


Rate equation limit for a combinatorial solution of a stochastic aggregation model

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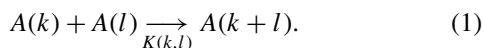
In a recent series of papers, an exact combinatorial solution was claimed for a variant of the so-called Marcus-Lushnikov model of aggregation. In this model, a finite number of aggregates are initially assumed to be present in the form of monomers. At each time step, two aggregates are chosen according to certain size-dependent probabilities and irreversibly joined to form an aggregate of higher mass. The claimed result given an expression for the full probability distribution over all possible size distributions in terms of the so-called Bell polynomials. In this paper, we develop the asymptotics of this solution in order to check whether the exact solution yields correct expressions for the average cluster size distribution as obtained from the Smoluchowski equations. The answer is surprisingly involved: For the generic case of an arbitrary reaction rate, it is negative, but for the so-called *classical* rate kernels, constant, additive, and multiplicative, the solutions obtained are indeed exact. On the other hand, for the multiplicative kernel, a discrepancy is found in the full solution between the combinatorial solution and the exact solution. The reasons for this puzzling pattern of agreement and disagreement are unclear. A better understanding of the combinatorial solution’s derivation is needed, the better to understand its range of validity.

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I. INTRODUCTION

In various systems irreversible aggregation of “clusters” $A(m)$ of mass m plays an important role. For instance, in aerosol physics, suspended particles coagulate (stick) driven by van der Waals forces; similar processes are important in polymer chemistry and astrophysics. The clusters are in general quite varied, going from galaxies to planetary systems. A standard reference for aggregation within aerosol physics is the book by Drake [1] for systems involving the physics of clouds and precipitation, see for instance Ref. [2]. A broad general introduction is also given in Ref. [3]. An overview of related problems that have interested the author is found in Ref. [4].

In such systems one is among other things interested in the cluster size distribution as a function of time. The simplest approach consists in the analysis of kinetic equations. We consider the reaction scheme



The $A(k)$ correspond to aggregates consisting of k monomers, denoted by $A(1)$, and the numbers $K(k, l)$ denote the *rates* at which $A(k)$ reacts with $A(l)$.

The kinetic description of such a system involves the time-dependent concentrations $c_k(t)$ of $A(k)$. The equations read:

$$\dot{c}_j(t) = \frac{1}{2} \sum_{k,l=1}^{\infty} K(k, l) c_k(t) c_l(t) [\delta_{k+l,j} - \delta_{k,j} - \delta_{l,j}]. \quad (2)$$

A basic property of (2) is the following: At a formal level, the total mass contained in the system is conserved:

$$\frac{d}{dt} \sum_{j=1}^{\infty} j c_j(t) = 0. \quad (3)$$

This property can fail, however, if at some finite critical time t_c

$$\sum_{k,l=1}^{\infty} k K(k, l) c_k(t) c_l(t) \quad (4)$$

diverges. In such a case the total mass starts decreasing with time after this divergence. Such systems are called gelling systems.

There exist many results concerning these equations. They can be solved exactly for the following rate kernels:

$$K(k, l) = 1 \quad \text{constant kernel}, \quad (5a)$$

$$K(k, l) = k + l \quad \text{additive kernel}, \quad (5b)$$

$$K(k, l) = kl \quad \text{multiplicative kernel}. \quad (5c)$$

The constant and additive kernels are nongelling, whereas the multiplicative kernel displays gelation. To show how this may arise, we display its solution for $c_j(t) = \delta_{j,1}$,

$$c_j(t) = \frac{j^{j-2}}{j!} t^{j-1} e^{-jt} \quad (t \leq 1), \quad (6a)$$

$$= \frac{j^{j-2} e^{-j}}{j!} \frac{1}{t} \quad (t \leq 1). \quad (6b)$$

For $t \leq 1$ it is seen that the mass indeed remains constant. On the other hand, for $t > 1$, all $c_j(t)$ are decreasing, and the mass does so as well. It is equal to $1/t$.

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Furthermore, an extensive scaling theory exists to describe the large-time and large-size behavior of the $c_k(t)$. In the nongelling cases, there exists a function $s(t)$ known as the characteristic size, with the following property: As $k \rightarrow \infty$ and $t \rightarrow \infty$ in such a way that $k/s(t) = x$ remains constant, there is a scaling function $\Phi(x)$ such that

$$\lim_{t \rightarrow \infty; k/s(t)=x} [k^2 c_k(t)] = \Phi(x). \tag{7}$$

For details see, for instance, Ref. [4]. For gelling systems, a similar behavior holds in the vicinity of the critical time:

$$\lim_{t \rightarrow t_c; k/s(t)=x} [k^\tau c_k(t)] = \Phi(x), \tag{8}$$

where τ is an exponent that depends on the specific kernel, which is, for instance, equal to 5/2 for the multiplicative kernel.

Let us shortly summarize the results of the scaling theory. To this end we define several quantities: The rate constants are assumed to be homogeneous in the sizes k and l with exponent λ , that is,

$$K(ak, al) = a^\lambda K(k, l). \tag{9}$$

We further define the exponents μ and ν by the relation

$$K(i, j) \simeq i^\mu j^\nu \quad (1 \ll i \ll j), \tag{10}$$

describing the behavior in the *strongly asymmetric* case $i \ll j$. Both the large- x and small- x behaviors of $\Phi(x)$ are determined by the above exponents: The system is gelling if $\lambda > 1$ and nongelling otherwise. If the system is nongelling, the small- x behavior of $\Phi(x)$ depends on whether $\mu > 0$, $\mu = 0$ or $\mu < 0$: In the former case, $\Phi(x)$ goes as $x^{1-\lambda}$, in the third it goes to zero faster than any power, whereas in the second it has a small- x behavior that must be determined separately in each particular case. The large- x behavior, on the other hand, is always of the type $x^{2-\lambda} \exp(-\text{const} \cdot x)$ except when $\nu = 1$, in which case the exponent arising before the exponential must be determined for every special case.

This paper concerns a combinatorial solution proposed in Refs. [5–9] of a discrete microscopic model underlying the Smoluchowski equations (2). We shall refer to this solution, which uses in a fundamental manner the so-called Bell polynomials, as the *Bell Polynomial Ansatz* (BPA).

The structure of the paper is the following: In Sec. II we present in detail the discrete Marcus-Lushnikov model and the BPA; in Sec. III we summarize the results to be shown in the rest of the paper; in Sec. IV we derive the formulas leading to an exact expression for the solution of (2) as a consequence of the BPA. We also show there that this solution cannot be generally valid; the exact validity of the approach for various classical kernels is discussed in Sec. V and we present conclusions in Sec. VI.

II. THE DISCRETE MARCUS-LUSHNIKOV MODEL AND ITS PROPOSED COMBINATORIAL SOLUTION

We start by describing a more microscopic model, known as the Marcus-Lushnikov model, describing the underlying stochastic dynamics of the aggregation process [10,11]. In this model, there are initially N particles, all of which are monomers, and the states of the system are described by the

vector of integers $\underline{n} = (n_1, \dots, n_N)$ which satisfy the condition $\sum_{k=1}^{\infty} kn_k = N$. Here n_k is the total number of aggregates $A(k)$ in the state \underline{n} .

