Weierstrass Institute for
Applied Analysis and Stochastics

Leibniz
Association

A large-deviation approach to coagulation

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based on joint work in progress with Luisa Andreis and Robert Patterson

Long-term objective:

coagulating Brownian motions in a box in the thermodynamic resp. hydrodynamic limit.

- At time zero, N i.i.d. uniformly distributed initial sites $B_1(0), \dots, B_N(0)$ in a box Λ.
- Each of them carries a mass $m_i(0) = 1$.
- The i-th motion runs independently in Λ with diffusion parameter $\frac{1}{m_i(t)} \in (0, \infty)$.
- Each two of them coagulate at time t with rate $K(|B_i(t) - B_j(t)|, m_i(t), m_j(t))$ to a new particle with mass $f(m_i(t), m_j(t))$ at the coagulation place.

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Our main question: Is there a gelation transition at some fixed time $t_c \in (0, \infty)$?

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Modeling difficulties: choice of coagulation kernel K and mass f and location of the coagulate.

Mathematical difficulties: handling the interplay of all the mechanisms (movement, locations, coagulation times, coagulate masses).

The MARCUS-LUSHNIKOV model is a non-spatial mean-field version [MARCUS 1968], [GILLESPIE 1972], [LUSHNIKOV 1978]:

Continuous-time Markov process of vectors of particle masses at time $t \in [0, \infty)$:

$$M_1^{(N)}(t) \geq M_2^{(N)}(t) \geq M_3^{(N)}(t) \geq \cdots \geq M_{n(t)}^{(N)}(t) \geq 1, \qquad \sum_{i=1}^{n(t)} M_i^{(N)}(t) = N.$$

Coagulation mechanism:

Particles with masses m and $\widetilde{m}$ coagulate after an exponential random time with parameter $K_N(m, \widetilde{m})$ (the coagulation kernel) independently of all the other particles.

Hydrodynamic regime:

Choosing $K_N(m, \widetilde{m}) \asymp \frac{1}{N}$ reflects the situation that each particle feels $\asymp N$ other particles and interacts with each of them after time $\asymp N$. Hence, each particle has $O(1)$ coagulations per time interval. This is the situation of a hydrodynamic limit, where the box Λ does not grow with N.

Here, we make the special choice of the multiplicative kernel:

$$K_N(m,\widetilde{m}) = \frac{m\,\widetilde{m}}{N}.$$

Advantage:

The model is now a function of a time-dependent version of the well-known ERDŐS-RÉNYI random graph model. Indeed, the vector $(M_i^{(N)}(t))_{i=1}^{n(t)}$ is in distribution equal to the collection of sizes of all the connected components of the graph $\mathcal{G}(N, 1-\mathrm{e}^{-t/N})$.

Explanation:

Equip each unordered pair $\{i,j\}$ of different numbers in $\{1,\dots,N\}$ independently with an exponentially distributed random time $\mathrm{e}_{i,j}$ with expected value $1/N$. After the elapsure of $\mathrm{e}_{i,j}$, there is a bond created between i and j. Then, at time t, for each pair, the probability to have a bond between them is equal to $1-\mathrm{e}^{-t/N}$.

After each of these elapsures, the new connected component of size $m+\widetilde{m}$ inherits all the bonds of the two other components of size m respectively $\widetilde{m}$, i.e., has from now $m\widetilde{m}$ active bonds.

[BUFFET, PULÉ 1990, 1991] calculated expectations of particle masses at time t in the limit $N \to \infty$ and detected a gelation phase transition d uring the time interval $[\log 2, 1]$ by looking exclusively on expectations of macroscopic particles:
At time $t \in (0, t_c)$, the total macroscopic particle part is $o(N)$, and at least one "giant particle" arises with mass $\asymp N$ at some time $t \in (1, \infty)$.

(No explicit formulas, no information about microscopic nor mesoscopic particles, no large deviations, but conjectures about exact size of macroscopic particle)

Our contribution:
Explicit large-deviation principle for the microscopic, the mesoscopic and the macroscopic part of the system at fixed time $t \in (0, \infty)$. Explicit identification of the gelation phase transition.

