Deterministic and Stochastic Models for Coalescence (Aggregation, Coagulation): a Review of the Mean-Field Theory for Probabilists

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Abstract

Consider N particles, which merge into clusters according to the rule: a cluster of size x and a cluster of size y merge at (stochastic) rate $K(x,y)/N$, where K is a specified rate kernel. This Marcus-Lushnikov model of stochastic coalescence, and the underlying deterministic approximation given by the Smoluchowski coagulation equations, have an extensive scientific literature. Some mathematical literature (Kingman's coalescent in population genetics; component sizes in random graphs) implicitly studies the special cases $K(x,y) = 1$ and $K(x,y) = xy$. We attempt a wide-ranging survey. General kernels are only now starting to be studied rigorously, so many interesting open problems appear.

Keywords. branching process, coalescence, continuum tree, density-dependent Markov process, gelation, random graph, random tree, Smoluchowski coagulation equation

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1 Introduction

Models, implicitly or explicitly stochastic, of coalescence (= coagulation, gelation, aggregation, agglomeration, accretion ...) have been studied in many scientific disciplines, but have only tangentially appeared in the "applied probability" literature. This is paradoxical, in that the "dual" process of splitting or fragmentation is, in an analogous mean-field model, very close to the classical topic of *branching processes* in applied probability. The purpose of this survey is to bring the existence of this large body of scientific literature to the attention of theoretical and applied probabilists. We shall provide pointers to the science literature, outline some of the mathematical results developed therein, comment on the duality between coalescence and branching processes, and pose some mathematical problems. That an opportunity arises to outline recent work of the author and colleagues is, of course, purely coincidental.

1.1 Verbal description of basic model

Clusters with different masses move through space. When two clusters (masses x and y, say) are sufficiently close, there is some chance that they merge into a single cluster of mass $x+y$. A completely detailed model would incorporate mass, position, velocity (or diffusive rates) of each cluster, together with the exact rule for coalescence of two clusters. Such models seem far too complicated for analysis, so a natural first approximation is the following. We may regard mass x as *discrete* ($x = 1, 2, 3, \ldots$, so the cluster consists of x *particles* of unit mass) or *continuous* ($0 < x < \infty$ a real number). Imagine the process to be spatially-stationary in infinite d-dimensional space, so that by stationarity there exist at time t densities $n(x,t)$ defined by:

$$n(x,t) = \text{ average number of clusters of mass } x \text{ per unit volume}$$

in the discrete case; and

$$n(x,t)dx = \begin{array}{l}\text{average number of} \\ \text{per unit volume}\end{array} \text{ clusters of mass } \in [x, x+dx]$$

in the continuous case. Next, there is a *rate kernel* $K(x,y)$ whose interpretation in the discrete setting is as follows. Consider a tagged cluster of mass x. We assume that the instantaneous rate at which it merges with some cluster of mass y is proportional to the density $n(y,t)$ of such clusters, and take $K(x,y)$ as the constant of proportionality. In other words, if we write a coalescence $\{x,y\} \to x+y$ as $(x,y) \to x+y$ or $(y,x) \to x+y$ with equal chance, then

average number of coalescences $(x,y) \to x+y$ per unit time per unit volume

$$= \tfrac{1}{2} n(x,t)n(y,t)\ K(x,y). \tag{1}$$

The idea is that the details of the local motion and local coalescence rule, which arise from the physics of what is being modeled, are subsumed into the rate function. In the continuous setting there is an obvious analog of (1): $\frac{1}{2}n(x,t)n(y,t)\ K(x,y)\ dx\ dy$ is the average number of coalescences with masses in $(x, x+dx)$ and $(y, y+dy)$. Based on this story we can write down differential equations (2,3) for the densities $n(x,t)$, and this is the starting point of section 2. A physicist would call this the "infinite-volume mean-field theory".

Some minor comments.

(i) $K(x,y)$ is not a "pure rate" because it has dimensions volume/time instead of 1/time.

(ii) We may assume K to be symmetric: $K(x,y) = K(y,x)$.

(iii) By scaling time, we can eliminate a multiplicative constant from the kernel, so we talk about e.g. $K(x,y) = xy$ instead of $K(x,y) = cxy$ for constant c.

(iv) Throughout the paper, *time t* is always a continuous variable; *discrete* and *continuous* refer to cluster masses.

Table 1 gives examples of kernels used in the physical chemistry literature. The table is taken from [74], who cite references to each case. Most of these examples, and others, are explained in Drake [26] section 4.3. Note that we parametrize the "size" of clusters by mass x rather than length l; these kernels are often written in terms of $l \propto x^{1/3}$ instead of x.

Table 1 [74] **Some specific kernels**

$K(x,y)$	Comment
$(x^{1/3}+y^{1/3})(x^{-1/3}+y^{-1/3})$	Brownian motion (continuum regime)
$(x^{1/3}+y^{1/3})^2(x^{-1}+y^{-1})^{1/2}$	Brownian motion (free molecular regime)
$(x^{1/3}+y^{1/3})^3$	Shear (linear velocity profile)
$(x^{1/3}+y^{1/3})^{7/3}$	Shear (non-linear velocity profile)
$(x^{1/3}+y^{1/3})^2\lvert x^{1/3}-y^{1/3}\rvert$	Gravitational settling
$(x^{1/3}+y^{1/3})^2\lvert x^{2/3}-y^{2/3}\rvert$	Inertia and gravitational settling
$(x-y)^2(x+y)^{-1}$	Analytic approximation of Berry's kernel
$(x+c)(y+c)$	Condensation/ branched-chain polymerization
$(x^{1/3}+y^{1/3})(xy)^{1/2}(x+y)^{-3/2}$	Based on kinetic theory

1.2 Why should probabilists care?

Section 2 reviews the deterministic Smoluchowski coagulation equations which formalize (1): this is the aspect of coalescence which has been most intensely studied in the scientific literature. This aspect is not "probabilistic", but the remainder of the survey is. Section 3 gives "probabilistic" interpretations of some deterministic results about the Smoluchowski coagulation equations, using duality with branching-type processes. But our main focus (sections 4 and 5) is on the "finite-volume mean-field theory" of the Marcus-Lushnikov process. This is a N-particle stochastic model, and we seek to understand its large-N behavior. In section 4 we emphasize the three simplest specific kernels K (constant, additive, and multiplicative), for which a rich and fairly explicit theory exists, with connections to other parts of mathematical probability (Kingman's coalescent, discrete and continuum random trees, random graphs). Section 5 discusses general kernels, where open problems outnumber rigorous results.

1.3 Digression: TP and SM mathematics

To ask "what is known" in this subject leads inexorably to philosophical issues concerning pure and applied mathematics. A typical paper [30, 35, 101] we cite from the scientific literature would be described by a layman as "mathematics" rather than "science": it is devoted to analysis of a mathematical model rather than description of experimental or observational results, although some reference to the latter is made in motivation and conclusion. I call this SM (*scientific modeling*) mathematics, as opposed to TP (*theorem-proof*) mathematics, which is the style of all "pure" and much of what is called "applied" mathematics. In SM mathematics, models may be incompletely or inconsistently specified; the focus is on obtaining conclusions about the model, allowing appeals to physical realism, unquantified approximations, and arguments by analogy. In TP mathematics one is supposed to have explicit assumptions and conclusions, as well as a rigorous argument linking them. A lively recent debate on these matters can be found in the discussion of [42]. Much of this survey deals with issues which have not been studied systematically as TP mathematics, and our "open problems" concern proofs of matters which mostly appear implicitly or explicitly in the SM literature.

1.4 Fields of application

Where possible I cite papers giving an accessible overview of a field, rather than the seminal paper in a field.

By far the largest application area is physical chemistry.

- *Aerosols* [26, 69]. That is, solid or liquid particles suspended in a gas: such as smoke, smog, dust; water droplet or snowflake formation in clouds.
- *Phase separation in liquid mixtures* [1].
- *Polymerization* [30].

The kernels shown in table 1 arise in such areas. Other areas include

- *Astronomy*: formation of large-scale structure in the universe [73]; formation of protostellar clusters within galaxies [72, 14]; formation of planets within solar systems [101]
- *Biological entities*, e.g. algae [2].
- *Bubble swarms* [79].

In all these settings, the clusters were physical entities in physical space, and have been studied as SM mathematics. A different area of application, which has caught the attention of TP mathematicians, is

- *Mathematical population genetics* [83].

Here the entities are 'lines of descent", i.e. number of ancestors in past generations of a sample of genes in the current generation, and the specific kernel $K(x,y) = 1$ arises (section 4.2). An area of TP mathematics which turns out to be related to our topic is

- *Random graph theory* [18]

where the specific kernel $K(x,y) = xy$ has implicitly been studied in great detail: see section 4.4.

In addition to the SM study of particular physical phenomena, there is a body of literature (e.g. [93, 87, 95] in *J. Statistical Physics*) devoted to mathematical study, with varying levels of rigor, of the kind of models we discuss here. When we get to discussing detailed mathematical results, we shall most often be referring to that literature. Let us also mention the graduate textbook of van Kampen [96] as a standard introduction to SM stochastic processes.

1.5 One specific application

In some of the application areas mentioned above, the use of our mean-field model would be regarded as old-fashioned: current research focuses on more physically realistic models. But to show this topic is not completely moribund, we mention recent experimental work of White and Wiltzius [103], recounted for laymen in *The Economist* [1]. Certain liquids (e.g. olive oil and alcohol) mix at high temperature but separate at low temperature; how in detail does separation occur as temperature is lowered very slowly through the critical point? At some point, microscopic droplets of one liquid form, but what then? One theory is that these droplets tend to form, and to dissolve back into the mixture, very quickly, except that two droplets which form adjacent to each other may merge into one. In this theory the process of pure droplets is rather like a branching process with immigration: above the critical temperature this is a subcritical process and the droplets stay small, but below the critical temperature the process becomes supercritical and a large component very rapidly forms. An alternative theory is that creation and dissolution of droplets occur comparatively slowly, and that the dominant mechanism is diffusion of droplets, which coalesce when they meet, and repeated coalescence creates large drops comparatively slowly. This is the "Brownian motion – continuum regime" case of our model. And [103] give experimental results showing (at least for a certain very viscous pair of liquids) a better fit to the diffusion and coalescence model.

2 Deterministic models

2.1 The Smoluchowski coagulation equations

Equation (1) and its continuous analog can be rewritten without words as the differential equations

$$\frac{d}{dt}n(x,t) = \frac{1}{2}\sum_{y=1}^{x-1} K(y,x-y)n(y,t)n(x-y,t) \quad - \quad n(x,t)\sum_{y=1}^{\infty} K(x,y)n(y,t) \qquad \text{(discrete } x\text{)} \tag{2}$$

$$\frac{d}{dt}n(x,t) = \frac{1}{2}\int_0^x K(y,x-y)n(y,t)n(x-y,t)dy \quad - \quad n(x,t)\int_0^\infty K(x,y)n(y,t)dy. \qquad \text{(continuous } x\text{)} \tag{3}$$

We will refer to (2,3) jointly as the *Smoluchowski coagulation equations.* (Note that the phrase "Smoluchowski equation" is used in a different context, diffusion under a potential). These equations have been studied in great detail in the SM community, and we outline some of their results. Note that from the verbal description of the model we expect solutions to have the property that mass density is preserved:

$$m_1(t) \equiv \sum_{x=1}^{\infty} xn(x,t) \text{ or } \int_0^\infty xn(x,t)\,dx \text{ is constant in } t. \tag{4}$$

We shall also use the *cluster density* $m_0(t)$ and the second moment $m_2(t)$ defined in the continuous case as

$$m_0(t) = \int_0^\infty n(x,t)dx.$$

$$m_2(t) = \int_0^\infty x^2 n(x,t)dx$$

Clearly $m_0(t)$ is decreasing and $m_2(t)$ is increasing.

The standard reference is the 1972 *de facto* monograph by Drake [26]. This cites 250 papers from the SM literature, and provides a very clear exposition of both the science background and the (fairly unsophisticated) mathematics being used at that time. I have not found any similarly wide-ranging survey of subsequent research. The 1994 monograph by Dubovskii [27] focuses narrowly on mathematical issues of existence and uniqueness of solutions. Snapshots of recent research results and interests are provided by the introductions to papers [70, 74, 85].

We now give a quick overview of three aspects of the Smoluchowski coagulation equations; exact solutions, gelation and self-similar solutions.

2.2 Exact solutions

It has long been recognized that three particular kernels $K(x, y)$ are mathematically tractable: 1, $x + y$ and xy. Table 2 gives, for each of these three kernels, a special solution to the equations (2,3). In the discrete case this is the ("obviously unique") solution with the *monodisperse* initial configuration $n(x, 0) = \delta_1(x)$; in the continuous case it is a solution arising from infinitesimally small initial clusters (where uniqueness is hardly obvious). Some involve the *Borel distribution* ([23] sec. 2.7), which for our purposes is best regarded as the total population size Z_λ in a Galton-Watson branching process with one progenitor and Poisson(λ) offspring distribution. Explicitly,

$$B(\lambda, x) \equiv P(Z_\lambda = x) = (\lambda x)^{x-1} e^{-\lambda x}/x!, \quad x = 1, 2, 3, \ldots ; 0 \leq \lambda \leq 1. \quad (5)$$

table 2: formulas for $n(x, t)$

$K(x,y)$	1	$x+y$	xy
discrete	$(1+\frac{t}{2})^{-2}(\frac{t}{2+t})^{x-1}$ $0 \leq t < \infty$ [76]	$e^{-t}B(1-e^{-t}, x)$ $0 \leq t < \infty$ [37]	$x^{-1}B(t, x)$ $0 \leq t \leq 1$ [57]
continuous	$4t^{-2}\exp(-2x/t)$ $0 < t < \infty$ [67]	$(2\pi)^{-1/2}e^{-t}x^{-3/2}e^{-e^{-2t}x/2}$ $-\infty < t < \infty$	$(2\pi)^{-1/2}x^{-5/2}e^{-t^2x/2}$ $-\infty < t < 0$

We included the conventional attributions of 4 of these formulas, which have been rediscovered many times. The remaining two continuous solutions arise by rescaling time in the corresponding discrete solutions and taking limits as $t \to \infty$ or $t \to 1$. These continuous solutions are more implicit than explicit in the SM literature. The continuous $x + y$ solution has $m_1(t) \equiv 1$

but infinite cluster density $m_0(t)$. The continuous xy solution has both $m_0(t)$ and $m_1(t)$ infinite, and is therefore often called "unphysical": see section 4.4 for its interpretation.