This model, and a purported solution for it, will occupy us throughout this paper. It may therefore be of interest to state briefly why this model is of interest. Clearly, it stands with respect to the continuous model of Smoluchowski in the same relation as a microscopic model of the molecular dynamics—or more precisely of the Langevin—type might stand to the equations of hydrodynamics. And indeed, the same differences exist. In the Monte Carlo model we study, many questions can be asked which have no meaning within the hydrodynamical framework: For instance, we may ask by how much the number of monomers at a given time t varies from run to run, or more generally yet, what is its distribution. Such questions have been studied, for instance, in Refs. [12,13].

Another issue concerns large clusters. The microscopic model under study only involves clusters of size less than a given number N , whereas the Smoluchowski equations involve infinitely many possible cluster sizes. When the system gels, it is assumed that part of the mass goes into an “infinite cluster.” But clearly the rate equations can tell us nothing about the nature of such clusters. However, the Marcus-Lushnikov model can be studied for large values of N , and the distribution of cluster sizes can be studied for both “small” and “large” clusters. Such was the purpose, for instance, of Lushnikov’s work on the Marcus-Lushnikov model applied to the multiplicative kernel [14–17], where it was shown that after gelation there is a single cluster of size of order N accounting for the mass deficit. It should be noted that this is not necessarily general: It was shown by Monte Carlo simulations in Ref. [18] that in certain systems with combined aggregation and fragmentation, the size of the “infinite clusters” grows as N^γ with $\gamma < 1$. The properties of such Monte Carlo simulations have also recently been studied in Ref. [19].

From all this follows that there are several properties of interest of aggregating systems—or related generalizations thereof—which cannot be obtained from the rate equations alone and for which the study of stochastic models, such as the Marcus-Lushnikov model, is of considerable interest.

Let us here make a general remark on notation: In the transition between the above mentioned microscopic model and the kinetic model given by (2), we must pass to a continuum limit, in which several variables, extensive in the microscopic model, are divided by N to yield a continuous variable of (2). With the *sole exception* of the quantities n_k , all such variables will be denoted by capital letters.

The aggregation process is then described as a stochastic process in which at each time step a transition takes place between a state \underline{n} and another resulting from the aggregation of one aggregate of size k and another of size l . Specifically, the transition probability between \underline{n} and \underline{n}' via an aggregation of $A(k)$ and $A(l)$ is only nonzero if

$$n'_j = n_j - 1 \quad (j = k, l), \tag{11a}$$

$$n'_{k+l} = n_{k+l} + 1, \tag{11b}$$

$$n'_j = n_j \quad (j \neq k, l, k + l). \tag{11c}$$

The rates $r_{k,l}$ of this transition is given by

$$\begin{aligned} r_{k,l}(\underline{n} \rightarrow \underline{n}') &= K(k,l)n_k n_l \quad (k \neq l), \\ &= K(k,k) \frac{n_k(n_k-1)}{2} \quad (k=l). \end{aligned} \quad (12)$$

Defining the normalization factors \mathcal{N}_k and the transition probabilities $p_{k,l}$ as

$$\mathcal{N}_k = \sum_l r_{k,l}, \quad p_{k,l} = \mathcal{N}_k^{-1} r_{k,l}, \quad (13)$$

we obtain the dynamics of the probability distribution $P(\underline{n}; S)$ by

$$P(\underline{n}; S+1) = \sum_{k,l=1}^N \sum_{\underline{n}'} p_{k,l}(\underline{n}' \rightarrow \underline{n}) P(\underline{n}'; S), \quad (14)$$

where S is the time, which in this model only takes integer values.

An essential difference between this model and the aggregation process described above should be immediately pointed out: In this stochastic model, an aggregation event occurs at each time step, whereas in the aggregation process, the $K(k,l)$ are rates in a continuous time process. As we shall see, this changes the time variable, but it does not affect anything else. The continuous variable equivalent to S is $\sigma = S/N$.

Let us here shortly discuss the somewhat complex issue of the relation between the time t of the original Marcus-Lushnikov model as defined by (15) and the variable σ of the corresponding discrete model. As noted above, the ‘‘time’’ variable is simply $N - K$, where K is the total number of particles at the step S . On the other hand, an infinitesimal increase of t in (15) corresponds to a random variation of the number of particles depending on the number of reactions taking place in the given time interval. Thus, at fixed t , in the continuous time Marcus-Lushnikov model, the number of particles is a random variable, whereas for the discrete variant, the number of particles is given at each time step. In the limit we are interested in, however, this has no influence, as the variance of the random number of particles at given time goes to zero as $N \rightarrow \infty$.

The original stochastic model introduced by Marcus [10] and Lushnikov [11] indeed involves transition rates, and not probabilities: These are defined as in (12), with no further normalisation; the continuous time equivalent of (14) is

$$\begin{aligned} \frac{\partial P(\underline{n}; t)}{\partial t} &= \sum_{k,l=1}^N \sum_{\underline{n}'} [r_{k,l}(\underline{n}' \rightarrow \underline{n}) P(\underline{n}'; t) \\ &\quad - r_{k,l}(\underline{n} \rightarrow \underline{n}') P(\underline{n}; t)]. \end{aligned} \quad (15)$$

This process is the true equivalent of the reaction rate equations (2), but we shall concentrate on the dynamics defined by (14), since it is for this that a combinatorial solution, the Bell Polynomial Ansatz (BPA), has been proposed [5–9]. To emphasize the difference, we shall call the model described by (14) the *discrete Marcus-Lushnikov model*

To state this solution we define some additional quantities: The sequence ξ_k is defined by the following recursion relation

$$(k-1)\xi_k = \sum_{l=1}^{k-1} K(l, k-l)\xi_l \xi_{k-l}, \quad (16a)$$

$$\xi_1 = 1, \quad (16b)$$

Here (16a) only applies for $k \geq 2$. These quantities play an important role in the short-time behavior of the solutions of (2). As $t \rightarrow 0$ one has for instance, for the initial condition $c_k(0) = \delta_{k,1}$

$$c_k(t) \simeq \xi_k t^{k-1}. \quad (17)$$

Their asymptotic behavior as $k \rightarrow \infty$ has been studied [4,20,21] and they behave as $k^{-\lambda}$ except for the case of kernels having $\nu = 1$, for which the behavior must be studied on a case-by-case basis.

