Remarks on a combinatorial solution of a stochastic aggregation model

F. Leyvraz

Instituto de Ciencias Físicas—Universidad Nacional Autónoma de México, Cuernavaca, Morelos, México

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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.
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.

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

$$A(k) + A(l) \xrightarrow{K(k,l)} A(k+l). \quad (1)$$

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:

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

A basic property of (2) is the following: at a formal level, the total mass $M_1$ 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 $t_c$

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

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 non-gelling, whereas the multiplicative kernel displays gelation. To show how this may arise, we display its solution for $c_j(t) = \delta_{j,1}$

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

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

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 $1/t$.

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

$$\lim_{t \to \infty; k/s(t) = x} \left[ k^2 c_k(t) \right] = \Phi(x). \quad (7)$$

For details see for instance [1]. For gelling systems, a similar behaviour holds in the vicinity of the critical time:

$$\lim_{t \to t_c; k/s(t) = x} \left[ k^x c_k(t) \right] = \Phi(x). \quad (8)$$
where $\tau$ is an exponent that depends on the specific kernel, which is, for instance, equal to $5/2$ for the multiplicative kernel.

Let us shortly summarise 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 $\lambda$, that is

$$K(ak, al) = a^\lambda K(k, l).$$

We further define the exponents $\mu$ and $\nu$ by the relation

$$K(i, j) \simeq i^\mu j^\nu \quad (1 \ll i \ll j)$$

Both the large-$x$ and small-$x$ behaviours of $\Phi(x)$ are determined by the above exponents: the system is gelling if $\lambda > 1$, non-gelling otherwise. If the system is non-gelling, the small-$x$ behaviour 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-$x$ behaviour that must be determined separately in each particular case. The large-$x$ behaviour 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 \[2–6\] 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 Section II we present in detail the discrete Marcus–Lushnikov model and its proposed combinatorial solution. In Section III we summarise the results to be shown in the rest of the paper; in Section IV we derive the formulae 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 Section V and we present conclusions in Section VI.

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

We start by describing a more microscopic model describing the underlying stochastic dynamics of the aggregation process \[4–8\]. 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 $\underline{n} = (n_1, \ldots, n_N)$ which satisfy the condition $\sum_{k=1}^\infty k n_k = N$. Here $n_k$ is the total number of aggregates $A(k)$ in the state $\underline{n}$.

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 $\underline{2}$. 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 non-zero if

$$n'_j = n_j - 1 \quad (j = k, l)$$

$$n'_{k+l} = n_{k+l} + 1$$

$$n'_j = n_j \quad (j \neq k, l, k + l)$$

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

$$r_{k,l}(\underline{n} \rightarrow \underline{n}') = K(k, l)n_k n_l \quad (k \neq l)$$

$$= K(k, k)\frac{n_k(n_k - 1)}{2} \quad (k = l)$$

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

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

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

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

(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 $\sigma = S/N$, and the connection between $\sigma$ and $t$ will be commented upon later.

The original stochastic model introduced by Marcus [7] and Lushnikov [8] indeed involves transition rates, and not probabilities: these are defined as in (12), with no further normalization; the continuous time equivalent of (14) is

$$\frac{\partial P(\tilde{w}; t)}{\partial t} = \sum_{k,l=1}^{N} \sum_{w'} \left[ r_{k,l}(u \rightarrow u') P(u'; t) - r_{k,l}(u' \rightarrow u) P(u; t) \right]$$

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 [2–6]. 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 $\xi_k$ is defined by the following recursion relation

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

(16a)

$$\xi_1 = 1$$

(16b)

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

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

Their asymptotic behaviour as $k \to \infty$ has been studied [1, 9, 10] and they behave as $k^{-\lambda}$ except for the case of kernels having $\nu = 1$, for which the behaviour must be studied on a case-by-case basis.

