Instantons in Aggregation Kinetics

Colm Connaughton[a], Roger Tribe[b] and Oleg Zaboronski[c]

[a]Complexity Centre, University of Warwick

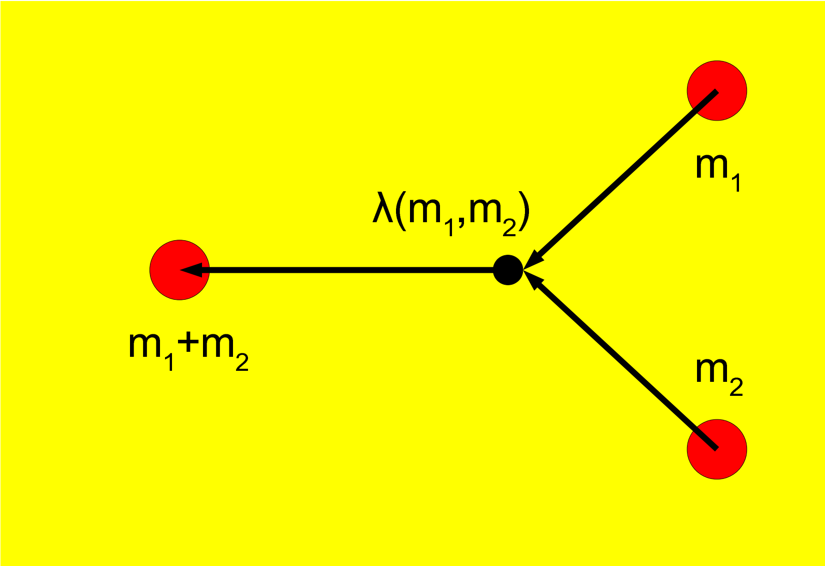
[b]Department of Mathematics, University of Warwick

[c]Department of Mathematics, University of Warwick

Plan

- The model
- Mean field theory
- The formalism
  - Rate functions via DZO path integrals
  - Instanton energy and mass conservation
- Fast and slow gelation probabilities: constant kernel
  - Large deviations principle
  - Solution of instanton equations
  - The statistics of mass flux
- Fast gelation and the non-gelling probability: multiplicative kernel
  - Fast gelation: LDP and instanton equations
  - Non-gelling near gelation time: LDP, results
- Conclusions

Markus-Luzhnikov model



Classical kernels:

$$\lambda(k,l) = 1 \text{ (Constant)}$$
$$\lambda(k,l) = kl \text{ (Multiplicative)}$$
$$\lambda(k,l) = (k+l)/2 \text{ (Sum)}$$

- Microstate: $\mathbf{N} = N_1, N_2, \ldots$
- $N_m = \#$ of particles of mass $m \in \{1, 2, 3, \ldots\}$
- Coagulation:
  - $N_{m_1} \to N_{m_1} - 1$
  - $N_{m_2} \to N_{m_2} - 1$
  - $N_{m_1+m_2} \to N_{m_1+m_2} + 1$
- Rate: $\lambda(m_1, m_2) N_{m_1} N_{m_2}$

Problem statement

- Monomer initial condition: $N_m(0) = M\delta(m, 1)$
- Mass conservation $\sum_m mN_m(t) = M$
- Complete gelation event: $N_m(t) = \delta(m, M)$
  - Equivalently, $N(t) \stackrel{def}{=} \sum_m N_m(t) = 1$
- Gelation time: $T_G = \mathbb{E}(\tau \mid N_\tau = 1)$
- **Find:** $Prob(N_t = 1)$ for $t << T_G$
- **Find:** $Prob(N_t >> 1)$ for $t > T_G$

Smoluchowski (mean field) theory

$$\dot{N}_m = \frac{1}{2}\sum_{m'=1}^{m}\lambda(m', m-m')N(m-m')N(m') - N(m)\sum_{m'=1}^{\infty}\lambda(m, m')N(m')$$

- Smoluchowski equation (SE)