We now introduce some further notation: Underlined letters such as \underline{z} and \underline{w} will always represent vectors with components as follows: $\underline{z} = (z_1, \dots, z_N)$. We shall use the following abbreviated notations involving the vector of complex variables:

$$\underline{z}^{\underline{w}} = \prod_{k=1}^N z_k^{w_k} \quad \underline{z} \underline{w} = (z_1 w_1, \dots, z_N w_N). \quad (18)$$

We further introduce the following abbreviations:

$$\underline{\xi} = (\xi_1, \dots, \xi_N) \quad \underline{m}! = (1!, 2!, \dots, N!). \quad (19)$$

We now define the generating function of the probability distribution $P(\underline{n}; S)$ as a function of

$$\Psi(\underline{z}; S) = \sum_{\underline{n}} P(\underline{n}; S) \underline{z}^{\underline{n}}, \quad (20)$$

The BPA yields the following expression for $\Psi(\underline{z}; S)$:

$$\Psi(\underline{z}, S) = \frac{B_{N,N-S}(\underline{m}! \underline{\xi} \underline{z})}{B_{N,N-S}(\underline{m}! \underline{\xi})}. \quad (21)$$

Here $B_{N,N-S}(\underline{x})$ is the *Bell polynomial* defined as follows: The series of polynomials $B_{n,m}(\underline{a})$, where \underline{a} is (exceptionally) an infinite sequence (a_1, a_2, \dots) , are given by the generating function

$$\sum_{n \geq m \geq 1} B_{n,m}(\underline{a}) \frac{x^n}{n!} y^m = \exp \left[y \left(\sum_{r=1}^{\infty} \frac{a_r}{r!} x^r \right) \right]. \quad (22)$$

It is, however, readily checked that $B_{n,m}(\underline{a})$ only depends on a_k for $1 \leq k \leq n - m + 1$, so that the expressions given above are well defined. For more details on Bell polynomials, see for instance Ref. [22].

III. SUMMARY OF RESULTS

The quantities $c_j(t)$ satisfying (2) correspond, in terms of the stochastic model described above, to the quantities

$$\bar{n}_j(S) = \sum_{\underline{n}} n_j P(\underline{n}; S). \quad (23)$$

Additionally to its S dependence, $\bar{n}_j(S)$ depends on N . It is well known [12,13,23] that, in the continuum limit, the

discrete Marcus-Lushnikov model tends to the kinetic equations in the following sense:

$$\lim_{\substack{S, N \rightarrow \infty \\ S/N = \sigma}} \frac{\bar{n}_j(S)}{N} = c_j(t), \quad (24a)$$

$$\sum_{k=1}^{\infty} c_k(t) = 1 - \sigma. \quad (24b)$$

This means that (24b) provides the correct connection between t and σ and that taking the $N \rightarrow \infty$ limit while maintaining σ constant leads to the correct concentration profile $c_j(t)$. Additionally, it can be shown that not only does the average value of $n_j(s)$ converge to the correct limit but that the probability distribution becomes infinitely sharp around the values defined by the kinetic equations (2).

Using an asymptotic formula for the Bell polynomials to be derived later, see (43), one finds an exact expression for the above described limit in terms of the BPA (21): Define

$$G(w) = \sum_{j=1}^{\infty} \xi_j w^j, \quad (25a)$$

$$w^*(\sigma) = \operatorname{argmin}_{0 < w < w_c} [(1 - \sigma) \ln G(w) - \ln w], \quad (25b)$$

where w_c is the convergence radius of $G(w)$. One then finds

$$\begin{aligned} \lim_{\substack{N, S \rightarrow \infty \\ S/N = \sigma}} \frac{\bar{n}_j(S)}{N} &= z_j \frac{\partial}{\partial z_j} \ln \Psi(z, S) \Big|_{z=1} = z_j \frac{\partial}{\partial z_j} \ln \\ &\times B_{N, N-S}(\underline{m}! \underline{\xi} z) \Big|_{z=1} = \frac{1 - \sigma}{G[w^*(\sigma)]} \xi_j w^*(\sigma)^j. \end{aligned} \quad (26)$$

Here we have used the definition of $\Psi(z; S)$, see (20), in the first equality and the BPA, see (21), in the second. The third will follow, as mentioned above, from asymptotic estimates on Bell polynomials to be derived in Sec. IV, see (43). From this we deduce that the right-hand side of (26) is an exact solution of (2) whenever (21) is a solution of the discrete Marcus-Lushnikov model defined by (14), and vice versa, we obtain that the BPA, see (21), cannot be an exact solution of the discrete Marcus-Lushnikov model unless (26) solves the Smoluchowski equations (2).

Generically, it is readily seen from what we know of scaling theory that (26) does not solve the Smoluchowski equations. Indeed, since the entire aggregation process described in the discrete Marcus-Lushnikov model stops when $S = N$, it follows that the infinite time limit corresponds to the $\sigma \rightarrow 1$ limit. As is also readily seen, if $G'(w) \rightarrow \infty$ as $w \rightarrow w_c$, then $w^*(\sigma) \rightarrow w_c$ as $\sigma \rightarrow 1$. Equation (26) thus leads to the following scaling form:

$$c_j(t) \simeq j^{-\lambda} \exp \left\{ -j \ln \left[\frac{w^*(\sigma)}{w_c} \right] \right\} \left[\sum_{k=1}^{\infty} c_k(t) \right], \quad (27)$$

the derivation of which is given in Appendix A. To describe this in terms of the scaling theory, we set

$$s(t) = \left\{ \ln \left[\frac{w^*(\sigma)}{w_c} \right] \right\}^{-1}. \quad (28)$$

Using as always the normalization

$$\sum_{k=1}^{\infty} k c_k(t) = 1, \quad (29)$$

we obtain after some straightforward manipulations that, for the nongelling case, the scaling function is of the form

$$\Phi(x) = \text{const} \cdot x^{2-\lambda} e^{-x}. \quad (30)$$

The elementary computations are given in Appendix A. A particularly problematic feature of this result is that it holds good for $\lambda < 2$. This means in particular that it does not yield gelling behavior for $\lambda > 1$.

While this is in good agreement with the large- j behavior as known from scaling theory, it is in strong disagreement with the known small- j behavior. Note that the discrepancy involves the size distribution and not the correspondence between t and σ . Further, since the formula does agree in the limit of sizes large with respect to typical size, the disagreement can also not be resolved by changing the definition of the sequence ξ_j : Such an attempt could introduce agreement at small values of j but would then spoil the agreement at large j .

Specifically, the kernel solved in Ref. [9], $K(k, l) = 1/k + 1/l$ has, as can be shown exactly, see Ref. [24], the following large time behavior

$$\lim_{t \rightarrow \infty} \left[\sum_{k=1}^{\infty} c_k(t) \right]^{-1} \exp \left[\int_0^t \sum_{k=1}^{\infty} c_k(t') dt' \right] c_1(t) = 1. \quad (31)$$

Clearly this result is incompatible with (27).

Yet another kind of behavior that cannot be subsumed under the scheme of (27) is the following: Define α_j and w_j via

$$\lim_{t \rightarrow \infty} [t^{w_j} c_j(t)] = \alpha_j. \quad (32)$$

Now it can be shown that the w_j in certain cases depend nontrivially on j . For instance, for the kernel $K(k, l) = 2 - q^k - q^l$ with $0 < q < 1$, which has been extensively treated in [25,26], one finds that

$$w_j = 2 - q^j. \quad (33)$$

Similar behavior also arises in the case in which the reaction rates $K(k, l)$ take three different constant values, depending on whether both masses are equal to 1, only 1, or neither [27].

