Coagulations with limited aggregations

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Smoluchowski's coagulation equations in a nutshell

Smoluchowski introduced a system of ODE's to describe the evolution of the concentrations of particles in a medium where pairs of particles merge.

The area has been intensively studied by physicists, chemists, and mathematicians.

A particle is characterized by its mass $m \in \mathbb{N}$.
$\kappa(m, m')$ specifies the rate at which a pair $\{m, m'\}$ coalesces.
$c_t(m)$ denotes the concentration of particles m at time t,

$$\frac{\mathrm{d}}{\mathrm{d}t} c_t(m) = \frac{1}{2} \sum_{m'=1}^{m-1} c_t(m') c_t(m - m') \kappa(m', m - m') - c_t(m) \sum_{m'=1}^{\infty} c_t(m') \kappa(m, m') .$$

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Dual formulation: write

$$\langle c_t, f\rangle = \sum_{m=1}^{\infty} f(m)c_t(m)\,,$$

where $f:\mathbb{N}^* \to \mathbb{R}$ has finite support.

Then

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\langle c_t, f\rangle\\ = \quad & \frac{1}{2}\sum_{m=1}^{\infty}\sum_{m'=1}^{\infty}(f(m+m')-f(m)-f(m'))\kappa(m,m')c_t(m)c_t(m')\end{aligned}$$

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Dynamics suggest that the average mass of particles

$$\langle c_t, \mathrm{Id} \rangle = \sum_{m=1}^{\infty} m c_t(m)$$

might be conserved.

Not always true. **Gelation** may occur :

$$T_{\mathrm{gel}} := \inf\{t > 0 : \langle c_t, \mathrm{Id} \rangle \neq \langle c_0, \mathrm{Id} \rangle\} < \infty$$

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Gelation can be interpreted as the formation of giant particles which are not taken into account in the average mass of particles.

The prototype of kernels for which this occurs is the multiplicative one:

$$\kappa(m, m') = m \cdot m' \,.$$

Suppose now that

$$\kappa(m, m') = m \cdot m'$$

and mono-disperse initial conditions $c_0(m) = \mathbf{1}_{m=1}$.

Then for $t < T_{\mathrm{gel}}$,

$$\frac{\mathrm{d}}{\mathrm{d}t} c_t(m) = \frac{1}{2} \sum_{m'=1}^{m-1} c_t(m') c_t(m - m') m'(m - m') - m c_t(m).$$

Solution step by step (McLeod):

$$c_t(m) = t^{m-1} m^{m-2} \mathrm{e}^{-mt} / m!\,, \qquad m \in \mathbb{N}^*.$$

Only valid before the gelation time !

Indeed

$$\sum_{m=1}^{\infty} \frac{t^{m-1} m^{m-1}}{m!} \mathrm{e}^{-tm} \begin{cases} = 1 & \text{if } t \leq 1 \\ < 1 & \text{otherwise.} \end{cases}$$

In particular $T_{\mathrm{gel}} = 1$.

Marcus and Lushnikov introduced finite systems of particles such that a pair (m, m') coagulates at a rate $\kappa(m, m')/n$, independently of the other pairs.

Hydrodynamic limits of Marcus-Lushnikov processes yield solutions to Smoluchowski equations before gelation; cf. Jeon, Norris, etc.

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For the multiplicative kernel, this is related to the random graph process of Erdős and Rényi, with edges appearing at rate $1/n$ between each pair of vertices.

The rate at which two clusters of size m and m' get connected is $(m \cdot m')/n$. The process of the sizes of the clusters is a Marcus-Lushnikov multiplicative coalescent.

Gelation $\Longleftrightarrow$ emergence of a **giant component** for $t > 1$.

McLeod's solution before gelation can be recovered from a statistical analysis of the clusters' sizes.

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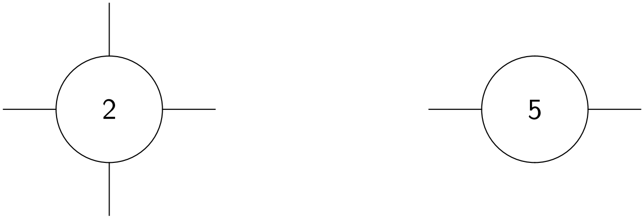
Macroscopic model for coagulation with limited aggregations

Toy model for the formation of polymers = clusters of atoms.