- Can be rigorously related to ML model in the scaling limit $N_t \to \infty$ for certain kernels
- Cannot be used to describe complete gelation ($N_t \sim 1$)
- Suffers from finite time singularities for some kernels (e. g. the multiplicative kernel)

The formalism

Path integral expression for $P(N_t = 1)$

$$P(N_t = 1) = \int \prod_{\tau'} \mathcal{D}\mu(\mathbf{z}(\tau'), \bar{\mathbf{z}}(\tau')) \exp[-S_{eff}]$$

$$S_{eff} = \int_0^t d\tau \left(\sum_m \dot{z}_m \bar{z}_m + \mathfrak{h}(\mathbf{z}, \bar{\mathbf{z}}) \right) - \log \left(z_M(t) \bar{z}_1^M(0) \right)$$

$$\mathfrak{h}(\mathbf{z}, \bar{\mathbf{z}}) = -\frac{1}{2} \sum_{m_1,\ m_2} \lambda_{m_1,m_2} (\bar{z}_{m_1+m_2} - \bar{z}_{m_1} \bar{z}_{m_2}) z_{m_1} z_{m_2}$$

Method: Doi-Zeldovich-Ovchinnikov. Note the presence of boundary terms.

Path integral expression for $P(N_t = fM)$

$$P(N_t = fM) = \frac{1}{(fM)!} \int \prod_{\tau'} \mathcal{D}\mu(\mathbf{z}(\tau'), \bar{\mathbf{z}}(\tau')) \exp[-S_{eff}],$$

$f \in (0,1)$.

$$S_{eff} = \int_0^t d\tau \left(\sum_m \dot{z}_m \bar{z}_m + \mathfrak{h}(\mathbf{z}, \bar{\mathbf{z}}) \right) - \log \left(\left(\sum_{k=1}^{M} z_k(t) \right)^{fM} \bar{z}_1^M(0) \right)$$

Note the difference in the boundary terms.

Laplace approximation for the path integral

- Laplace formula:

$$P(N_t = 1) \sim \exp\{-S_{eff}[z^c, \bar{z}^c]\}$$

- Here $(z_m^c(\tau), \bar{z}_m^c(\tau))$ solve $\delta S_{eff} = 0$ subject to:

$$z_m(0)\bar{z}_m(0) = M\delta_{m,1}, \; z_m(t)\bar{z}_m(t) = \delta_{m,M} \text{ (Fast gelation)}$$

$$z_m(0)\bar{z}_m(0) = M\delta_{m,1}, \; \sum_{k=1}^{M} z_k(t)\bar{z}_m(t) = fM \text{ (Non-gelation)}$$

- General applicability condition: the PI is dominated by trajectories close to the instanton trajectory

Euler-Lagrange (instanton) equations

$$\dot{z}_m = \frac{1}{2} \sum_{m_1,m_2} \lambda_{m_1,m_2} \left(\delta_{m,m_1+m_2} - \bar{z}_{m_1}\delta_{m,m_2} - \bar{z}_{m_2}\delta_{m,m_1}\right) z_{m_1} z_{m_2}$$

$$\dot{\bar{z}}_m = -\frac{1}{2} \sum_{m_1,\, m_2} \lambda_{m_1,m_2}(\bar{z}_{m_1+m_2} - \bar{z}_{m_1}\bar{z}_{m_2})(z_{m_1}\delta_{m,m_2} + z_{m_2}\delta_{m,m_1})$$

- Integrals of motion:
  - $E = \mathfrak{h}(z^c, \bar{z}^c)$ ('Instanton energy')
  - $M = \sum_m m z_m^c \bar{z}_m^c$ (Mass)
- Special solution: $\bar{z} \equiv 1$; z solves Smoluchowski equation, $E = 0$
- $N_m(t) = z_m(t)\bar{z}_m(t)$ - the symbol of the occupation number operator