We therefore see that the claim of general validity made for the BPA in Refs. [5–9], cannot be upheld. The reasoning presented in these papers must thus contain some flaw, which is however by no means obvious. In order to illustrate the nature and the extent of the possible disagreement between the BPA and the results of a Monte Carlo simulation of the discrete Marcus-Lushnikov model, let us consider the specific case illustrated in Fig. 1, the details of which are given in the caption: As we see, there is a very strong disagreement for low sizes, specifically for monomers, whereas the two cluster size

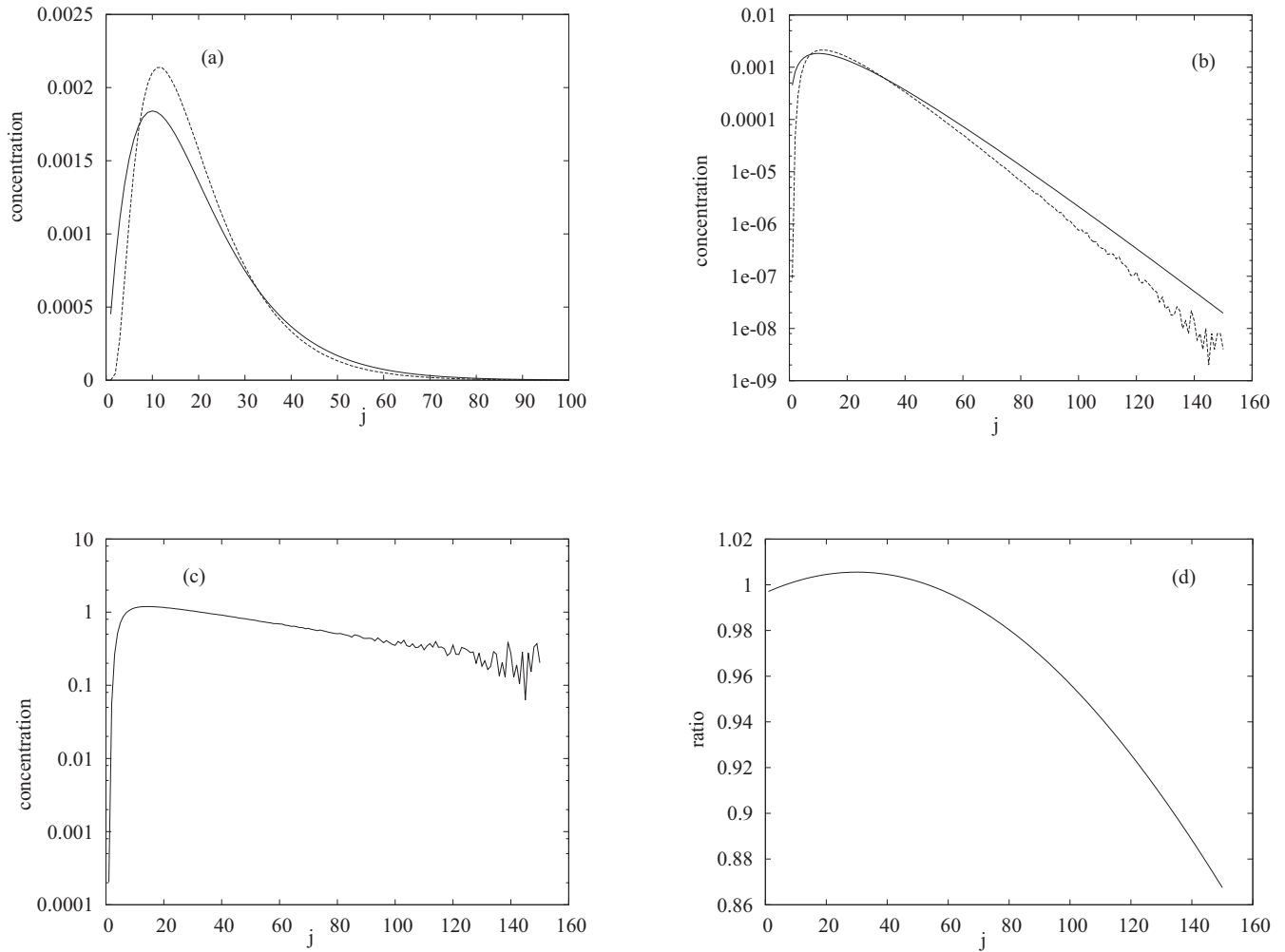


FIG. 1. Here we compare the cluster size distribution obtained through the BPA to that obtained through direct simulation of the discrete Marcus-Lushnikov model. The case considered is a system with the reaction rates $K(k, l) = 1/k + 1/l$, with $N = 5000$ and $S = 4750$, implying a total number of particles of 250. This corresponds to a number density $\sum_k c_k(t)$ of $1/20$, and hence from the scaling theory of Type III kernels [4], the typical size is of the order of 20. Since the total number of monomers is 5000, we are not strongly affected by finite-size effects. On all figures, the x axis corresponds to the cluster size. The simulations performed involved 10^5 runs. Panel (a) displays the two cluster size distributions on a linear scale, the full line denoting the BPA and the dotted line the simulation results. Panel (b) shows the same on a log-log scale, which indicates the very strong deviations at the origin, together with reasonable agreement at large sizes. Panel (c) tests this more precisely by showing the logarithm of the quotient of the numerical solution to the BPA one. There we see how, after very strong initial variations, the quotient slowly decreases instead of tending to a constant, as predicted here. The reason for the discrepancy appears to lie in the nonasymptotic behavior of the BPA expression for the concentration profile, shown in panel (d) which displays the quotient of the exact BPA results and its asymptotic behavior.

distributions are roughly proportional for sufficiently large sizes.

Nevertheless, the identity between the small- j and the large- j behaviors is characteristic for the so-called classical kernels, namely the constant, additive, and multiplicative kernels, as well as their combinations. We shall in fact explicitly show that (26) does provide an exact solution in those cases, for the multiplicative kernel at least before the gel time.

The fact that the average value of n_j/N is exact for these kernels clearly does not guarantee the accuracy of the full probability distribution. An explicit comparison between the exact distribution of the discrete Marcus-Lushnikov model and the BPA was performed for the case $N = 20$ and $S = 4$,

starting from the initial condition $n_1 = 20$ and $n_j = 0$ for $j \geq 2$. The former is readily evaluated for small systems using explicit enumeration of (14).

