Large Deviation Functions in Aggregation

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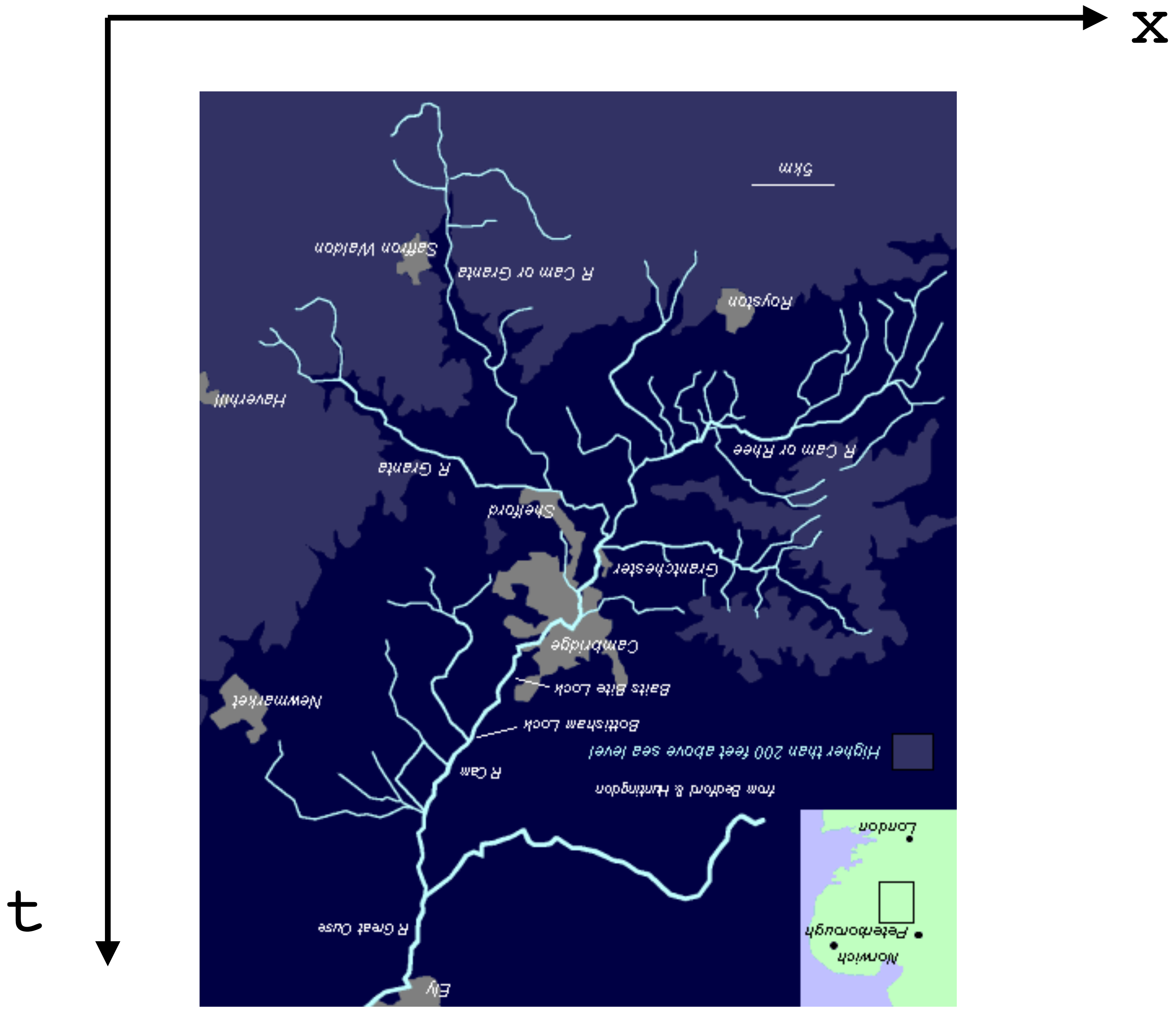
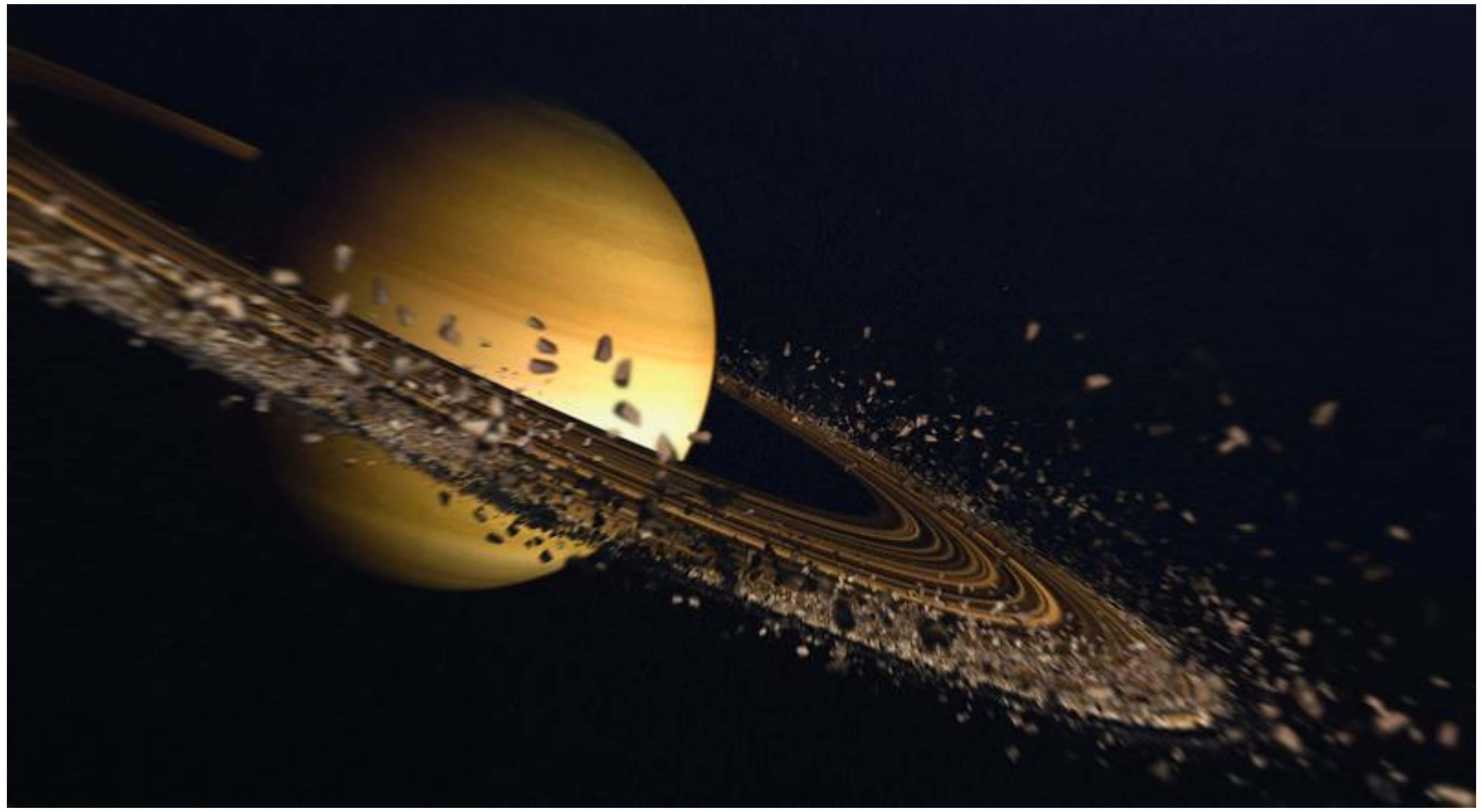
RR, V. Subashri, O. Zaboronski, in preparation