On the calculation of $inf[S_{eff}]$

- **Claim.** $S^c_{eff} = -E \cdot t +$ boundary terms
- **Derivation:** $\mathfrak{h}(\mathbf{z}, \bar{\mathbf{z}})$ is homogeneous function of $\mathbf{z}$ of order 2:

$$\int_0^t d\tau \left(\sum_{m=1}^{M} \dot{z}_m \bar{z}_m + \mathfrak{h} \right)$$

$$= \sum_{m=0}^{M} z_m \bar{z}_m \,|_0^t + \int_0^t d\tau \left(-\sum_{m=1}^{M} z_m \frac{\partial \mathfrak{h}}{\partial z_m} + \mathfrak{h} \right)$$

$$= \sum_{m=0}^{M} z_m \bar{z}_m \,|_0^t - E(t) t$$

- **N.B.** $E = 0$ corresponds to mean field

Fast and slow gelation probabilities: the constant kernel

The large deviations principle for fast gelation.

The limit: $t << 1$, $M = \infty$

$$\log P(N_\tau) \sim -\frac{S^c_{eff}}{\tau} + \log\left(\frac{z_M(1)\bar{z}_1^M(0)}{\tau}\right),$$

where

$$S^c_{eff} = \inf_{\{z(t),\bar{z}(t)\}} \int_0^1 d\tau[\sum_m \dot{z}_m \bar{z}_m + \mathfrak{h}(z,\bar{z})],$$

$$\begin{cases} z_m(0+)\bar{z}_m(0+) & = \infty \cdot \delta_{m,1}, \\ z_m(1-)\bar{z}_m(1-) & = 0 \end{cases}$$

Solving the instanton equations.

- Euler-Lagrange equation for $N(\tau) = \sum_m z_m(\tau)\bar{z}_m(\tau)$:

$$\dot{N}(\tau) = -\frac{1}{2}N^2(\tau) + E,$$

- Boundary conditions: $N(0) = \infty$, $N(1) = 0$
- $E = -\frac{p^2}{2} < 0$
- $N(\tau) = p \tan\left(\frac{p}{2}(\tau - \tau_0)\right)$
  - $E = -\frac{\pi^2}{2}$
- Rate function: $\log P(N_t = 1) \sim -\frac{\pi^2}{2t} + O(t^0)$
- Really hard step: the estimate of the contribution from the boundary terms

Statistics of mass flux

- Non-equilibrium ’turbulent’ state: constant flux of mass through mass scales of the system.
- The average mass flux: $J = M/\tau$ (random quantity)
- Mean field flux: $J_{mf} = M/T_G = M$.

$$P\left(J > J_+\right) = \Pr\left(\tau < \frac{M}{J_+}\right) = \Pr\left(N_{M/J_+} = 1\right) \overset{J_+\to\infty}{\sim} e^{-\frac{\pi^2}{2}\frac{J_+}{J_{mf}}}$$

- Left tail of flux distribution:

$$P\left(J < J_-\right) = Pr\left(\tau > \frac{M}{J_-}\right) \sim Pr\left(N_{M/J_-} = 2\right) \overset{J_-\to 0}{\sim} e^{-\frac{J_{mf}}{J_-}}$$

- Fluctuation relation: $\log\left(\frac{\Pr(J>J_{mf}L)}{\Pr(J<J_{mf}/L)}\right) \overset{L\to\infty}{\sim} \left(1 - \frac{\pi^2}{2}\right) L$