These were found to coincide exactly for both the constant and the additive kernel, yet to differ in the case of the multiplicative kernel. We state the results for the latter case. At $S = 4$, five states only have nonzero probabilities:

$$\begin{aligned} \underline{n}_1 &= (12, 4, \dots) & \underline{n}_2 &= (13, 2, 1, \dots) \\ \underline{n}_3 &= (14, 0, 2, \dots) & \underline{n}_4 &= (14, 1, 0, 1, \dots) \\ \underline{n}_5 &= (15, 0, 0, 0, 1, \dots), \end{aligned} \tag{34}$$

where the final zeros have not been written explicitly. The exact probabilities for the multiplicative kernel are given by

$$\begin{aligned}
 P(\underline{n}_1; 4) &= \frac{130}{517} = 0.2515\dots \\
 P(\underline{n}_2; 4) &= \frac{22\,400}{48\,081} = 0.4659\dots \\
 P(\underline{n}_3; 4) &= \frac{22\,480}{336\,567} = 0.0668\dots \\
 P(\underline{n}_4; 4) &= \frac{460\,485}{2\,580\,347} = 0.1785\dots \\
 P(\underline{n}_5; 4) &= \frac{96\,552}{2\,580\,347} = 0.0374\dots, \tag{35}
 \end{aligned}$$

whereas the ones arising from the BPA are

$$\begin{aligned}
 P(\underline{n}_1; 4) &= \frac{273}{1\,081} = 0.2525\dots \\
 P(\underline{n}_2; 4) &= \frac{504}{1\,081} = 0.4662\dots \\
 P(\underline{n}_3; 4) &= \frac{72}{1\,081} = 0.0666\dots \\
 P(\underline{n}_4; 4) &= \frac{192}{1\,081} = 0.1776\dots \\
 P(\underline{n}_5; 4) &= \frac{40}{1\,081} = 0.0370\dots \tag{36}
 \end{aligned}$$

While it is seen that these are numerically quite close, the two are clearly different. On the other hand, for the additive and constant kernels, even for the case $N = 20$ and $S = 16$, which has 70 accessible states, the comparison between the BPA and an exact enumeration, yields perfect agreement. There is thus essentially no doubt concerning the exactness of these two solutions. Indeed, Lushnikov [11,28] has presented exact solutions for these kernels for the corresponding continuous model. These can presumably be carried over to the discrete case.

IV. THE $N \rightarrow \infty$ AVERAGE CLUSTER SIZE DISTRIBUTION

Let us first derive an explicit expression for \bar{n}_j as a function of $\Psi(\underline{z}; S)$. One finds

$$\bar{n}_j = z_j \frac{\partial}{\partial z_j} \ln \Psi(\underline{z}; S)|_{\underline{z}=1}. \tag{37}$$

Substituting the BPA (21) into (37) yields

$$\bar{n}_j = z_j \frac{\partial}{\partial z_j} \ln [B_{N,N-S}(\underline{m}! \underline{\xi} \underline{z})]|_{\underline{z}=1}. \tag{38}$$

To evaluate this in the limit of large N and S with $S/N = \sigma$, and $0 < \sigma < 1$, we need an appropriate asymptotic expression for the Bell polynomial.

From the definition of Bell polynomials, see (22), we obtain using Cauchy's expression for the coefficients of a power series:

$$\sum_{m=1}^{\infty} \frac{1}{n!} B_{n,m}(\underline{a}) y^m = \frac{1}{2\pi i} \oint_C \frac{dw}{w^{n+1}} \exp \left[y \left(\sum_{r=1}^{\infty} \frac{a_r}{r!} w^r \right) \right]. \tag{39}$$

Here C is a contour enclosing the origin but no singularity of the integrand. Now, comparing the coefficients of y one obtains the following well-known relation:

$$\frac{m!}{n!} B_{n,m}(\underline{a}) = \frac{1}{2\pi i} \oint_C \frac{dw}{w^{n+1}} \left(\sum_{r=1}^{\infty} \frac{a_r}{r!} w^r \right)^m. \tag{40}$$

A substitution now yields straightforwardly

$$\frac{(N-S)!}{N!} B_{N,N-S}(\underline{m}! \underline{\xi} \underline{z}) = \frac{1}{2\pi i} \oint_C \frac{G(w|\underline{z})^{N-S}}{w^{N+1}} dw, \tag{41a}$$

$$G(w|\underline{z}) = \sum_{j=1}^{\infty} \xi_j z_j w^j. \tag{41b}$$

Here C is a contour enclosing the origin but no singularity of $G(w|\underline{z})$. Specifically, we may think of a circle around the origin with a radius $r < w_c$. Since the Taylor series of $G(w)$ has positive coefficients, the maximum value of $G(w)$ on this circle is assumed as the real axis is crossed. The same remark holds for the integrand of (41).

It therefore follows, using the method of stationary phase, that

$$\begin{aligned}
 \lim_{\substack{S,N \rightarrow \infty \\ S/N = \sigma}} \frac{1}{N} \ln \left[\frac{(N-S)!}{N!} B_{N,N-S}(\underline{m}! \underline{\xi} \underline{z}) \right] \\
 = (1-\sigma) \ln G[w^*(\sigma|\underline{z})|\underline{z}] - \ln w^*(\sigma|\underline{z}), \tag{42}
 \end{aligned}$$

where $w^*(\sigma|\underline{z})$ is defined similarly to (25b)

$$w^*(\sigma|\underline{z}) = \underset{0 < w < w_c(\underline{z})}{\operatorname{argmin}} [(1-\sigma) \ln G(w|\underline{z}) - \ln w]. \tag{43}$$

The somewhat messy details are relegated to Appendix B. Summarizing, however, it may be said that this is a straightforward application of the method of stationary phase, as described in Bender and Orszag [29]. Note that the asymptotic expression (43) does not hold universally for all sequences ξ_j . Essential use is made both of the positivity of the ξ_j and of the fact that the ξ_j grow regularly (in the sense, for instance, that the nearest singularity to the origin is on the positive real axis, to the exclusion of other singularities at the same distance). The above derivation of (43) is quite elementary, and I assume it to be already known but have not found a reference for it.

We now need to evaluate the derivative with respect to z_j of the right-hand side of (43). We first use the following well-known fact: For an arbitrary function $\phi(x, \lambda)$, let

$$x^*(\lambda) = \underset{x}{\operatorname{argmin}} (f(x, \lambda)) \quad g(\lambda) = f(x^*(\lambda), \lambda), \tag{44}$$

then

$$g'(\lambda) = \frac{\partial f}{\partial \lambda}(x^*(\lambda), \lambda). \tag{45}$$

To use this result, we take the function

$$(1-\sigma) \ln G(w(\sigma|\underline{z})|\underline{z}) - \ln w(\sigma|\underline{z}), \tag{46}$$

as $f(x, \lambda)$, where w plays the role of x and z_j the role of λ .

Using this result, we only need to take the derivative with respect to the \underline{z} dependence of $G(w(\sigma|\underline{z})|\underline{z})$. This leads to

$$\lim_{\substack{S,N \rightarrow \infty \\ S/N = \sigma}} \frac{\bar{n}_j}{N} = \frac{1-\sigma}{G[w(\sigma)]} \xi_j w(\sigma)^j, \tag{47}$$

as stated earlier.

Let us now fill in some of the missing details: We first show that, on the interval $0 \leq w \leq w_c$ the function $(1 - \sigma) \ln G(w) - \ln w$ indeed takes a minimum at $w(\sigma)$. Indeed, the second derivative is given by

$$\frac{1 - \sigma}{G(w)^2} [G(w)G''(w) - G'(w)^2] + \frac{1}{w^2} > 0, \quad (48)$$

where the positivity follows from the positivity of the ξ_j and the Cauchy-Schwarz inequality. As a consequence, because of the Cauchy-Riemann equations, the same function has a local maximum in the imaginary direction, which is the one of the contour.