Aggregation is ubiquitous



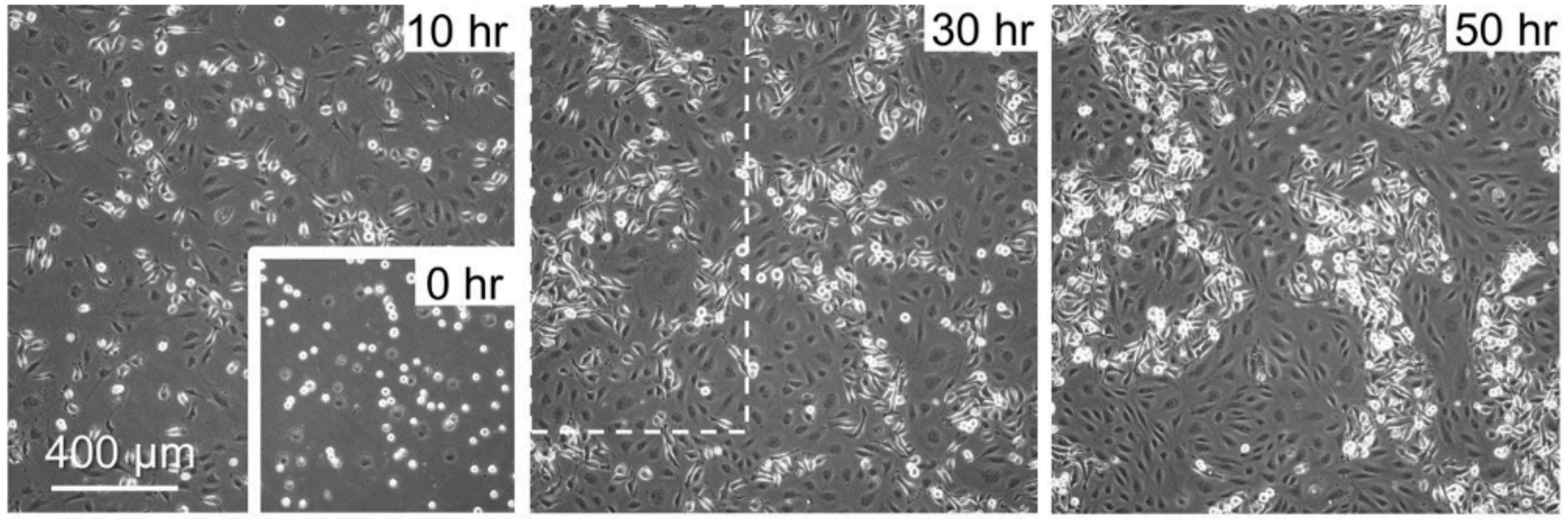
River Networks



Saturn rings

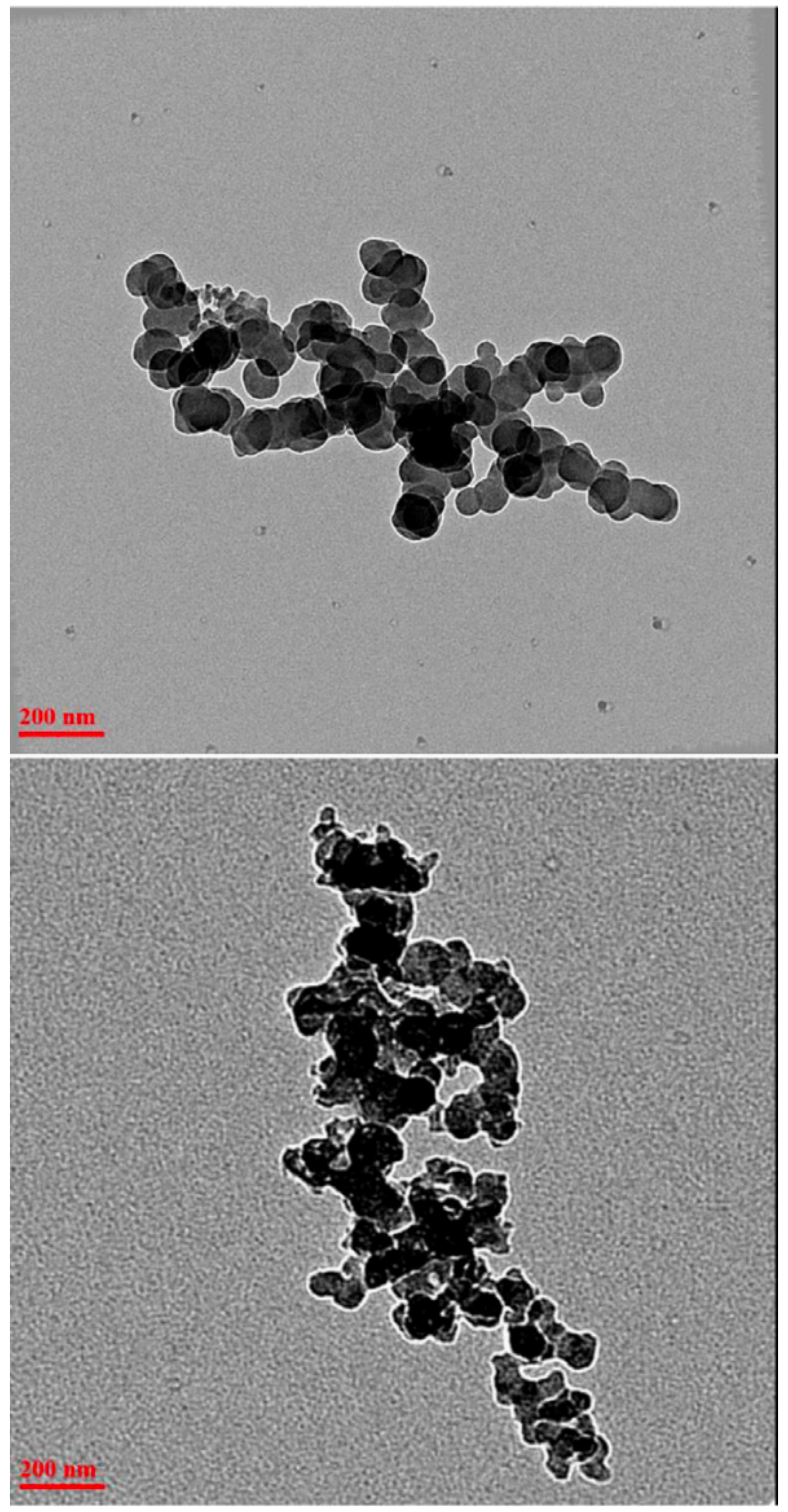
Shutterstock

Aggregation is ubiquitous



Bone marrow cancer cells

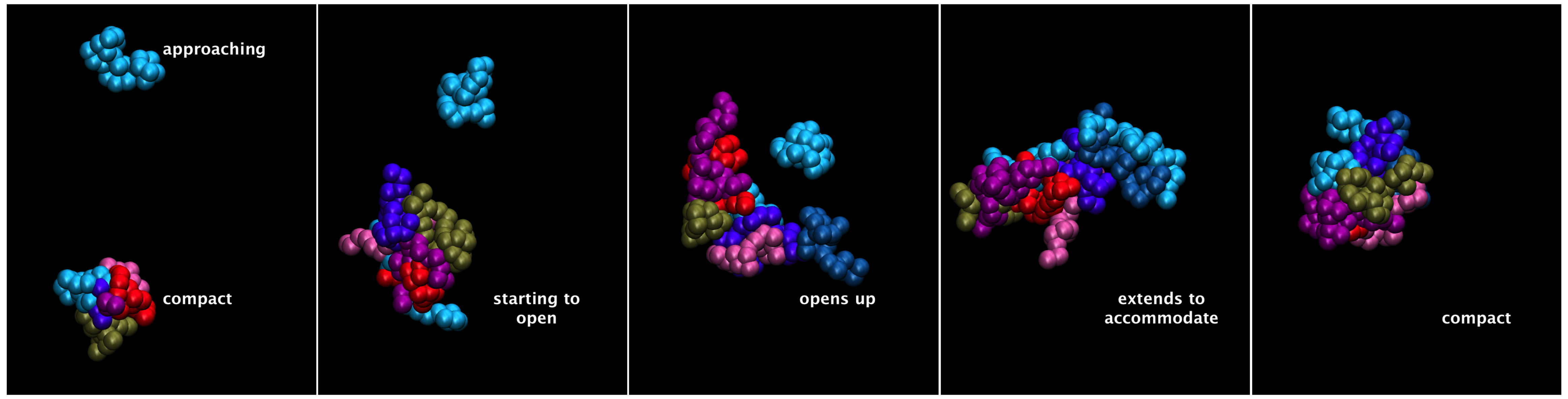
Liu et al, Phys. Rev. Res, 2021



Soot aggregates

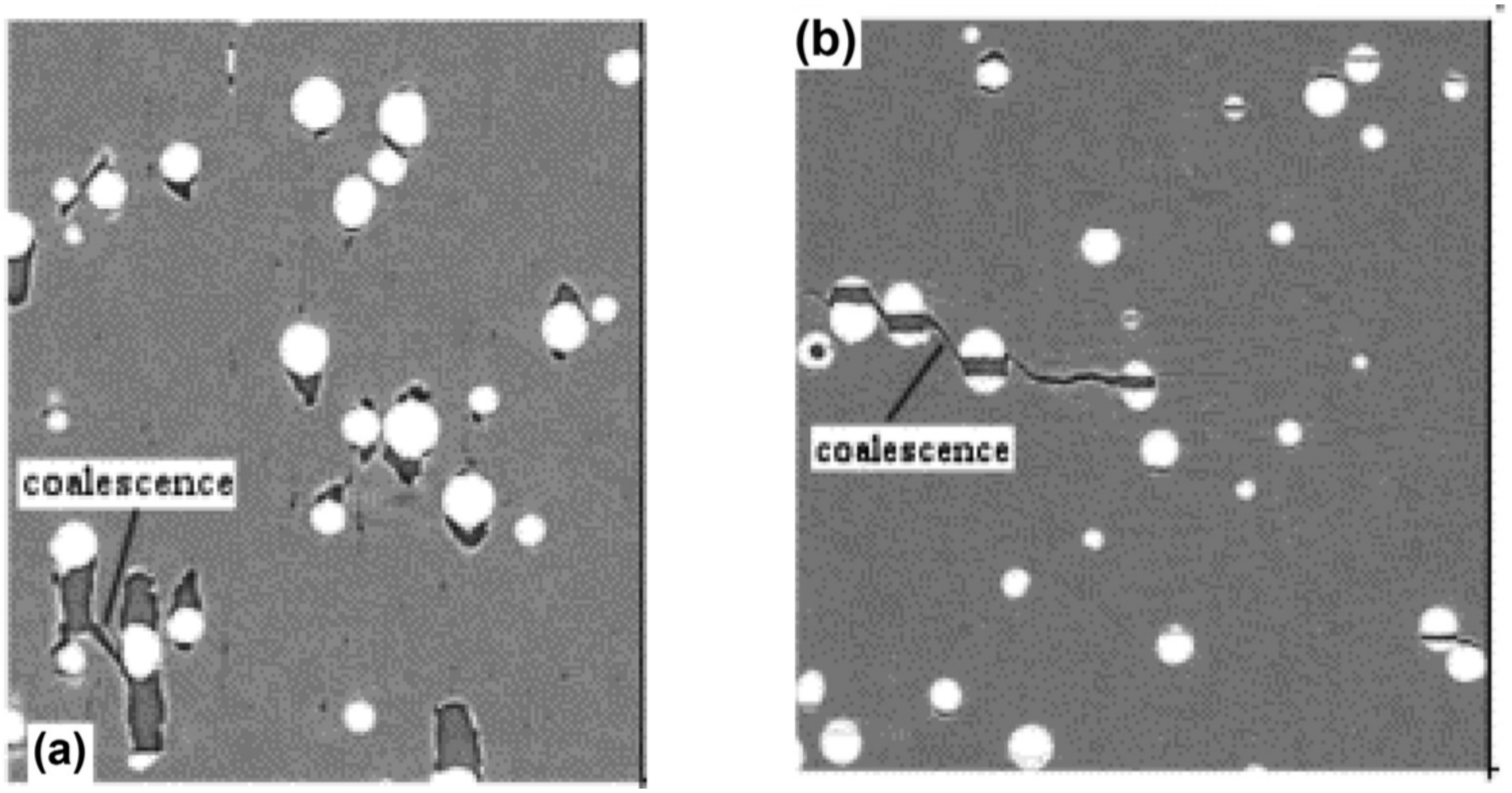
Zhang et al, J. Quant Spect Radiative Transfer, 2020

Aggregation is ubiquitous



Charged-polymers

Tom et al, J. Chem. Phys. (2017)



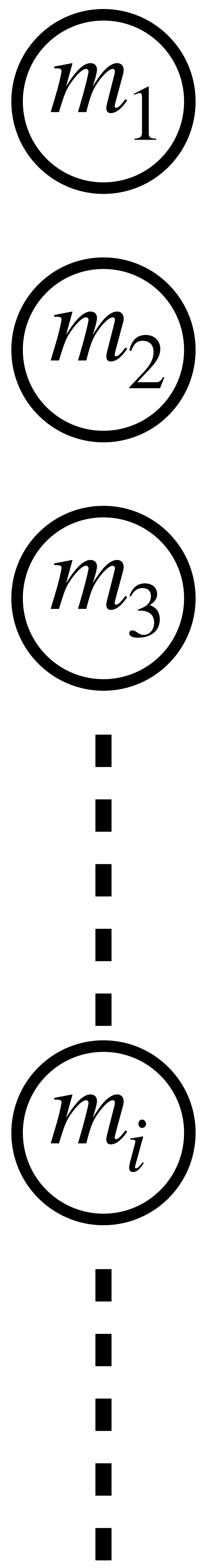
Void coalescence in ductile fracture

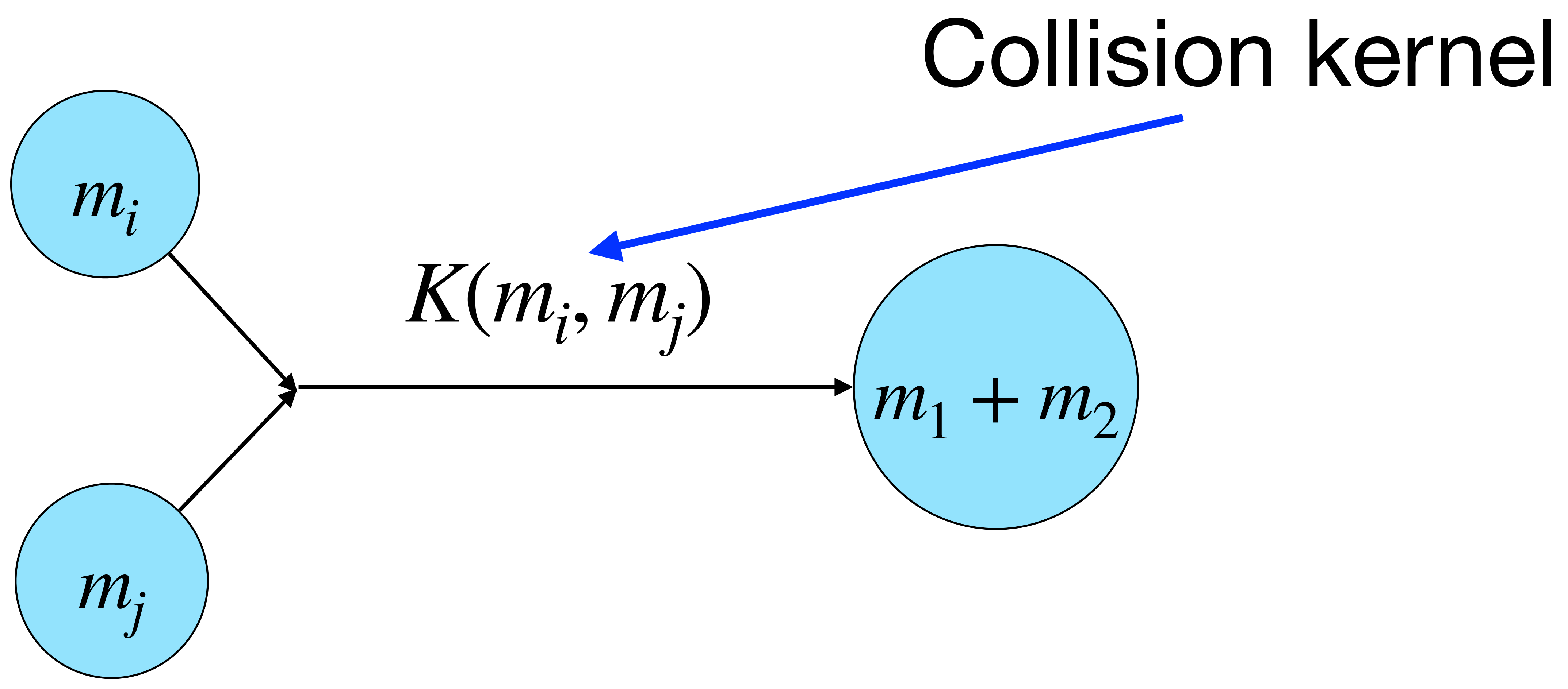
Pineau et al, Acta Materialia (2016)

Two features

- Two kinetic processes
  - Transport to bring clusters together
  - Aggregation on contact
- Modelling options
  - Model both processes separately
  - Combine them both into an effective collision kernel
  - For example: ballistic transport
    - $|v_1 - v_2|(r_1 + r_2)^{d-1}$

Model (Cluster-Cluster Aggregation)





- Initial condition: M particles of mass 1
- Mass conserved; Number decreases with time
- Marcus-Lushnikov model

Kernel for ballistic particles

$$K(m_1, m_2) \propto |v_1 - v_2|(r_1 + r_2)^{d-1}$$

$$\sim \sqrt{v_1^2 + v_2^2}(m_1^{1/d} + m_2^{1/d})^{d-1}$$

Momentum conservation

$$K(m_1, m_2) \sim \sqrt{m_1^{-1} + m_2^{-1}}(m_1^{1/d} + m_2^{1/d})^{d-1}$$

The standard approach (a brief review)

- Mean mass distribution
- Smoluchowski coagulation equation (1917)

$$\frac{dN(m,t)}{dt} = \frac{1}{2}\sum_{m_1=1}^{\infty}\sum_{m_2=1}^{\infty} K(m_1,m_2)N(m_1)N(m_2)\delta(m_1+m_2-m) - \sum_{m_1=1}^{\infty} K(m,m_1)N(m,t)N(m_1,t)$$

Gain term

Loss term

- Appears to conserve mass

$$\frac{d\langle m\rangle}{dt} = \frac{1}{2}\sum_{m_1=1}^{\infty}\sum_{m_2=1}^{\infty} K(m_1,m_2)N(m_1)N(m_2)(m_1+m_2) - \sum_{m=1}^{\infty}\sum_{m_1=1}^{\infty} K(m,m_1)mN(m,t)N(m_1,t)$$

$$\frac{d\langle m\rangle}{dt} = 0$$

Leyvraz, Phys. Rep 2003,
Aldous, Bernoulli, 1999,
Wattis, Physica D, 2006

- But not always true!

Smoluchowski Equation (Mass conservation)

- Consider mass flux from mass utmost m to greater than m

$$J(m) = \sum_{m_1=1}^{m} \sum_{m_2=m+1-m_1}^{\infty} K(m_1, m_2) m_1 N(m_1) N(m_2)$$

$$\frac{d(mN(m))}{dt} = J(m-1) - J(m)$$

$$\frac{d\langle m \rangle}{dt} = -J(\infty)$$

- Only is $J_\infty = 0$ will mass be conserved

Smoluchowski Equation (solution)

- Scaling solution (mass conservation)

$$N(m,t) \approx \frac{1}{\mathscr{M}(t)^2} f\left(\frac{m}{\mathscr{M}(t)}\right), \beta < 1 \qquad K(hm_1, hm_2) = h^{\beta} K(m_1, m_2)$$

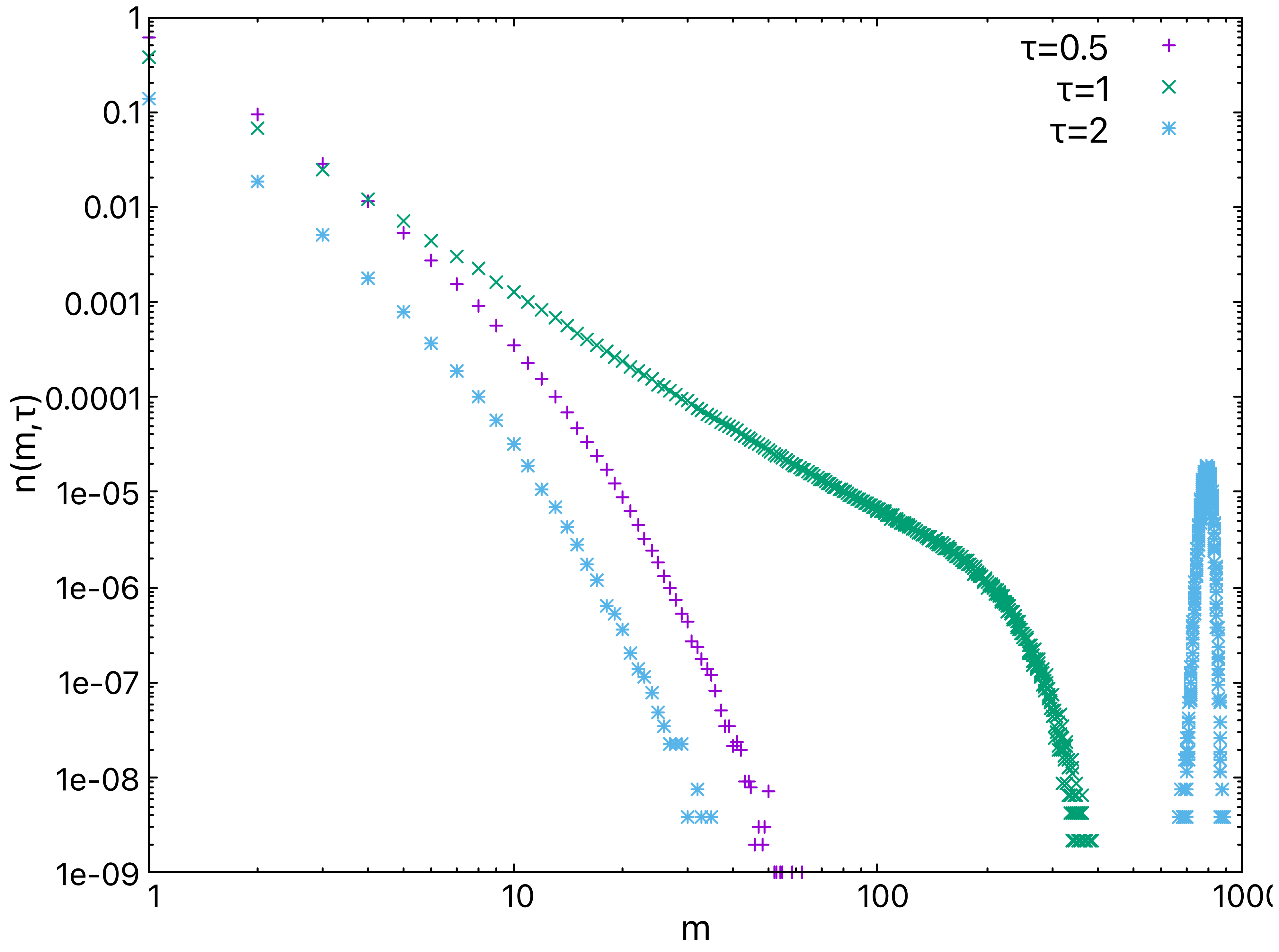
- Substitute into Smoluchowski equation
- Can obtain scaling of $\mathscr{M}(t)$
- Cannot calculate f for arbitrary kernel

