ldots, N_N) = \mathrm{e}^{-\beta(N+\mu p - \log\Omega(N_1,\ldots,N_N)/\beta)}.$$

Defining the entropy

$$S_{\beta,\mu}(N_1, \ldots, N_N) = \log\Omega_{\beta,\mu}(N_1, \ldots, N_N)$$

we have that the most probable group size distributions are the ones of maximal entropy.

Thus, we are left with the minimization program: minimize over the vector $(N_1, \ldots, N_N)$ the quantity

$$-S_{\beta,\mu}(N_1, \ldots, N_N) = \beta(N + \mu p) - \log\Omega(N_1, \ldots, N_N)$$

with the constraints (1) and (2).

Putting

$$p_j \stackrel{df}{=} \frac{N_j}{p} \qquad j = 1, \ldots, N$$

the standard Lagrange multipliers method allows us to reformulate this problem as the following. Minimize

$$\sum_{j=1}^{N} p_j \left(\beta(j+\mu) + \log\left(p_j \frac{j!}{c_j}\right) + \lambda_1 + \lambda_2 j\right) = \sum_{j=1}^{N} p_j \log\left(\left(p_j \frac{j!}{c_j}\right)\mathrm{e}^{\beta(j+\mu)+\lambda_1+\lambda_2 j}\right)$$

under the constraints $\sum_{j=1}^{N} p_j = 1$, $\sum_{j=1}^{N} j p_j = N/p \stackrel{df}{=} 1/\alpha$, with $\alpha \in [0, 1]$.

Therein, (λ_1, λ_2) are the Lagrange multipliers.

The minimum is reached when the argument of the logarithm is one, so that $p_j^* = c_j \mathrm{e}^{\beta(j+\mu)-\lambda_2 j}/j!_j \mathrm{e}^{\lambda_1}$, $j = 1, \ldots, N$, where the Lagrange multipliers are determined by the constraints.

As $N, p \to \infty$, while the group density is held fixed $p/N = \alpha$, the first Lagrange multiplier is given by the first constraint. It is

$$\mathrm{e}^{\lambda_1} = \sum_{j\geqslant 1} \frac{c_j \mathrm{e}^{\beta(j+\mu)-\lambda_2 j}}{j!} = \mathrm{e}^{-\beta\mu} z(\beta + \lambda_2)$$

where

$$z(\beta) \stackrel{df}{=} \sum_{j\geqslant 1} c_j \frac{\mathrm{e}^{-\beta j}}{j!}$$

for the three different choices of the sequence c_j given in section 3.

For the second Lagrange multiplier, $\sum_{j=1}^{N} j p_j^* = 1/\alpha$ gives the characterization

$$-\alpha \frac{\mathrm{d}}{\mathrm{d}\beta} \log z(\beta + \lambda_2) = 1\,. \tag{18}$$

Finally,

$$p_j^* = -\frac{c_j}{z(\beta+\lambda_2)} \frac{\mathrm{e}^{-(\beta+\lambda_2)j}}{j!} \qquad j \geqslant 1$$

$$q_j^* \stackrel{df}{=} j\alpha p_j^* = -\frac{c_j}{\frac{\mathrm{d}}{\mathrm{d}\beta} z(\beta+\lambda_2)} \frac{j\mathrm{e}^{-(\beta+\lambda_2)j}}{j!} \qquad j \geqslant 1$$

are, respectively, the most probable cluster-size distributions and probability of finding a particle in a cluster of size j, where λ_2 is determined by (18).

Detailing the equations for the three different models yields (i) $z(\beta) = \mathrm{e}^{-\beta}/\left(1-\mathrm{e}^{-\beta}\right)$, (ii) $z(\beta) = \mathrm{e}^{\mathrm{e}^{-\beta}} - 1$, (iii) $z(\beta) = -\log\left(1-\mathrm{e}^{-\beta}\right)$ where it should be noted from (14) that $z(\beta) = \log Z(0, \beta)$.

In case (i), the solutions are explicitly computable from the relation $\alpha = 1 - \theta$.

They are

$$p_j^* = \alpha(1-\alpha)^{j-1} \qquad j \geqslant 1$$

(the geometrical Pascal distribution)

$$q_j^* = \alpha^2(1-\alpha)^{j-1} \qquad j \geqslant 1\,.$$

In case (ii), the distributions are Poisson-like

$$p_j^* = \frac{1}{\mathrm{e}^{\theta}-1} \frac{\theta^j}{j!} \qquad j \geqslant 1$$

$$q_j^* = \mathrm{e}^{-\theta} \frac{\theta^{j-1}}{(j-1)!} \qquad j \geqslant 1$$

where θ is the (unique) positive solution to $\alpha = (1-\mathrm{e}^{-\theta})/\theta$.