There has also been considerable attention paid to the *general bilinear* kernel $K(x, y) = A + B(x + y) + Cxy$, for which some more complicated explicit solutions are available [86, 90, 77, 78].

2.3 Gelation

Consider the second moment of cluster mass $m_2(t) = \int_0^\infty x^2 n(x,t)dx$. Because a coalescence $\{x, y\} \to x + y$ increases the sum-of-squares-of-masses by $2xy$, the continuous Smoluchowski coagulation equation implies

$$\tfrac{d}{dt} m_2(t) = \int\int xy\ K(x, y)\ n(x, t) n(y, t)\ dx\ dy \tag{6}$$

and analogously in the discrete case. Now consider the assumption

$$K(x, y) \le k_0(1 + x + y). \tag{7}$$

Inserting into (6),

$$\tfrac{d}{dt} m_2(t) \le k_0(2m_2(t)m_1(t) + m_1^2(t)).$$

For an initial configuration with $m_0(0)$ and $m_2(0)$ finite, this becomes (since $m_0(t)$ is decreasing and $m_1(t)$ is constant)

$$\tfrac{d}{dt} m_2(t) \le k_0(2m_2(t)m_1(0) + m_1^2(0))$$

implying $m_2(t) < \infty$ for all $t < \infty$.

It is not difficult to make this type of argument rigorous. See White [102] and Heilmann [39] for the discrete case, and chapters 3 and 4 of Dubovskii [27] for the continuous case (in the more general setting of coagulation and fragmentation), and extensive references to the literature. The exact results are rather technical in the continuous case, but can be summarized informally as

Principle 1 *For a kernel K satisfying (7) and extra technical conditions in the continuous case, and an initial configuration $n(x, 0)$ such that*

$$m_1(t) = 1,\ \ m_0(t) < \infty,\ \ m_2(t) < \infty \tag{8}$$

holds for $t = 0$, the Smoluchowski coagulation equation has a unique solution, and this solution satisfies (8) for all $0 \le t < \infty$.

In contrast, consider the case $K(x, y) = xy$. Here (6) reduces to

$$\frac{d}{dt} m_2(t) = (m_2(t))^2 \tag{9}$$

in both discrete and continuous cases. Thus in the monodisperse discrete case ($n(1, 0) = 1$) we have

$$m_2(t) = (1 - t)^{-1},\ 0 \leq t < 1$$

while in the continuous case we have

$$m_2(t) = \left(\tfrac{1}{m_2(0)} - t\right)^{-1},\ 0 \leq t < \tfrac{1}{m_2(0)}.$$

Note that the continuous case special solution in table 2 has $m_2(t) = 1/|t|,\ -\infty < t < 0$, consistent with (9).

As discussed by numerous authors, this kernel xy is the prototype example where the process exhibits a *phase transition*, typically called *gelation* in the context of coalescence models. As the reader may know from a casual acquaintance with percolation theory, there is a tendency in the scientific literature to define such concepts via moment behavior. Thus one could say *gelation occurs*, or K is a *gelling kernel*, if the discrete model with the monodisperse initial condition has no solution with

$$m_2(t) < \infty,\ 0 \leq t < \infty. \tag{10}$$

Then one can define a critical time t_c as the largest time such that $m_2(t) < \infty$ for all $t < t_c$, and seek e.g.
(i) proofs that, for discrete and continuous mass, *no* initial configuration has a solution satisfying (10);
(ii) estimates of the critical time in terms of the initial configuration.

Mathematically, it is more natural to define critical times in terms of existence of solutions of the Smoluchowski coagulation equations which have the mass-conserving property (4): T_{gel} is the largest time such that the discrete model with the monodisperse initial condition has a solution with $m_1(t) = 1$ for all $t < T_{\text{gel}}$. The SM literature tends to assume these two definitions are equivalent. The physical interpretation of gelation is that after the critical time, a strictly positive proportion of mass lies in infinite-mass clusters, the *gel*. One can model post-gelation behavior by explicitly modeling [106] interaction between the gel and the *sol* (finite-mass clusters), but in this survey we shall only consider pre-gelation behavior, except for brief comments on the $K(x, y) = xy$ case in section 4.4.

For probabilists, the interpretation of gelation in terms of *stochastic* models is a natural question, to be discussed in section 5.2.

In discussing general kernels, we shall often assume the kernel K is *homogeneous* with some exponent γ:

$$K(cx, cy) = c^{\gamma} K(x, y),\ 0 < c, x, y < \infty. \tag{11}$$

In fact one could use a weaker notion of asymptotic homogeneity:

$$\lim_{c \to \infty} c^{-\gamma} K(cx, cy) = \bar{K}(x, y),\ 0 < x, y < \infty. \tag{12}$$

Note that all except one of the kernels in table 1 is homogeneous, with exponents $-\frac{1}{6}, 0, \frac{1}{6}, \frac{7}{9}, 1, \frac{4}{3}$. Principle 1 says that for $\gamma \leq 1$ the kernel is non-gelling. For some time it has been widely accepted in the SM literature [92, 95] that for $\gamma > 1$ the kernel is gelling. The first general rigorous result was given only recently by Jeon [44, 45], who showed that $T_{\mathrm{gel}} < \infty$ provided

$$\exists \gamma > 1,\ 0 < c_1, c_2 < \infty \text{ such that } c_1 (xy)^{\gamma/2} \leq K(x, y) \leq c_2 xy.$$

Moreover it is believed that for $\gamma > 2$ the kernel is *instantaneously gelling*, that is $T_{\mathrm{gel}} = 0$. Precisely, an argument in [88] (rewritten rigorously in [22] in the discrete case) shows that $T_{\mathrm{gel}} = 0$ provided

$$\exists \gamma > 2\alpha > 2 \text{ such that } x^{\alpha} + y^{\alpha} \leq K(x, y) \leq (xy)^{\gamma/2}\ \forall x, y.$$

2.4 Self-similarity

Consider the continuous setting, and as above suppose the kernel K is homogeneous with some exponent γ. It is natural [35] to seek a solution which is *self-similar* (also called *self-preserving* or *scaling*), in the following sense.

$$n(x, t) = s^{-2}(t) \psi(x/s(t)) \tag{13}$$

where $\psi(x) \geq 0$ satisfies

$$\int_0^{\infty} x \psi(x)\, dx = 1. \tag{14}$$

Here the "1" is a normalization convention. As at (4), we want the mean density $\int x n(x, t)\, dx$ to be constant in time, which explains the s^{-2} term in (13). Of course, the interpretation of (13) is that clump mass scales with time as $s(t)$.

Following [95], here is a brief analysis of self-similarity. By substituting into (3), routine manipulations show that (13) is a solution provided

$$\frac{1}{2}\int_0^x K(y,x-y)\psi(y)\psi(x-y)\,dy \;-\; \psi(x)\int_0^\infty K(x,y)\psi(y)\,dy = w(2\psi(x)+x\psi'(x)) \qquad (15)$$

for some constant $w \neq 0$, and we may take $s(t)$ as the solution of

$$s'(t) = ws^\gamma(t). \qquad (16)$$

In fact the integrals may diverge at zero, in which case we simply replace (15) by its integrated version (the $\tau = 2$ case of (20) later). Solving (16),

$$s(t) \propto t^{\frac{1}{1-\gamma}},\ -\infty < \gamma < 1 \qquad s(t) \propto e^{wt}, \gamma = 1. \qquad (17)$$

The SM literature tends to take for granted the existence and uniqueness (up to scaling) of solutions of (15), and proceeds to speculations (see section A.1) on the asymptotic ($x \to 0,\ x \to \infty$) form of $\psi(x)$. Apparently nothing has rigorously been proved, outside the realm of the exact solutions. The solution in table 2 for $K(x,y) = 1$ (where $\gamma = 0$) is of form (13,17), with $\psi(x) = e^{-x}$ and $s(t) = t/2$. And the solution for $K(x,y) = x+y$, where $\gamma = 1$, is also of form (13,17), with $\psi(x) = (2\pi)^{-1/2}x^{-3/2}e^{-x/2}$ and $s(t) = e^{2t}$. In this connection, it has long been known that the two kernels $x+y$ and $\max(x,y)$ have no self-similar solution satisfying (14) and $\int_0^\infty \psi(x)dx < \infty$: see Drake [26] section 6.4 and Knight [48] respectively.

If a unique self-similar solution exists, it is natural to expect convergence to self-similarity from rather general initial configurations. See section 3.1 for a simple proof for $K(x,y) = 1$.

It has long been noted by numerical methods that certain of the kernels arising in table 1 (e.g. $K(x,y) = (x^{1/3}+y^{1/3})(x^{-1/3}+y^{-1/3})$ [35]) appear to have self-similar solutions which are roughly log-Normal. See [61, 98, 49] for recent work. It is sometimes stated in the SM literature that this is to be expected when large-small coalescences (rather than large-large) predominate. I haven't found any convincing mathematical elaboration of this assertion: see Appendix A.4 for further comments.

For the record, let us state explicitly some open problems implicit in this and previous sections.

Open Problem 2 *Consider a homogeneous kernel K with exponent $\gamma \leq 1$. Give rigorous proofs, under explicitly stated extra hypotheses, that* *(a) there exists a unique ψ satisfying (14) such that (13,17) is a solution of the continuous Smoluchowski coagulation equation.*

(b) For $\gamma < 1$ we have $\int_0^\infty \psi(x)dx < \infty$.

(c) The solution $n(x,t)$ of the discrete Smoluchowski coagulation equation with monodisperse initial configuration is asymptotically self-similar, in the sense that

$$\sup_x |s^2(t)n(x,t-t_0) - \psi(x/s(t))| \to 0 \text{ as } t \to \infty, \text{ for some } t_0. \tag{18}$$

(d) (18) remains true for initial configurations $n(x,0)$ satisfying specified "not too spread out" conditions, in continuous and discrete space, assuming aperiodicity of $n(x,0)$ in the discrete case.

In (18) we have asked for local (as in the *local* CLT) convergence of densities, but proving the weaker notion of convergence of distributions would be just as welcome.

For gelling kernels, we can seek self-similarity as $t \uparrow T_{\text{gel}}$. The continuous solution in table 2 for $K(x,y) = xy$ can be written as the special case

$$\psi(x) = (2\pi)^{-1/2}x^{-5/2}e^{-x/2}; \quad s(t) = |t|^{-2}, \tau = 5/2$$

of the general form

$$n(x,t) = s^{-\tau}(t)\psi(x/s(t)), \ -\infty < t < 0 \tag{19}$$

In this case $\int x\psi(x) = \infty$, that is the mass density is infinite, so we cannot (as in the non-gelling case) use conservation of mass density to say $\tau = 2$. Substituting into the Smoluchowski coagulation equation shows that (19) is a solution provided it satisfies the analog of (15) with τ in place of 2; but to avoid divergent integrals at zero we replace (15) by its integrated version

$$w\int_{x_0}^\infty \left(\tau x\psi(x) + x^2\psi'(x)\right)dx = -\int_0^{x_0} dx \int_{x_0-x}^\infty dy \ xK(x,y)\psi(x)\psi(y). \tag{20}$$

[95] give a non-rigorous analysis of the gelling case, and we incorporate their conclusions into the following open problem.

Open Problem 3 *Consider a homogeneous kernel K with exponent $1 < \gamma \le 2$, and suppose $0 < T_{\text{gel}} < \infty$. Give rigorous proofs, under explicitly stated extra hypotheses, that*

(a) There is a unique (up to scaling) solution ψ of (20), and for this solution $\tau = (3+\gamma)/2$. And $\int_0^\infty x\psi(x)dx = \infty$ while $\int_0^\infty x^2\psi(x)dx < \infty$.

(b) The solution $n(x,t)$ of the discrete Smoluchowski coagulation equation with monodisperse initial configuration is asymptotically self-similar as $t \uparrow T_{\mathrm{gel}}$, in the sense that for some a

$$n(x,t) \sim a(T_{\mathrm{gel}} - t)^{\frac{3+\gamma}{1-\gamma}} \ \psi(x(T_{\mathrm{gel}} - t)^{\frac{2}{\gamma-1}}) \text{ as } t \uparrow T_{\mathrm{gel}}, \tag{21}$$

uniformly on $\{x(T_{\mathrm{gel}} - t)^{\frac{2}{\gamma-1}} > x_0\}$.

(c) (21) remains true for initial configurations $n(x,0)$ satisfying specified "not too spread out" conditions, in continuous and discrete space, assuming aperiodicity of $n(x,0)$ in the discrete case, and where T_{gel} now depends on the initial configuration.

To connect (b) with (a), the conclusion of (a) implies (by setting up and solving the equation analogous to (16)) that

$$n(x,t) = |t|^{\frac{3+\gamma}{1-\gamma}} \ \psi(x|t|^{\frac{2}{\gamma-1}}) \tag{22}$$

is a self-similar solution of the Smoluchowski coagulation equation.

2.5 Other aspects of the Smoluchowski coagulation equations

(a) For the record, we mention some other aspects of the Smoluchowski coagulation equations which we shall not pursue in this review.

- *General polydisperse initial conditions.* The solutions presented in table 2 are the special solutions. Much of the literature studies solutions of the Smoluchowski coagulation equations from general ("polydisperse") initial configurations. Some explicit solutions for the three special kernels in table 2 and the general bilinear kernel $K(x,y) = A + B(x+y) + Cxy$, under polydisperse initial conditions, are discussed in [26] section 6.3., [17, 68, 71, 77, 78, 84]. Some discussion of physically reasonable or mathematically tractable initial configurations (e.g. in the continuous setting, the Gamma, log-Normal or $n(x,0) = x^{-\beta}, x \geq x_0$ densities) in the context of the "applied" kernels in table 1 can be found in [26] section 4.5.

- *Time to approach self-similarity* [98].

- *Numerical methods.* See [49] for references, and [66] for Monte Carlo procedures.

- *The inverse problem.* How to estimate the rate kernel K from experimental or observational data. [2, 59, 75].

(b) This paper deals only with "pure coalescing" models. But much of the scientific literature considers coalescence together with other effects, in particular

- fragmentation (splitting) [27]
- removal of clusters (sedimentation, condensation, crystalization) [41]
- continuous addition of new particles. [74]

In fact, much of the literature we cite relating to existence of solutions of the Smoluchowski coagulation equations deals with such more general settings. Whittle [104] provides a mathematical introduction to reversible mean-field models of coalescing and fragmentation, and Ernst [30] relates this topic to broader topics in statistical physics.