A particle is described by its number of available connexions (arms) and its size (number of atoms).

Arms serve to perform aggregations.

A pair of arms is consumed for each aggregation.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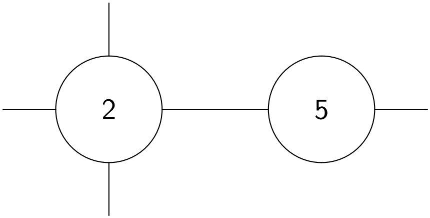
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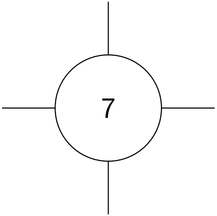
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Generic particle (a, m), a is the number of arms, m the mass.

$c_t(a, m) =$ concentration of particles (a, m) at time t.

Every pair of arms is activated at the same rate.

Transition

$$\{(a, m), (a', m')\} \longrightarrow (a + a' - 2, m + m')$$

occurs at time t with intensity

$$ac_t(a, m) \times a'c_t(a', m')\,.$$

Evolution of the concentrations is specified by variation of Smoluchowski's equation

$$\begin{aligned} & \frac{\mathrm{d}}{\mathrm{d}t} c_t(a,m) \\ = \quad & \frac{1}{2} \sum_{a'=1}^{a+1} \sum_{m'=1}^{m-1} a' c_t(a',m') \cdot (a-a'+2) c_t(a-a'+2, m-m') \\ & - \sum_{a'=1}^{\infty} \sum_{m'=1}^{\infty} a c_t(a,m) \cdot a' c_t(a',m'). \end{aligned}$$

This resembles multiplicative Smoluchowski's equation.

Assume that the initial condition is purely atomic, i.e.

$$c_0(a,m) = \mu(a)\mathbf{1}_{m=1}\,,$$

where μ is a measure on $\mathbb{N}$ with finite first two moments

$$A_j := \sum_{a=1}^{\infty} a^j \mu(a) < \infty \quad \text{for } j = 1, 2\,.$$

The system can be solved explicitly following the key steps :

- Introduce generating functions of concentrations.
- This yields a non-linear PDE which can be reduced to a quasi-linear and then solved by the method of characteristics.
- One inverts the generating functions and recovers the concentration (requires a version of Lagrange inversion formula).

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The gelation time is then given by

$$T_{\text{gel}} = \begin{cases} \infty & \text{if } A_2 \leq 2A_1, \\ 1/(A_2 - 2A_1) & \text{if } A_2 > 2A_1, \end{cases}$$

Note that T_{gel} can be infinite, a situation which never occurs for Smoluchowski's equation with the multiplicative kernel !

Theorem

There is a unique solution on $[0, T_{\mathrm{gel}})$ *:*

$$c_t(a,m) = \frac{(a+m-2)!}{a!m!} A_1^m t^{m-1} (1+A_1 t)^{-(a+m-1)} \nu^{*m}(a+m-2)\,,$$

where

$$\nu(j) = \frac{j+1}{A_1}\,\mu(j+1)\,, \qquad j \in \mathbb{N}$$

and

$$\nu^{*m} = \underbrace{\nu * \cdots * \nu}_{m \text{ times}}$$

is the m-th convolution power of ν.