Finally, in case (iii)

$$p_j^* = -\frac{1}{\log(1-\theta)} \frac{\theta^j}{j} \qquad j \geqslant 1$$

$$q_j^* = (1-\theta)\theta^{j-1} \qquad j \geqslant 1$$

where θ is the (unique) solution of the interval $(0, 1)$ to $\alpha = -[(1-\theta)/\theta]\log(1-\theta)$.

6. Cluster–cluster aggregation

We now come to the question of including cluster aggregation into our models.

We first introduce a combinatorial tree structure which shall prove useful for our purpose. Suppose N atoms (or nodes) have been labelled as $\{1, \ldots, N\}$. A labelled increasing tree is a rooted simply connected tree for which labels along any branch from the root are forced to go in increasing order. The enumeration of such trees has been undertaken in [15]. Suppose

there are $(c_N)_{N\geqslant 1}$such trees with N atoms. Then introduce a generating function for this sequence, say $\phi(\theta)$, as

$$\phi(\theta) \stackrel{df}{=} \sum_{N\geqslant 1} \frac{c_N}{N!}\theta^N .$$

The main result of these authors is that $\phi(\theta)$ is the unique solution to the autonomous ordinary differential equation

$$\dot{\phi}(\theta) = g(\phi(\theta)) \tag{19}$$

with initial condition $\phi(0) = 0$, and for various g such that

$$g(\theta) = 1 + \sum_{k\geqslant 1} \frac{g_k}{k!}\theta^k$$

where $(g_k)_{k\geqslant 1}$is any sequence of integral numbers.

The function g is called the branch generating function. It describes locally the variability of the edges pointing outwards from any node of the tree.

The general unordered increasing tree (or non-plane tree) is thus defined recursively by appending an atom to a set of similar sub-trees. This amounts to choosing $g(\theta) = \mathrm{e}^{\theta}$, for which $g_k = 1, k \geqslant 1$. Note that for such trees, there is no order distinction between the sub-trees dangling from their common root. Ordered trees, or plane trees, could be obtained in a similar way, when considering the modified functional equation (19) with $g(\theta) = 1/(1-\theta)$, for which $g_k = k!,\ k \geqslant 1$: for such trees, there are $k!$ ways to arrange k sub-trees, taking 'chirality' into account. Therefore, modifying the 'branch'-generating function g gives rise to a variety of tree structures implicitly defined by (19). For example, unordered binary trees are enumerated while using $g(\theta) = 1 + \theta^2/2$ in the above functional equation, whereas ordered binary trees can be obtained from $g(\theta) = 1 + \theta^2$. Linear increasing trees are enumerated using $g(\theta) = 1 + \theta$ and constitute the simplest such structures.

If an explicit solution for the ordinary differential equation (19) exists, we shall call the model *solvable*. For example, choosing for g the following particular functions:

$$1 + \theta,\ (1 + \theta)^p (\text{with integer } p \geqslant 2),\ 1 + \theta^2,\ 1 + \theta^2/2!,\ 1/(1 - \theta),\ \mathrm{e}^{\theta}$$

yields, respectively, for $\phi(\theta)$,

$$\exp\theta - 1,\ -1 + [1 - (p - 1)\theta]^{-1/(p-1)},\ \tan\theta,\ \sqrt{2}\tan(\theta/\sqrt{2}),\ 1 - \sqrt{1 - 2\theta},$$
$$-\log(1 - \theta).$$

Considering a forest of increasing trees leads to the generating function $\mathrm{e}^{\phi(\theta)}$, the Taylor coefficient of which, say σ_N, counts the number of forests of increasing trees that one can form with N atoms, relaxing the connectedness condition for trees.

Next consider the bivariate 'marked' exponential generating function

$$\Phi(\gamma, \theta) \stackrel{df}{=} \mathrm{e}^{\gamma\phi(\theta)} . \tag{20}$$

Developing

$$\Phi(\gamma, \theta) \stackrel{df}{=} 1 + \sum\nolimits_{N\geqslant 1} \frac{\theta^N}{N!}\Phi_N(\gamma)$$

with

$$\Phi_N(\gamma) \stackrel{df}{=} \sum_{p=1}^{N} \sigma_N(p)\gamma^p .$$

In this interpretation, $\sigma_N(p)$ counts the number of forests made of p increasing trees that one can form with N atoms.

We now come to our cluster aggregation models.

Differentiating (20) with respect to θ gives from (19)

$$\partial_\theta \Phi(\gamma,\theta) = \gamma \dot{\phi}(\theta)\Phi(\gamma,\theta) = \gamma \sum_{k\geqslant 0} \frac{g_k}{k!}(\phi(\theta)^k \Phi\big(\gamma,\theta)\big)\,.$$

This leads to the following recurrences for the function sequence $(\Phi_N(\gamma))_{N\geqslant 1}$:

$$\Phi_{N+1}(\gamma) = \gamma \sum_{k\geqslant 0} \frac{g_k}{k!}\partial_\gamma^{(k)} \Phi_N(\gamma)$$

where $\partial_\gamma^{(k)}$ indicates derivation with respect to γ (k times).