(c) There has been much study, mostly using Monte Carlo simulation, of fractal structure of cluster-cluster aggregation models, in the spirit of the well known DLA model of cluster growth by adding single particles. See Vicsek [99] Chapter 8 for a survey. In the setting of the Smoluchowski coagulation equations this possibility has classically been ignored (in specifying rate kernels, it is often assumed that clusters are spherical), but an assumed fractal exponent could be built into the kernel.

2.6 Hydrodynamic limits and reaction-diffusion processes

From the viewpoint of TP mathematics, the verbal description of the Smoluchowski coagulation equations in section 1.1 is just motivation: we can use the Smoluchowski coagulation equations as starting point for mathematical analysis, but we have not attempted to say that they arise as part of a more detailed rigorous stochastic model. To establish these rigorously as a *limit* of the type of model in section 1.1 is a topic called *hydrodynamics* or *propagation of chaos*. Lang and Nguyen [52] study a model of discrete particles performing Brownian motion in 3 dimensions, coalescing when they approach within a fixed distance, the diffusion rate of clusters being unaffected by cluster size. In an appropriate limit they justify that the cluster-size distribution does converge to the solution of the Smoluchowski coagulation equation with $K(x, y) = 1$. Undoubtedly more general results of this type can be proved, though there is a conceptual problem. Derivation of specific rate kernels K often presupposes that physical parameters are within certain ranges, so taking mathematical limits may not make much sense if we cannot preserve such constraints.

Conversely, there is SM discussion [46, 85] of models in the spirit of section 1.1 where the Smoluchowski coagulation equations do *not* provide satisfactory solutions over time-intervals of interest.

A more substantial body of recent mathematical literature concerns hydrodynamic limits for *reaction-diffusion* processes, where several types of particle diffuse and interact to produce new particles. But that work mostly focuses on equilibrium behavior and on finite number of types (see section 5.1 for elaboration), so has a different flavor from our size-asymptotics in irreversible coalescence.

3 Stochastic structures encoding solutions of the Smoluchowski coagulation equations

One answer to the question "what is the relationship between the deterministic Smoluchowski coagulation equations and stochastic models?" is to seek the type of limit theorems indicated in section 2.6. But we can pose the question differently: is there *any* rigorous stochastic model involving coalescence in which the exact solutions of the Smoluchowski coagulation equations appear as ergodic averages? It turns out that in 5 of the 6 cases in table 2 there are special constructions, to be described in section 3.1. Loosely, these involve replacing "physical space" of section 1.1 (in which we imagine particle clusters moving) with an "artificial" spatial structure. In section 3.2 we discuss duality (via time-reversal) between the deterministic Smoluchowski coagulation equations and deterministic pure fragmentation equations, which can be interpreted as expectations within branching-type stochastic processes. This idea of coalescence as the time-reversal of splitting is implicit in the special constructions of section 3.1, and is used explicitly in section 3.3 to give a general constructions for general kernels.

3.1 Special constructions

Construction 4 $K(x,y) = 1$*; continuous.*

Take the line $L = (-\infty, \infty)$ as "space". At each time t create a Poisson point process of marks on L, with rate $r(t)$, where $r(t) > 0$ is decreasing with t. Couple the point processes as t varies in the natural way: each point present at time t_1 remains present at time $t_2 > t_1$ with probability $r(t_2)/r(t_1)$, independently for different points.

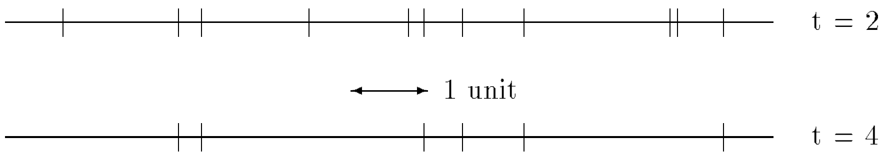

Figure 1. Construction for $K(x, y) = 1$; continuous

At time t there is a process of line segments (between successive marks). Writing "mass" for "length" and "cluster" for "line segment", the probability density for mass x per cluster is $\rho_t(x) = r(t) \exp(-xr(t))$ and the density of mass per unit length of L is

$$n(x, t) = r^2(t) \exp(-xr(t)). \tag{23}$$

As t increases, a mark disappears at rate $-r'(t)/r(t)$, so a tagged cluster of mass x will merge with a neighboring cluster of some mass y with rate

$$2\frac{-r'(t)}{r(t)}\rho_t(y) = 2\frac{-r'(t)}{r(t)}\frac{n(y,t)}{r(t)}.$$

Here the "2" comes from the two endpoints, and we appeal to the fact that adjacent line segments have independent lengths, as a property of the Poisson process. Choosing $r(t) = 2t^{-1}$ to solve $r'(t) = -\frac{1}{2}r^2(t)$ makes this rate equal $n(y, t)$. So the $n(x, t)$ satisfy the continuous Smoluchowski coagulation equation with $K(x, y) = 1$, and (23) is the density in table 2.

Remarks. Here $L = (-\infty, \infty)$ is our "artificial space". Construction 4 describes a stochastic model with extra structure (an ordering of intervals) and incorporating this extra structure gives a coalescing model rather different from the Smoluchowski coagulation equation. But the point is that the "ergodic densities" $n(x, t)$ in the model do indeed satisfy the Smoluchowski coagulation equation, even if this is not *a priori* obvious.

Construction 5 $K(x, y) = 1$*; discrete.*

This is the discrete analog of the previous construction. Put unit mass at each integer $-\infty < i < \infty$. Let an edge from i to $i + 1$ appear at a random time T with $P(T > t) = 2/(t+2) = G(t)$, say, independently for different edges.

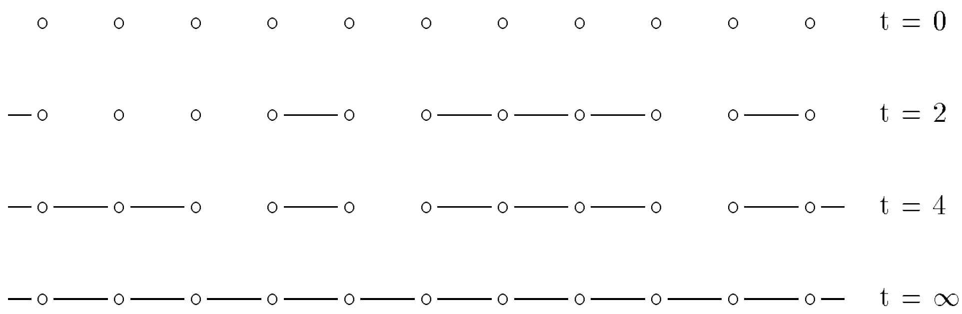

Figure 2. Construction for $K(x, y) = 1$; discrete

At time t a connected clusters has mass x with probability $\rho_t(x) = (1 + \frac{t}{2})^{-1}\left(\frac{t}{t+2}\right)^{x-1}$ and hence the density of mass-x clusters per unit length is

$$n(x, t) = (1 + \tfrac{t}{2})^{-2}\left(\frac{t}{t+2}\right)^{x-1}, \quad x = 1, 2, 3, \ldots. \tag{24}$$

Arguing as above, a tagged cluster of mass x will merge with a neighboring cluster of some mass y with rate

$$2\ \frac{-\frac{d}{dt}P(T > t)}{P(T > t)}\ \rho_t(y) = n(y, t).$$

So the $n(x, t)$ satisfy the discrete Smoluchowski coagulation equation with $K(x, y) = 1$, and (24) is the density in table 2.

The general solution for $K(x, y) = 1$. We can use the same method to show that for any initial configuration (discrete or continuous) with $0 < m_1(0) < \infty$ and $m_0(0) = 1$ we have asymptotic self-similarity in the following sense:

$$t\int_0^{at} n(x, t)dx \to 1 - e^{-a/m_1(0)} \text{ as } t \to \infty,\ 0 < a < \infty. \tag{25}$$

Start at time $t = 0$ with a stationary renewal process of marks on $L = (-\infty, \infty)$, with inter-renewal density $n(x, 0)$. Let the marks disappear at independent times T with $P(T > t) = 2/(t+2) = G(t)$. At time t the marks form a renewal process with some inter-renewal distance L_t. Writing the density of L_t as $n(x, t)/G(t)$, the analysis above shows that $n(x, t)$ satisfies the Smoluchowski coagulation equation. But classical (and easy) results on thinning of renewal processes (see e.g. [24] Prop. 9.3.1) imply that $G(t)L_t$ converges in distribution to the exponential$(1/m_1(0))$ distribution, establishing (25).

Without this easy probability argument, rather tedious analysis [50] seems needed to prove (25).

Remark. The key feature of these two constructions is that there is an "invariance" property (stationarity under shifts of the line) which enables us to define the deterministic quantities $n(x,t)$ as ergodic averages. The next constructions have more sophisticated invariance properties, which we will not attempt to say precisely, but which enable the $n(x,t)$ to be defined rigorously as ergodic averages.

Construction 6 *$K(x,y) = x + y$; discrete.*

Take unit mass at positions $0, 1, 2, \ldots$ and connect with edges $(i, i+1)$. Make each of these atoms the progenitor of a Galton-Watson branching process with Poisson(1) offspring distribution, and draw the individuals as unit masses and the parent-child relationships as edges. This construction gives a random infinite tree, with root $\star$ at position 0, illustrated in the bottom part of figure 3. Grimmett [38] first described this tree, and showed that it arises as a $n \to \infty$ limit of uniform random n-vertex trees. The finite-n property that "the tree has the same distribution relative to each vertex" extends to the limit infinite tree: see [3] for one statement of this invariance property. Now regard each edge as appearing at a random time T with exponential(1) distribution, independently for different edges. At times $0 < t < \infty$ we see a configuration of "clusters" (finite trees), rooted at the vertex nearest the path-to-infinity. By invariance, the distribution of cluster size at time t is the distribution of the cluster rooted at $\star$, given that $\star$ is the root of a cluster, and this is just the size of total population in a Galton-Watson branching process with Poisson$(1 - e^{-t})$ offspring distribution. This total population has mean e^t, and so the density of clusters of size x is

$$n(x,t) = e^{-t} B(1 - e^{-t}, x); \ x = 1, 2, 3, \ldots. \tag{26}$$

A computation ([10] Lemma 3.2(b)) shows that the way clusters merge in this example follows the Smoluchowski coagulation equation with $K(x,y) = x + y$. Section 4.3 elaborates this construction.

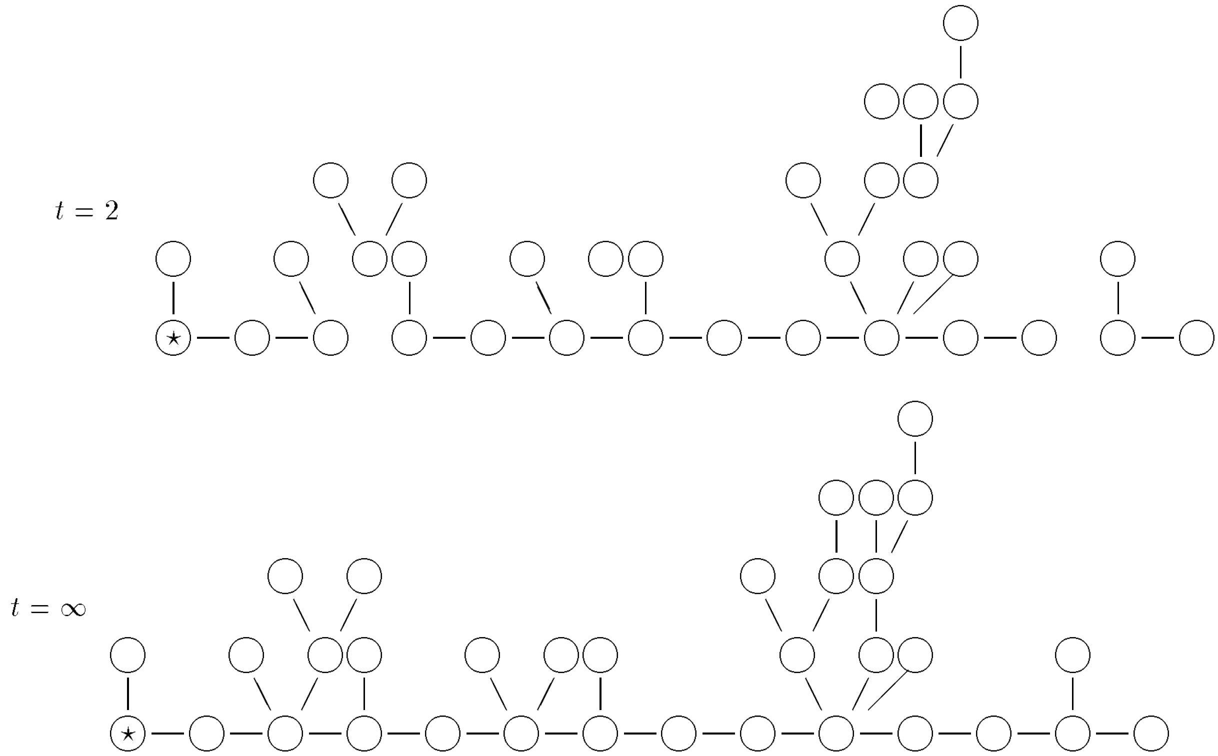

Figure 3. Construction for $K(x, y) = x + y$; discrete

Construction 7 *$K(x, y) = x + y$; continuous.*

It is natural to regard Construction 4 as the continuous limit of Construction 5. It is true, but less obvious, that we can take an analogous continuous limit in Construction 6. Recall the $t = \infty$ random graph in Construction 6. We viewed each vertex as having mass 1, and each edge as having length 1. It turns out that the number of vertices withing distance d of a specified vertex grows as order d^2. So if we rescale by taking each vertex to have mass $1/n$ and each edge to have length $1/n^{1/2}$, then the mass of the region within distance 1 of a specified point is bounded away from 0 and ∞, and we can take a $n \to \infty$ limit. The limit is called the *self-similar continuum random tree* (SSCRT), and is described rigorously in [4], [5] section 2.5. Figure 4 illustrates the SSCRT: of course, by (statistical) self-similarity there are smaller and smaller branches not shown. The lines in figure 4 are part of the "skeleton" of the SSCRT; all the mass is on the "leaves".