Corollary

Suppose no gelation ($A_2 \leq 2A_1$). Then as time tends to ∞, there is a limiting concentration

$$c_\infty(a, m) = \lim_{t\to\infty} c_t(a, m)$$

which is 0 *for* $a \neq 0$ *and*

$$c_\infty(0, m) = \frac{A_1}{m(m-1)} \nu^{*m}(m-2) \,.$$

A similar formula holds for in the case when gelation occurs:

Corollary (Normand and Zambotti)

Suppose gelation occurs ($A_2 > 2A_1$). Then for some $\beta > 1$,

$$\lim_{t\to\infty} c_t(0,m) = \frac{A_1}{m(m-1)}\beta^{m-1}\nu^{*m}(m-2)\,.$$

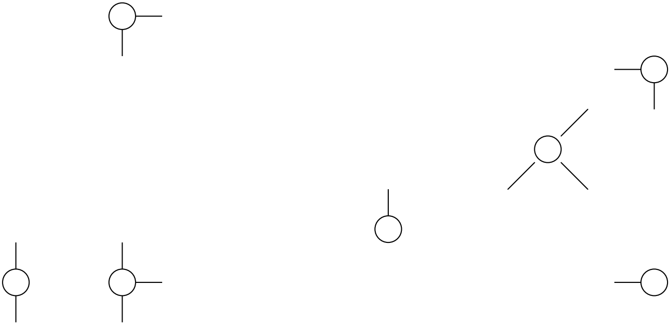
The formula resembles that for the distribution of the total population in a Galton-Watson branching process with reproduction law ν and 2 ancestors !

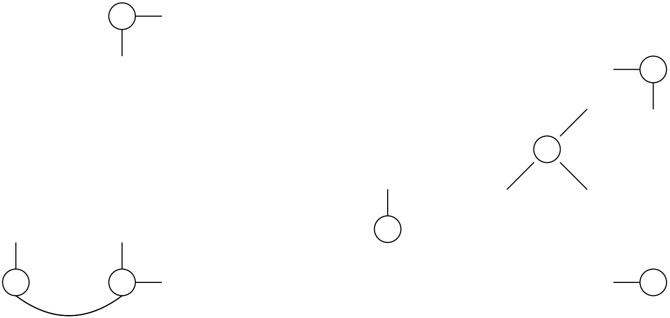
Microscopic version in the sub-critical case

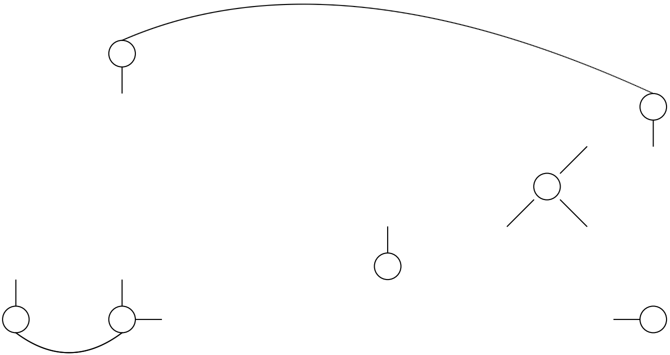
Simple stochastic algorithm which produces random multi-graphs with pre-described degrees:

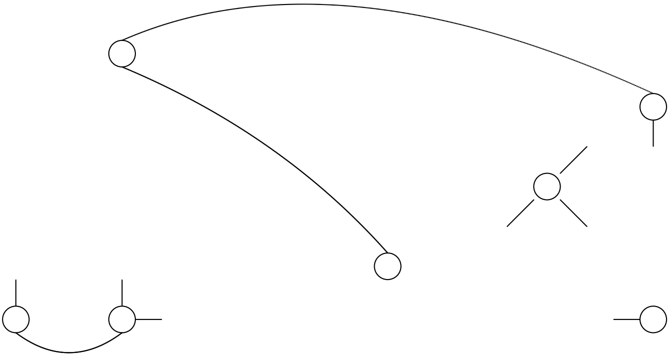
Consider a set of vertices $\mathcal{V}$ where each vertex v has a *degree* $d(v)$ (number of arms attached to v).

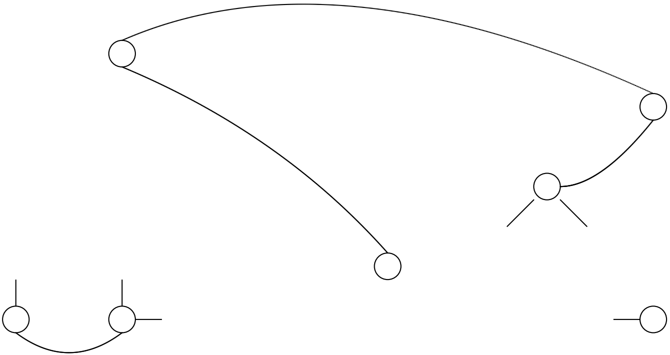
A configuration is obtained by joining pairs of arms uniformly at random to create edges.

