

Instantons, Non-Convexity, and Ensemble Inequivalence in Product-Kernel Aggregation

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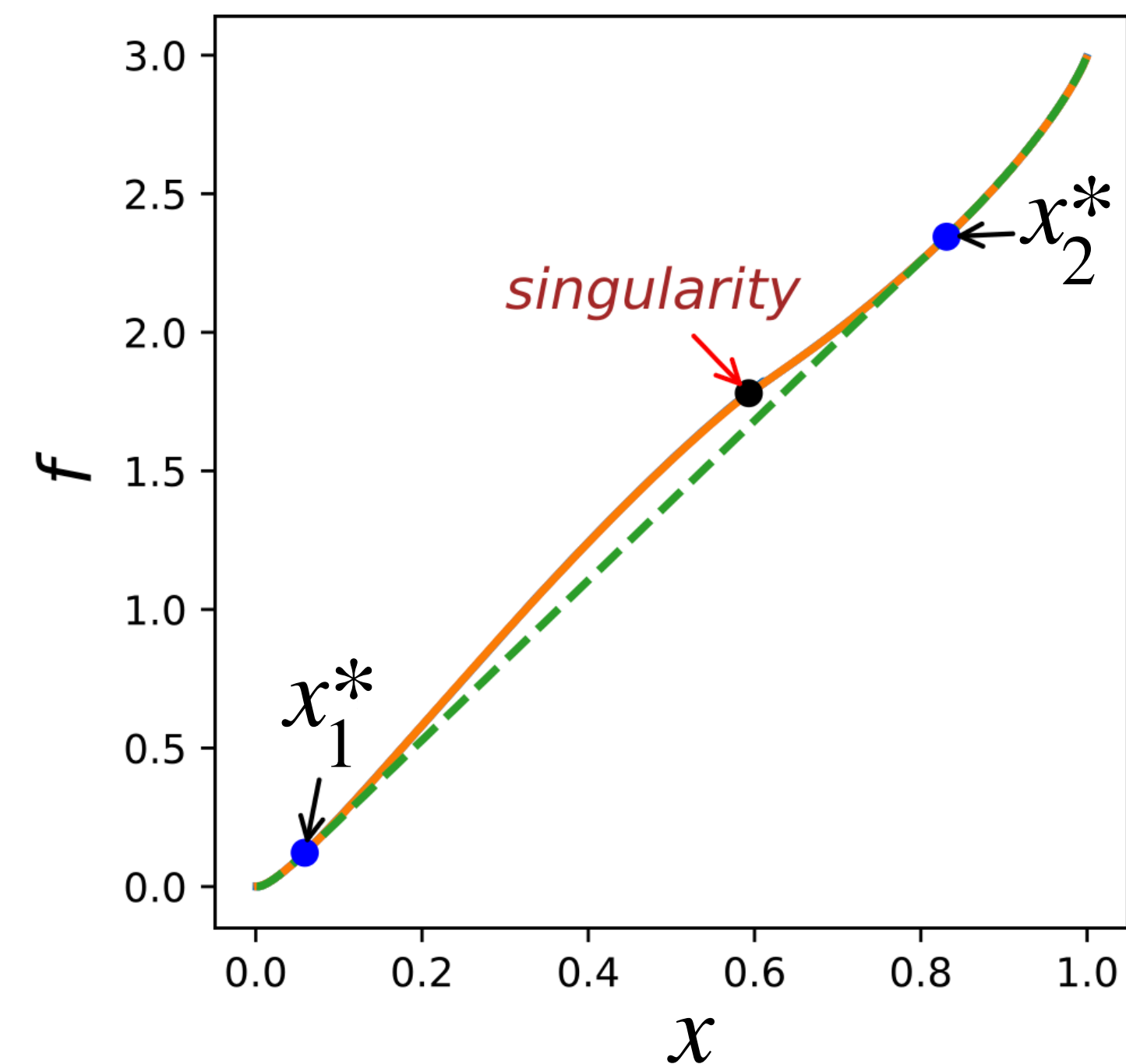
R. Rajesh, V. Subashri, and O. Zaboronski, Physical Review Letters, **133**, 097101 (2024)