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

$$\tilde{z}^{\tilde{w}} = \prod_{k=1}^{N} z_k^{w_k} \quad \tilde{z} \tilde{w} = (z_1 w_1, \ldots, z_N w_N)$$

(18)

We further introduce the following abbreviations

$$\xi = (\xi_1, \ldots, \xi_N) \quad m! = (1!, 2!, \ldots, N!)$$

(19)

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

$$\Psi(\tilde{z}; S) = \sum_{\tilde{w}} P(\tilde{w}; S) \tilde{z}^{\tilde{w}}$$

(20)

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

$$\Psi(\tilde{z}; S) = \frac{B_{N,N-S}(m! \xi)}{B_{N,N-S}(m!)}$$

(21)

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

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

(22)

It is, however, readily checked that $B_{n,m}(a)$ 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 [11].
III. SUMMARY OF RESULTS

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

$$\pi_j(S) = \sum_n n_j P(n; S).$$  \hspace{1cm} (23)

Additionally to its $S$ dependence, $\pi_j(S)$ depends on $N$. It is well-known \[12–14\] that, in the continuum limit, the discrete Marcus–Lushnikov model tends to the kinetic equations in the following sense:

$$\lim_{S,N \to \infty} \frac{\pi_j(S)}{N} = c_j(t) \hspace{2cm} (24a)$$
$$\sum_{k=1}^{\infty} c_k(t) = 1 - \sigma \hspace{2cm} (24b)$$

This means that (24b) provides the correct connection between $t$ and $\sigma$, and that taking the $N \to \infty$ limit while maintaining $\sigma$ 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, one finds an exact expression for the above described limit in terms of the BPA (21): define

$$G(w) = \sum_{j=1}^{\infty} \xi_j w^j \hspace{2cm} (25a)$$
$$w^*(\sigma) = \arg\min_{0 < w < w_c} [(1 - \sigma) \ln G(w) - \ln w] \hspace{2cm} (25b)$$

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

$$\lim_{N,S \to \infty} \frac{\pi_j(S)}{N} = \frac{1 - \sigma}{G[w(\sigma)]} \xi_j w(\sigma)^j \hspace{2cm} (26)$$

From this we deduce that the r.h.s. of (26) is an exact solution of (2) whenever (21) is a solution of the discrete Marcus–Lushnikov model defined by (14), and viceversa, 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 $\sigma \to 1$ limit. As is readily seen as well, if $G^\prime(w) \to \infty$ as $w \to w_c$, $w^*(\sigma) \to w_c$ as $\sigma \to 1$. (26) thus leads to the scaling form

$$c_j(t) \simeq j^{-\lambda} \exp \left[ -j \ln \left( \frac{w^*(\sigma)}{w_c} \right) \right] \left( \sum_{k=1}^{\infty} c_k(t) \right) \hspace{2cm} (27)$$

To describe this in terms of the scaling theory, we set

$$s(t) = \left[ \ln \left( \frac{w^*(\sigma)}{w_c} \right) \right]^{-1}. \hspace{2cm} (28)$$

Using as always the normalisation

$$\sum_{k=1}^{\infty} k c_k(t) = 1 \hspace{2cm} (29)$$

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

$$\Phi(x) = \text{const.} \cdot x^{2-\lambda} e^{-x}. \hspace{2cm} (30)$$
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 behaviour for \( \lambda > 1 \).

While this is in good agreement with the large-\( j \) behaviour as known from scaling theory, it is in strong disagreement with the known small-\( j \) behaviour. Note that the discrepancy involves the size distribution, and not the correspondence between \( t \) and \( \sigma \). 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 \( \xi_j \): 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 \( \{2\} \), \( K(k, l) = 1/k + 1/l \) has, as can be shown exactly, see \( \{15\} \), the following large time behaviour

\[
\lim_{t \to \infty} \left[ (kt)^{-1/2} \exp[-(kt)^{1/2}]c_1(t) \right] = 1
\]  

\[
\lim_{t \to \infty} \left[ (kt)^{1/2} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} c_k(t) \right] = 1
\]

where \( k \) is a numerical constant. Clearly this result is incompatible with \( \{27\} \). Yet another kind of behaviour that cannot be subsumed under the scheme of \( \{27\} \) is the following: define \( \alpha_j \) and \( w_j \) via

\[
\lim_{t \to \infty} \left[ t^{w_j} c_j(t) \right] = \alpha_j
\]

Now it can be shown that the \( w_j \) in certain cases depend non-trivially 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 \( \{17, 18\} \), one finds that

\[
w_j = 2 - q^j.
\]

Similar behaviour also arises in the case in which the reaction rates \( K_{i,j} \) take 3 different constant values, depending on whether both masses are equal to one, only one, or neither \( \{19\} \).

We therefore see that the claim of general validity made for the BPA in \( \{2–6\} \), cannot be upheld. The reasoning presented in these papers must thus contain some flaw, which is however by no means obvious.