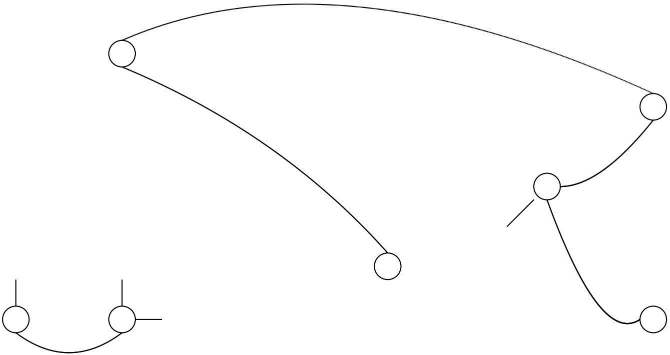


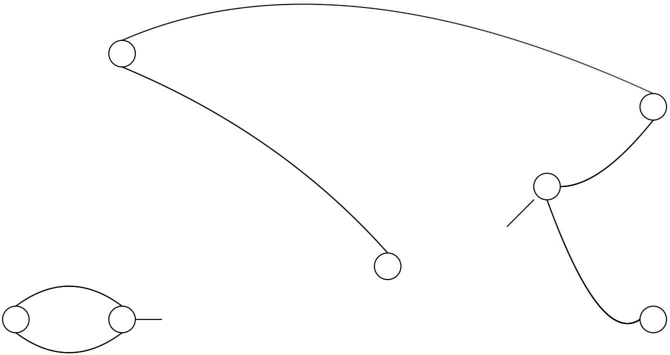


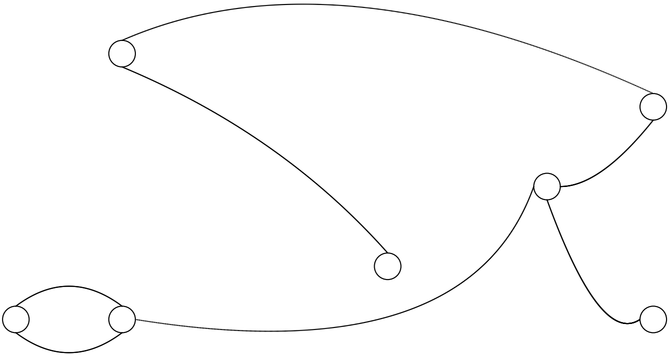








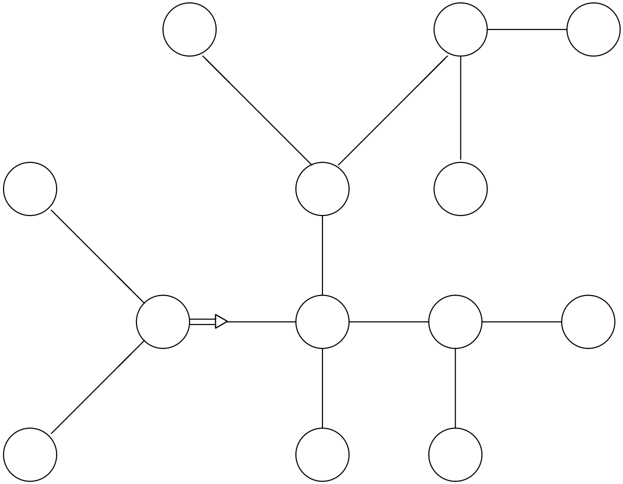


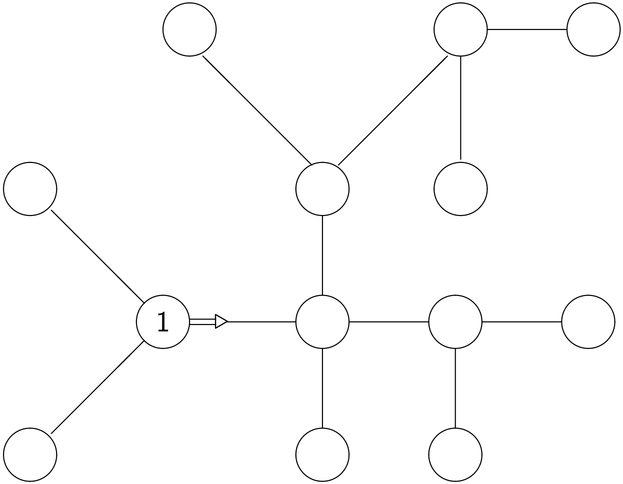


Our aim is to analyze statistically clusters (connected components) in a large random configuration.

When the degrees of vertices are not too large, most clusters are **tree** = simple connected graph with no loops or cycles.