Smoluchowski Equation (solution)

- Exact solution possible for three kernels
  - Constant: $K(m_1, m_2) = \lambda \;\; [\mathscr{M}(t) \sim t]$
  - Sum: $K(m_1, m_2) = \frac{\lambda}{2}(m_1 + m_2) \;\;\; [\mathscr{M}(t) \sim e^t]$
  - Product: $K(m_1, m_2) = \lambda m_1 m_2$ [mass not conserved]

Product Kernel

- $N(m,t) = \dfrac{m^{m-3} t^{m-1} e^{-mt}}{(m-1)!}$
- $\langle m^2 \rangle$ diverges at $t = 1$ (gelation transition)

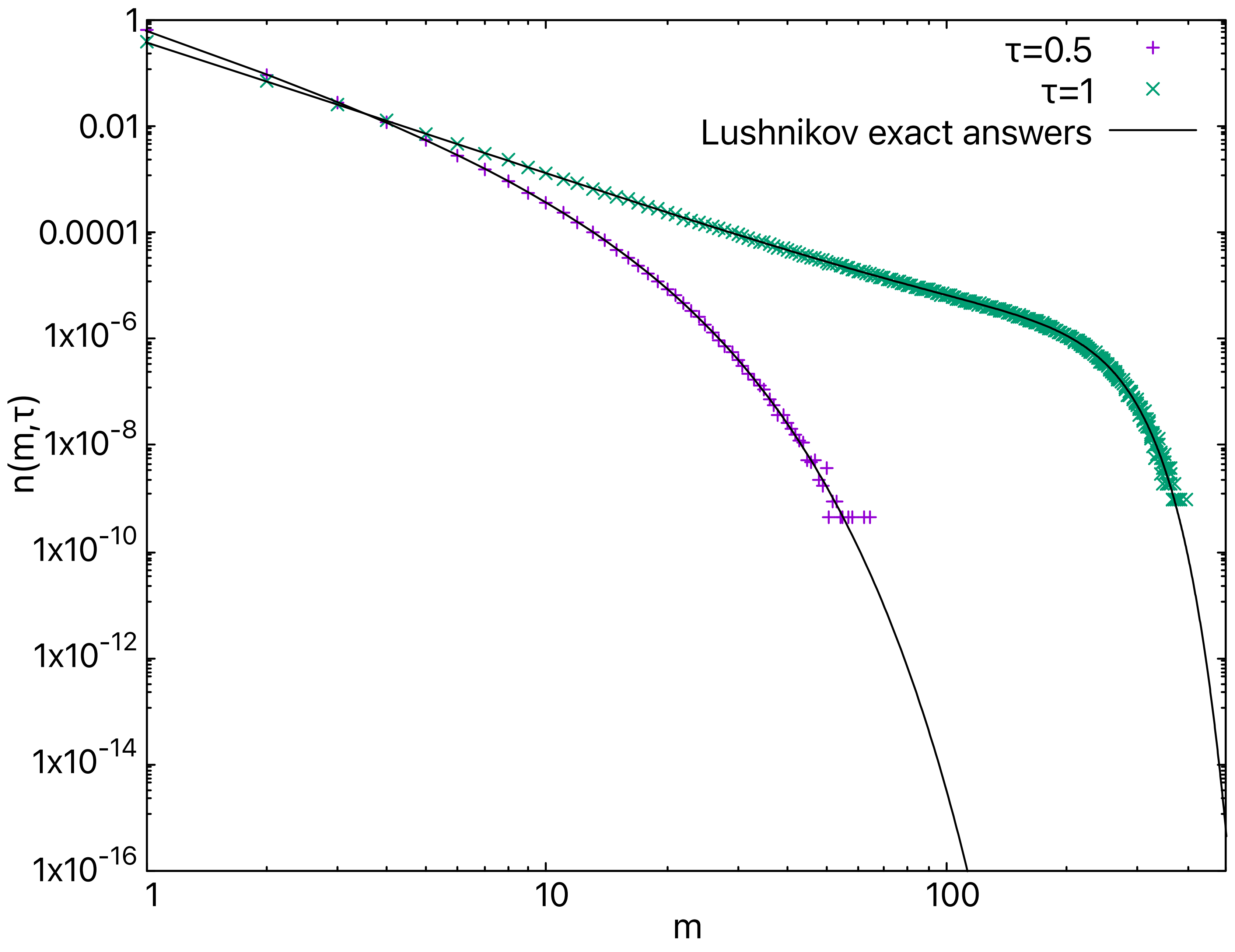


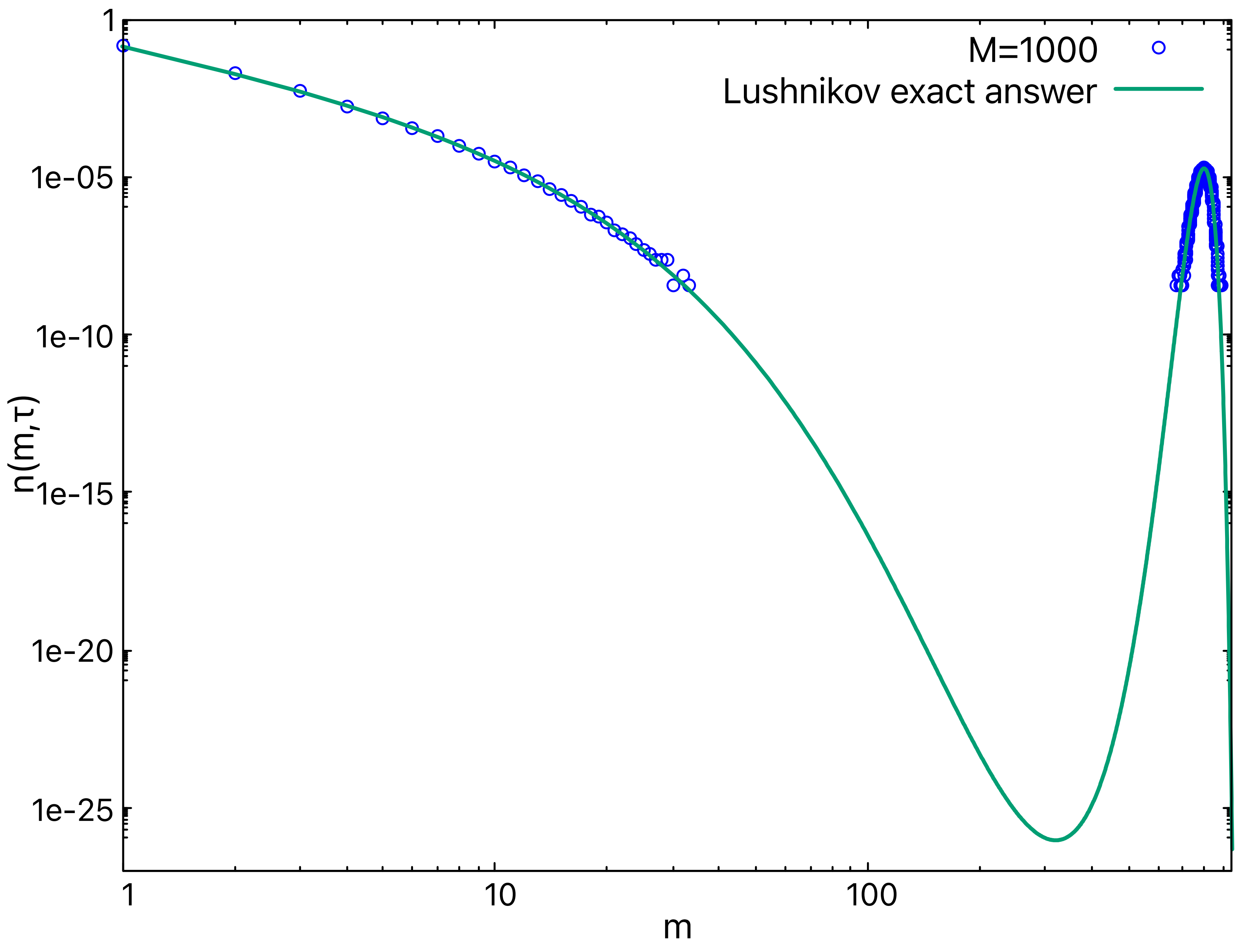
Lushnikov Solution

- A remarkable solution in terms of Mallows–Riordan polynomials

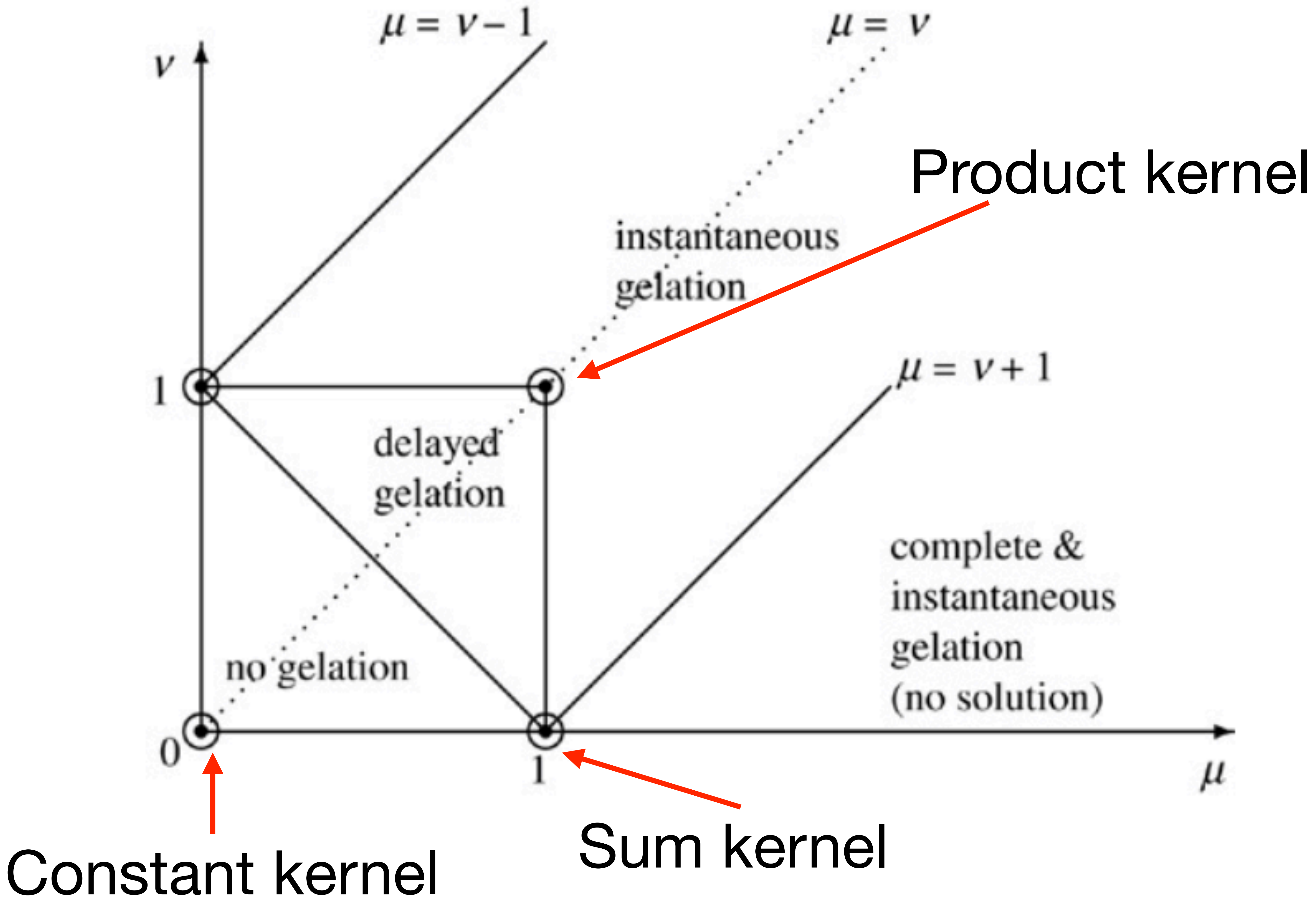
$$N(m,\tau) = \binom{M}{m} e^{(m^2-2mM+m)\tau}(e^{2\tau}-1)^{m-1}F_{m-1}(e^{2\tau})$$