Microscopic and macroscopic empirical measures of the particle sizes:

$$\mathrm{Mi}^{(N)}(t) = \frac{1}{N}\sum_{i=1}^{n(t)} \delta_{M_i^{(N)}(t)} \qquad \text{and} \qquad \mathrm{Ma}^{(N)}(t) = \sum_{i=1}^{n(t)} \delta_{\frac{1}{N} M_i^{(N)}(t)}.$$

Then $\mathrm{Mi}^{(N)}(t)$ is a random member of the set $\mathcal{N} = \mathcal{N}(1)$, where

$$\mathcal{N}(c) = \Big\{\lambda \in [0,\infty)^{\mathbb{N}} \colon \sum_{k\in\mathbb{N}} k\lambda_k = c\Big\} \qquad \text{(coordinatewise top.)}.$$

$\mathrm{Ma}^{(N)}(t)$ is a random element of $\mathcal{M}_{\mathbb{N}_0} = \mathcal{M}_{\mathbb{N}_0}(1)$, where

$$\mathcal{M}_{\mathbb{N}_0}(c) = \Big\{\alpha \in \mathcal{M}_{\mathbb{N}_0}((0,1]) \colon \int_{(0,1]} x\,\alpha(\mathrm{d}x) = c\Big\} \qquad \text{(vague top.)}.$$

and $\mathcal{M}_{\mathbb{N}_0}((0,1])$ is the set of all measures on $(0,1]$ with values in $\mathbb{N}_0$.

Note that the total masses

$$c_\lambda = \sum_{k\in\mathbb{N}} k\lambda_k \qquad \text{and} \qquad c_\alpha = \int_{(0,1]} x\,\alpha(\mathrm{d}x)$$

are not continuous functions of λ resp. α.

LDP for the micro- and macroscopic parts

As $N \to \infty$, the pair $(\mathrm{Mi}^{(N)}(t), \mathrm{Ma}^{(N)}(t))$ satisfies an LDP with rate function

$$I(\lambda, \alpha; t) = \begin{cases} I_{\mathrm{Mi}}(\lambda; t) + I_{\mathrm{Ma}}(\alpha; t) + (1 - c_\lambda - c_\alpha)\Big(\frac{t}{2} - \log t\Big), & \text{if } c_\lambda + c_\alpha \leq 1, \\ \infty & \text{otherwise,} \end{cases}$$

where

$$\begin{aligned} I_{\mathrm{Mi}}(\lambda; t) &= \sum_{k=1}^{\infty} \lambda_k \log \frac{k! t \lambda_k}{\mathrm{e}\, k^{k-2}} + c_\lambda \Big(1 + \frac{t}{2} - \log t\Big), \\ I_{\mathrm{Ma}}(\alpha; t) &= \int_0^1 \Big[x \log \frac{x}{1 - \mathrm{e}^{-tx}} + \frac{t}{2} x(1 - x)\Big]\, \alpha(\mathrm{d}x). \end{aligned}$$

Corollary 1: LDP for micro-particle size statistics

As $N \to \infty$, $\mathrm{Mi}^{(N)}(t)$ satisfies an LDP with rate function

$$\mathcal{I}_{\mathrm{Mi}}(\lambda;t) = \inf_{\alpha \in \mathcal{M}_{\mathbb{N}}} I(\lambda,\alpha;t) = I_{\mathrm{Mi}}(\lambda;t) - (1-c_\lambda)\left(\log \frac{1-\mathrm{e}^{(c_\lambda-1)t}}{1-c_\lambda} - \frac{c_\lambda t}{2}\right).$$

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Corollary 2: LDP for macroscopic particles

As $N \to \infty$, $\mathrm{Ma}^{(N)}(t)$ satisfies an LDP with rate function

$$\mathcal{I}_{\mathrm{Ma}}(\alpha;t) = \inf_{\lambda\in\mathcal{N}} I(\lambda,\alpha;t) = I_{\mathrm{Ma}}(\alpha;t) + (1-c_\alpha)\left(\frac{t}{2} - \log t\right) + C_{t,\alpha}\left(\log(t\,C_{t,\alpha}) - \frac{t}{2}C_{t,\alpha}\right),$$

where $C_{t,\alpha} = (1-c_\alpha)\wedge\frac{1}{t}$.

- We also show that the map $\alpha \mapsto I_{\mathrm{Ma}}(\alpha;t)$ is minimal only in delta-measures.
- From this, we see a non-analyticity at the point where $1-c_\alpha = \frac{1}{t}$ (only for $t\in(1,\infty)$).