We now discuss under what circumstances $w(\sigma)$ is an interior minimum satisfying the equation

$$(1 - \sigma)w(\sigma) \frac{G'[w(\sigma)]}{G[w(\sigma)]} = 1. \quad (49)$$

As we move from $w = 0$ to $w = w_c$, both $G'(w)$ and $G(w)$ increase. If as $w \rightarrow w_c$ $G'(w)$ diverges, then the existence of a (unique) solution of (50) follows straightforwardly. On the other hand, if $G'(w_c) < \infty$, then there is a value $0 < \sigma < 1$ such that (50) has no interior solution. As we shall see, this is what happens in the case of the postgel solution of the multiplicative kernel.

V. EXACT VALIDITY FOR THE CLASSICAL KERNELS

Let us now check that for the three classical cases, the solution given by (26) indeed corresponds to the known exact solution. In all cases, the quantities ξ_j defined in (16) and the corresponding generating function $G(w)$ defined in (25a) are known exactly, so that verifying the correctness of the solution (26) is in principle straightforward.

Let us consider the case of the multiplicative kernel, since the average n_j for the other two can be expressed in terms of binomial coefficients, for which the results are readily obtained.

In the following we perform the computations required to evaluate the BPA solution, but all steps are part of the standard approach to solving the multiplicative kernel, as reviewed, for instance, in Reference [4]. It follows from the recursion relation (16) that the generating function for the ξ_j , namely $G(w)$, satisfies the ordinary differential equation:

$$wG'(w) - G(w) = \frac{1}{2}[wG'(w)]^2 \quad G'(0) = 1. \quad (50)$$

This has the unique implicit solution

$$w = (1 - \sqrt{1 - 2G}) \exp(\sqrt{1 - 2G} - 1). \quad (51)$$

We now substitute (51) into

$$(1 - \sigma) \ln G - \ln w \quad (52)$$

and minimize with respect to G . One obtains

$$G = 2\sigma(1 - \sigma) \quad w = 2\sigma e^{-2\sigma}. \quad (53)$$

If we finally substitute these expressions into the right-hand side of (26), one obtains

$$c_j(t) = \xi_j(2\sigma)^{j-1} e^{-2j\sigma}. \quad (54)$$

Finally, we need to connect σ and t . We know the expression (24b) for σ . But we can obtain the sum over all $c_k(t)$ from the Smoluchowski equations

$$\sum_{k=1}^{\infty} c_k(t) = 1 - \frac{t}{2} \quad (t \leq 1), \quad (55a)$$

$$= \frac{1}{2t} \quad (t \geq 1). \quad (55b)$$

The limitation on the value of t arises, of course, from the fact that the equation for $\sum_{k=1}^{\infty} c_k$ depends on the mass, which itself is only equal to 1 for $t \leq 1$.

Note that (54) is only true for $t \leq 1$, so we only consider (55a), which leads to $\sigma = t/2$, and thus to the exact equation for the concentrations, compare with (6). Here we use the fact that, for the multiplicative kernel, $\xi_j = j^{j-2}/j!$.

We do not yet know the solution for $\sigma > 1/2$, which corresponds to the postgel phase. It is clear that the maximum of the function (52) is now at the end of the convergence interval, that is, at $w = w_c = e^{-1}$ and $G = G_c = \frac{1}{2}$ independently of σ . If we now substitute these into the right-hand side of (26) we obtain

$$c_j(t) = 2\xi_j e^{-j}(1 - \sigma) = \frac{\xi_j e^{-j}}{t}, \quad (56)$$

where we have used the expression (55b) for the particle number. This is in fact the correct solution of (2) as it stands.

Note that this result is only valid for the values of j which are of order one, not for those which are of order N : This is, of course, a relevant remark, since beyond the gel point there are such aggregates and they form a finite part of the total mass. But since the asymptotic developments derived above fail for $j \sim N$, we cannot make any remarks on the gel particles.

This is a rather remarkable result. Indeed, for the postgel multiplicative kernel, the Smoluchowski equations can be meaningfully given two forms, which lead to different solutions:

$$\dot{c}_j(t) = \frac{1}{2} \sum_{k=1}^{j-1} k(j-k)c_k(t)c_{j-k}(t) - jc_j(t) \sum_{k=1}^{\infty} kc_k(t), \quad (57a)$$

$$\dot{c}_j(t) = \frac{1}{2} \sum_{k=1}^{j-1} k(j-k)c_k(t)c_{j-k}(t) - jc_j(t). \quad (57b)$$

Here (57a) is simply (2) for $K(k, l) = kl$ and (57b) is obtained from (57a) by assuming the constancy of the mass, even though the equation's solution eventually violates it. The solution of (57a) is (6), whereas the solution of (57b) is simply (6a) for all times, that is, the solution is analytic. After $t = 1$, of course, the solution of (57b) no more satisfies the assumption of conserved mass, which was used for its derivation.

Both these formulations are expected to be valid, each in an appropriate context. The former given by (57a) is known as the Stockmayer solution and is expected to hold when no interaction between the finite (sol) particles and the gel is possible. In the opposite case, the solution described by (57b), known as the Flory solution, is expected to hold. For a detailed discussion of this issue see Ref. [30].

The BPA thus leads to the exact Stockmayer solution. In the case of the Marcus-Lushnikov model, the correct result

depends on details of the model. Thus, in a related model, that of a random graph, we have initially N sites and link at each time step two randomly chosen sites. Before gelation, this is equivalent to the discrete Marcus-Lushnikov model as $N \rightarrow \infty$. After gelation, the random graph model is known to follow the Flory solution [30]. However, the random graph model's equivalence to the discrete Marcus-Lushnikov model does not hold after the gel time: indeed, in the random graph model, it occurs with finite probability that two sites both belonging to the infinite cluster are chosen and joined, thereby leaving the cluster size distribution unmodified. Such a process has no equivalent in the discrete Marcus-Lushnikov model. A variant of the random graph model in which cycles are forbidden was analysed in Ref. [30]. There it was shown that the decay of $c_j(t)$ as $t \rightarrow \infty$ was exponential, thereby contradicting the Stockmayer solution.

The BPA thus rather remarkably yields exactly a well-known gelling solution. With respect to the discrete Marcus-Lushnikov model, it appears most likely that the solution obtained via the BPA does not describe the model correctly, but the coincidence with a correct solution of a version of the Smoluchowski's equations remains striking.

For the other two kernels, we have the well-known relations

$$Ge^{-G} = w \quad (58)$$

for the additive kernel and

$$G = \frac{w}{2-w} \quad (59)$$

for the constant kernel, from which the exact solutions can be derived in an elementary manner. The fact that these solutions correspond to the exact solutions of (2) is readily confirmed.

VI. CONCLUSIONS

Summarizing, we have derived analytically the solution to the Smoluchowski equations that arises from the solution of the discrete Marcus-Lushnikov model proposed in Refs. [5–9]. As is readily verified, in the general case these expressions do not satisfy the properties known from the general scaling theory of the Smoluchowski equations as described in Ref. [4]. Specifically, the concentration profile thus obtained agrees qualitatively well in the limit of cluster sizes large with respect to the typical size but deviates strongly from the known behavior in the opposite limit.