AA Lushnikov, PRL 2004, Physica D 2006





Summary of Smoluchowski equation

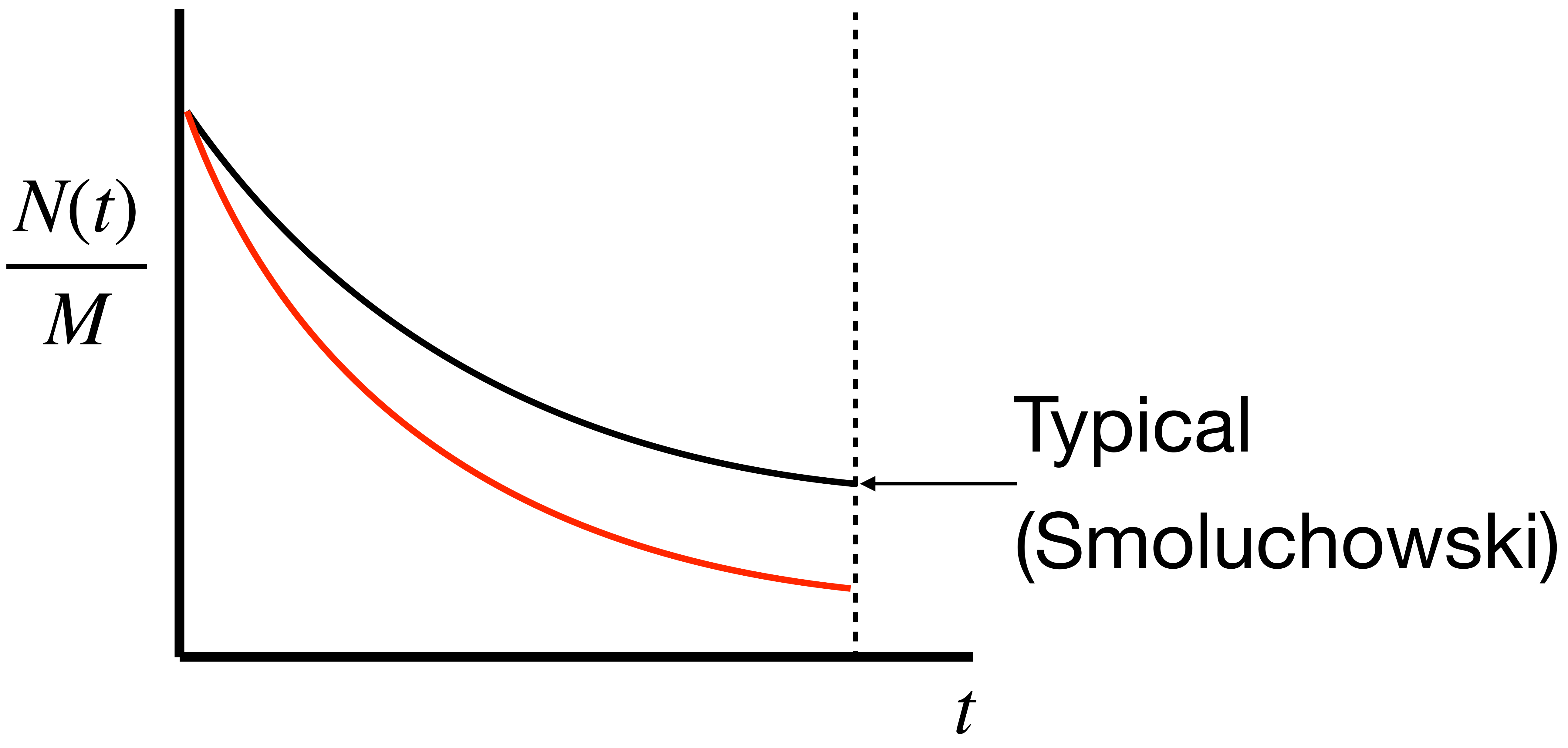


$$K(m_1, m_2) = \frac{1}{2}(m_1^\mu m_2^\nu + m_1^\nu m_2^\mu)$$

Wattis, Physica D, 2006

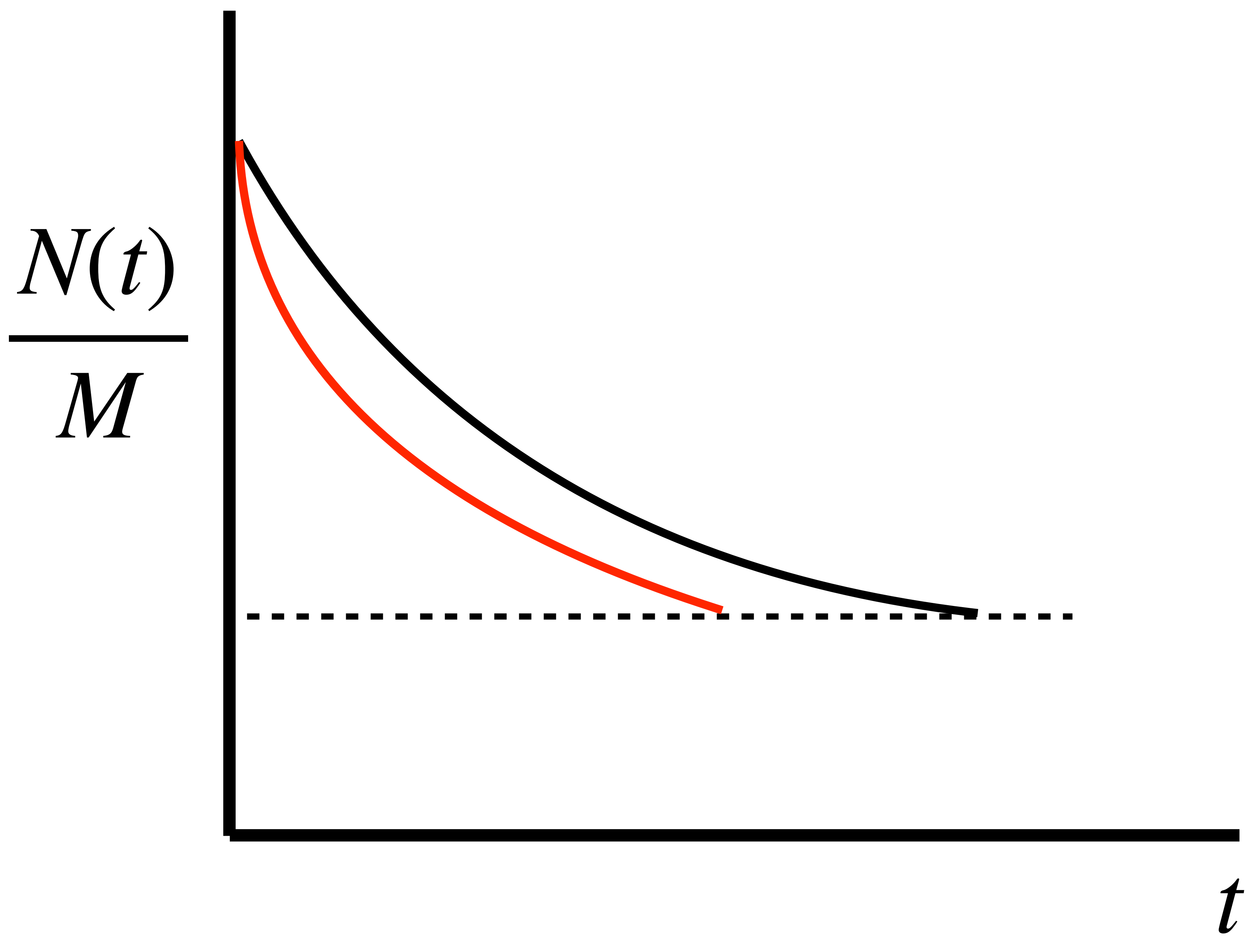
What are the probabilities of rare events?

This question is unanswered despite the long history



$P(M, N, t)$?

Probability of N particles at time t



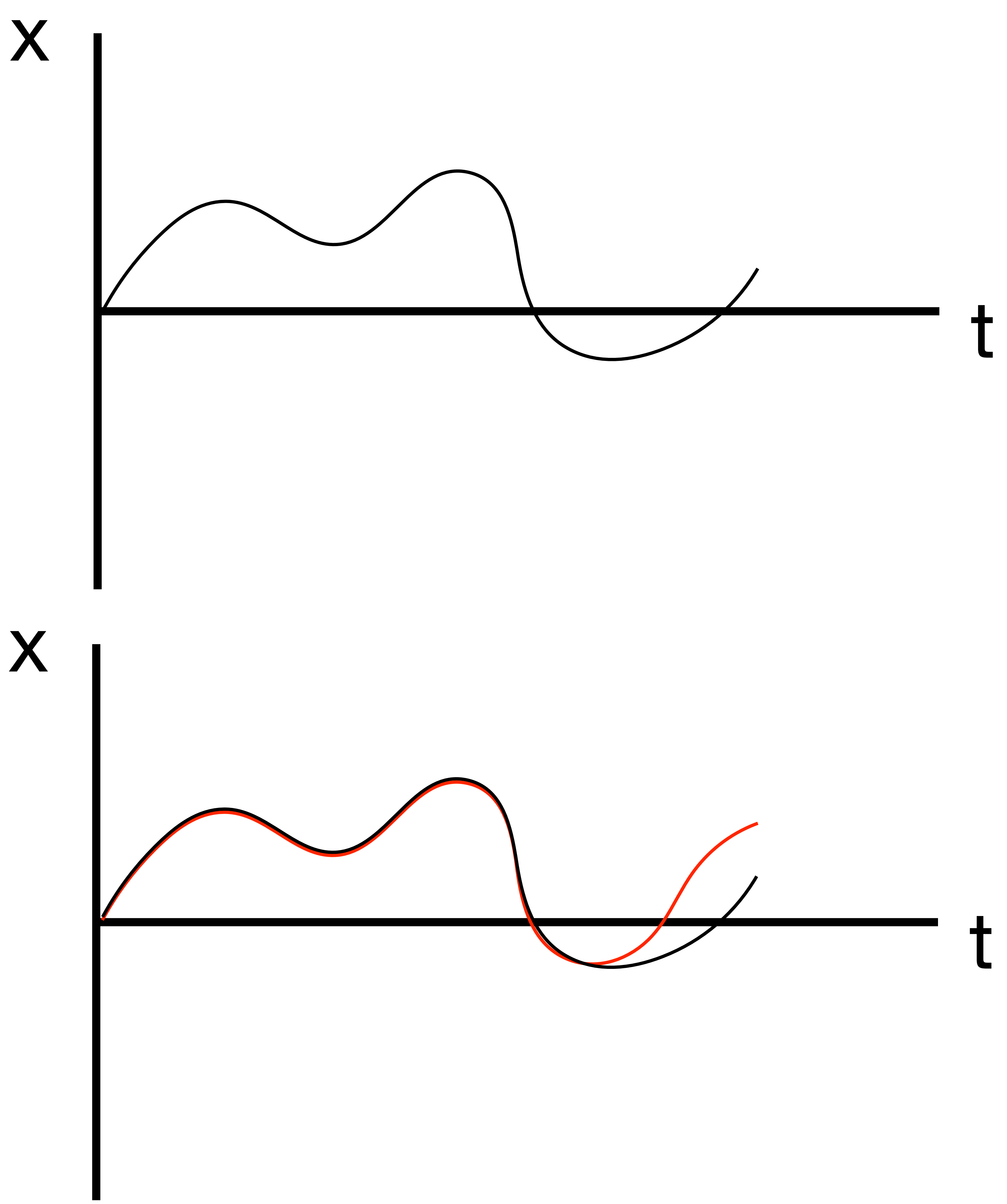
$\tilde{P}(M, N, t)$?

Probability of (M-N)-th collision at time t

Remainder of talk

- Will present
  - A numerical algorithm that works for any kernel
  - An analytical approach for constant, sum and product kernels

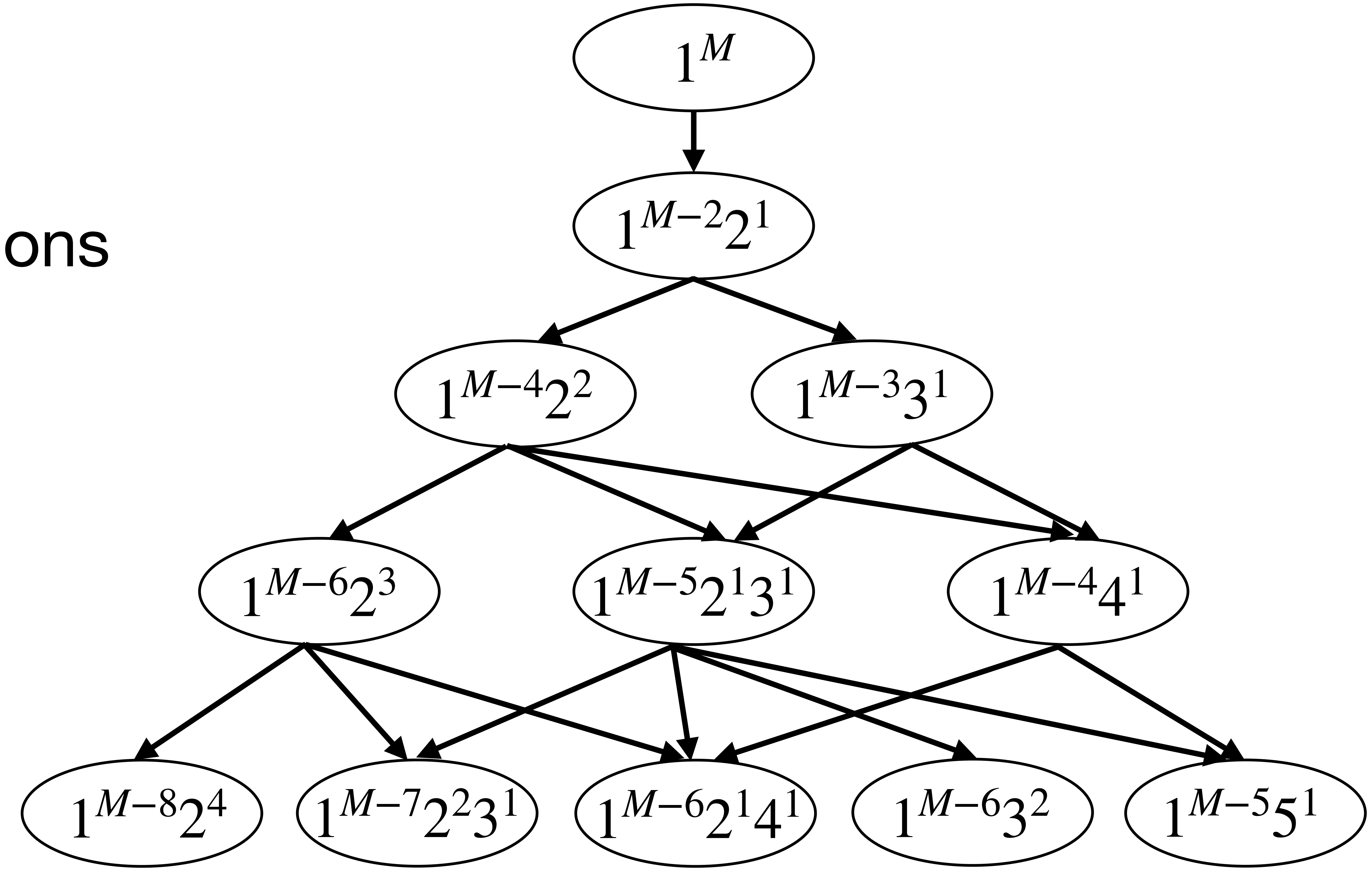
Biased Monte Carlo simulations



- Example of random walks
  - Weight trajectory with e^{wx}
  - Modify trajectory by changing one random number
  - Apply standard Metropolis rule to choose between trajectory: an equilibrium simulation between non equilibrium trajectories
  - Unweight bias