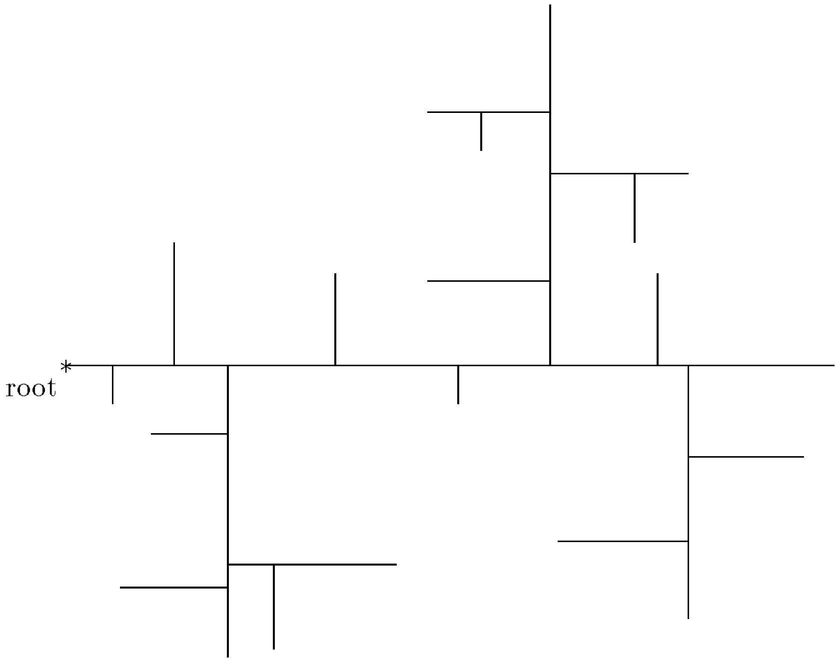

Figure 4. The SSCRT

For our purposes here, the SSCRT plays the role that the line $L = (-\infty, \infty)$ plays in Construction 4. Take time interval $-\infty < t < 0$. At each time t, construct a Poisson process of marks on the skeleton, with rate $|t|$ per unit length, coupled in the natural way as t varies. Cutting the SSCRT at these marks splits it into subtrees of finite mass; write $n(x, t)$ for the density of mass-x subtrees. For fixed t, this is the rescaled limit of Construction 6 with t' defined via $e^{-t'} = e^{-t} n^{-1/2}$. Taking limits in (26) gives

$$n(x, t) = (2\pi)^{-1/2} e^{-t} x^{-3/2} e^{-e^{-2t} x/2}$$

the formula we recorded in table 2.

Construction 8 $K(x,y) = xy$; *discrete.*

This construction, illustrated in figure 5, was used for different purposes in [6].

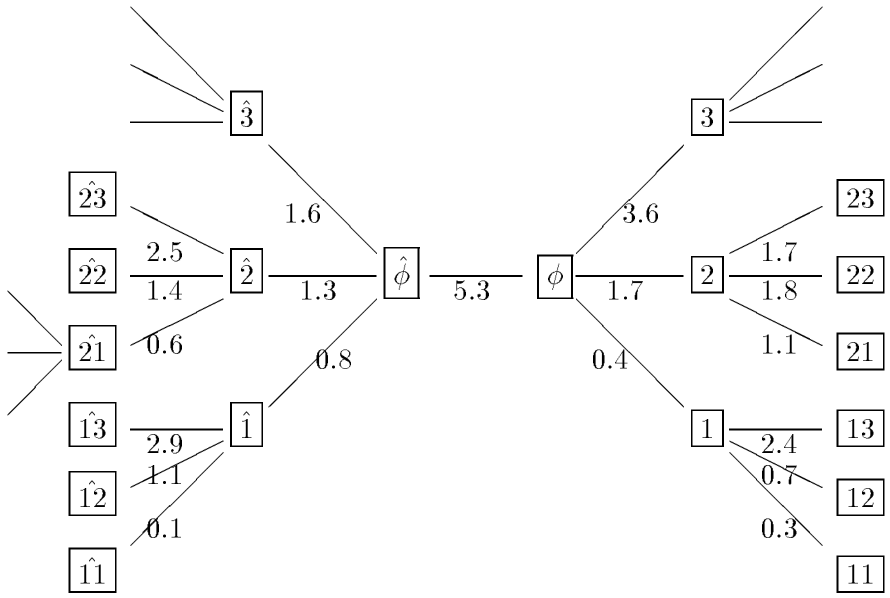

Figure 5. An infinitary tree

Start with a distinguished edge between vertices ϕ and $\hat{\phi}$. Let $0 < \tau_1^\phi < \tau_2^\phi < \ldots$ be the points of a Poisson (rate 1) point process on R^+, create new vertices $1, 2, \ldots$ and create edges (ϕ, i) with edge-weights τ_i^ϕ. Recursively, for each created vertex v let $0 < \tau_1^v < \tau_2^v < \ldots$ be the points of a Poisson (rate 1) point process on R^+, create new vertices $v1, v2, \ldots$ and create edges (v, vi) with edge-weights τ_i^v. (Figure 5 shows only the first 3 children and early generations.) Repeat for descendants of $\hat{\phi}$. Finally, give the distinguished edge a weight chosen from the uniform (Lebesgue) measure on $(0, \infty)$. This construction yields a σ-finite measure on the space of all edge-weights. As explained rigorously in [6], we can view this random object as a $n \to \infty$ limit of a process of i.i.d. random edge-weights on the complete bipartite graph on $2n$ vertices, and the finite-n invariance property extends to an invariance property for the limit object: "the tree has the same distribution relative to each vertex".

At each time $t > 0$ we may consider the subgraph consisting of only those edges with weight $\leq t$, and let the clusters at time t be the connected components of this subgraph. Figure 6 illustrates $t = 0.75$.

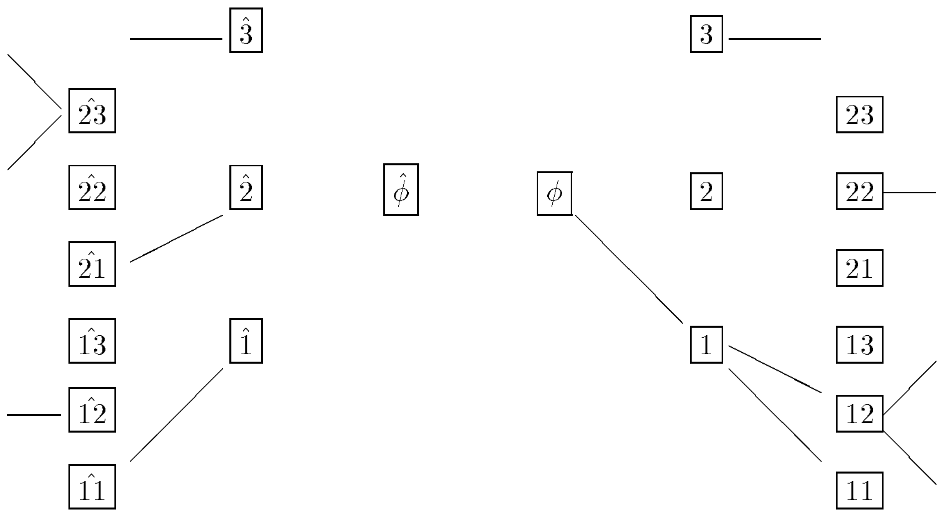

Figure 6. Construction for $K(x, y) = xy$; discrete

The cluster containing a specified vertex at time $t \leq 1$ is a Galton-Watson branching process with Poisson(t) offspring, and so has size distribution $B(t, x)$ given by (5). This is the size-biasing of the cluster-size density $n(x, t)$, and so

$$n(x, t) = x^{-1} B(t, x).$$

For a cluster of size x at time t, as t increases each vertex grows a new edge at rate 1, and so the rate of merging with some size-y cluster is

$$xB(t, y) = xyn(y, t).$$

So the $n(x, t)$ satisfy the discrete Smoluchowski coagulation equation with $K(x, y) = xy$,

Remark. In contrast to the previous constructions, there seems no easy way to take limits to obtain a construction for the *continuous* case $K(x, y) =$

xy. Rather sophisticated ideas are needed – see section 4.4.

Remark. There is a long history, going back to Flory [34], of using branching process models in the theory of polymerization. The idea that certain such models were equivalent to the Smoluchowski coagulation equation with certain kernels seems to have emerged slowly: a clear discussion is given by Ziff [106]. Our three discrete constructions are in the same spirit as the discussion in [106], but that paper has in mind some imprecise notion of "ensemble of clusters", while our point is that by using the constructions with σ-finite invariant measures we can rigorously define stochastic models where ergodic averages evolve as the Smoluchowski coagulation equation.

3.2 Dual splitting models

In the spirit of the Smoluchowski coagulation equations for pure coalescence, one can write down deterministic equations for pure fragmentation. We adopt the continuous setting (the discrete case is analogous). Consider a *splitting kernel* $S(l;x),\ 0 < x < l$. Assume that a cluster of mass l splits at rate $S(l;x)$ into two fragments of masses x and $l-x$, where the ordering of $\{x, l-x\}$ is random, so $S(l;x) = S(l;l-x)$. Write as usual $n(x,t)dx$ for the average number of clusters of mass $\in [x, x+dx]$ per unit volume. Then the deterministic *pure fragmentation* equation is

$$\tfrac{d}{dt}n(l;t) = -n(l;t) \int_0^l S_t(l;x)\, dx \ + \ 2\int_0^\infty n(l+y;t)S_t(l+y;l)\, dy \quad (27)$$

where we have more generally allowed time-dependence in the splitting kernel.

Consider now the *duality formula*

$$n(x,t)n(y,t)K_t(x,y) = 2n(x+y,t)S_t(x+y;x). \quad (28)$$

The duality relationship is as follows. If $n(x,t)$ is a solution of the Smoluchowski coagulation equation with time-dependent kernel K_t, then (reversing the direction of time) $n(x,t)$ is a solution of (27) for S_t defined at (28); and conversely. As we shall see, duality typically changes a time-independent kernel to a time-dependent kernel, Table 3 gives the dual splitting kernels for the special solutions in table 2. In these examples, the dual splitting kernel has the form $S_t(l;x) = a(t)S(l;x)$ and so the time-dependence can be removed by a deterministic time-change.

Write $b(i) = i^{i-2}/i!$.

table 3: the dual splitting kernel $S_t(l;x)$

$K(x,y)$	1	$x+y$	xy
discrete	$\frac{2}{t(t+2)}$ $0 \leq t < \infty$	$\frac{e^{-t}}{2(1-e^{-t})}\frac{x(l-x)b(x)b(l-x)}{b(l)}$ $0 \leq t < \infty$	$\frac{1}{2t}\frac{x(l-x)b(x)b(l-x)}{b(l)}$ $0 \leq t \leq 1$
continuous	$2t^{-2}$ $0 \leq t < \infty$	$(8\pi)^{-1/2}e^{-t}l^{5/2}x^{-3/2}(l-x)^{-3/2}$ $-\infty < t < \infty$	$(8\pi)^{-1/2}l^{5/2}x^{-3/2}(l-x)^{-3/2}$ $-\infty < t < 0$

Given a splitting kernel S, there is a natural stochastic model of fragmentation, the Markovian branching-type process where different clusters fragment independently according to the rate kernel S. There is a simple connection between the stochastic process and the deterministic equations (27): the mean frequency of cluster-masses in the stochastic model evolves *exactly* as (27). (We mention this because the analogous assertion for pure coalescence is false – cf. section 4.1). The issue of self-similar solutions (clearly analogous to *stable type structure* [60] for supercritical branching processes) for pure fragmentation was studied by Brennan and Durrett [19]. We summarize their results in Appendix A.3. An initially promising idea is to use branching process theory with tractable special splitting kernels to obtain, via the duality relation (28), explicit solutions of the Smoluchowski coagulation equation for further kernels K, but unfortunately (53) this leads to time-dependent kernels. Appendix A.4 explores this idea further.

3.3 General constructions

In this section we outline one approach to the problem of defining abstract probabilistic structures which encode the solutions of the Smoluchowski coagulation equation for a general kernel K. This approach is closely analogous to the theory [3] of *asymptotic fringe distributions*. We consider the discrete case, and abstract the idea of Construction 5. Figure 7 illustrates the construction, where we imagine the initial $t = 0$ configuration having a single mass-1 particle at each integer position $-\infty < x < \infty$. At a typical time t we see clusters, each cluster being an interval of particles (pictured as the particles between successive vertical lines). Mathematically, such a process is succinctly represented by a sequence $(\xi_i; -\infty < i < \infty)$, where $\xi_i > 0$ indicates the time at which the cluster ending with particle i coalesces with the cluster beginning with particle $i+1$.

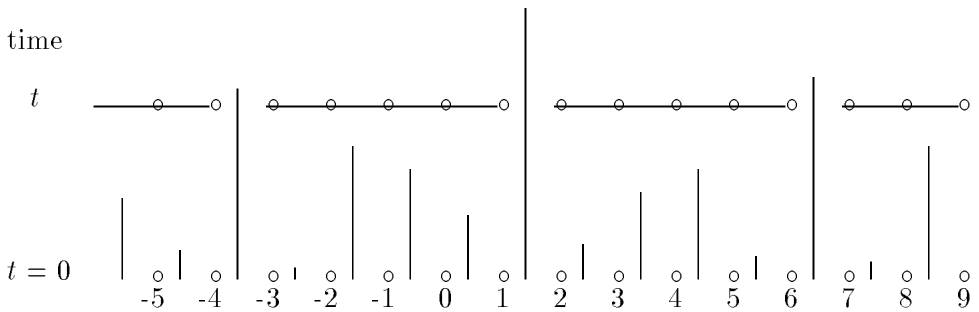

Figure 7. A general construction

It can be shown that such a construction is possible, for $0 \le t < T_{\mathrm{gel}}$, with the property:

> (*) at each time t the left endpoints of clusters form a stationary ergodic process with cluster-size distribution $m_1(t)n(x,t)$.