To define the **shape** of a tree, we distinguish an arm called the root and use the **breadth-first enumeration** of vertices :

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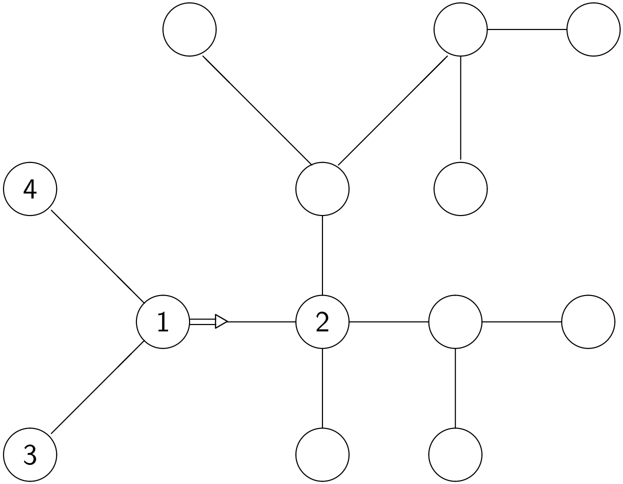
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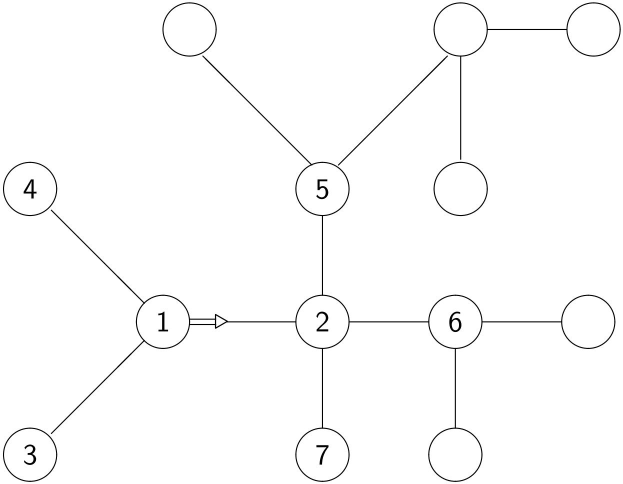
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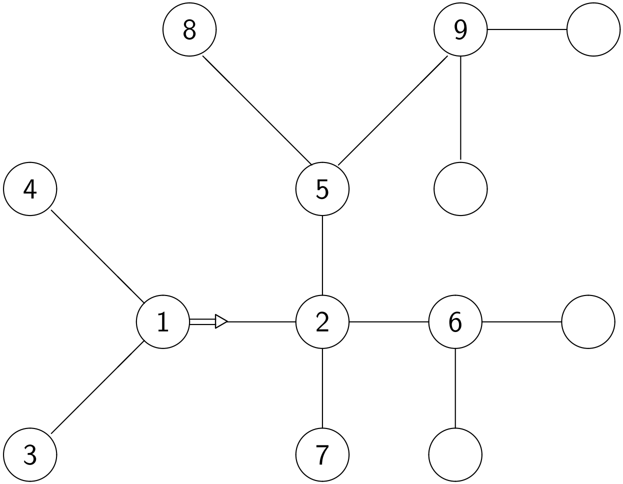