Nevertheless, the identity between the small-\( j \) and the large-\( j \) behaviours 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 non-zero probabilities:

\[
\begin{align*}
\bar{u}_1 &= (12, 4, \ldots) & \bar{u}_2 &= (13, 2, 1, \ldots) \\
\bar{u}_3 &= (14, 0, 2, \ldots) & \bar{u}_4 &= (14, 1, 0, 1, \ldots) \\
\bar{u}_5 &= (15, 0, 0, 0, 1, \ldots)
\end{align*}
\]

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

\[
\begin{align*}
P(\bar{u}_1; 4) &= \frac{130}{944} = 0.2515 \ldots & P(\bar{u}_2; 4) &= \frac{22400}{4800} = 0.4659 \ldots \\
P(\bar{u}_3; 4) &= \frac{38995}{7900} = 0.0668 \ldots & P(\bar{u}_4; 4) &= \frac{2504}{4500} = 0.1785 \ldots \\
P(\bar{u}_5; 4) &= \frac{2580}{317} = 0.3034 \ldots
\end{align*}
\]

whereas the ones arising from the BPA are

\[
\begin{align*}
P(\bar{u}_1; 4) &= \frac{273}{128} = 0.2525 \ldots & P(\bar{u}_2; 4) &= \frac{504}{1081} = 0.4662 \ldots \\
P(\bar{u}_3; 4) &= \frac{120}{40} = 0.0666 \ldots & P(\bar{u}_4; 4) &= \frac{1081}{40} = 0.1776 \ldots \\
P(\bar{u}_5; 4) &= \frac{308}{1081} = 0.0370 \ldots
\end{align*}
\]

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 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, for these two kernels, Lushnikov \( \{8, 16\} \) has presented exact solutions for these kernels, for the corresponding continuous model. These can presumably be carried over to the discrete case.
IV. THE $N \to \infty$ AVERAGE CLUSTER SIZE DISTRIBUTION

Let us first derive an explicit expression for $\pi_j$ as a function of $\Psi(z; S)$. One finds

$$\pi_j = z_j \frac{\partial}{\partial z_j} \ln \Psi(z; S) \bigg|_{z=1}$$

(37)

Substituting the BPA (24) into (37) yields

$$\pi_j = z_j \frac{\partial}{\partial z_j} \ln \left[ B_{N,N-S}(m^1 \xi_j) \right] \bigg|_{z=1}$$

(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

$$\frac{(N-S)!}{N!} B_{N,N-S}(m^1 \xi_j) = \frac{1}{2\pi i} \oint_C G(w|z)^{N-S} w^{N-S} dw$$

(39a)

$$G(w|z) = \sum_{j=1}^{\infty} \xi_j z^j w^j$$

(39b)

Here $C$ is a contour enclosing the origin, but no singularity of $G(w|z)$. 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 (39).

It therefore follows, via a saddle point approximation, that

$$\lim_{S,N \to \infty} \frac{1}{N} \ln \left[ \frac{(N-S)!}{N!} B_{N,N-S}(m^1 \xi_j) \right] = (1 - \sigma) \ln G(w^*|z) - \ln w^* \ln w$$

(40)

where $w^*(\sigma|z)$ is defined similarly to (24a).

$$w^*(\sigma|z) = \arg\min_{0 < w < w_c(z)} \left[ (1 - \sigma) \ln G(w|z) - \ln w \right].$$

(41)

Note that the asymptotic expression (40) does not hold universally for all sequences $\xi_j$. Essential use is made both of the positivity of the $\xi_j$ and of the fact that the $\xi_j$ 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 (40) 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 $\xi_j$ of the r.h.s. of (40). As a first remark, one notes that the dependence of $w(\sigma)$ on $\xi_j$ due to the dependence of $\sigma$ on $\xi_j$ can be neglected: due to the definition of $w(\sigma|z)$, there is no first order dependence on $\sigma$ of

$$(1 - \sigma) \ln G(w(\sigma|z)|z) - \ln w(\sigma|z).$$

(42)

We thus only need to take the derivative with respect to the $z$-dependence of $G(w(\sigma|z))$. This leads to

$$\lim_{S,N \to \infty} \frac{\pi_j}{N} = \frac{1 - \sigma}{G^2(w)} \xi_j w(\sigma)^{i}$$

(43)

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

$$\frac{1}{G^2(w)} [G(w)G''(w) - G'(w)^2] + \frac{1}{w^2} > 0.$$
where the positivity follows from the positivity of the $\xi_j$ 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