In terms of the coefficients $\sigma_N(p)$ describing $\Phi_N(\gamma)$, this yields the recurrences

$$\sigma_{N+1}(p) = \sigma_N(p-1) + \sum_{k=1}^{N-(p-1)} a_{p,k}\sigma_N(p+k-1) \tag{21}$$

with

$$a_{p,k} = \frac{g_k}{k!}\prod_{j=0}^{k-1}(p+k-j-1).$$

In an alternative way

$$\sigma_{N+1}(p) = \sigma_N(p-1) + \sum_{q=p}^{N} b_{p,q}\sigma_N(q) \qquad p = 1,\ldots,N \qquad N \geqslant 1$$

with

$$b_{p,p+r} = a_{p,r+1} = \frac{g_{r+1}}{(r+1)!}\prod_{j=0}^{r}(p+j) \qquad r \geqslant 0 \qquad p \geqslant 1\,. \tag{22}$$

Recurrences (21) constitute the announced generalization of (5).

We now interpret recurrences (21) in terms of nucleation–aggregation phenomena, as described in section 2.

Indeed, in such extended models the additional atom in the transition $N \to N+1$, when it sees a cluster situation with p groups, may connect to k groups simultaneously, $k = 1,\ldots,\min(K,p)$, where $K \stackrel{df}{=} \max(k \geqslant 1 : g_k \neq 0)$ is the (possibly infinite) order of the branch generating function $g(\theta)$. This k-connection (fusion) occurs with transition probability

$$\boldsymbol{Q}_{N,p}(k) \stackrel{df}{=} \frac{a_{p,k}}{\left(1+\sum_{k=1}^{N-(p-1)} a_{p,k}\right)}.$$

By doing so, the number of groups shifts from p to $(p-k+1)$ and decreases as soon as $k \geqslant 2$ (cluster–cluster aggregation).

Of course, nucleation occurs with probability

$$\boldsymbol{Q}_{N,p}(0) \stackrel{df}{=} \frac{1}{\left(1+\sum_{k=1}^{N-(p-1)} a_{p,k}\right)}$$

and still remains possible.

In other words, equation (4) of section 2 has to be replaced by

$$P_{N+1} = P_N\,\mathbf{1}_{K_N=0} + (P_N - K_N + 1)\,\mathbf{1}_{K_N>0}$$

where K_N is the random variable giving the number of connections with transition distribution

$$\boldsymbol{Q}(K_N = k \mid P_N = p) = \boldsymbol{Q}_{N,p}(k) \qquad k \geqslant 0.$$

The coefficients $a_{p,k}$ entering in the definition of these probabilities are now easy to interpret: they are the number of ways that the inserted atom will select k distinguishable (resp. indistinguishable) connection groups out of p possible groups, as soon as $g_k = k!$ (resp. $g_k = 1$).

Remark 4. As a result of (21) and (22), the sequence $\sigma_N(p),\ p = 1, \ldots, N$, can be obtained from the Nth iterate (power) of the unbounded operator in ℓ_1:

$$A : (x_1, \ldots, x_p, \ldots) \to \left(x_1, \ldots, x_{p-1} + \sum_{q \geqslant p} b_{p,q} x_q, \ldots \right) \tag{23}$$

acting on the initial condition $X_0 \stackrel{df}{=} (1, 0, \ldots, 0, \ldots)$.

Example 1. Let us give some examples that show that models (ii) and (iii) are actually particular cases of this new interpretation.

(ii) $g(\theta) = 1 + \theta$ for which $g_1 = 1,\ g_k = 0,\ k \geqslant 2$ leads to $\phi(\theta) = \exp\theta - 1$ and $\Phi(\gamma, \theta) = \mathrm{e}^{\gamma(\mathrm{e}^{\theta}-1)}$ and from (21) we get (equation 5(ii))

$$\sigma_{N+1}(p) = \sigma_N(p-1) + p\sigma_N(p).$$

(iii) $g(\theta) = \mathrm{e}^{\theta}$ for which $g_k = 1,\ k \geqslant 1$ leads to $\phi(\theta) = -\log(1-\theta)$ and $\Phi(\gamma, \theta) = (1-\theta)^{-\gamma}$.

Recurrences (21) obtained while inserting $g_k = 1,\ k \geqslant 1$ in (22) constitute an alternative interpretation to (equation 5(iii)). In this case, connection with any number of pre-existing groups is allowed to take place.