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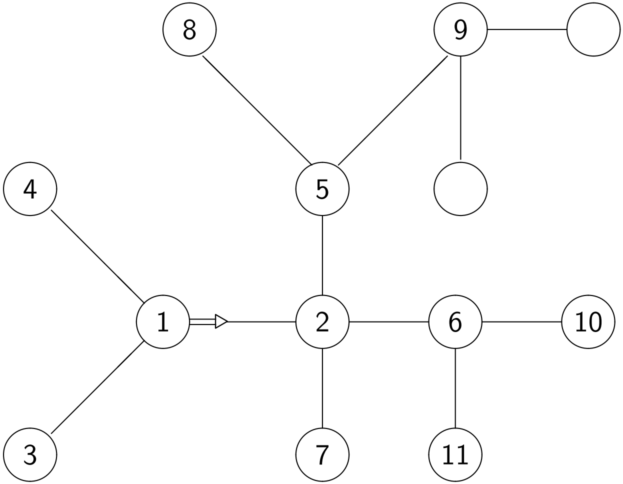
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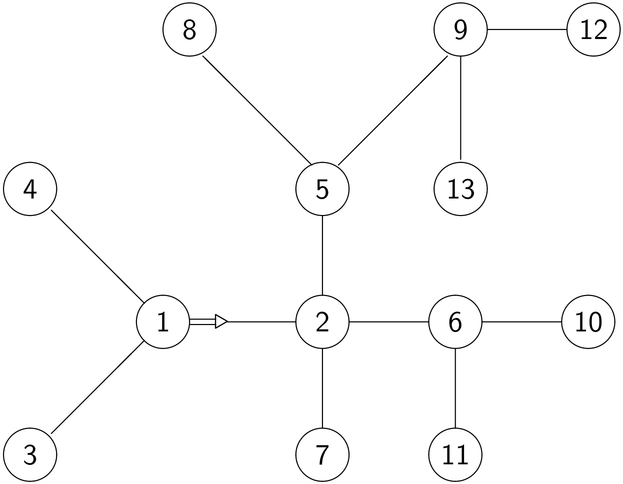
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Once vertices of a tree have been enumerated, $v_1, v_2, \ldots$, the **shape** of the tree is determined by the sequence of degrees