As is well-known, however, the three exactly solvable cases, the constant, additive, and multiplicative kernels, have the remarkable property that their small-size and large-size behaviors coincide. In that case, it is verified that the analytic solution derived in this paper from the Bell Polynomial Ansatz (BPA) does indeed coincide exactly with the corresponding solution of the Smoluchowski equation, with the exception of the postgel multiplicative kernel, for which the solution obtained via the BPA is the Stockmayer result, whereas the exact result is presumably the Flory solution.

To complicate matters further, it turns out that the BPA for the full probability distribution is almost certainly exact for all N in the case of the additive and constant kernels but that such is not the case for the multiplicative kernel. Conjecturally, one

might assume that, in the large- N limit, the BPA converges to the exact pregel solution for the full probability distribution, and similarly that it converges to a probability distribution different of that of the Marcus-Lushnikov model in the postgel case, namely one that yields the Stockmayer solution. Since, for small N , there is no sharp difference between pregel and postgel stages, the existence of a discrepancy at small N and small times is perhaps understandable.

Considering the remarkable successes of the BPA, it would clearly be extremely desirable to obtain a better understanding of the mechanism underlying of its failure in the general case.

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APPENDIX A: THE SCALING FUNCTION FROM (26)

In all cases except when $\nu = 1$, the ξ_j behave as $j^{-\lambda}$ [21]. This implies that $G(w)$ goes as $(w_c - w)^{\lambda-1}$, where this should be understood as meaning the singular part only. Thus, constant and linear terms dominating this behavior may exist, depending on the value of λ .

Consider first $\lambda < 1$, that is, the nongelling case. We then have $G(w) \rightarrow \infty$ as $w \rightarrow w_c$. The equation determining $w(\sigma)$ reads

$$(1 - \sigma)w(\sigma) \frac{G'[w(\sigma)]}{G[w(\sigma)]} = 1. \quad (A1)$$

Since $\lambda < 1$, both $G(w)$ and $G'(w)$ diverge, and their ratio goes as $(w_c - w)^{-1}$. It follows that $w(\sigma) - w_c$ is proportional to $1 - \sigma$ as $\sigma \rightarrow 1$. $G[w(\sigma)]$ then diverges as $(1 - \sigma)^{\lambda-1}$. Substituting into (26) then yields

$$\frac{n_j(\sigma)}{N} = \text{const} \cdot j^{-\lambda} (1 - \sigma)^{2-\lambda} \exp\left(-\text{const} \cdot \frac{j}{1 - \sigma}\right), \quad (A2)$$

which has the scaling form indicated in (30).

If $1 < \lambda < 2$, then $G(w_c)$ remains finite, but $G'(w)$ diverges as $(1 - \sigma)^{\lambda-2}$ as $\sigma \rightarrow 1$. A similar computation then yields

$$\frac{n_j(\sigma)}{N} = \text{const} \cdot j^{-\lambda} (1 - \sigma) \exp\left[-\text{const} \cdot \frac{j}{(1 - \sigma)^{1/(2-\lambda)}}\right], \quad (A3)$$

which again confirms the scaling form (30). This is particularly problematic, since it implies that no gelation arises for $1 < \lambda < 2$, in contradiction to well-known exact results [31].

APPENDIX B: DERIVATION OF THE SADDLE-POINT APPROXIMATION (43)

As a first step, let us show the following elementary result: Let $f(x)$ be a real valued function on the real interval $[a, b]$, which has a unique maximum at x^* which is strictly inside $[a, b]$. Then

$$I \lim_{N \rightarrow \infty} \frac{1}{N} \ln \int_a^b \exp[Nf(x)] dx = f(x^*). \quad (B1)$$

In the following we denote the integral above by I_N . Without loss of generality we assume x^* to be zero.

We now express $f(x)$ as

$$f(x) = f(0) + f''(0)\frac{x^2}{2} + g(x), \tag{B2}$$

where $g(x) = O(x^3)$ as $x \rightarrow 0$. We now separate the integral I_N in two parts, $I_N = J_N + K_N$, with

$$J_N = \int_{-N^{-\alpha}}^{N^{-\alpha}} \exp[Nf(x)]dx, \tag{B3a}$$

$$K_N = \left(\int_a^{-N^{-\alpha}} + \int_{N^{-\alpha}}^b \right) \exp[Nf(x)]dx, \tag{B3b}$$

where $1/3 < \alpha < 1/2$.

We shall show that J_N satisfies (B1) and $K_N/J_N \rightarrow 0$ as $N \rightarrow \infty$, thereby proving the result. Since $\alpha > 1/3$, we find that $Ng(x) \rightarrow 0$ on the whole range of integration of J_N , so that

$$\begin{aligned} J_N &= e^{Nf(0)} \int_{-N^{1/2-\alpha}}^{N^{1/2-\alpha}} \exp[-N|f''(0)|x^2/2]dx \\ &\simeq e^{Nf(0)} \sqrt{\frac{2\pi}{|f''(0)|N}}, \end{aligned} \tag{B4}$$

where the final approximate equality follows from $\alpha < 1/2$ and $N \gg 1$. Note that, since $f(0)$ is a maximum, $f''(0) < 0$, explaining the notation using absolute values. Of course, the multiplicative term of order $N^{-1/2}$ disappears on evaluating the left-hand side of (B1)

On the other hand, at the border between the integration domains of J_N and K_N , the integrand can still be evaluated using (B2) neglecting $g(x)$. K_N/J_N is therefore negligible, since it is of the order $\exp(-N^{1-2\alpha}|f''(0)|)$. Since the maximum is unique, the part of the integral K_N for which the representation (B2) cannot be used is also exponentially small against J_N and also negligible.

We now need to cast the integral

$$I(N, S) = \frac{1}{2\pi i} \oint_C \frac{G(w|\underline{z})^{N-S}}{w^{N+1}} dw \tag{B5}$$

in the form (B1). In the following, we shall use mainly the fact that the power series of $G(w|\underline{z})$ in terms of w has only positive coefficients, and that these asymptotically behave as a power law $z_k \sim k^{-\lambda}$.

Defining $\sigma = S/N$, we have

$$I(N, N\sigma) = \frac{1}{2\pi i} \oint_C \exp\{N[(1-\sigma)\ln G(w|\underline{z}) - \ln w]\} \frac{dw}{w}. \tag{B6}$$

We define the abbreviation:

$$H(w|\underline{z}) = (1-\sigma)\ln G(w|\underline{z}) - \ln w. \tag{B7}$$

The quantity $w^*(\sigma|\underline{z})$ corresponds to the minimum of the function $H(w|\underline{z})$ on the real interval $[0, w_c(\underline{z})]$. In the following, we shall use as a contour C the circle of radius $w^*(\sigma|\underline{z})$.

Now, since $G(w|\underline{z})$ has only positive coefficients, by a standard theorem of complex analysis [32], its maximum modulus on C lies on the positive real axis, and the same holds for $G(w|\underline{z})/w^{1/(1-\sigma)}$, since $|w|$ is constant on C . The same thus holds as well for the logarithm and hence for the real part of $H(w|\underline{z})$. Therefore the only maximum on C of $\text{Re } H(w|\underline{z})$ is at $w^*(\sigma|\underline{z})$.