R. Goutham, R. Rajesh, V. Subashri, and O. Zaboronski, Physical Review E **114**, 014152 (2026)

R. Goutham, R. Rajesh, V. Subashri, and O. Zaboronski, ArXiv: (2026)

Large Deviation Theory

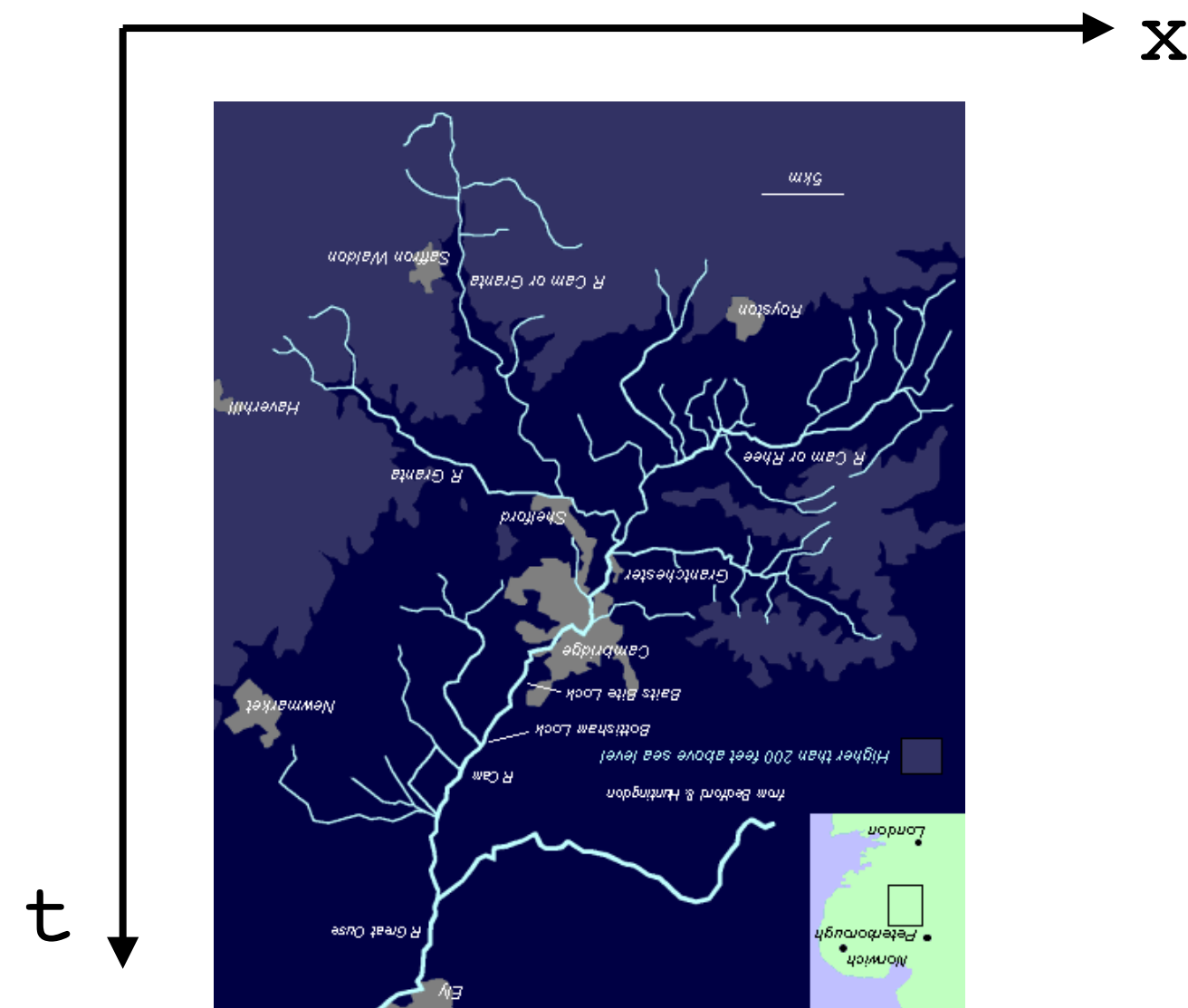
- Large deviation principle:
 - $P(X_M \approx x) \asymp e^{-Mf(x)}$
 - $f(x)$: large deviation function (LDF); M : rate
- Scaled Cumulant Generating Function:
 - $\lambda(p) = \lim_{M \rightarrow \infty} \frac{1}{M} \ln \langle e^{pMX} \rangle$
- Gärtner-Ellis Theorem:
 - if $\lambda(p)$ is differentiable, $f(x)$ is the Legendre transform of $\lambda(p)$
 - Else Legendre transform of $\lambda(p)$ gives convex envelope of $f(x)$