$$S = (d(v_1), d(v_2), \ldots) .$$

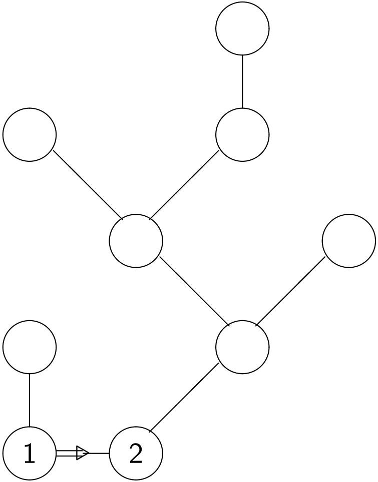
Let ν be a probability measure on $\mathbb{N}$ with $\sum i\nu(i) \leq 1$.

Consider a Galton-Watson branching process with reproduction law ν and started from two ancestors, denoted by 1 and 2.

The genealogy can be represented by a pair of trees.

Further connect the two ancestors by an additional oriented edge $1 \to 2$.

The distribution on the space of finite trees is denoted by $\mathbb{GW}_2^\nu$.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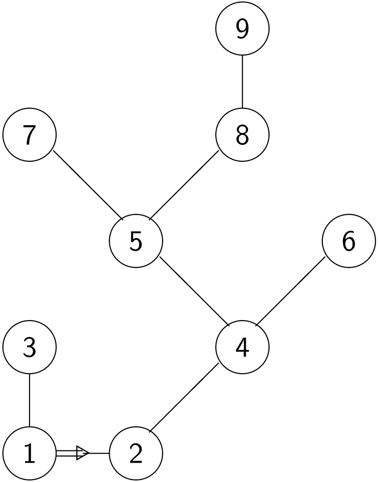
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For each n, consider a set $\mathcal{V}_n$ of n vertices and a degree function $d_n : \mathcal{V}_n \to \mathbb{N}^*$. Introduce the empirical distribution of the degrees

$$\mu_n(i) := \frac{1}{n}\#\{v \in \mathcal{V}_n : d_n(v) = i\}, \qquad i \in \mathbb{N}^*.$$

Assume that for every $i \in \mathbb{N}^*$

$$\lim_{n\to\infty} \mu_n(i) := \mu(i) \text{ and } \lim_{n\to\infty} \langle \mu_n, \mathrm{Id} \rangle = \langle \mu, \mathrm{Id} \rangle.$$

Introduce the empirical measure of the shapes of clusters :

$$\epsilon_n = \frac{1}{D_n} \sum_a \delta_{S_n(a)}$$

where $S_n(a)$ denotes the shape of the cluster rooted at the arm a and

$$D_n = \sum_{v \in \mathcal{V}_n} d(v) \,.$$

Theorem

Suppose

$$\sum_{i=1}^{\infty} i(i-2)\mu(i) \leq 0.$$

Then for every shape S

$$\lim_{n\to\infty} \epsilon_n(S) = \mathbb{GW}_2^{\nu}(S) \qquad \text{in probability,}$$

where

$$\nu(i) = \frac{(i+1)\mu(i+1)}{\sum j\mu(j)}, \qquad i \in \mathbb{N}\,.$$

The condition

$$\sum_{i=1}^{\infty} i(i-2)\mu(i) \leq 0.$$

is necessary and sufficient for the absence of giant clusters in the configuration model (Molloy and Reed).

It is equivalent to non-gelation ($A_2 \leq 2A_1$) in the setting of coagulation equations with limited aggregations.

It terms of the reproduction law ν, it can be rephrased as

$$\sum i\nu(i) \leq 1.$$

We can now recover with probabilistic arguments the formula for the limiting concentrations of coagulation equations with limited aggregations:

Corollary

For $k \geq 2$ denote by $C_n(k)$ the number of clusters of size k in the random configuration on $\mathcal{V}_n$. Then

$$\lim_{n\to\infty} n^{-1} C_n(k) = \frac{A_1}{k(k-1)} \nu^{*k}(k-2) \qquad \textit{in probability},$$

where $A_1 = \sum i\mu(i)$.

Indeed it is known (Dwass) that the distribution of the total population generated by two ancestors in a branching process with reproduction law ν

$$\mathbb{GW}_2^{\nu}(k) = \frac{2}{k}\nu^{*k}(k-2)\,,$$

where ν^{*k} stands for the k-th convolution power of ν.

Note that a tree of size k has exactly $2(k-1)$ arms, and thus is counted $2(k-1)$ times in the empirical measure ϵ_n.

The corollary then follows from the previous theorem, taking into account this bias.

Gelation and self-organized critically

We present succinctly and informally some recent results due to **Merle** and **Normand** in the supercritical case.

Gelation is modeled in the stochastic case by introducing a threshold $\alpha(n)$ such that 'giant'polymers with size greater than $\alpha(n)$ **fall into the gel**.

Only particles with size less than $\alpha(n)$ are allowed to coagulate, the other are removed from the system.

Merle and Normand show that the empirical measure μ_t^n of the number of used arms in the solution at time t converges to a deterministic measure μ_t.

μ_t is sub-critical when $t < T_{\text{gel}}$ and exactly critical for $t \geq T_{\text{gel}}$.

This is an illustration of **self-organized criticality**.

Further the empirical distribution of the shapes of polymers at time t converges to the law of a Galton-Watson tree with reproduction distribution ν_t and two ancestors,

$$\mathbb{GW}_2^{\nu_t}.$$

Using Dwass' formula, this yields probabilistic explanations of the deterministic results on coagulation equations with limited aggregations.

Smoluchowski's equations and stochastic coalescence

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