In other words, the chance that particle 0 is the first particle in a size-x cluster is $n(x,t)$. To outline the construction, fix t_0 and create at time t_0 a stationary renewal process with inter-renewal distribution $m_1(t_0)n(x,t_0)$. Then run time backwards from t_0 to 0, and split each cluster according to the dual splitting kernel (28), independently for each cluster. This defines a process with property (*) on $0 \le t \le t_0$, representable as $(\xi_i^{(t_0)})$, where $\xi_i^{(t_0)} = \infty$ if i is the final particle in a time-t_0 cluster, and otherwise is the time at which particles i and $i+1$ are split into distinct clusters. We now let $t_0 \to \infty$ and define (ξ_i) as a subsequential weak limit of the $(\xi_i^{(t_0)})$. It is not hard to check that property (*) remains true in the limit.

One might hope that we could arrange that the left endpoints of the clusters formed a *renewal process* at each time t, but the following argument shows this is impossible in general. Consider the kernel with $K(1,2) > 0$ and $K(x,y) = 0$ otherwise. Take an initial configuration with clusters of masses 1 and 2. Suppose this process was represented as a renewal process at time 0 and at time ∞. Then at time ∞ there would be clusters of masses $1,2$ and 3, but there could be no successive clusters of masses $(1,2)$, so it could not be a renewal process.

We pictured the clusters as linear chains, but it is perhaps more natural to regard them as trees, by specifying that when two clusters merge we pick at random (uniformly) one vertex from each cluster, and join these two vertices by an edge. Thus the cluster containing vertex 0 in figure 7 merges just after time t with the cluster shown on its left, and this merger might create a new edge $\leftrightarrow$ as follows.

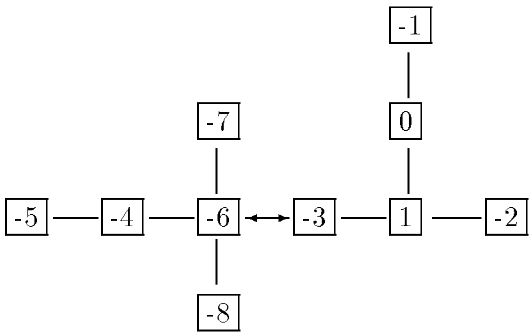

Figure 8. The general construction, pictured as a tree

We may define the stochastic process $(\mathcal{T}(t); t \geq 0)$ where $\mathcal{T}(t)$ is the tree containing vertex 0 at time t. This provides a rigorous formalization of the notion of "the history of coalescences containing a typical particle in the Smoluchowski coagulation equation". Detailed study of the cases $K(x,y) = x+y$ and xy is in [13].

The construction extends without essential change to the continuous setting. Here property (*) becomes

> at each time t there is a stationary ergodic point process on the line, in which the inter-point distances have density $m_1(t)n(x,t)$.

And the tree-process $(\mathcal{T}(t))$ becomes a process of "continuum trees" in the spirit of Construction 7.

4 Stochastic Models: the finite-volume setting

4.1 The stochastic coalescent

The Smoluchowski coagulation equations provide an *infinite-volume* mean-field description of coalescence in terms of deterministic equations. The corresponding *finite-volume* mean-field description is intrinsically stochastic. In the discrete setting, fix N and consider a state-space consisting of unordered (multi)-sets $\mathbf{x} = \{x_1, \ldots, x_m\}$ where the x_i are positive integers summing to N. So $\mathbf{x}$ represents a configuration with clusters of masses $x_1, \ldots, x_m$. We can now define a continuous-time finite-state Markov chain by declaring

$$\text{each pair } \{x_i, x_j\}, j \neq i \text{ coalesces into a cluster of mass } x_i + x_j$$
$$\text{at rate } K(x_i, x_j)/N. \tag{29}$$

The elementary way to formalize this idea is by taking the state-space as $\mathbf{n} = (n_1, n_2, \ldots, n_N)$, where n_x represents the number of mass-x clusters and $\sum_x n_x = N$. Then the transitions are of the form

$$(n_1, \ldots, n_N) \to$$
$$(n_1, \ldots, n_{i-1}, n_i - 1, n_{i+1}, \ldots, n_{j-1}, n_j - 1, n_{j+1}, \ldots, n_{i+j-1}, n_{i+j} + 1, n_{i+j+1}, \ldots)$$

with rate $K(i,j)n_i n_j/N$. This model was perhaps first introduced by Marcus [56], and re-introduced by several authors [36, 81], in particular by Lushnikov [54] as a model of gelation. We call it the *Marcus-Lushnikov process* $\mathbf{ML}^{(N)}(t)$. The state of this process at time t may be written in two equivalent ways. We may write $\mathbf{ML}^{(N)}(x,t)$ for the (random) number of mass-x clusters. Alternatively, we may write $\mathbf{ML}_i^{(N)}(t)$ for the mass of the i'th largest cluster. The Marcus-Lushnikov process is the natural stochastic analog of the discrete Smoluchowski coagulation equation, when we study only finite-sized clusters (see section 5.1).

For developing a mathematical theory, a slightly different formulation is often more convenient. For any model of coalescence with finite total mass, the total mass is conserved over time, so we may rescale and assume the total mass equals 1. So consider the state space consisting of finite or infinite configurations $\mathbf{x} = \{x_i\}$ with $x_1 \geq x_2 \geq \ldots > 0$ and $\sum_i x_i = 1$. Define the *stochastic coalescent* with kernel K to be the Markov process

$\mathbf{X}(t) = (X_i(t); i \geq 1)$ on this state space whose time-dynamics are described informally by

$$\text{each pair } \{x_i, x_j\}, j \neq i \text{ coalesces into a cluster of mass } x_i + x_j$$

$$\text{at rate } K(x_i, x_j). \tag{30}$$

This differs from (29) in that the coalescence rate is does not depend on N. But note that for a homogeneous kernel, i.e.

$$K(cx, cy) = c^\gamma K(x, y),\ 0 < c, x, y < \infty,$$

the Marcus-Lushnikov process and the stochastic coalescent are the same process up to time-space rescaling:

$$X_i(t) = N^{-1}\mathbf{ML}_i^{(N)}(tN^{1-\gamma}). \tag{31}$$

Thus for a homogeneous kernel, whereas the Marcus-Lushnikov process is formally a different process with different state-space for different N, (31) permits rephrasing in terms of a single process with a single state-space, the stochastic coalescent. In particular, the stochastic coalescent provides a natural setting for studying $N \to \infty$ asymptotics of Marcus-Lushnikov type processes. Our discussion deals with homogeneous kernels for simplicity, but one expects the same asymptotic behavior to hold for asymptotically homogeneous (12) kernels, using the limit $\bar{K}$ to specify the stochastic coalescent.

We defer to section 5.4 technical issues in making precise the definition of *stochastic coalescent*. In the following three sections we discuss, from the modern theoretical stochastic processes viewpoint, the standard stochastic coalescent for the three special kernels 1, $x + y$ and xy (*Standard* as in "standard Brownian motion", i.e. a scaling convention). These standard stochastic coalescents have constructions closely related to those of section 3, and appear naturally as $N \to \infty$ limits of the Marcus-Lushnikov processes. The SM literature on Marcus-Lushnikov processes emphasizes combinatorial methods, briefly reviewed in section 4.5.

4.2 Kingman's coalescent

We start by giving a construction. Take independent exponential, rate $\binom{k}{2}$, r.v.'s $(\xi_k, k \geq 2)$. Since $E\sum_{k=2}^\infty \xi_k = \sum_{k=2}^\infty 1/\binom{k}{2} = 2$ we can define random times $0 < \ldots < \tau_3 < \tau_2 < \tau_1 < \infty$ by $\tau_j = \sum_{k=j+1}^\infty \xi_k$. Take $(U_j, j \geq 1)$

independent uniform on $(0,1)$. For each j, draw a vertical line from (U_j, τ_j) down to $(U_j, 0)$. See figure 9.

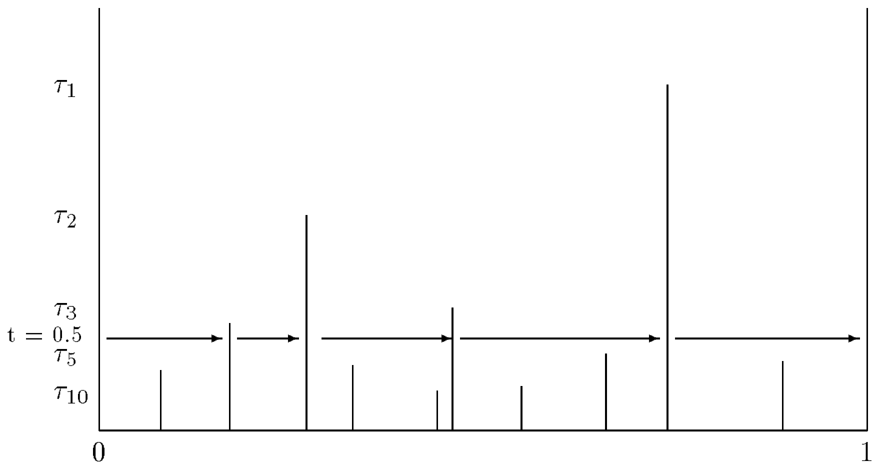

Figure 9. Kingman's coalescent

The vertical axis shows time. At time t the construction splits the unit interval $(0,1)$ into j subintervals, where j is defined by $\tau_j < t < \tau_{j-1}$, and where the endpoints of the subintervals are $\{0, 1, U_1, \ldots, U_{j-1}\}$. Figure 9 illustrates $t = 0.5$, with 5 subintervals. Writing $\mathbf{X}(t)$ for the lengths of these subintervals, the process $\mathbf{X}$ is a version of the stochastic coalescent with $K(x,y) = 1$, and this version is called *Kingman's coalescent.* The construction goes back to Kingman [47]. Kingman's coalescent has been used extensively in mathematical population genetics [83], where the emphasis is of the number of "lines of descent" (clusters, in our terminology) and mutations along lines of descent. This emphasis is rather different from our emphasis on masses of clusters.

It is easy to show (see Appendix A.5) that Kingman's coalescent is the *unique* version of the $K(x,y) = 1$ stochastic coalescent such that

$$X_1(t) = \max_i X_i(t) \to 0 \text{ a.s. as } t \downarrow 0. \tag{32}$$

In our terminology, (32) singles out $\mathbf{X}$ as the *standard* $K(x,y) = 1$ stochastic coalescent. The connection with the $K(x,y) = 1$ Marcus-Lushnikov process is that, if the initial distributions satisfy

$$N^{-1}\mathbf{ML}_1^{(N)}(0) \ \stackrel{d}{\to}\ 0 \text{ as } N \to \infty \tag{33}$$

then

$$(N^{-1}\mathbf{ML}^{(N)}(Nt), 0 < t < \infty) \ \xrightarrow{d}\ (\mathbf{X}(t), 0 < t < \infty) \qquad (34)$$

in the natural sense of weak convergence of l_1-valued processes on the time-interval $(0, \infty)$.

Note that

$$E\tau_j = \sum_{k=j+1}^{\infty} 1/\binom{k}{2} = \frac{2}{j}; \ \ \mathrm{var}\ \tau_j = \sum_{k=j+1}^{\infty} 1/\binom{k}{2}^2 \sim \frac{4}{3j^3},$$

and that τ_j satisfies the assumptions of the (non-identically-distributed) central limit theorem for independent sums. As in the CLT for renewal processes, it follows that $N(t)$, the number of clusters at time t, is asymptotically Normal$(\frac{2}{t}, \frac{2}{3t})$ as $t \downarrow 0$. From this, and standard results about i.i.d. uniform order statistics, it is routine to derive various $t \downarrow 0$ asymptotics for Kingman's coalescent. Writing $C(x, t)$ for the number of clusters of mass $\leq x$ at time t,

$$\sup_{0 \leq x < \infty} |C(xt, t) - \tfrac{2}{t}(1 - e^{-2x})| \to 0 \text{ a.s. } . \qquad (35)$$

The first-order $N \to \infty$ asymptotics of the $K(x, y) = 1$ Marcus-Lushnikov process under initial assumption (33) are now rather clear. For fixed $t > 0$, (34) implies that for large N the Marcus-Lushnikov process at time Nt has a finite number of clusters with masses distributed approximately as $N\mathbf{X}(t)$. And (35) implies that, if $t_N \downarrow 0$ sufficiently slowly, then $\mathbf{ML}^{(N)}(Nt_N)$ consists of about $2/t_N$ clusters with empirical mass distribution approximately exponential (mean $Nt_N/2$). How fast can t_N decrease, for this to remain true? It is not hard to see that the following natural condition is sufficient: the proportion of mass initially in mass $\Omega(Nt_N)$ clusters is negligible, that is

$$N^{-1} \sum_{x > \varepsilon N t_N} \mathbf{ML}^{(N)}(x, 0) \ \xrightarrow{p}\ 0, \ \ \text{each } \varepsilon > 0.$$

It is interesting to observe that a Gaussian limit for fluctuations of cluster frequencies of $\mathbf{X}(t)$ as $t \downarrow 0$ follows from classical results. Recall that *Brownian bridge* $B^0(\cdot)$ appears as a limit of empirical distributions for i.i.d.r.v.'s (η_i) with continuous distribution function F:

$$N^{-1/2}\left(\sum_{i=1}^{N} 1_{(\eta_i \leq x)} - NF(x);\ x \geq 0\right) \ \xrightarrow{d}\ (B^0(F(x)); x \geq 0).$$

Now the N spacings obtained from $N-1$ independent uniform points on $[0,1]$ are distributed as $(\frac{\eta_1}{S},\ldots,\frac{\eta_N}{S})$, where the (η_i) are independent exponential(1) and $S=\sum_{i=1}^N \eta_i$. It follows that

$$A(x,N) = \text{number of spacings of length} \leq x$$

satisfies

$$N^{-1/2}\left(A(x/N,N) - N(1-e^{-x})\right) \stackrel{d}{\to} B^0(1-e^{-x}).$$

This is classical, e.g. [65] Theorem 6.4. Since $C(x,t) = A(x,N(t))$, we find

$$(t/2)^{1/2}\left(C(xt,t) - \tfrac{2}{t}(1-e^{-2x})\right) \stackrel{d}{\to} B^0(1-e^{-2x}) + \sqrt{2/3}(1-e^{-2x})Z \quad (36)$$

where Z is standard Normal, independent of B^0.

Variance calculations of this type for the constant-rate stochastic coalescent can be found in [87, 25], only the latter making the explicit connection with Kingman's coalescent.