(iv) $g(\theta) = (1+\theta)^2$ for which $g_1 = g_2 = 2,\ g_k = 0,\ k \geqslant 3$ leads to $\phi(\theta) = \theta/(1-\theta)$ and $\Phi(\gamma, \theta) = \mathrm{e}^{\gamma\theta/(1-\theta)}$:

$$\sigma_{N+1}(p) = \sigma_N(p-1) + 2p\sigma_N(p) + p(p+1)\sigma_N(p+1) \qquad p = 1, \ldots, N\,.$$

(v) $g(\theta) = 1 + \theta^2$ for which $g_1 = 0,\ g_2 = 2,\ g_k = 0,\ k \geqslant 3$ leads to $\phi(\theta) = \tan\theta$ and $\Phi(\gamma, \theta) = \mathrm{e}^{\gamma\tan\theta}$:

$$\sigma_{N+1}(p) = \sigma_N(p-1) + p(p+1)\sigma_N(p+1).$$

7. Concluding remarks

This paper presents a statistical physics approach to the modelling of nucleation–aggregation phenomena of atoms in the thermodynamic limit $N \to \infty$.

Three different models have been developed within the same statistical framework, showing that small causes can produce large effects. These models were designed to represent simple aggregation by single-particle adjunction (monomer addition). These examples have been shown to be entirely solvable. The main reason for this solvability is that in (4) both nucleation and aggregation transition probabilities were independent of the cluster size distribution that exists. This will, for example, not be the case if one is to model an aggregation process for which the inserted atom is more likely to connect with a group of small size, simply because state-space equations (3) and (4) become strongly dependent on one another, for these 'anti-social' atoms! Therefore more work is needed to understand the equilibrium structures that will prevail.

It has also been shown, however, using the 'cavity method' approach discussed herein, how to include in aggregation models the possibility for an atom to connect simultaneously to more than one group at the same time. In this situation the number of groups in the transition $N \to N + 1$ may decrease because clusters themselves can aggregate.

Real experimental data have been related to model (ii) by Cohen in [16–18]. In these papers, the author claims to model simultaneous aggregation and fragmentation phenomena, when we only see nucleation and aggregation in such models, as has been shown. It is our opinion that more work is needed to include fragmentation in this language which remains an open problem.

References

[1] Sintes T, Toral R and Chakrabarti A 1994 Reversible aggregation in self-associating polymer systems *Phys. Rev.* E **50** 2967–76

[2] Elminyawi I M, Gangopadhyay S and Sorensen C M 1991 Numerical solutions to the Schmoluchowski aggregation–fragmentation equations *J. Colloid Interf. Sci.* **144** 315

[3] Schroeder M R 1989 *Number Theory in Science and Communication* (Berlin: Springer)

[4] Ayoub R 1963 *An Introduction to the Analytic Theory of Numbers* (Providence, RI: American Mathematical Society)

[5] Riordan J 1958 *An Introduction to Combinatorial Analysis* (New York: Wiley)

[6] Moser L and Wyman M 1955 An asymptotic formula for the Bell numbers *Trans. R. Soc. Canada* **49** 49–54

[7] Harper L H 1967 Stirling behavior is asymptotically normal *Ann. Math. Statist.* **38** 410–4

[8] Feller W 1968 *An introduction to Probability Theory and its Applications* vol I (New York: Wiley)

[9] De Bruijn N G 1970 *Asymptotic Methods in Analysis* (Amsterdam: North-Holland)

[10] Ellis R S 1985 Entropy, large deviations and statistical mechanics *Grundl. der Math. Wiss.* (New York: Springer)

[11] Mendès F M and Tenenbaum G 1993 A one dimensional model with phase transition *Commun. Math. Phys.* **154** 603–11

[12] Mandelbrot B, Evertsz C and Hayakawa Y 1990 Exactly self-similar left-sided multifractal measures *Phys. Rev.* A **42** 4528–36

[13] Rosenkrantz R D 1983 *Papers on Probability, Statistics and Statistical Physics* vol 158, ed E T Jaynes (Dordrecht: Reidel)

[14] Levine R D and Tribus M (eds) 1979 *The Maximum Entropy Formalism* (Cambridge, MA: MIT Press)

[15] Bergeron F, Flajolet P and Salvy B 1992 Varieties of increasing trees *CAAP's 92* ed J C Raoult (Lecture Notes in Computer Science **581**) pp 24–48

[16] Cohen R D 1992 Development of the cluster-size distribution in flowing suspensions *AICHE Jal* **38** 1129–34

[17] Cohen R D 1990 Steady-state cluster size distribution in stirred suspensions *J. Chem. Soc. Faraday Trans.* **86** 2133–8

[18] Cohen R D 1991 Evolution of the cluster size distribution in stirred suspensions *J. Chem. Soc. Faraday Trans.* **87** 1163–8