By exclusively considering the microscopic total-mass rate function,

$$\begin{aligned}\mathcal{J}_{\mathrm{Mi}}(c;t) &= \inf_{\lambda\in\mathcal{N}(c)} \mathcal{I}_{\mathrm{Mi}}(\lambda;t)\\ &= \inf_{\lambda\in\mathcal{N}(c)} \Big[\text{const.} + \sum_{k=1}^{\infty} \lambda_k \log \frac{k!\lambda_k}{k^{k-2}}\Big]\\ &= tc + (1-c)\log\frac{1-c}{1-\mathrm{e}^{t(c-1)}} + \begin{cases} c\log c - tc^2 & \text{for } c < \frac{1}{t},\\ -\frac{1}{2t} - \frac{t}{2}c^2 - c\log t & \text{for } c \geq \frac{1}{t},\end{cases}\end{aligned}$$

we now detect the gelation phase transition.

Microscopic total mass phase transition

1. For $t \in (0,1)$, the minimum of $\mathcal{I}_{\mathrm{Mi}}$ is attained precisely at

$$\lambda_k^*(c;t) = \frac{k^{k-2} c^k t^{k-1} \mathrm{e}^{-ctk}}{k!}, \qquad k \in \mathbb{N},$$

and the minimum of $\mathcal{J}_{\mathrm{Mi}}(\cdot;t)$ is attained precisely at $c = 1$ with value $\mathcal{J}_{\mathrm{Mi}}(1;t) = 0$. Therefore the infimum of the joint rate function $I(\cdot,\cdot;t)$ is attained at $(\lambda, \alpha) = (\lambda_k^*(1;t), \mathbf{0})$.

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2. For $t \in (1,\infty)$, the minimum of $\mathcal{J}_{\rm Mi}(\cdot;t)$ is attained precisely at $c=\beta_t$ for some $\beta_t \in (0, \frac{1}{t})$, given as the smallest positive solution to $\log \beta_t = t\beta_t - t$. The infimum is attained precisely at $(\lambda,\alpha) = (\lambda^*(\beta_t;t), (1-\beta_t, 0, \dots))$.

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2. For $t \in (1,\infty)$, the minimum of $\mathcal{J}_{\mathrm{Mi}}(\cdot;t)$ is attained precisely at $c = \beta_t$ for some $\beta_t \in (0, \frac{1}{t})$, given as the smallest positive solution to $\log \beta_t = t\beta_t - t$. The infimum is attained precisely at $(\lambda, \alpha) = (\lambda^*(\beta_t;t), (1-\beta_t, 0, \dots))$.

Hence, $t_c = 1$ is the gelation transition time. On a linear level, we can say:

- Before time 1, all particles are finitely large, and the statistics of their sizes follow the Borel distribution.
- After time 1, there is precisely one macroscopic particle of size $(1-\beta_t)N$, and a Borel-distributed statistics of remaining particle sizes.

LDP for mesoscopic total mass

Fix $t \in [0, \infty)$ and $\varepsilon > 0$ and $R \in \mathbb{N}$. Then the mesoscopic (ε, R)-total mass,

$$\overline{\mathrm{Me}}_{R,\varepsilon}^{(N)}(t) = \frac{1}{N} \sum_{i\colon R < M_i^{(N)}(t) < \varepsilon N} M_i^{(N)}(t).$$

satisfies an LDP with some rate function $\mathcal{J}_{\mathrm{Me}}^{(\varepsilon,R)}(\cdot; t)$ whose limit for $\varepsilon \downarrow 0$ and $R \to \infty$ is equal to

$$\mathcal{J}_{\mathrm{Me}}(c; t) = (1-c)\Big(\log(1-c)t - \frac{(1-c)t}{2}\Big) + \frac{t}{2} - \log t.$$

- $\mathcal{J}_{\mathrm{Me}}(\cdot; t)$ is strictly increasing and has a unique zero at $c = 0$.
- We presume that $\overline{\mathrm{Me}}_{R_N,\varepsilon_N}^{(N)}(t)$ satisfies an LDP with rate function $\mathcal{J}_{\mathrm{Me}}(\cdot; t)$ if $1 \ll R_N \leq N\varepsilon_N \ll N$.

Put

$$\mu_t^{(N)}(k) = \mathtt{P}\Big(\mathcal{G}(k, 1 - \mathrm{e}^{-\frac{t}{N}}) \text{ is connected}\Big),$$

then we have

Distribution of statistics

For any N and any $\ell = (\ell_k)_k \in \mathbb{N}_0^{\mathbb{N}}$ satisfying $\sum_k k\ell_k = N$, write

$$A_{N,t}(\ell) = \bigcap_{k\in\mathbb{N}} \{\#\{i\colon M_i^{(N)}(t) = k\} = \ell_k\},$$

then

$$\mathbb{P}_N(A_{N,t}(\ell)) = N! \prod_k \frac{\mu_t^{(N)}(k)^{\ell_k} \mathrm{e}^{-\frac{t}{2N} k(N-k)\ell_k}}{k!^{\ell_k}\, \ell_k!}.$$

This follows directly from the characterisation of the Lushnikov model as a function of the Erdős-Rényi graph.