There is a simple connection between Kingman's coalescent and Construction 4 (which exhibited the solution of the continuous Smoluchowski coagulation equation for $K(x,y)=1$ via a process of coalescing intervals on the *infinite* line). Given Kingman's construction, rescale the unit interval $[0,1]$ to the interval $[-\frac{m}{2},\frac{m}{2}]$ and rescale the times (τ_j) to $(m\tau_j)$. Then the $m\to\infty$ limit is the process in construction 5. Of course, the appearance of the exponential distribution in (35) fits in with its appearance as the self-similar solution of the continuous Smoluchowski coagulation equation. See (49) for the corresponding conjecture for general non-gelling kernels.

4.3 The additive coalescent and the continuum random tree

Cayley's formula (see e.g. [97] Chapter 2) says there are N^{N-2} trees on N labeled vertices. Pick such a tree T_∞ at random. To the edges e of T_∞ attach independent exponential(1) r.v.'s ξ_e. Write $F(t)$ for the forest obtained from T_∞ by retaining only the edges e with $\xi_e \leq t$. Write $\mathbf{Y}^{(N)}(t)$ for the vector of sizes of the trees comprising $F(t)$. It can be shown that $(\mathbf{Y}^{(N)}(t); 0\leq t<\infty)$ is the Marcus-Lushnikov process associated with the additive kernel $K(x,y)=x+y$, with monodisperse initial conditions. This construction was apparently first explicitly given by Pitman [63], although various formulas associated with it had previously been developed in the combinatorial literature [62, 105] and the SM literature [40]. Here are two examples of simple formulas. The number $D^{(N)}(t)$ of clusters satisfies

$$D^{(N)}(t) - 1 \stackrel{d}{=} \text{Binomial}(N-1, e^{-t})$$

> The cluster-sizes (in random order) of $\mathbf{Y}^{(N)}(t)$, given $D^{(N)}(t) = d$, are distributed as $(\eta_i; 1 \le i \le d | \sum_{i=1}^{d} \eta_i = N)$, where the (η_i) are i.i.d. Borel(1).

Construction 6 was the discrete $N \to \infty$ limit of this construction, and we saw in (26) how the solution of the discrete Smoluchowski coagulation equation for $K(x,y) = x+y$ arises in this limit. We can make a continuous-space construction analogous to Construction 7. That is, take the construction above and rescale by taking each vertex to have mass $1/N$ and each edge to have length $1/N^{1/2}$. The $N \to \infty$ limit is called the *continuum random tree* (CRT), and is described rigorously in [5, 7]. (In the SSCRT of Construction 7 the root is attached to an infinite baseline; the CRT here is compact, with total mass 1). Now similarly to Construction 7, at each time $-\infty < t < \infty$ construct a Poisson process of marks on the skeleton, with rate e^{-t} per unit length, coupled in the natural way as t varies. Figure 10 illustrates the CRT and the marks, for some fixed t. Cutting the CRT at these marks splits it into subtrees of finite mass; write $\mathbf{X}(t)$ for the vector of masses of these subtrees at time t. Then (as we expect by analogy with the discrete case above) the process $(\mathbf{X}(t), -\infty < t < \infty)$ evolves as the stochastic coalescent for $K(x,y) = x+y$. This process, the *standard additive coalescent*, is studied in detail in [12].

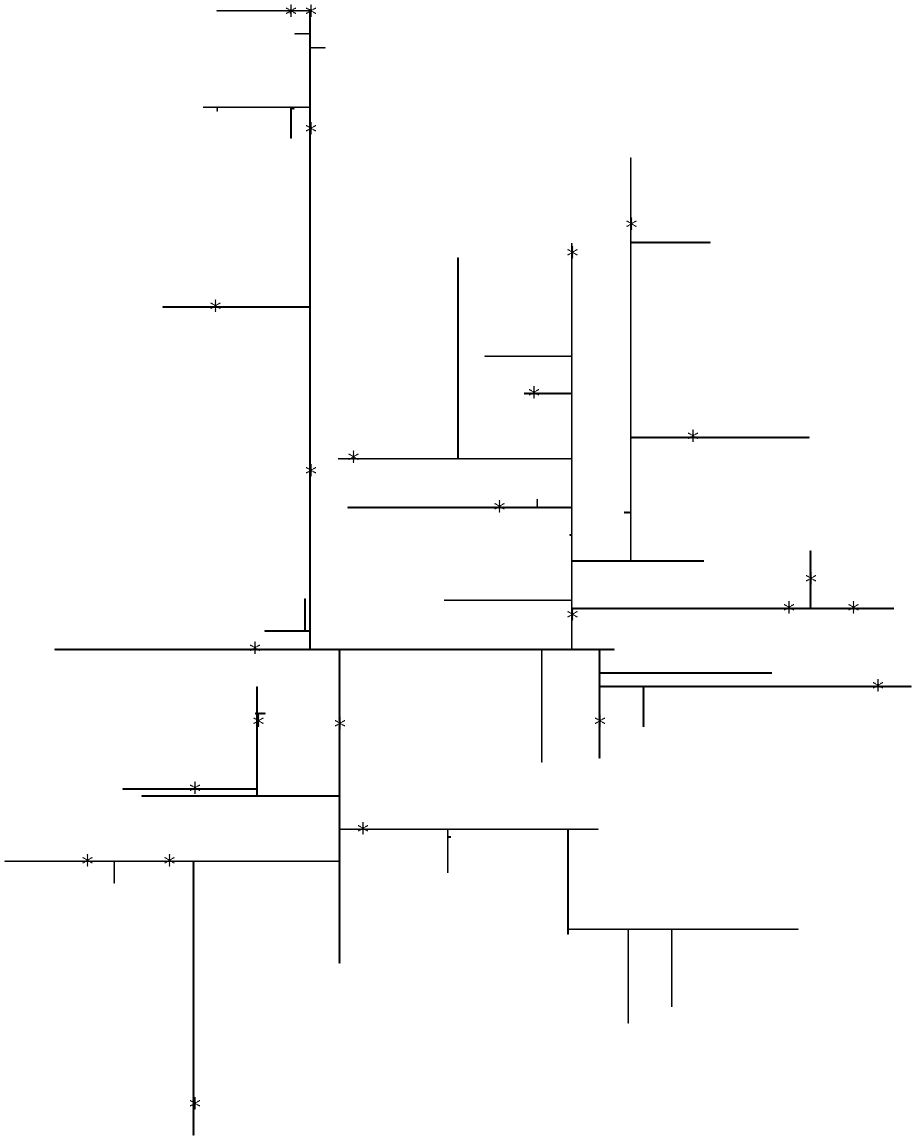

Figure 10. The CRT and the additive coalescent

4.4 Random graphs and the multiplicative coalescent

In the random graph model $\mathcal{G}(N,p)$, there are N vertices, and each of the $\binom{N}{2}$ possible edges is present with probability p, independently for different edges. Study of this model goes back to Erdős and Rényi [28, 29], and the monograph Bollobás [18] surveys results up to 1984. Sizes of the connected components have been a classical topic of study. A moment's thought shows that for the kernel $K(x,y) = xy$ the Marcus-Lushnikov process $\mathbf{ML}^{(N)}(t)$ with monodisperse initial configuration is exactly the process of component sizes in $\mathcal{G}(N, 1-e^{-t/N})$. Recall from table 2 that $n(x,t) = x^{-1}B(t,x)$ is the solution of the Smoluchowski coagulation equation for $K(x,y) = xy$ in the discrete setting. The fact that expectations behave like the deterministic solution in the pre-gelation interval, i.e. that

$$N^{-1}E\mathbf{ML}^{(N)}(x,t)(t) \to n(x,t) \text{ as } N \to \infty \text{ for fixed } x \geq 1, t < 1 \tag{37}$$

is classical [28] and easy (relative to a given vertex, the random graph looks locally like a Galton-Watson branching process). Barbour [15] proved the central limit theorem: for fixed x,

$$N^{-1/2}(\mathbf{ML}^{(N)}(x,t)(t) - Nn(x,t)) \xrightarrow{d} \text{Normal}(0, n(x,t)(1+(t-1)x^2 n(x,t))) \tag{38}$$

and Pittel [64] established joint convergence to the mean-zero Gaussian process with covariances

$$(t-1)xyn(x,t)n(y,t), \ y \neq x. \tag{39}$$

(Note that these results are stated in the literature for tree-components, but for $t < 1$ only $O(1)$ vertices are outside tree-components: [18] p. 97). Remarkably, van Dongen and Ernst [93] had previously given formula (39) and its extension to two times (t_1, t_2), in the context of the multiplicative Marcus-Lushnikov process.

It is interesting to probe more deeply into the behavior of the stochastic model around the "critical time" corresponding to the gelation time $T_{\text{gel}} = 1$ in the deterministic model. Rather detailed rigorous results are known: see [43] for recent exhaustive analysis. We give a probabilistic discussion, following [9]. Recall $\mathbf{ML}_1^{(N)}(t)$ is the mass of the largest cluster in the Marcus-Lushnikov process, that is the size of the largest component of $\mathcal{G}(N, 1-e^{-t/N})$. It is classical [28, 18] that

$$\mathbf{ML}_1^{(N)}(t) \quad = \Theta(\log N) \quad , t < 1$$

$$= \Theta(N^{2/3}) \quad ,t = 1$$
$$= \Theta(N) \quad ,t > 1.$$

The next step is the idea that the giant component emerges over the time interval $1 \pm \Theta(N^{-1/3})$. That is, for large s, at time $t = 1 - s/N^{1/3}$ there are numerous components whose sizes are small constants times $N^{2/3}$, and no larger components, whereas at time $t = 1 + s/N^{1/3}$ there is a unique component whose size is a large multiple of $N^{2/3}$, and other components whose sizes are small constants times $N^{2/3}$. Bollobás [18] Chapter 6 develops some aspects of this idea, via $s \to \infty$ asymptotics. It was subsequently realized that it is natural to study emergence of the giant component by studying the process $(\mathbf{Z}_N(t) : -\infty < t < \infty)$, where $\mathbf{Z}_N(t)$ is defined to be $N^{-2/3}$ times the vector of component sizes of $\mathcal{G}(N, N^{-1} + tN^{-4/3})$. Aside from a negligible time-change, $\mathbf{Z}_N(t)$ evolves as the stochastic coalescent, started at time $-N^{-1/3}$ with N clusters of masses $N^{-2/3}$ each. We can now let $N \to \infty$, and it turns out [9] that

$$\mathbf{Z}_N \stackrel{d}{\to} \mathbf{Z} \tag{40}$$

where the limit process $(\mathbf{Z}(t); -\infty < t < \infty)$ is defined to be the *standard multiplicative coalescent.* The novel feature is that the total mass $\sum_i Z(t,i)$ is infinite. As shown in [9], the natural state space is the space l_2 of configurations $\mathbf{x} = (x_i)$ with $\sum_i x_i^2 < \infty$. As remarked in section 3.1, we do not have any simple "process" explanation of the special solution in table 2 for the continuous kernel $K(x,y) = xy$

$$n(x,t) = (2\pi)^{-1/2} x^{-5/2} \exp(-t^2 x/2). \tag{41}$$

So it is surprising that there is a process description of the standard multiplicative coalescent $\mathbf{Z}$, or at least of its distribution $\mathbf{Z}(t)$ at fixed time t. Take $(B(s); 0 \leq s < \infty)$ to be inhomogeneous reflecting Brownian motion on $[0, \infty)$ with drift rate $t - s$ at time s, and with $B(0) = 0$. Then the vector of lengths of excursions of B from 0 is distributed as $\mathbf{Z}(t)$ [9]. One simple corollary of this representation applies when t is large and positive. There, the process $B(s)$ initially stays close to the deterministic path $b(s) = ts - \frac{1}{2}s^2$, over $0 < s < 2t$, implying that the "giant component" of $\mathbf{Z}(t)$ has mass approximately $2t$. The connection between the standard multiplicative coalescent and the special solution (41) is as follows. Write

$$\tilde{n}(x,t)dx = E(\text{ number of clusters of } \mathbf{Z}(t) \text{ with mass } \in [x, x + dx]).$$

Then as $t \to -\infty$, the function $\tilde{n}(\cdot, t)$ approaches $n(\cdot, t)$ in the following sense: if $x_a(t)$ is defined by

$$\int_{x_a(t)}^{\infty} n(x,t)dx = a$$

then

$$\int_{x_a(t)}^{\infty} \tilde{n}(x,t)dx \to a. \tag{42}$$

In particular,

$$\max_i Z_i(t) \to 0 \text{ a.s. as } t \to -\infty. \tag{43}$$

It is natural to guess that the standard multiplicative coalescent is in some sense the "essentially unique" version of the multiplicative coalescent on $-\infty < t < \infty$ satisfying (43): the precise result is proved in [11].

The convergence (40) extends to polydisperse Marcus-Lushnikov processes as follows. For $r = 2, 3$ write $\sigma_r(N) = \sum_i (\mathbf{ML}_i^{(N)}(0))^r$, and write $c(N) = (\sigma_3(N))^{2/3}/(\sigma_2(N))^2$. The appropriate scaling is

$$\mathbf{Z}_N(t) = c^{1/2}(N)\mathbf{ML}^{(N)}(N(c(N)t + \tfrac{1}{\sigma_2(N)}))$$

and Proposition 4 of [9] shows that the conclusion

$$\mathbf{Z}_N \stackrel{d}{\to} \mathbf{Z}$$

remains valid provided

$$\mathbf{ML}_1^{(N)}(0) = o(\sigma_3^{1/3}(N)). \tag{44}$$

Note that in the case where $\mathbf{ML}^{(N)}(x, 0) \approx N\rho(x)$ for some $\rho(x)$ not depending on N, with $\rho(x) = x^{-\beta+o(1)}$ as $x \to \infty$, the condition $\beta > 4$ is enough to imply (44).

Turning to the SM literature, the solution (41) of the Smoluchowski coagulation equation is usually called "unphysical" because the total mass density $m_1(t)$ is infinite. The description of the multiplicative coalescent illuminates what's going on: we are measuring mass relative to the size of large clusters at the critical time, rather than in absolute terms.