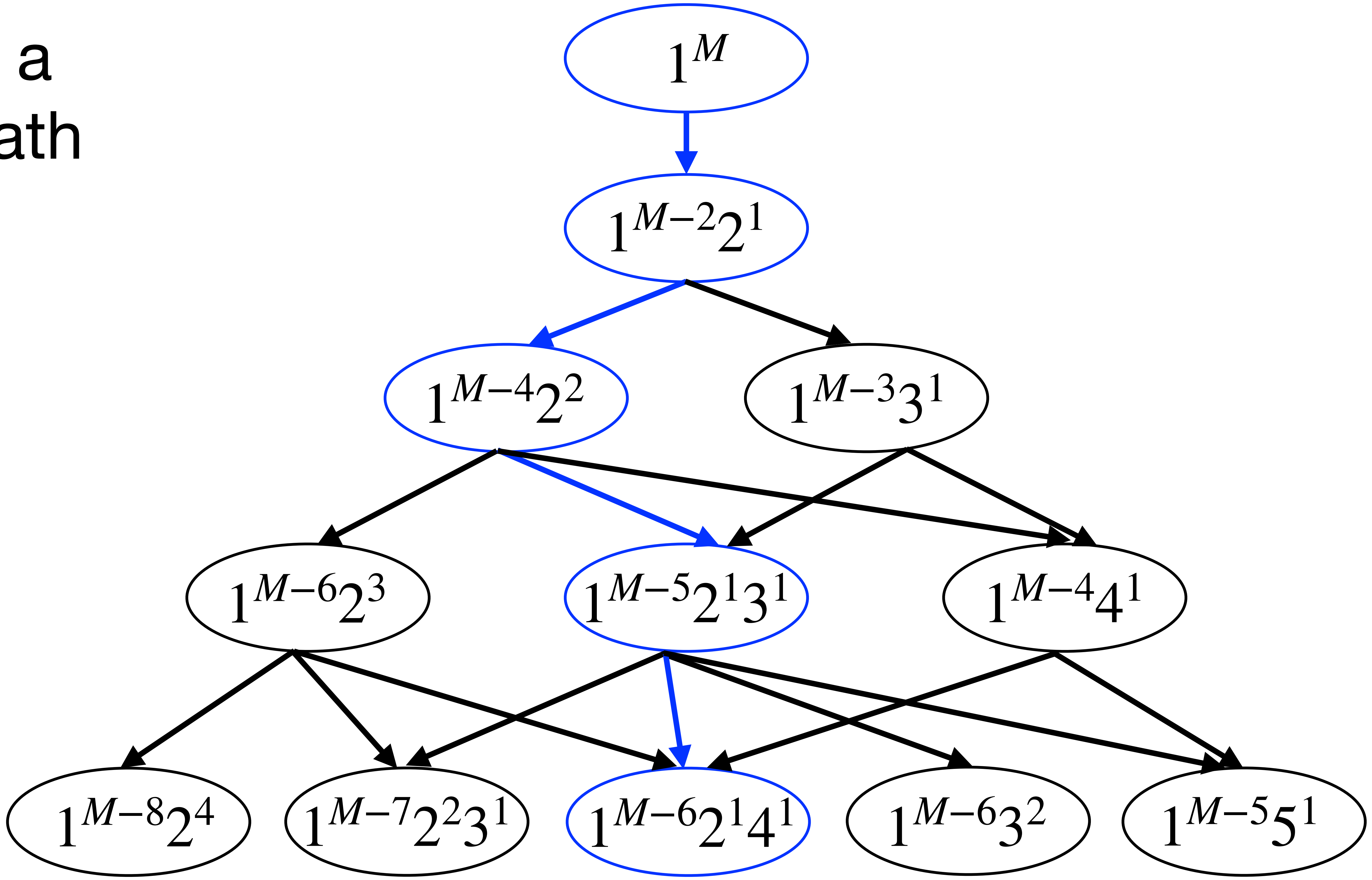
Algorithm

- Evolution: A directed graph
- Waiting times between configurations
- Total number of collisions



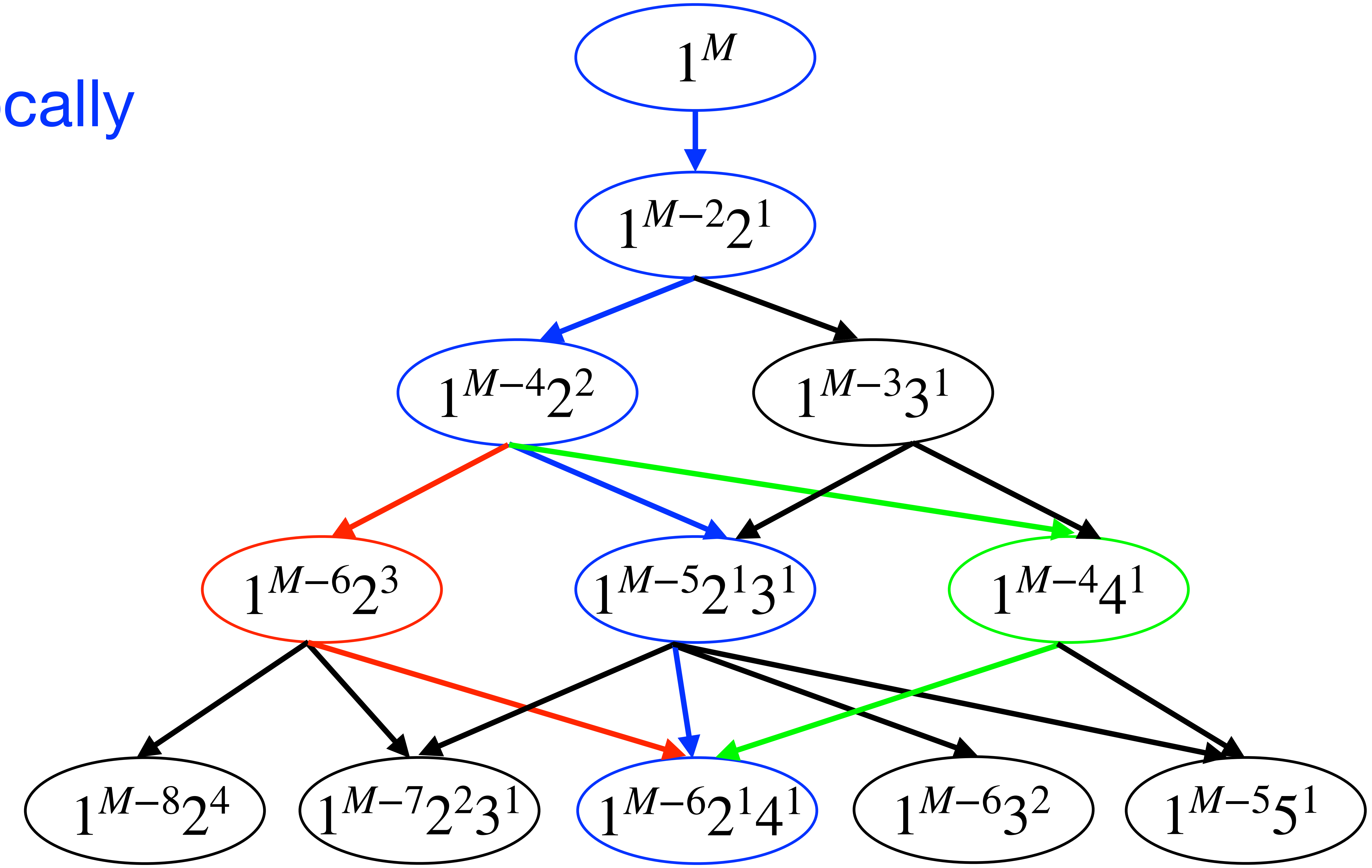
Algorithm

- Trajectory: a directed path



Algorithm

- Transform locally along loops



Ergodicity

- We prove ergodicity of loop interchange move
- Any trajectory can be transformed into a standard trajectory though only such reversible moves

Biasing the simulation

- Attaching weights to number of collisions/time
- In addition to modifying trajectory
  - Adding/deleting collisions
  - Modify the weighting times
- Kernel independent
- Mostly rejection free

Benchmarking (constant kernel)

$$\mathcal{R}_i = \frac{\lambda(M-i)(M-i-1)}{2}$$

$$P(M,N,t) = \int_0^\infty d\Delta t_0 \int_0^\infty d\Delta t_1 \ldots \int_{t=0}^\infty d\Delta t_{C-1} \quad \mathcal{R}_0 e^{-\mathcal{R}_0 \Delta t_0}$$

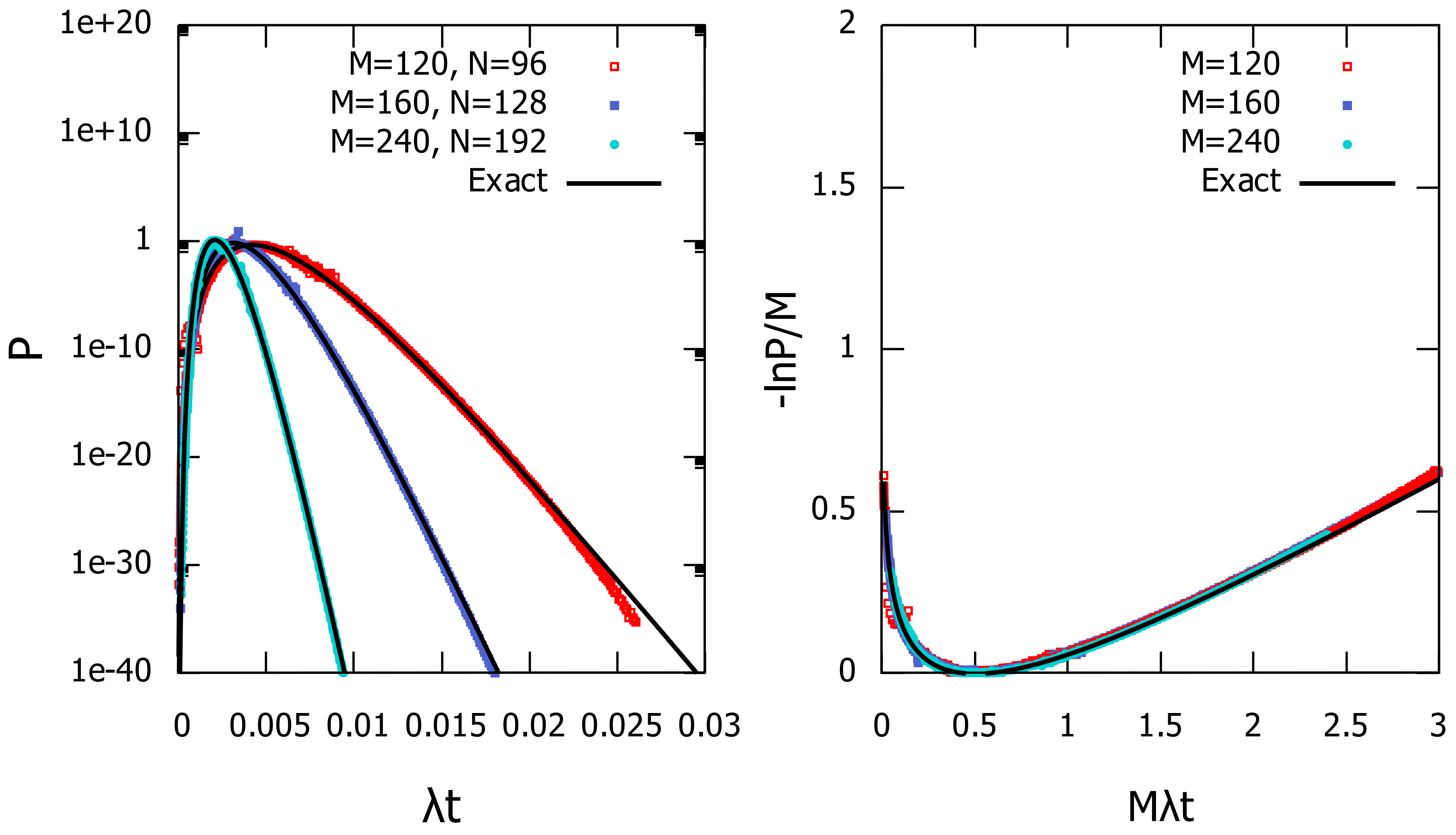
$$\mathcal{R}_1 e^{-\mathcal{R}_1 \Delta t_2} \ldots \mathcal{R}_{C-1} e^{-\mathcal{R}_{C-1} \Delta t_{C-1}} \delta\left(\sum_{i=0}^{C-1} \Delta t_i - t\right).$$

Laplace transform and inverse Laplace tranform

$$P(M,N,t) = \left(\prod_{k=0}^{C-1} \mathcal{R}_k\right) \sum_{i=0}^{C-1} e^{-\mathcal{R}_i t} \prod_{j \neq i, j=0}^{C-1} \frac{1}{\mathcal{R}_j - \mathcal{R}_i}$$

Algorithm able to obtain LDF

Constant kernel



Reproduces exact solution of $\tilde{P}(M, N, t)$ (by biasing time)

V. Subashri et al, Computer Phys. Comm. 2023

Analytics (summary of results)

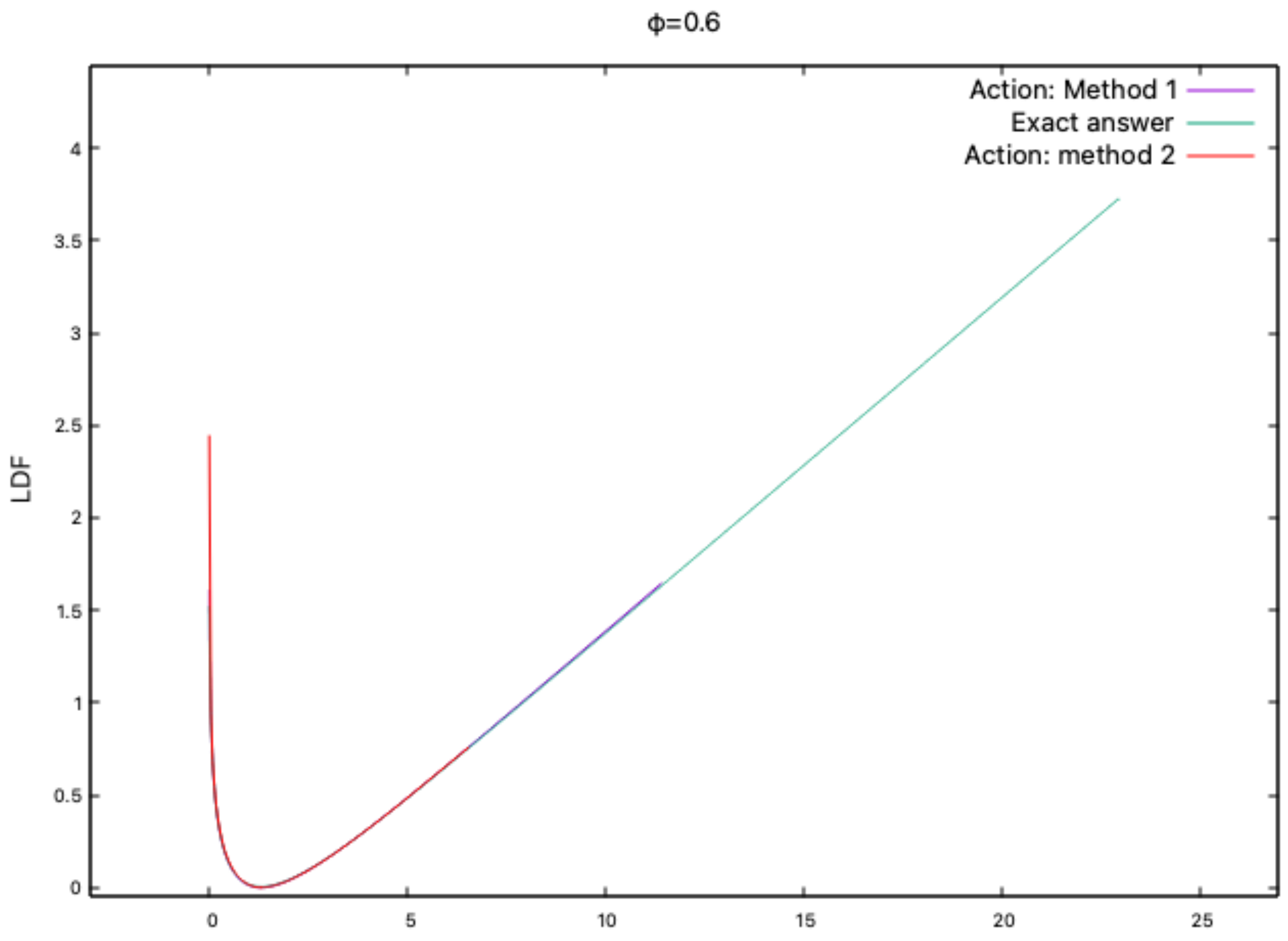
- For an arbitrary kernel: $P(M, N, t) \sim \exp\left[-Mf\left(\frac{N}{M}, Mt\right)\right]; \phi = \frac{N}{M}, \tau = Mt$
- $M \to \text{rate}$
- Exact expressions of $f(\phi, \tau)$ for constant, sum, and product kernel
- Exact expression for the instant trajectory for constant and sum kernel and some regimes of product kernel
- For the product kernel, $\frac{d^2 f(\phi, \tau)}{d\phi^2}$ has a discontinuity for $\tau \gtrsim 1$