Micro and macro asymptotics

As $N \to \infty$,

$$\mu_t^{(N)}(k) \sim k^{k-2}\Big(\frac{t}{N}\Big)^{k-1}, \qquad k \in \mathbb{N}.$$

and

$$\frac{1}{N}\log \mu_t^{(N)}(\lfloor \alpha N \rfloor) \to \alpha \log\big(1 - \mathrm{e}^{-t\alpha}\big), \qquad \alpha \in (0,1).$$

- The first one is basically standard.
- The second is based on estimates from [VAN DER HOFSTAD/SPENCER 2006].
- This large-deviation assertion seems to be new in the investigation of Erdős-Rényi graphs.
- We have also a conditional LLN for the number of open bonds given that the graph $\mathcal{G}(\lfloor \alpha N \rfloor, 1 - \mathrm{e}^{-t/N})$ is connected.
- Now the main LDP follows by using Stirling's formula and the fact that the cardinality of the relevant λ's is $\mathrm{e}^{o(N)}$.

- In [SMOLUCHOWSKI 1916] a system of ODEs is introduced for the evolution of the (microscopic) particle sizes (as part of his famous work on Brownian motion).
- Convergence of stochastic coagulation processes towards these ODEs was expected for long time, but the first rigorous proof was given only in [LANG, NGUYEN 1980].
- In [LUSHNIKOV 1978] the formation of a gel is realized and explained.
- Pathwise large deviations appear cumbersome, but doable. Such LDPs have been derived by [MIELKE et. al (2017)] following a Freidlin-Wentsel approach, but the rate function is rather inexplicit and not easy to evaluate at a fixed time.

Consider the non-interacting Bose gas in the thermodynamic limit at temperature $1/\beta \in (0,\infty)$ with particle density $\rho \in (0,\infty)$. Then the partition function is given by

$$Z_{\Lambda_N}^{(\beta)} = \sum_{(\ell_k)_{k\in\mathbb{N}}\in\mathbb{N}_0^{\mathbb{N}} \colon \sum_k k\ell_k = N} \prod_k \frac{N^{\ell_k}}{\ell_k!\, k^{\ell_k}} [\rho(4\pi\beta k)^{\frac{d}{2}}]^{-\ell_k},$$

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$$f(\beta,\rho) = \lim_{N\to\infty}\frac{1}{N}\log Z_{\Lambda_N}^{(\beta)} = -\inf_{\lambda\in\mathcal{N}(\rho)} I(\lambda), \quad \text{where} \quad I(\lambda) = \sum_k \lambda_k \log\frac{\lambda_k k}{(4\pi\beta k)^{\frac{d}{2}}\,\mathrm{e}}.$$

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Comparison: In Lushnikov's model, we face roughly

$$t^N \mathrm{e}^{\frac{t}{2}N} \sum_{(\ell_k)_{k\in\mathbb{N}}\colon\ \sum_k k\ell_k = N} \prod_k \frac{k^{(k-2)\ell_k} t^{-\ell_k}}{\ell_k!\, k!^{\ell_k}}.$$

The two respective minimizers are

$$k\lambda_k^{(\mathrm{Lush})}(c;t) = \frac{1}{t}\,\frac{(cte^{-ct})^k}{k^{1-k}\,k!} \quad \text{and} \quad k\lambda_k^{(\mathrm{BEC})}(\alpha;t) = \frac{1}{\rho(4\pi\beta)^{\frac{d}{2}}}\,\frac{\mathrm{e}^{-\alpha k}}{k^{\frac{d}{2}}},$$

where c and α control the value of $\sum_k k\lambda_k$ (note that $k^{1-k}\,k! \asymp k^{3/2}$).

In the Bose gas, increasing β drives more and more particles into the finite cycles. There is a natural threshold, the critical inverse temperature $\beta_{\rm c}$, characterised by

$$(4\pi\beta)^{\frac{d}{2}}\rho = \sum_{k\in\mathbb{N}} k^{-\frac{d}{2}}.$$

Only when all finite cycles are filled entirely, the first “infinite” cycle arises.

The BEC is a saturation transition.

In contrast, in the Lushnikov model, increasing t makes each particle larger, until some decide to make the jump to infinity. After this happens for the first time, the other micro particles keep growing (recall that $\beta_t < \frac{1}{t}$).

The gelation phase transition is an explosion transition.