The Smoluchowski coagulation equations with $K(x, y) = xy$ have been studied many times in the SM literature. In particular, Ziff et al [107, 31] observe (41) arising as a "scaling limit" as $t \uparrow 1$ for the monodisperse initial conditions, and discuss the extent to which this remains true for more general initial conditions, and also discuss different models of post-gelation behavior. McLeod [58] showed that with the initial configuration $n(x,0) = \alpha e^{-\alpha x}$ the continuous Smoluchowski coagulation equation has explicit solution

$$n(x,t) = \frac{\alpha e^{-(t+\alpha)x} I_1(2x\alpha^{1/2}x^{1/2})}{x^2 t^{1/2}}$$

on $0 \le t \le \alpha$, where I_1 is the modified Bessel function. In the stochastic setting, van Dongen and Ernst [93] gave a detailed study of the multiplicative Marcus-Lushnikov process. They derived the variance-covariance formulas (38,39), and also (p. 911) give a heuristic discussion of the $1 \pm \Theta(N^{-1/3})$ transition, from the viewpoint of the breakdown in the Gaussian approximation. It is not clear exactly when the explicit connection with random graph theory was made in the SM literature: [21] is one account from 1991. Conversely, even present-day accounts of random graphs [43] make no mention of the Smoluchowski coagulation equation connection.

Let us briefly discuss post-gelation behavior. For $t > 1$, the deterministic quantities $n(x,t)$ derived as the limit (37) densities of size-x components in the random graph model are no longer solutions of the Smoluchowski coagulation equation, because in the random graph model the gel and the sol are interacting. In physics terminology, these $n(x,t)$ arise in a *Flory* model of gelation. The Smoluchowski coagulation equation itself represents the *Stockmayer* model in which sol and gel do not interact, and in this case the post-gelation solution has the surprisingly simple form

$$n(x,t) = n(x,1)t^{-1}, \ t \ge 1$$

which goes back to [80]. This hasn't been studied in the random graphs literature, but a probabilistic elaboration will be given in [10] section 3.7.

4.5 Combinatorial approaches

A different approach to the monodisperse Marcus-Lushnikov process is to seek to write down and exploit a combinatorial expression for the exact distribution $p(\mathbf{n};t) = P(\mathbf{ML}^{(N)}(x,t) = n_x, x \ge 1)$. For the multiplicative kernel (i.e. the classical random graph process) this is easy because $\mathcal{G}(N, 1 - e^{-t/N})$ has an intrinsic description which does not involve analyzing time-evolution, and we obtain

$$p(\mathbf{n};t) = N! \prod_k \frac{1}{n_k!} \left(\frac{q(k, 1-e^{-t/N}) e^{-tk(N-k)/N}}{k!} \right)^{n_k}$$

where $q(k,p)$ is the chance that $\mathcal{G}(k,p)$ is connected. And $q(k,p)$ is determined by an elementary recurrence formula ([18] exercise 7.1).

Similarly, there is a discrete reformulation of the construction of Kingman's coalescent which enables one to write down a partition function [16].

In the additive case, such results go back to Lushnikov [55], and have two somewhat different extensions. Hendricks et al. [40] give an expression for the partition function for the kernel $K(x,y) = A + B(x+y)$. And implicit in [55] (see [40, 20] for clearer expositions) is the following result.

Lemma 9 *Consider the Marcus-Lushnikov process with $K(x,y) = xf(y) + yf(x)$ for some f, with monodisperse initial configuration. Then*

$$p(\mathbf{n};t) = N! \prod_k \frac{(b_k(t))^{n_k}}{n_k!}$$

where $(b_k(t))$ are the solutions of the differential equations

$$\frac{d}{dt} b_k(t) = \sum_{i=1}^{k-1} i f(k-i) b_i(t) b_{k-i}(t) - (N-k) f(k) b_k(t)$$

with $b_k(0) = 1_{(k=1)}$.

van Dongen and Ernst [93, 87] give the most detailed SM treatment of the special cases of the stochastic coalescent: see also Tanaka and Nagazawa [81, 82].

5 Stochastic coalescence with general kernels

In sections 4.2 - 4.4 we saw that the behavior of the Marcus-Lushnikov process and the stochastic coalescent for the three special kernels is mostly well understood. In contrast, very little is rigorously known about general kernels. Our main purpose in this section is to pose explicit open problems for general kernels.

5.1 The WLLN for the Marcus-Lushnikov process

In looking at the SM literature from a TP viewpoint, perhaps the most striking feature is the lack of attention paid to the fundamental "weak law of large numbers" issue: does the discrete Smoluchowski coagulation equation really represent a limit in the Marcus-Lushnikov process? We state this in the simplest setting of monodisperse initial configurations, though there are parallel problems in the polydisperse and the continuous-space settings. To see why the problem arises at all, note that (in contrast to the setting of pure fragmentation – section 3.2) the mean frequencies $N^{-1}\ E\mathbf{ML}^{(N)}(x,t)$ in the Marcus-Lushnikov process do *not* evolve exactly as the discrete Smoluchowski coagulation equation.

Open Problem 10 *For a general kernel K, let $n(x,t)$ be the solution of the discrete Smoluchowski coagulation equation and let $\mathbf{ML}^{(N)}(t)$ be the Marcus-Lushnikov process, each with monodisperse initial conditions. Prove that, as $N \to \infty$ for fixed t,*

$$N^{-1}\ \mathbf{ML}^{(N)}(x,t)\ \stackrel{p}{\to}\ n(x,t),\ x \geq 1 \tag{45}$$

provided either of the following hold.
(a) $K(x,y) = o(xy)$.
(b) $t < T_{\mathrm{gel}}$.

This problem is closely related to the question of *uniqueness* of the solution $n(x,t)$, which in section 2 we implicitly assumed, but in fact the only general result [39] proving uniqueness assumes $K(x,y) = O(x+y)$, which implies non-gelling. In case (a), recent results of Jeon [44, 45] imply (45), *assuming* uniqueness. Tom Kurtz (personal communication) outlines similar results. Note that in the multiplicative case (45) fails for $t > T_{\mathrm{gel}} = 1$, so that the hypothesis "(a) or (b)" is about as weak as possible.

Open Problem 10 is related to standard results on *density-dependent population processes* ([32] Chapter 11). Roughly, such a process has a finite number of types of "molecules" which react in some finite number of ways, the total number N of "atoms" being constant in time. For such a process one has not only a weak law of large numbers but also Gaussian approximations (see section 5.5). But the "finite number of types" condition is essential, and hence in our setting (interpret a cluster of mass x as a type-x molecule) these standard results can seldom be applied. The recent results mentioned above rely on truncation arguments to approximate by the finite case. Note that the kernel $K(x,y) = xy$ has the special property that the evolution of $(\mathbf{ML}^{(N)}(x,t), 1 \leq x \leq x_0)$ is itself Markov (in other words, we can lump together clusters of mass $> x_0$), so that the standard results do imply Gaussian asymptotics of form (38,39) for fixed x, y as noted in [93].

5.2 Gelling kernels

Perhaps the most interesting aspect of the subject is the general interpretation of gelation in terms of stochastic models of coalescence. The natural counterpart to Open Problem 10, dealing with post-gelation behavior, is as follows.

Open Problem 11 *In the setting of Open Problem 10, prove that for fixed* $t > T_{\mathrm{gel}}$ *there exists* $\varepsilon(t) > 0$ *such that*

$$\lim_{x_0 \uparrow \infty} \limsup_{N \to \infty} P\left(N^{-1} \sum_{x > x_0} x \mathbf{ML}^{(N)}(x,t) > \varepsilon(t)\right) = 1.$$

In words, after gelation some non-vanishing proportion of the total mass is in clusters whose size is not $O(1)$.

Open Problem 11 is one weak interpretation of gelation, but further conjectures are pure speculation concerning how much of the well-understood qualitative behavior for the multiplicative coalescent extends to more general gelling kernels. Consider the following three known properties of the Marcus-Lushnikov process for $K(x,y) = xy$.

(a) At time $t > T_{\mathrm{gel}}$ the giant component has mass $\Omega(N)$.

(b) At time $t > T_{\mathrm{gel}}$ the WLLN assertion of Open Problem 10 no longer holds.

(c) The times T_N (resp. T'_N) at which $N^{-1}\mathbf{ML}_1^{(N)}(t)$ first exceeds ε (resp. $1-\varepsilon$) satisfy $(T'_N - T_N)/T_N \stackrel{p}{\to} 0$.

Property (c) is too weak to use as a criterion for gelation, because it holds for $K(x,y) = x + y$. I conjecture that (a) and (b) are too strong, in that they do not hold for gelling kernels with exponent $1 < \gamma < 2$. A more plausible stochastic interpretation of gelation is

> a unique "giant cluster" of $\mathbf{ML}^{(N)}(t)$ can be identified while its mass is still $o(N)$.

More precisely:

Open Problem 12 *If* $T_{\mathrm{gel}} < \infty$, *prove there exist random times* $T_N \stackrel{p}{\to} T_{\mathrm{gel}}$ *such that*

$$\sup_{t \geq T_N} \mathbf{ML}_2^{(N)}(t)/\mathbf{ML}_1^{(N)}(t) \stackrel{p}{\to} 0$$

$$N^{-1}\, \mathbf{ML}_1^{(N)}(T_N) \stackrel{p}{\to} 0.$$

Lemma 9 suggests one approach to studying the issues in Open Problems 11 and 12 for kernels of the special form $K(x,y) = xf(y) + yf(x)$. An alternative special form of kernel (noted in [106]) is

$$K(x,y) = \frac{2f(x)f(y)}{f(x+y) - f(x) - f(y)} \tag{46}$$

where $f(1) = 1$ and $f(x+y) > f(x) + f(y)$. Consider the solution $n(x,t)$ of the discrete Smoluchowski coagulation equation for such a kernel with monodisperse initial configuration, and consider

$$s(t) = \sum_x f(x)n(x,t).$$

It is easy to check $\frac{d}{dt}s(t) = s^2(t)$ and hence $s(t) = (1-t)^{-1}$, $0 \leq t < 1$. This suggests (but does not quite prove) that $T_{\text{gel}} = 1$. It is shown in [8] that for kernels of this special form (46) one can use stochastic calculus to analyze the Marcus-Lusnikov process and prove the conclusion of Open Problem 12.

5.3 Dynamical scaling and entrance boundaries

We digress to mention an issue of mathematical formulation. When studying stochastic processes, a natural way to take limits is as time increases to infinity or to a critical point, as in Open Problems 2 and 3, which in the language of statistical physics assert *dynamical scaling* under the monodisperse initial distribution, and assert *universality* when the same behavior holds in the polydisperse setting. In the context of a finite-volume stochastic model such as the Marcus-Lushnikov process, as $t \to \infty$ the mass ultimately forms a single cluster; the interesting question to study is how this happens. For a $N \to \infty$ limit stochastic coalescent process, this question asks for the behavior at *small* time rather than at large time. We saw in sections 4.2 - 4.4 the existence of a *standard* stochastic coalescent for the three special kernels 1, $x+y$ and xy, which originates with the mass in infinitesimally small clusters. Parts of Open Problems 14 and 15 below seek generalizations of this behavior. In the language of theoretical stochastic processes, we are seeking the *entrance boundary* for the general stochastic coalescent. Physically, the underlying story from section 1.1 will typically make sense only when cluster-masses are in some finite range $[x_0, x_1]$, so neither of the limit procedures ($x_0 \downarrow 0$ or $x_1 \uparrow \infty$) corresponding to small-time and large-time limits seems more natural than the other.

5.4 Open problems for the general stochastic coalescent

Intuitively, the state space for the stochastic coalescent $\mathbf{X}(t)$ specified at (30) consists of unordered sets $\{x_i\}$ of cluster-masses, with $x_i > 0$ and $\sum_i x_i = 1$. We can formalize this in several ways, e.g.
(i) by taking the decreasing ordering $x_1 \geq x_2 \geq \ldots$ of cluster-masses, so the state space becomes the infinite-dimensional simplex;
(ii) identifying $\{x_i\}$ with the measure $\sum x_i \delta_{x_i}(\cdot)$.
Evans and Pitman [33] give a careful account of the "technical bookkeeping" issues involved in formalization (e.g. one wishes to track the previous history of mergers of a particular cluster at time t). The details are not important for us: we shall just write l_1 for the state space. To use general theory of continuous-space Markov processes we desire some regularity property, and it seems natural to expect the *Feller property*: the distribution at a fixed time t varies continuously with the initial distribution. Evans and Pitman [33] prove the Feller property under the conditions

$$K(0,0) = 0;\ |K(x_1,y_1) - K(x_2,y_2)| \leq k_0(|x_2 - x_1| + |y_2 - y_1|)\ \forall 0 \leq x_i, y_i \leq 1.$$

This condition holds for 6 of the 9 kernels in table 1. A natural minimal assumption, satisfied by all 9 kernels, is

$$K(x,y) \text{ is a symmetric, continuous function } (0,1)^2 \to [0,\infty). \tag{47}$$

Open Problem 13 *Prove that, under assumption (47), the stochastic coalescent exists as a Feller process on l_1.*

This is conceptually just a technical issue: of more substance are the following open problems, representing the stochastic analogs of Open Problems 2 and 3. Write

$$\mathbf{F}(x,t) = \sum_i X_i(t) 1_{(X_i(t) > x)}$$

for the total mass in clusters of mass $> x$, in some version $\mathbf{X}(t)$ of the stochastic coalescent. Write $\mathbf{X}^{(N)}$ for the stochastic coalescent started with N clusters of mass $1/N$ each, i.e. the rescaling (31) of the monodisperse Marcus-Lushnikov process. As usual, we also seek analogs of convergence assertions for suitable polydisperse initial distributions.

Open Problem 14 *Consider a homogeneous kernel K with exponent $\gamma \leq 1$. Suppose there exists a unique ψ satisfying (14) such that $n(x,t) = s^{-2}(t)\psi(x/s(t))$ is a solution of the continuous Smoluchowski coagulation* *equation, for $s(t)$ satisfying (17). Write $T_{\text{init}} = 0$ if $\gamma < 1$, $T_{\text{init}} = -\infty$ if $\gamma = 1$. Give rigorous proofs, under explicitly stated extra hypotheses, that*

(a) there exists a version $(\mathbf{X}(t), T_{\text{init}} < t < \infty)$ of the stochastic coalescent such that

$$\sup_x |\mathbf{F}(xs(t), t) - \int_x^\infty y\psi(y)dy| \to 0 \ a.s. \ as \ t \downarrow T_{\text{init}},$$

and so in particular

$$\max_i X_i(t) \to 0 \ a.s. \ as \ t \downarrow T_{\text{init}}. \tag{48}$$

(b) If $\gamma < 1$ then the version in (a) is the unique *version satisfying (48).*

(c) As $N \to \infty$,

$$(\mathbf{X}^{(N)}(-s^{-1}(\tfrac{1}{N}) + t); s^{-1}(\tfrac{1}{N}) < t < \infty) \ \xrightarrow{d} \ (\mathbf{X}(t); T_{\text{init}} < t < \infty)$$

for some t_0, where s^{-1} is the inverse function of $s(t)$.