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

(45)

As we move from $w = 0$ to $w = w_c$, both $G'(w)$ and $G(w)$ increase. If as $w \to w_c$ $G'(w)$ diverges, then the existence of a (unique) solution of (45) follows straightforwardly. On the other hand, if $G'(w_c) < \infty$, then there is a value $0 < \sigma < 1$ such that (45) has no interior solution. As we shall see, this is what happens in the case of the post-gel 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 $\xi_j$ 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. It follows from the recursion relation (16), that the generating function for the $\xi_j$, namely $G(w)$, satisfies the ordinary differential equation:

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

(46)

This has the unique implicit solution

$$
w = \left(1 - \sqrt{1 - 2G}\right) \exp\left(\sqrt{1 - 2G} - 1\right)
$$

(47)

We now substitute (47) into

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

and minimize with respect to $G$. One obtains

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

(49)

If we finally substitute these expressions into the r.h.s. of (26), one obtains

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

(50)

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

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

(51a)

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

(51b)

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 (50) is only true for $t \leq 1$, so we only consider (51a), 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, $\xi_j = j^{i-2}/j!$.

We do not yet know the solution for $\sigma > 1/2$, which corresponds to the post-gel phase. It is clear that the maximum of the function (18) 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 $\sigma$. If we now substitute these into the r.h.s. of (26) we obtain

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

(52)
where we have used the expression (51b) 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 post-gel multiplicative kernel, the Smoluchowski equations can be meaningfully given two forms, which lead to different solutions:

$$\dot{c}_j(t) = \frac{1}{2} \sum_{k=1}^{j-1} k(j-k)c_k(t)c_{j-k}(t) - j c_j(t) \sum_{k=1}^{\infty} k c_k(t)$$  \hspace{1cm} (53a)

$$\dot{c}_j(t) = \frac{1}{2} \sum_{k=1}^{j-1} k(j-k)c_k(t)c_{j-k}(t) - j c_j(t)$$  \hspace{1cm} (53b)

Here (53a) is simply (2) for $K(k, l) = kl$ and (53b) is obtained from (53a) by assuming the constancy of the mass, even though the equation’s solution eventually violates it. The solution of (53a) is (6), whereas the solution of (53b) is simply (6a) for all times, that is, the solution is analytic. After $t = 1$, of course, the solution of (53b) 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 (53a) 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 (53b), known as the Flory solution, is expected to hold. For a detailed discussion of this issue see [20].

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 $N \to \infty$. After gelation, the random graph model is known to follow the Flory solution [20]. 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 [20]. There it was shown that the decay of $c_j(t)$ as $t \to \infty$ 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

$$Ge^{-G} = w$$  \hspace{1cm} (54)

for the additive kernel, and

$$G = \frac{w}{2 - w}$$  \hspace{1cm} (55)

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

Summarising, we have derived analytically the solution to the Smoluchowski equations that arises from the solution of the discrete Marcus–Lushnikov model proposed in [2–6]. 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 [1]. 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 behaviour 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 behaviours coincide. In that case, it is verified that the analytic solution derived in this paper from the BPA does indeed coincide exactly with the corresponding solution of
the Smoluchowski equation, with the exception of the post-gel 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 pre-gel 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 post-gel case, namely one that yields the Stockmayer solution. Since, for small $N$, there is no sharp difference between pre-gel and post-gel stages, the existence of a discrepancy at small $N$ and small times is perhaps understandable.

Considering the remarkable successes of the Bell Polynomial Ansatz, 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 $\xi_j$ behave as $j^{-\lambda}$ [10]. 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 behaviour may exist, depending on the value of $\lambda$.

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

$$(1 - \sigma)w(\sigma)\frac{G'[w(\sigma)]}{G[w(\sigma)]} = 1.$$  \hspace{1cm} (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 $\sigma \to 1$. $G[w(\sigma)]$ then diverges as $(1 - \sigma)^{\lambda - 1}$. Substituting into (26) then yields

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

which has the scaling form indicated in (30).

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

$$\frac{n_j(\sigma)}{N} = \text{const.}\cdot j^{-\lambda}(1 - \sigma) \exp\left(-\text{const.}\cdot \frac{j}{(1 - \sigma)^{1/(2 - \lambda)}}\right)$$  \hspace{1cm} (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 [21].

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