Fast gelation and the non-gelling probability: the multiplicative kernel

Fast gelation event

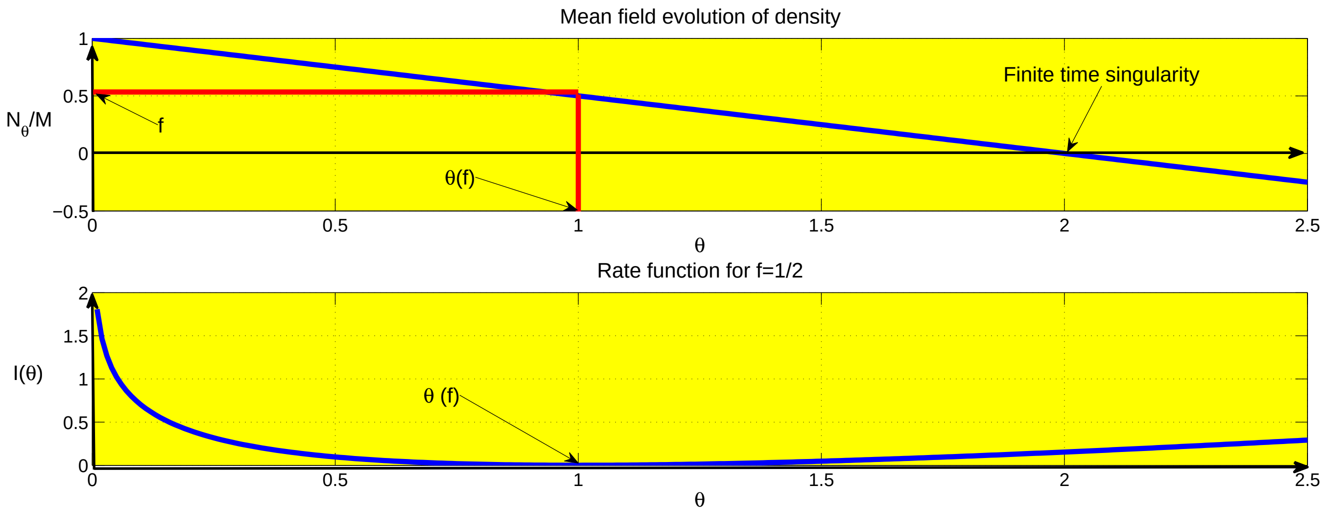
- Typical gelation time: $T_G = \frac{Const}{M}$
- The scaling limit: M is fixed, $t = \theta/M$, $\theta << 1$
- Small time LD principle still applies: $\log Pr(N_t = 1) \sim -\frac{1}{t}S_{eff}+$ boundary terms
- Equations of motion:
  - $\dot{N}(\tau) = E - \frac{M^2}{2}, 0 < \tau < t$
  - $N(0) = M,\ N(t) = 1$
- Instanton energy: $E = \frac{M^2}{2} + \frac{1-M}{t}$
- Boundary terms dominate
- $\log P(N_t = 1) \sim -M \log\left(\frac{1}{\theta}\right) + O(\theta^0) \Rightarrow$ Algebraic decay of gelation probability

LDP for $P(N_t = fM)$, $f \in f(0,1)$

- Scaling limit: $M \to \infty$, $t = \theta/M$, $\theta \sim 1$
- LD principle:

$$\frac{1}{M}\log \Pr\left(N_{\frac{\theta}{M}} = fM\right) = -I(\theta) + O(\log(M)/M)$$

- Rate function: $I(\theta) = \frac{1}{2}(\theta - \theta_{mf}(f)) - \frac{\theta_{mf}(f)}{2}\log(\theta/\theta_{mf}(f))$
- $\theta_{mf}(f) = 2(1-f)$- mean field time to $N = fM$. Potential non-analyticity!



A note for mathematicians.

- ML model can be restated as a stochastic differential equation driven by Poisson noise
- All scaling limits considered in the presentation correspond to the limit of weak noise
- All large deviation principles discussed in the talk follow from the standard Wentzel-Freidlin theory for SDE's with Poisson noise.

Conclusions

- Large deviations turned out to be an effective tool in the analysis of aggregation
- Rate function$=$Instanton energy$\times$time$+$boundary terms
- Instanton energy$=0$ corresponds to MF approximation
- Instanton equations: Mean field equation $=$ Optimal noise fluctuation
- Solutions to instanton equations are globally well defined even for gelling kernels
- **Reference**: Colm Connaughton, Roger Tribe, Oleg Zaboronski *On the statistics of rare events in Markus-Luzhnikov model*, still in preparation