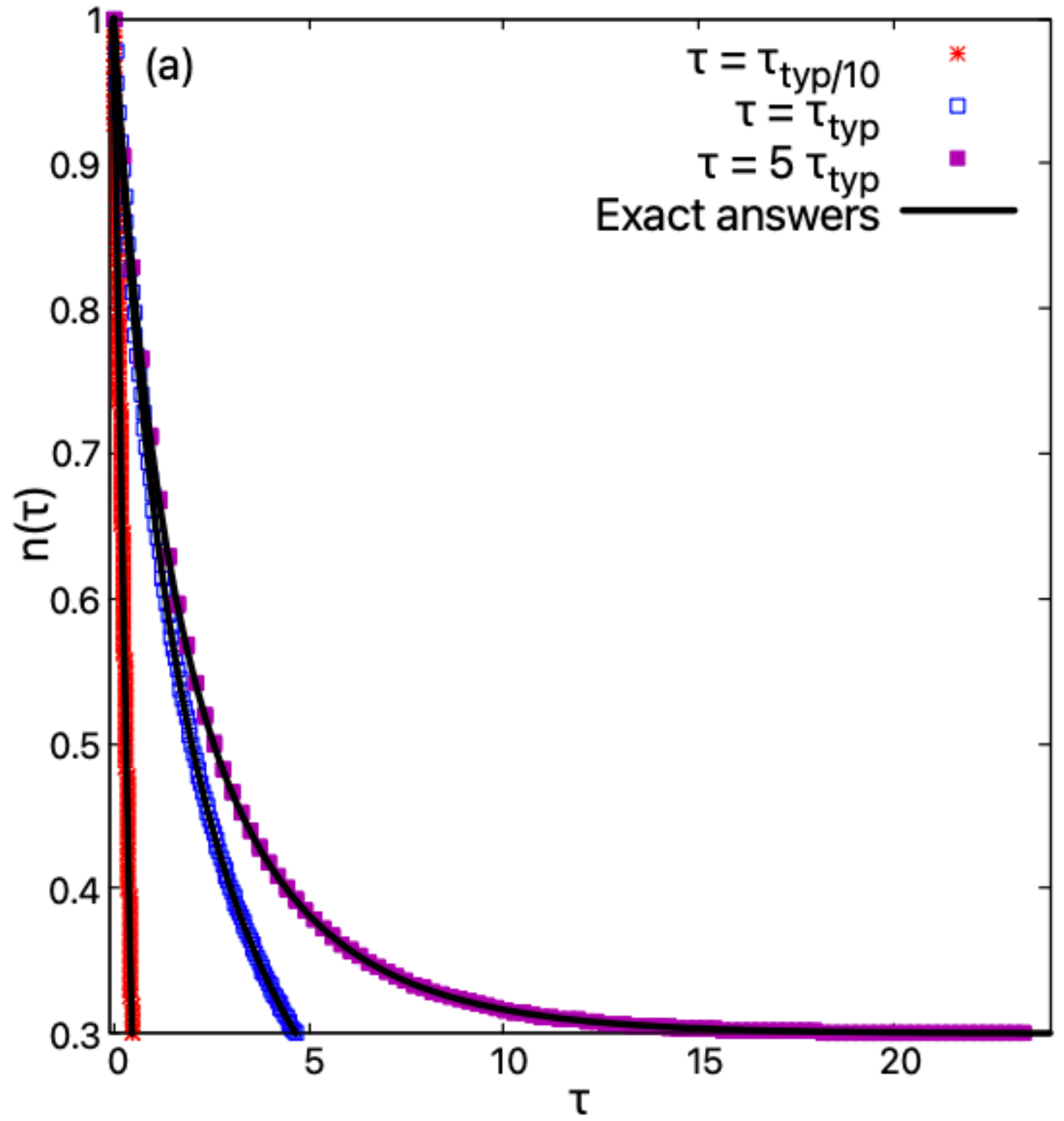
Constant Kernel

$$\frac{dn}{dt} = -\frac{n^2}{2} + E, \quad n(0) = 1; n(\tau) = \phi$$

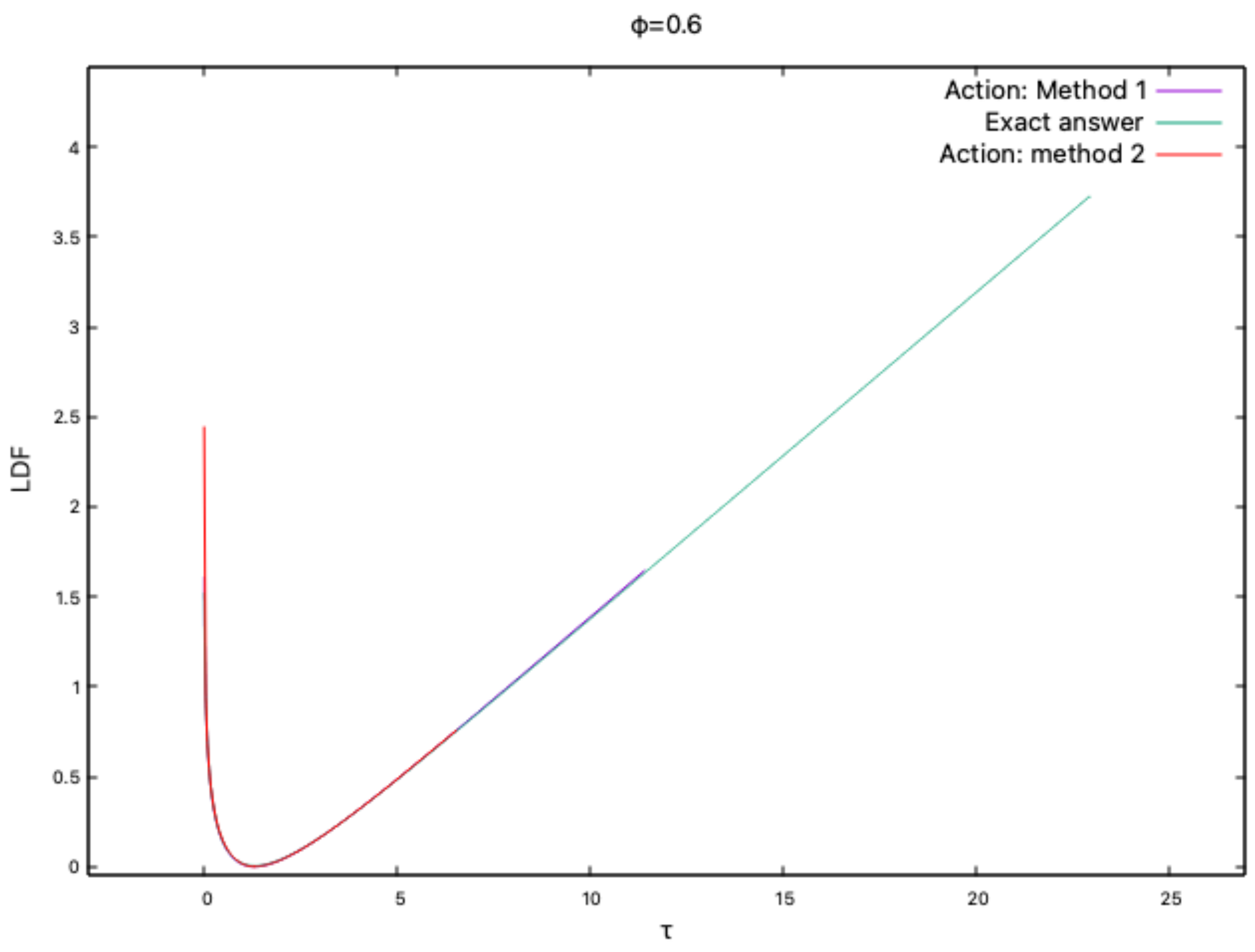
$$f(\phi,\tau) = \begin{cases} 2\phi\ln\phi + \ln(1-E) - \phi\ln(-E+\phi^2) - \frac{E\tau}{2}, & E<0, \\ 0, & E=0, \\ -E\tau - 2\phi\ln 2E\phi - (1-\phi)\ln\frac{\sinh\tau\sqrt{E/2}}{1-\phi} + \\ (1+\phi)\ln(\sqrt{2E}\cosh\tau\sqrt{E/2} + \sinh\tau\sqrt{E/2}), & E>0. \end{cases}$$

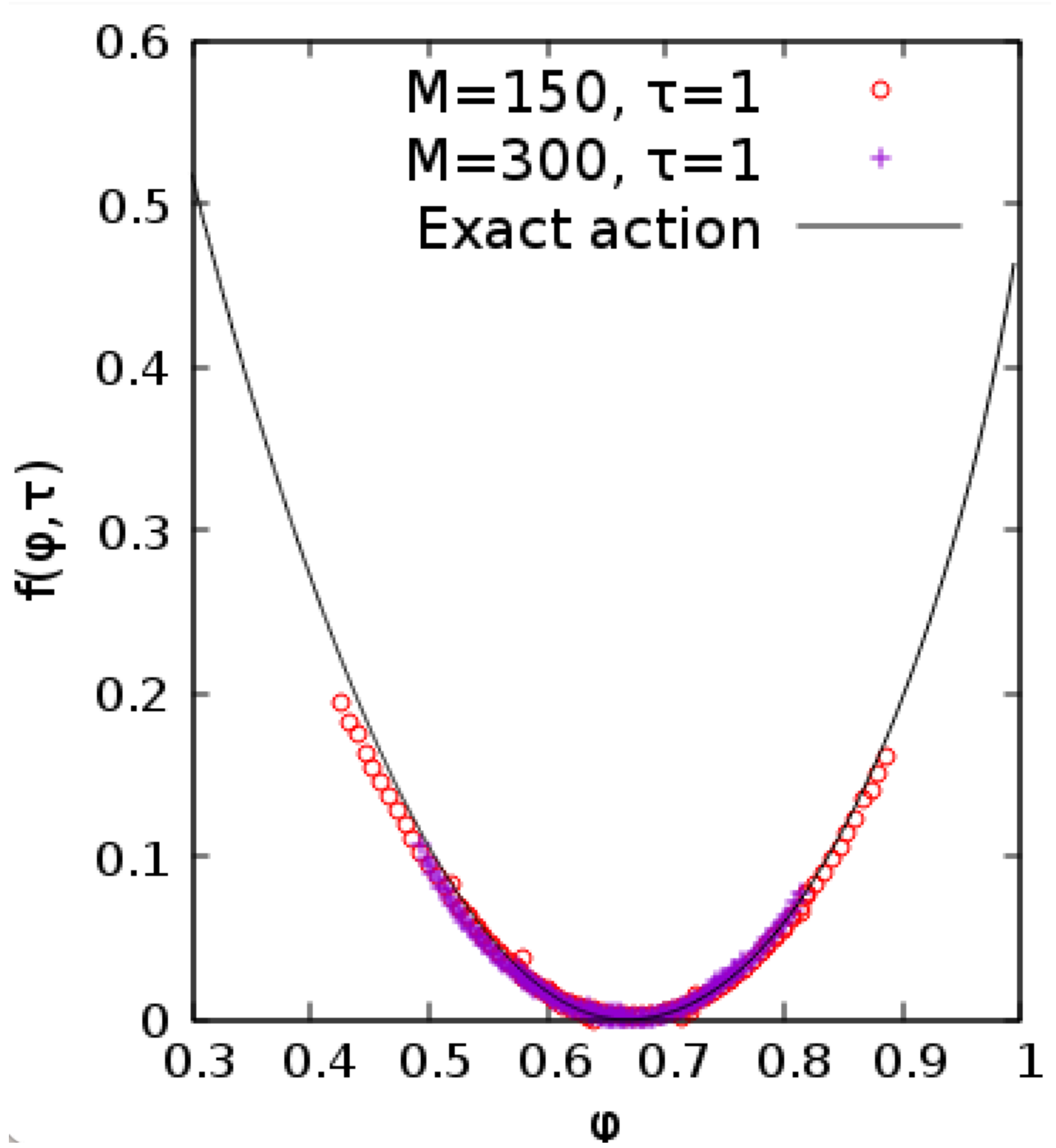
$$E = 0 \implies f = 0 \text{ and Smoluchowski equation}$$