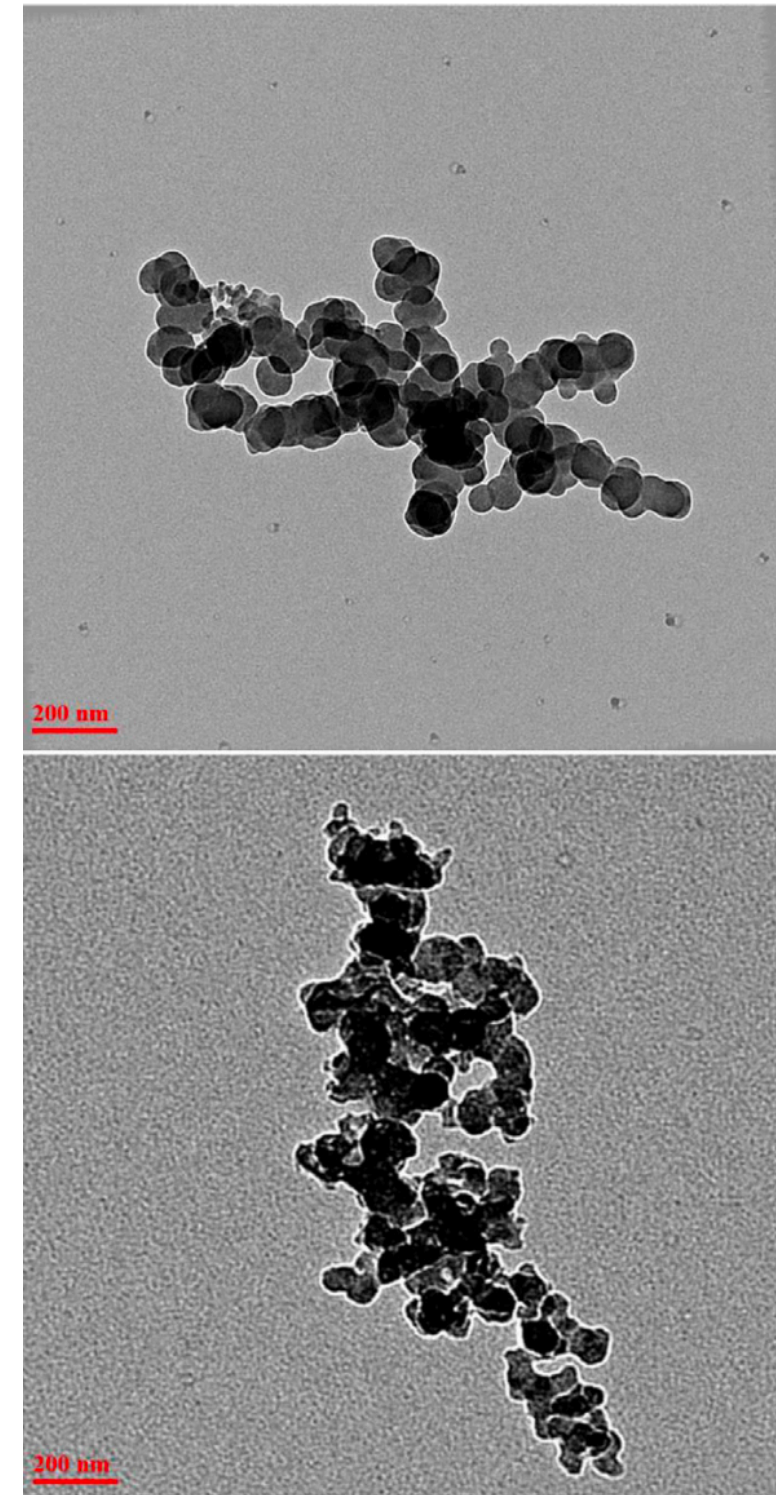
3 Questions in Nonequilibrium Large Deviations