Note, however, that, in order additionally to ensure that the maximum modulus arising on the real axis is the only one on C , we must exclude such irregular growth as might occur, for instance, if the coefficients of the power series of G are only nonzero for even values of k . We therefore implicitly assume that such behavior does not arise.

We therefore understand the behavior of the modulus of H . Let us now look at its real and imaginary parts. The real part coincides with the function itself on the real axis and is minimum at $w^*(\sigma|\underline{z})$ with respect to purely real variations. From the Cauchy-Riemann differential equations [32] one finds that the imaginary part also has vanishing derivative with respect to imaginary variations. Thus, since the contour C is vertical at $w^*(\sigma|\underline{z})$, the imaginary part has zero derivative along C . But since H is real on the real axis, by the Schwarz reflection principle [32], the imaginary part of H is odd, so that it grows cubically (or possibly faster) as the distance to the real axis, and can thus be neglected in the immediate vicinity of the point $w^*(\sigma|\underline{z})$. We may now apply (B1) without problems and obtain the desired result (42).

Finally, it should be pointed out that the above approximation describes the z_s dependence of the integral (B6) only for $s \ll N$. Indeed, $G(w|\underline{z})$ in can be replaced without changing the results by $G_N(w|\underline{z})$ given by

$$G_N(w|\underline{z}) = \sum_{j=1}^N \xi_j z_j w^j. \tag{B8}$$

In particular, it follows that such integrals as (B6) are independent of z_s for $s > N$ and the above approximate approach does not apply for s of order N .

[1] R. L. Drake, in *Topics in Current Aerosol Research*, edited by G. M. Hidy, J. R. Brock, Part 2 (Pergamon Press, New York, 1972), Vol. 3.
 [2] H. Pruppacher and J. Klett, *Microphysics of Clouds and Precipitations* (Kluwer, Dordrecht 1998).
 [3] P. L. Krapivsky, S. Redner, and E. Ben-Naim, *A Kinetic View of Statistical Physics*, (Cambridge University Press, Cambridge, UK, 2010).

[4] F. Leyvraz, Scaling theory and exactly solved models in the kinetics of irreversible aggregation, *Phys. Rep.* **383**, 95 (2003).
 [5] A. Fronczak, A. Chmiel, and P. Fronczak, Exact combinatorial approach to finite coagulating systems, *Phys. Rev. E* **97**, 022126 (2018).
 [6] M. Łepek, P. Kukliński, A. Fronczak, and P. Fronczak, Exact combinatorial approach to finite coagulating systems through recursive equations, *Rep. Math. Phys.* **84**, 117 (2019).

- [7] A. Fronczak, M. Łeppek, P. Kukliński, and P. Fronczak, Coagulation with product kernel and arbitrary initial conditions: Exact kinetics within the Marcus-Lushnikov framework, *Phys. Rev. E* **99**, 012104 (2019).
- [8] M. Łeppek, A. Fronczak, and P. Fronczak, Coalescence with arbitrary-parameter kernels and monodisperse initial conditions: A study within combinatorial framework, *Rep. Math. Phys.* **88**, 89 (2021).
- [9] M. Łeppek, A. Fronczak, and P. Fronczak, Combinatorial solutions to coagulation kernel for linear chains, *Physica D* **415**, 132756 (2021).
- [10] A. H. Marcus, Stochastic coalescence, *Technometrics* **10**, 133 (1968).
- [11] A. A. Lushnikov, Coagulation in finite systems, *J. Colloid Interface Sci.* **65**, 276 (1978).
- [12] P. G. J. van Dongen and M. H. Ernst, Fluctuations in coagulating systems, *J. Stat. Phys.* **49**, 879 (1987).
- [13] P. G. J. van Dongen, Fluctuations in coagulating systems. II, *J. Stat. Phys.* **49**, 927 (1987).
- [14] A. A. Lushnikov, Exact kinetics of the sol-gel transition, *Phys. Rev. E* **71**, 046129 (2005).
- [15] A. A. Lushnikov, From Sol to Gel Exactly, *Phys. Rev. Lett.* **93**, 198302 (2004).
- [16] A. A. Lushnikov, Gelation in coagulating systems, *Physica D* **222**, 37 (2006).
- [17] A. A. Lushnikov, Exact post-critical behavior of a source-enhanced gelling system, *J. Phys. A: Math. Theor.* **41**, 072001 (2008).
- [18] N. V. Brilliantov, W. Otieno, and P. L. Krapivsky, Nonextensive Supercluster States in Aggregation with Fragmentation, *Phys. Rev. Lett.* **127**, 250602 (2021).
- [19] A. Kalinov, A. I. Osinsky, S. A. Matveev, W. Otieno, and N. V. Brilliantov, Direct simulation Monte Carlo for new regimes in aggregation-fragmentation kinetics, *J. Comput. Phys.* **467**, 111439 (2022).
- [20] M. H. Ernst, E. M. Hendriks, and F. Leyvraz, Smoluchowski's equation and the θ -exponent for branched polymers, *J. Phys. A: Math. Gen.* **17**, 2137 (1984).
- [21] P. G. J. Van Dongen, Solutions of Smoluchowski's coagulation equation at large cluster sizes, *Physica A* **145**, 15 (1987).
- [22] L. Comtet, *Advanced Combinatorics: The Art of Finite and Infinite Expansions* (Springer Science & Business Media, New York, 2012).
- [23] J. R. Norris, Smoluchowski's coagulation equation: uniqueness, nonuniqueness and a hydrodynamic limit for the stochastic coalescent, *Ann. Appl. Probab.* **9**, 78 (1999).
- [24] F. Leyvraz, Exact asymptotic solution of an aggregation model with a bell-shaped distribution, *Phys. Rev. E* **103**, 022123 (2021).
- [25] F. Calogero and F. Leyvraz, A new solvable model of aggregation kinetics, *J. Phys. A: Math. Gen.* **32**, 7697 (1999).
- [26] F. Leyvraz, Scaling and crossover properties of a new solvable model of aggregation kinetics, *J. Phys. A: Math. Gen.* **32**, 7719 (1999).
- [27] M. Mabilia, P. L. Krapivsky, and S. Redner, Kinetic anomalies in addition-aggregation processes, *J. Phys. A: Math. Gen.* **36**, 4533 (2003).
- [28] A. A. Lushnikov, Exact kinetics of a coagulating system with the kernel $K = 1$, *J. Phys. A: Math. Theor.* **44**, 335001 (2011).
- [29] C. M. Bender and S. Orszag, *Advanced Mathematical Methods for Scientists and Engineers I: Asymptotic Methods and Perturbation Theory* (Springer Science & Business Media, New York, 1999), Vol. 1.
- [30] R. M. Ziff and G. Stell, Kinetics of polymer gelation, *J. Chem. Phys.* **73**, 3492 (1980).
- [31] I. Jeon, Existence of gelling solutions for coagulation-fragmentation equations, *Commun. Math. Phys.* **194**, 541 (1998).
- [32] L. V. Ahlfors, *Complex Analysis: An Introduction to the Theory of Analytic Functions of One Complex Variable* (McGraw-Hill, New York 1953), p. 177.