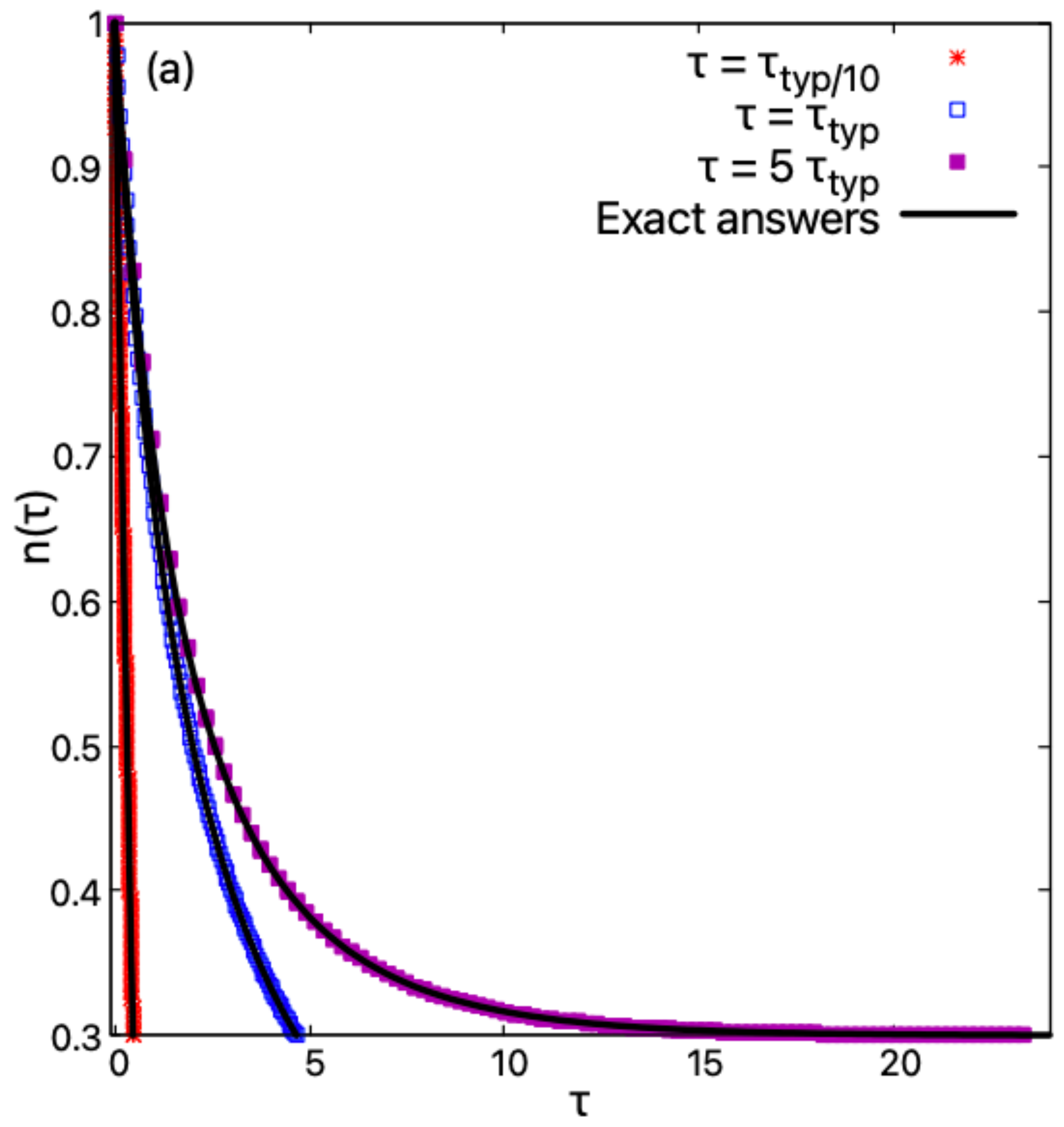




Constant Kernel







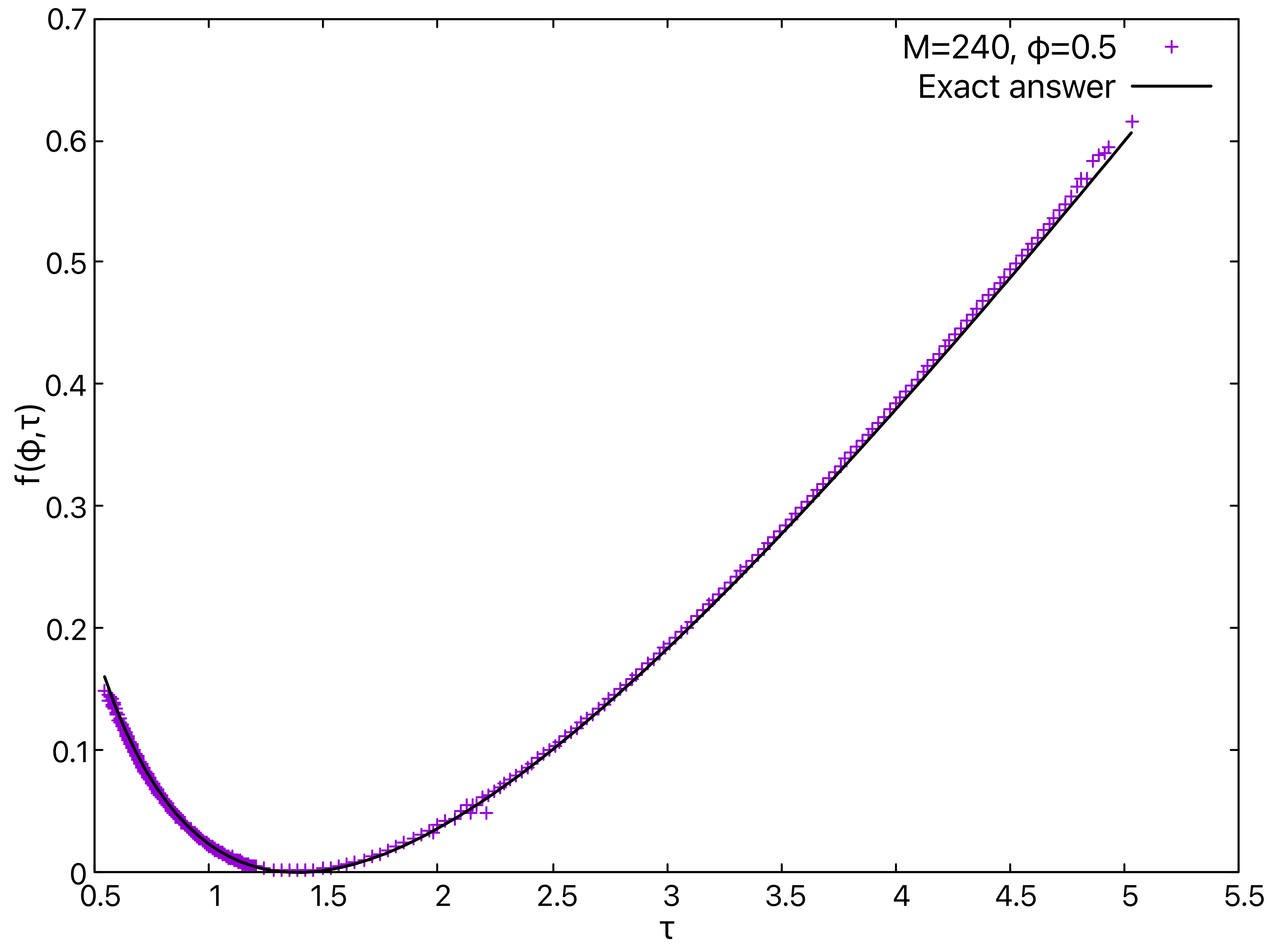
$\phi = 0.3$

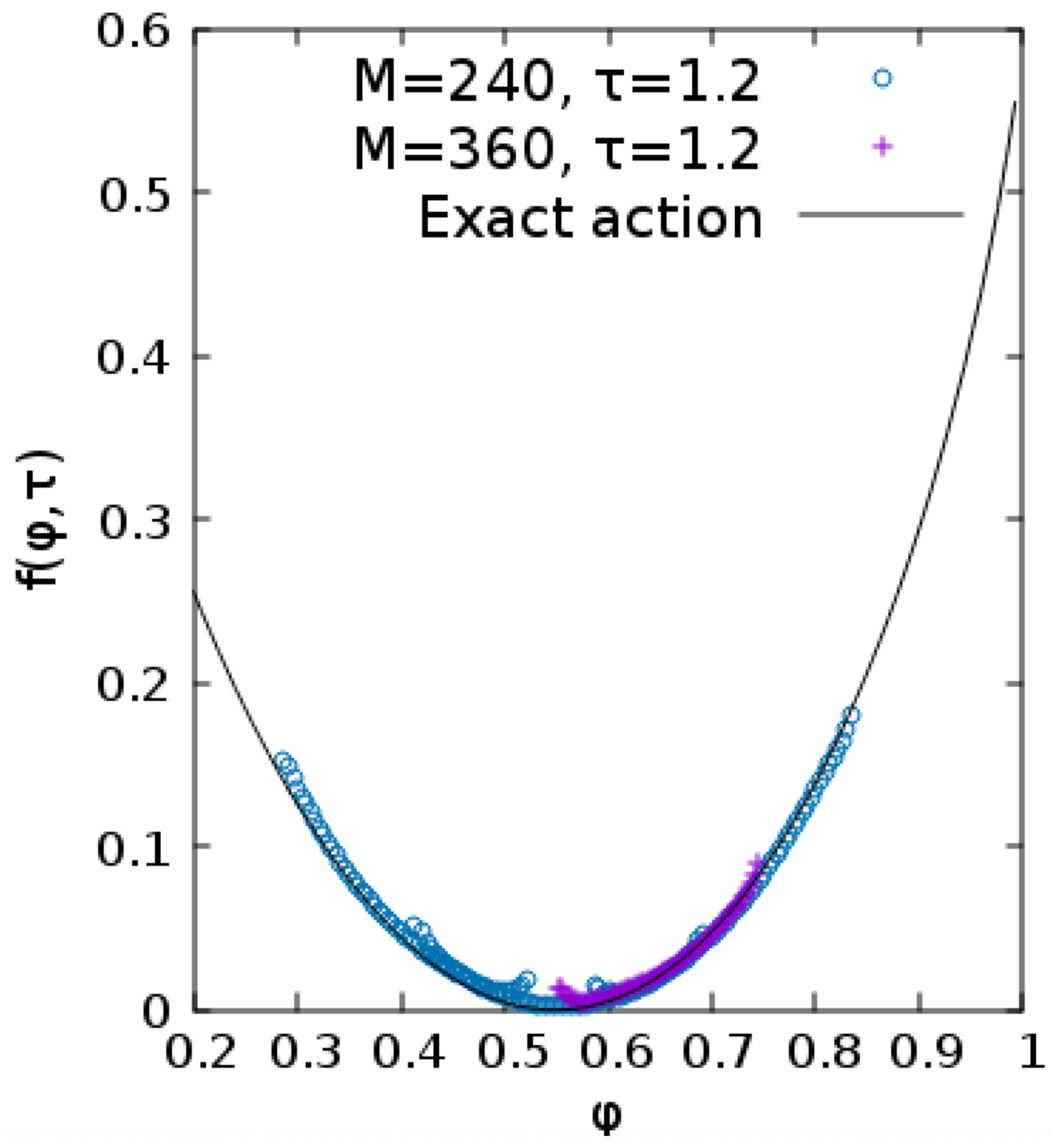
Sum Kernel

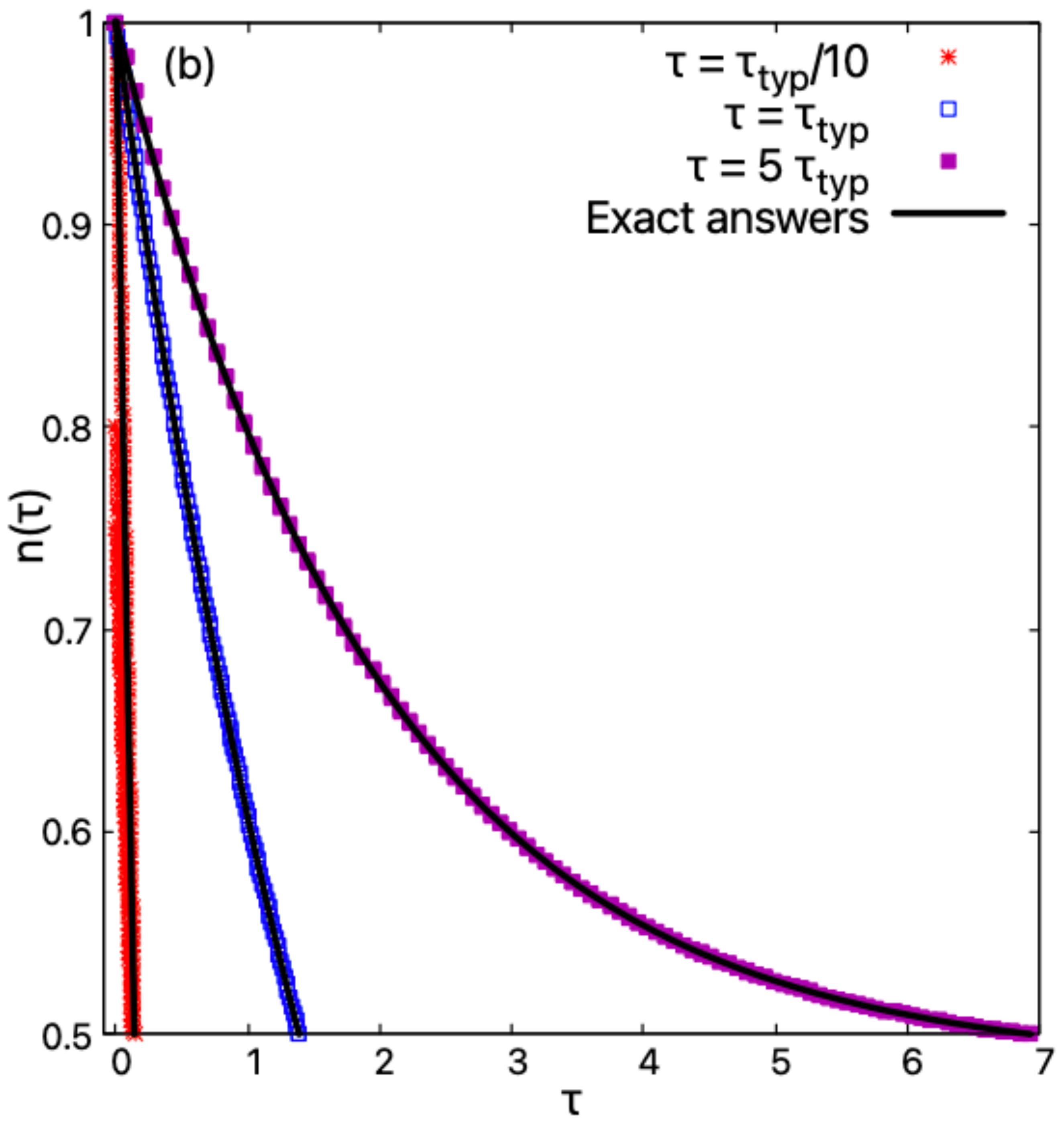
$$n(t) = 2E - (2E-1)e^{-\frac{\tau}{2}}, \quad n(\tau) = \phi$$

$$f(\phi,\tau) = -(1-\phi)\ln(1-e^{-\frac{\tau}{2}}) + \frac{\tau\phi}{2} + \phi\ln\phi + (1-\phi)\ln(1-\phi)$$