For Kingman's coalescent, these results are straightforward, and indeed contained (in slightly different form) in our section 4.2 discussion. For the additive coalescent see [12].

Note that Open Problems 10 and 14 involve the behavior of the Marcus-Lushnikov process for non-gelling kernels over different time-regimes. Specifically, for a homogeneous kernel with $\gamma < 1$, Open Problem 10 involves $t = \Omega(1)$ whereas Open Problem 14 involves $t = \Omega(N^{1-\gamma})$. The corresponding conjecture for intermediate times, that is for $t_N \to \infty$ with $t_N = o(N^{1-\gamma})$, is that

$$\sup_x |N^{-1} \sum_{x' > xs(t)} x' \mathbf{ML}^{(N)}(x', t_N) - \int_x^\infty y\psi(y)dy| \ \xrightarrow{p} \ 0 \text{ as } N \to \infty. \tag{49}$$

The next Open Problem seeks to generalize deeper structure of the multiplicative coalescent. Recall that the multiplicative coalescent took values in l_2.

Open Problem 15 *Consider a homogeneous kernel K with exponent $1 < \gamma \leq 2$. Suppose $0 < T_{\text{gel}} < \infty$, and suppose the conclusions (a,b) of Open Problem 3 hold. Give rigorous proofs, under explicitly stated extra hypotheses, that there exists a version $(\mathbf{X}(t); -\infty < t < \infty)$ of the l_2-valued stochastic coalescent with the following properties.*

(a) Writing $\mathbf{X}(t) = (X_{(1)}(t), X_{(2)}(t), \ldots)$ *in decreasing order of cluster-masses,*

$$X_{(1)}(t) \to 0 \ a.s. \ as \ t \downarrow -\infty$$

$$X_{(1)}(t) \to \infty \ and \ X_{(2)}(t) \to 0 \ a.s. \ as \ t \uparrow \infty.$$

(b) There is a self-similar solution (22) of the Smoluchowski coagulation equation

$$n(x,t) = |t|^{\frac{3+\gamma}{1-\gamma}} \ \psi(x|t|^{\frac{2}{\gamma-1}})$$

which satisfies the analog of (42).

(c) As $N \to \infty$

$$\left(\sigma_N^{-1/\gamma} \mathbf{X}^{(N)}(t_N + \sigma_N t); \ -\tfrac{t_N}{\sigma_N} \leq t < \infty\right) \ \xrightarrow{d} \ (\mathbf{X}(t); -\infty < t < \infty)$$

for certain constants t_N, σ_N.

One expects the constants t_N, σ_N in (c) to grow as powers of N, with exponents depending on γ, but it is not clear (even heuristically) whether these exponents can be obtained from the exponent in Open Problem 3 which relates only to the behavior near the critical point. *Uniqueness* of the stochastic coalescent is a subtle issue even in the multiplicative and additive cases [11, 12], so we hesitate to speculate about general kernels.

5.5 Gaussian fluctuations

The weak law of large numbers (Open Problem 10) asserts that the solution of the Smoluchowski coagulation equation gives the first-order approximation of the Marcus-Lushnikov process for large N. It is natural to seek a second-order approximation involving Gaussian fluctuations of order $N^{1/2}$. As noted in section 5.1, in the restricted case where there are only a finite number of different cluster-sizes (so the limit Gaussian process takes values in some R^d), such a result is part of the general weak convergence theory of [32] Chapter 11. But presumably the conclusions continue to hold without that restriction, at least under mild extra assumptions.

Open Problem 16 *In the setting of Open Problem 10 (with perhaps extra regularity hypotheses), show that*

$$N^{-1/2}(\mathbf{ML}^{(N)}(x,t) - Nn(x,t)) \ \xrightarrow{d} \ Z(x,t)$$

in the sense of weak convergence of R^∞-valued processes, where $(Z(x,t); x = 1,2,\ldots, 0 \le t < T_{\rm gel})$ is the mean-zero R^∞-valued Gaussian diffusion specified by

$$\begin{aligned} dZ(x,t) &= -\sum_y K(x,y)Z(x,t)n(y,t)\,dt \\ &\quad + \sum_y \sqrt{K(x,y)n(x,t)n(y,t)}\,dB_{\{x,y\}}(t) \qquad (50) \end{aligned}$$

where the $B_{\{x,y\}}(t)$ are independent standard Brownian motions.

See van Dongen [87] for SM discussion of approximations in the spirit of Open Problem 16.

Another way to think about Gaussian approximations is in the context of the (continuous-space) stochastic coalescent at small times – cf. (36) for the case of the constant kernel.

Open Problem 17 *Suppose, as in Open Problem 14(a), that $(\mathbf{X}(t), T_{\rm init} < t < \infty)$ is the standard version of the stochastic coalescent for a kernel K which is homogeneous with exponent $\gamma \le 1$. Prove that as $t \downarrow T_{\rm init}$,*

$$\left(\frac{1}{s^{1/2}(t)}\left(\mathbf{F}(xs(t),t) - \int_x^\infty y\psi(y)dy\right); 0 < x < \infty\right) \stackrel{d}{\to} (Z(x); 0 < x < \infty)$$

where $Z(x)$ is a certain mean-zero Gaussian process.

As stated, this involves looking at single times, but there is a natural extension to a time-indexed Gaussian process $(Z(x,t'))$. Finally, is the spirit of the intermediate-time empirical WLLN (49) there is a corresponding Gaussian approximation conjecture, featuring the same limit Gaussian process $(Z(x))$ as in Open Problem 17. Ways of seeking to calculate the covariance structure of $Z(x)$ are mentioned in section A.6.

6 Envoi

With gross oversimplification, we can point to two waves of interest in our topic. The first was the deterministic theory developed by physical chemists in the 1960s and surveyed by Drake [26]. The second was the stochastic theory developed by statistical physicists in the early 1980s, culminating in the work of van Dongen, Ernst, Hendriks and others. Perhaps the open problems in this survey and concurrent technical work such as [9, 33, 45] will stimulate a third wave of interest amongst theoretical probabilists.

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A Appendix

A.1 Self-similarity and tail behavior

In the settings where one expects self-similar solutions of the Smoluchowski coagulation equation (section 2.4), there is some SM literature ([53, 89, 91, 94] – surveyed in [95]) on the $t \to \infty$ behavior of $n(x,t)$ for *fixed* x, or for $x(t) \gg s(t)$. To illustrate the type of result, in the homogeneous setting [94] argues that for fixed $t < T_{\mathrm{gel}}$, as $x \to \infty$

$$n(x,t) \sim A(x,t)e^{-xz(t)}$$

where

$$(\nu < 1) \quad A(x,t) \approx A(t)x^{-\theta}$$

and when $\nu = 1$ there is also the possibility

$$A(x,t) \approx \exp(-d(t)x^{\beta}), \text{ some } 0 < \beta < 1.$$

Here ν is the "balance" parameter

$$K(1,y) \sim y^{\nu+o(1)} \text{ as } y \to \infty.$$

This result is derived from heuristic self-consistency arguments: essentially, what is shown is that

$$n(x,t) \sim A(x,t)e^{-x^{\omega}z(t)}$$

is not possible for $\omega \neq 1$.

It is generally believed that these "large deviation" results reflect $x \to 0$ or ∞ behavior of the presumed self-similar solution $\psi(x)$. This is far from clear from the TP viewpoint.

See [51] for numerical results for the kernels $(x+y)^\gamma$ and $(xy)^{\gamma/2}$.

A.2 Synthesizing self-similar solutions

A way of synthesizing self-similar solutions is described in [26] section 6.4 and attributed to Wang [100]. Write

$$K(x,y) = \frac{F(x,y)}{\psi(x)\psi(y)} \tag{51}$$

and substitute into (15). Then (15) becomes

$$\tfrac{1}{2}\int_0^x F(y, x-y)dy \;-\; \int_0^\infty F(x,y)dy = w(2\psi(x) + x\psi'(x)). \tag{52}$$

Thus if we start with some arbitrary positive kernel function F, and if we can solve (52) for ψ which can be normalized to (14), then ψ is a self-similar solution to the Smoluchowski coagulation equation with kernel K defined at (51).

A.3 Self-similar solutions for the pure fragmentation equation

We summarize results in Brennan and Durrett [19], promised from section 3.2. Consider a splitting kernel which is homogeneous

$$S(cl; cx) = c^{\alpha-1}S(l;x)$$

for some $\alpha > 0$. Then the pure fragmentation equation (27) has a self-similar solution

$$n(x,t) = t^{2/\alpha}\psi(xt^{1/\alpha})$$

where ψ is defined as follows. Let $\ldots < V_{-1} < 0 < V_0 < V_1 < \ldots$ be the renewal times of a stationary renewal process with inter-renewal density

$$P(V_{i+1} - V_i \in dv) = e^{-v}S(1; e^{-v}).$$

Let ϕ be the probability density function of the random variable

$$Y = \sum_{m=0}^{\infty} \xi_m \exp(-\alpha V_m)$$

where the (ξ_m) are independent exponential(1) r.v.'s. Then

$$\psi(x) = \alpha x^{\alpha-2}\phi(x^\alpha).$$

Moreover in the special case $S(l;x) = l^{\alpha-1}$ we have

$$\psi(x) = \alpha \exp(-x^\alpha)/\Gamma(2/\alpha).$$

This looks promising, suggesting that by duality we can get coalescing kernels K with these ψ as self-similar solutions. Unfortunately, applying the duality formula (28) gives

$$K_t(x,y) = \frac{2\Gamma(2/\alpha)(x+y)^{\alpha-1}}{\alpha t^{2/\alpha}} \exp\left((x^\alpha + y^\alpha - (x+y)^\alpha)t\right) \tag{53}$$

and we cannot time-change to a time-independent kernel, except in the case $\alpha = 1$ which corresponds to the familiar kernel $K(x,y) = \text{constant}$.

A.4 Constant-rate interval-splitting

Recall from section 3.2 the notion of *dual splitting kernel* $S_t(l;x)$. Here is another example. Take $[0,1]$ as our "artificial space". At time $t = 0$ we see the unit interval; as t increases, the interval is split into subintervals according to the rule: each interval $[a,b]$ splits at rate 1 at a uniform random position. Thus the splitting kernel is

$$S_t(l;x) = l^{-1}. \tag{54}$$

Write L_t for the size-biased interval length density at time t, so that the density of L_t is

$$f_t(l) = ln(l,t)/a(t) \tag{55}$$

where $a(t) = \int ln(l,t)\, dl$. It is easy to see that $\log L_t$ has exactly the distribution of $\prod_{i=1}^{Q_t} \log \xi_i$, where Q_t has Poisson(t) distribution and ξ_i has the "size-biased uniform" density $2x$ on $0 < x < 1$. So for large t the distribution of $\log L_t$ is approximately Normal$(-\mu t, \sigma^2 t)$ for certain constants μ, σ. Combining with (55) gives an approximation

$$n(x,t) \approx \frac{a(t)x^{-2}}{\sigma\sqrt{2\pi t}} \exp\left(-\frac{(\mu t + \log x)^2}{2\sigma^2 t}\right).$$

Combining with (54) and substituting into (28) shows that the dual coalescence rate kernel is approximately of the form $b(t)K(x,y)$ for

$$K(x,y) = x^2 y^2 (x+y)^{-3}. \tag{56}$$

This calculation suggests that kernel (56) may have a self-similar density which is approximately log-Normal.

A.5 Embedding the $K(x,y) = 1$ coalescent

A special feature of the $K(x,y) = 1$ setting is that asymptotics for the Marcus-Lushnikov process can be obtained by embedding into Kingman's coalescent. More exactly, let us consider the standard stochastic coalescent $(\mathbf{X}(t); t \geq 0)$ constructed in section 4.2, and let $\mathbf{X}^{(k)}$ be the stochastic coalescent started with configuration $(x_i^{(k)}, 1 \leq i \leq k)$, where

$$\sum_i x_i^{(k)} = 1. \tag{57}$$

Recall the definition of τ_k. At time τ_k we attach the weights $(x_i^{(k)})$ to the k clusters of $\mathbf{X}(\tau_k)$, in random order, and then define $\mathbf{X}^{(k)}(t)$ to be the weights of the clusters of $\mathbf{X}(\tau_k + t)$. This provides an *embedding* of $\mathbf{X}^{(k)}$ into $\mathbf{X}$. Now recall the functional WLLN for sampling without replacement.

Lemma 18 *Suppose $(x_i^{(k)})$ satisfies (57) and $\max_i x_i^{(k)} \to 0$ as $k \to \infty$. Let $S^{(k)}(t) = \sum_{i \leq kt} x_{\pi(i)}^{(k)}$, where π is a uniform random permutation of $\{1, \ldots, k\}$. Then $\sup_{0<t<1} |S^{(k)}(t) - t| \xrightarrow{p} 0$.*

Applying the lemma to the embedding, we deduce (34) and the uniqueness property (32) of Kingman's coalescent.

A.6 Variance calculations

Open Problem 17 involves a Gaussian process $(Z(x); 0 < x < \infty)$ intended to represent fluctuations of cluster-size counts in the intermediate-time regime. For the three special kernels, explicit description of this process is most easily done by exploiting special structure (36,39). For a general K, a direct approach is to write down the differential equations implied by (50) for $EZ(x,t)Z(y,t)$, pass to the continuous-space limit, and then use the presumed scaling invariance to derive an equation in the spirit of (15) for the covariance function of $Z(x)$.

A different approach to variance calculations is to use the general construction in section 3.3, in which cluster sizes at time t in a certain model are represented as a stationary one-dimensional process. Perhaps one can use a suitable CLT for stationary processes to obtain a rigorous Gaussian limit in this model, and then relate this model to the Marcus-Lushnikov process featured in Open Problem 16.

A.7 What was new in this paper?

As befits a survey, little in this paper is new. In the big picture, the general viewpoint of section 3 does seem rather novel, as does the sketched general construction in section 3.3. In details, the sketched "slick proofs" of (25) and (36) seem novel.