$\phi = 0.5$







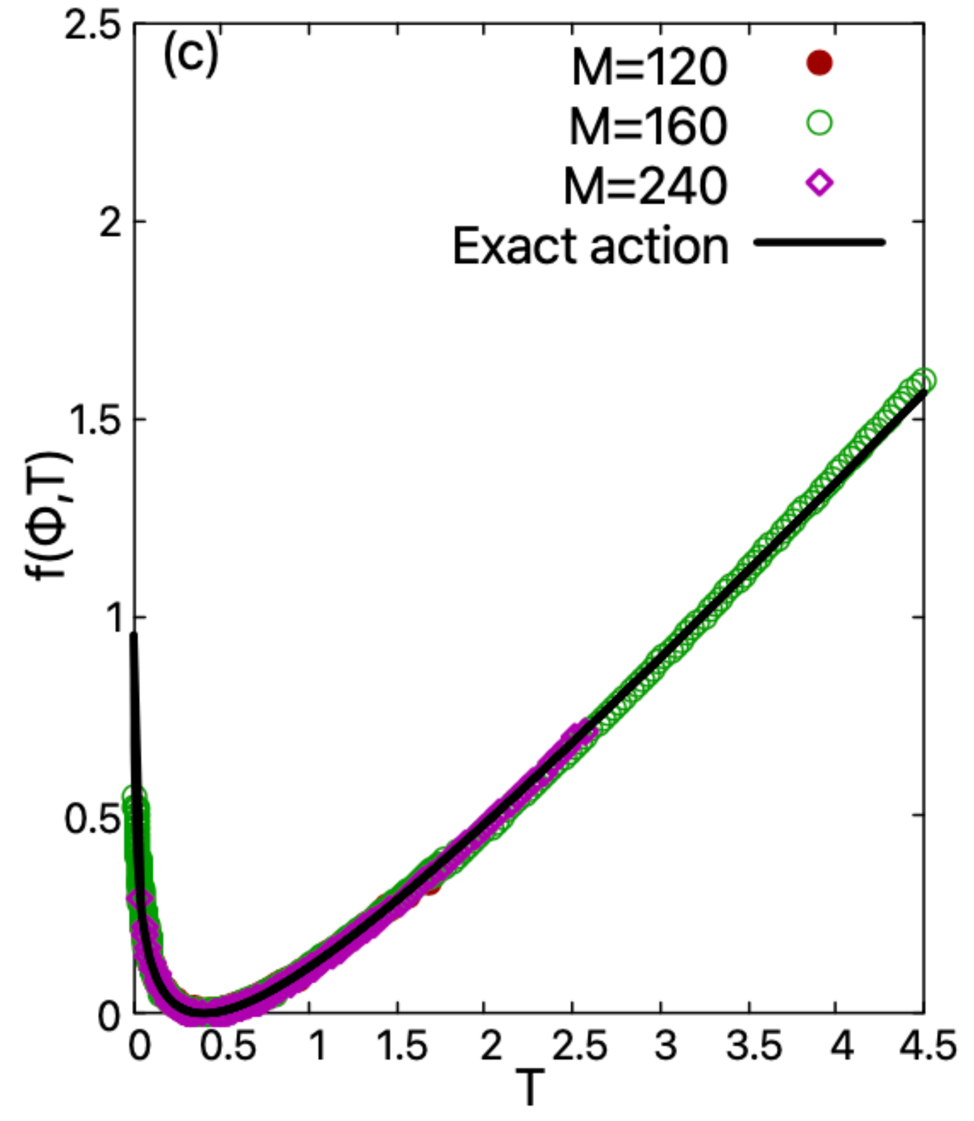
Product Kernel

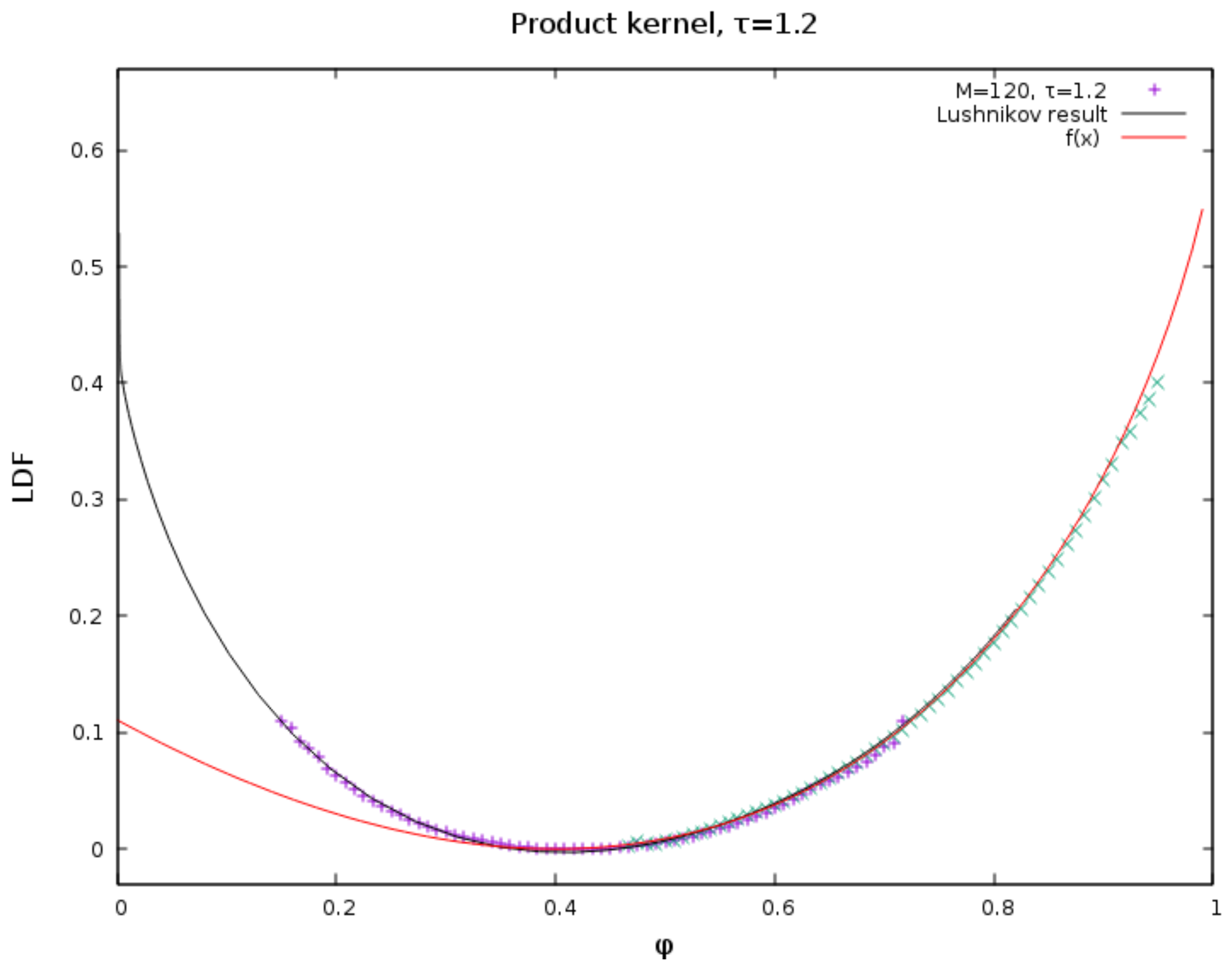
$$f(\phi,\tau) = \phi\ln\phi - (\phi-1) + \frac{\tau}{2} - (1-\phi)\ln\tau + g(\phi)$$

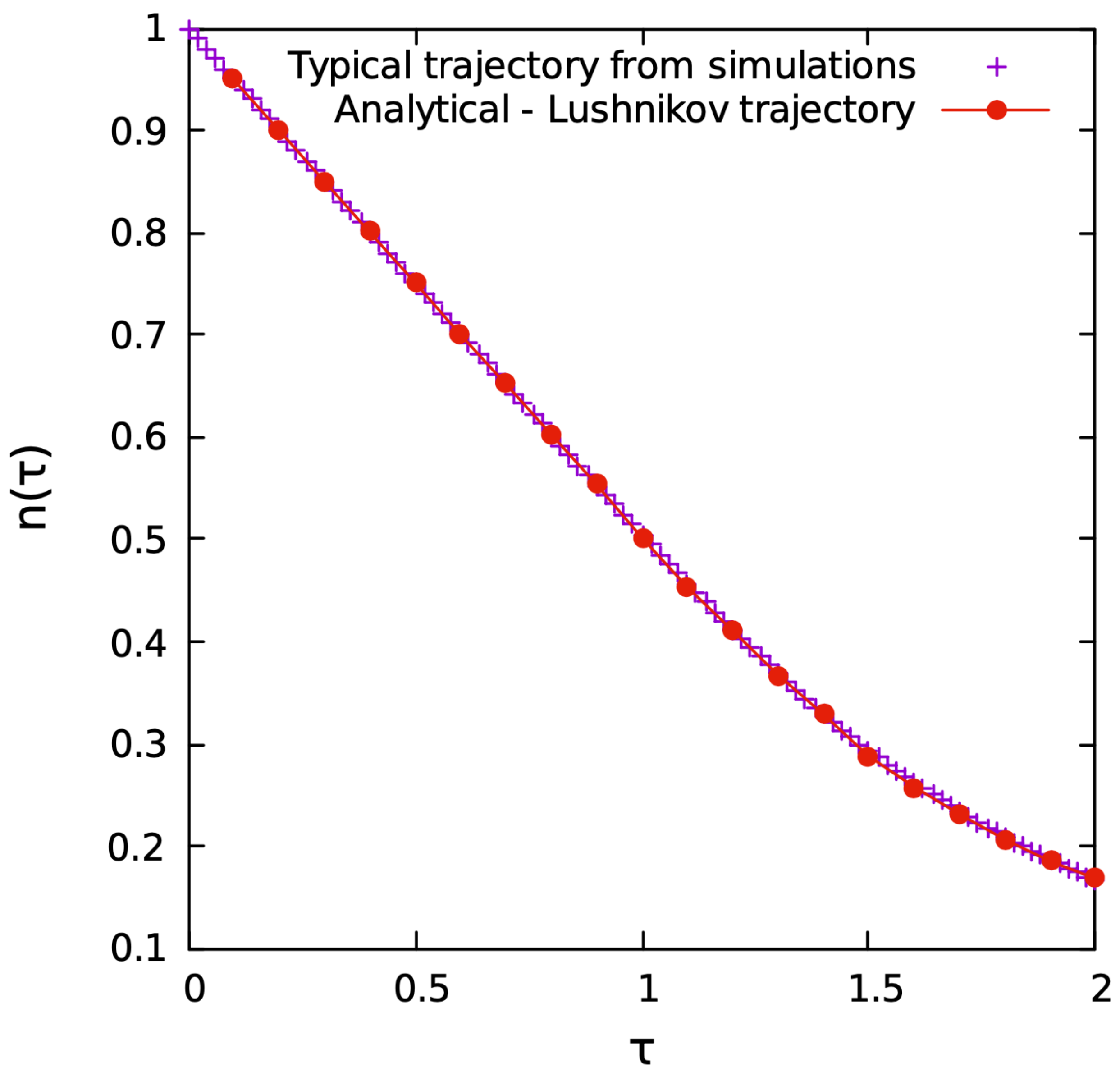
$$g(\phi) = \max_x \left[\ln x - \phi\ln\left[\sum_{k=1}^{M}\binom{M}{m} x^k e^{k^2\tau/M} F_{k-1}(e^{2\tau/M})\right]\right]$$

Evaluate numerically

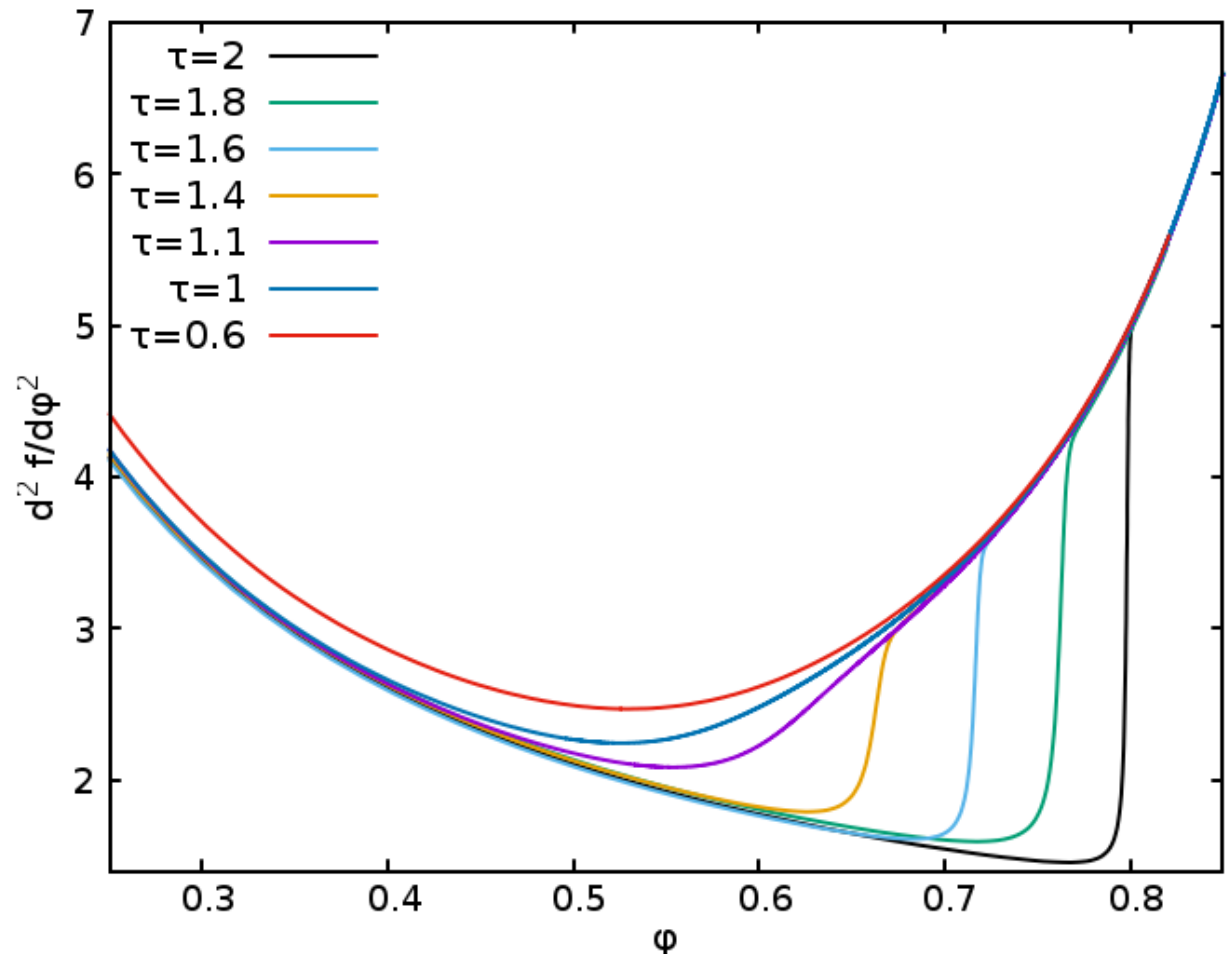
$\phi = 0.8$







Product kernel singularity



Method of solution

- Start with master equation
- Follow Doi-Zeldovich procedure
  - Introduce annihillation, creation operators to rewrite as Schrödinger equation and derive effective Hamiltonian
  - Introduce coherent states to derive effective action

$$P(M,N,t) \sim \frac{1}{N!}\int \mathscr{D}\tilde{z}_i(t)\mathscr{D}y_i(t) \sum_{k_1,k_2,\ldots k_N=1}^{M} \delta\left(\sum_i k_i - M\right)\exp\left(-M\int_0^\tau dt\left(\sum_{m=1}^{M}\tilde{z}_m\dot{y}_m + E(\{y_i,\tilde{z}_i\}) + \delta(t) - \frac{1}{M}\sum_{n=1}^{N}\ln y_{k_n}(\tau)\delta(t-\tau)\right)\right)$$

$$E(\{z_i\},\{\tilde{z}_i\}) = -\frac{1}{2}\sum_{i,j} K(i,j)(\tilde{z}_{i+j} - \tilde{z}_i\tilde{z}_j)z_i z_j$$ (“Hamiltonian”, a constant of motion)

- Solve Euler-Lagrange equations with appropriate boundary conditions
- Evaluate δ function by saddle point method

Conclusions and Outlook

- Aggregation an infinite species system
- Able to calculate LDF for standard kernels
  - Goes beyond the usual paradigm in aggregation
- LDF singular for product kernel. Expect it to hold for gelling kernels
- For product kernel different approaches give different action, and different LDF!
  - Correctness decided based on Lushnikov equation
- Mass distribution along trajectory can also be calculated
- Questions
  - $P(M,1,t)$?
  - Probability of fluctuations about instant trajectory?
  - LDF when there is an input of particles
  - k-nary collisions?
  - Other kernels numerically