- For an interacting stochastic system with infinite degrees of freedom
 - **Q1.** Can we obtain the **complete LDF**, rather than merely its convex envelope?
 - **Q2.** Can we solve for the **instanton trajectories** that realize these rare events?
 - **Q3.** Does **ensemble inequivalence**, familiar from equilibrium long-range interacting systems, extend to purely nonequilibrium stochastic dynamics?
- We will answer these questions for **product kernel aggregation**

Aggregation is ubiquitous



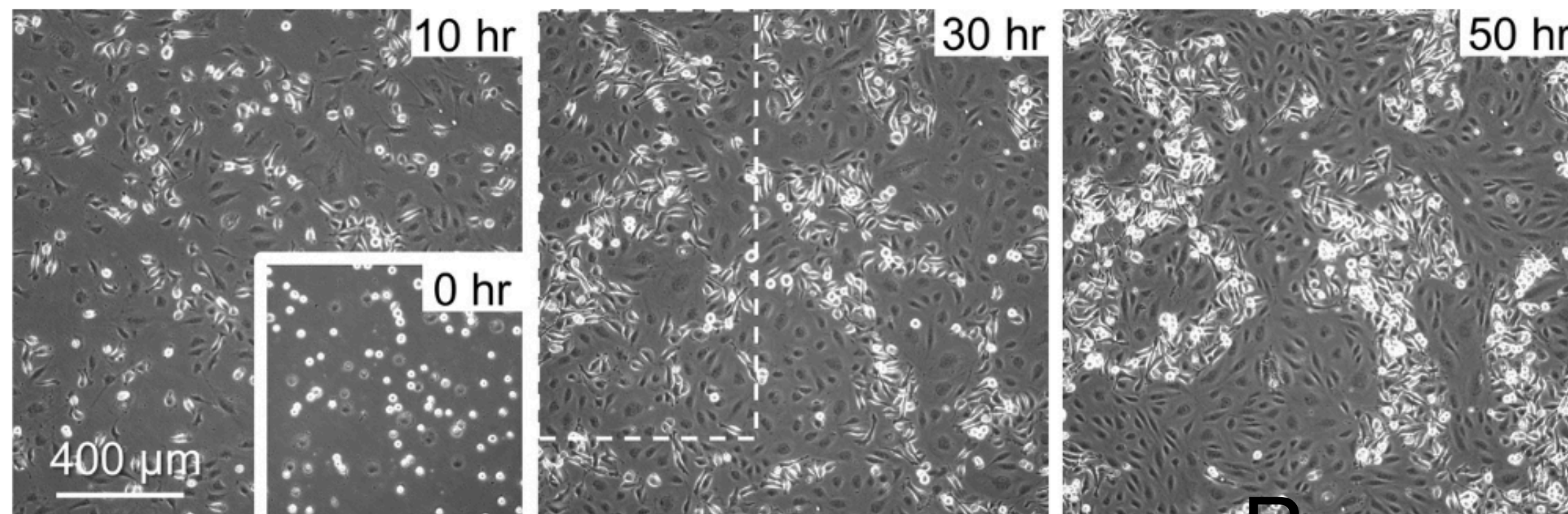
River Networks



Soot

aggregates

- 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 $K(m_1, m_2)$



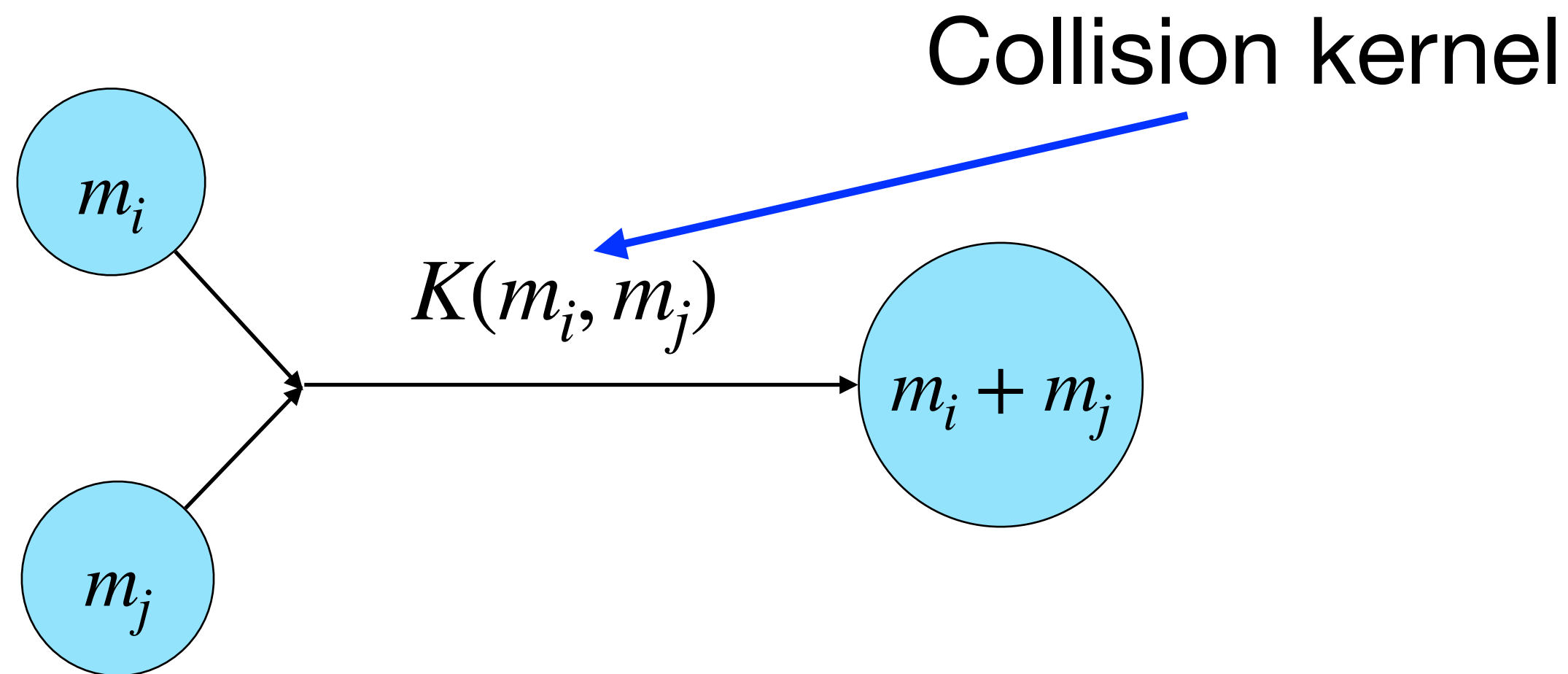
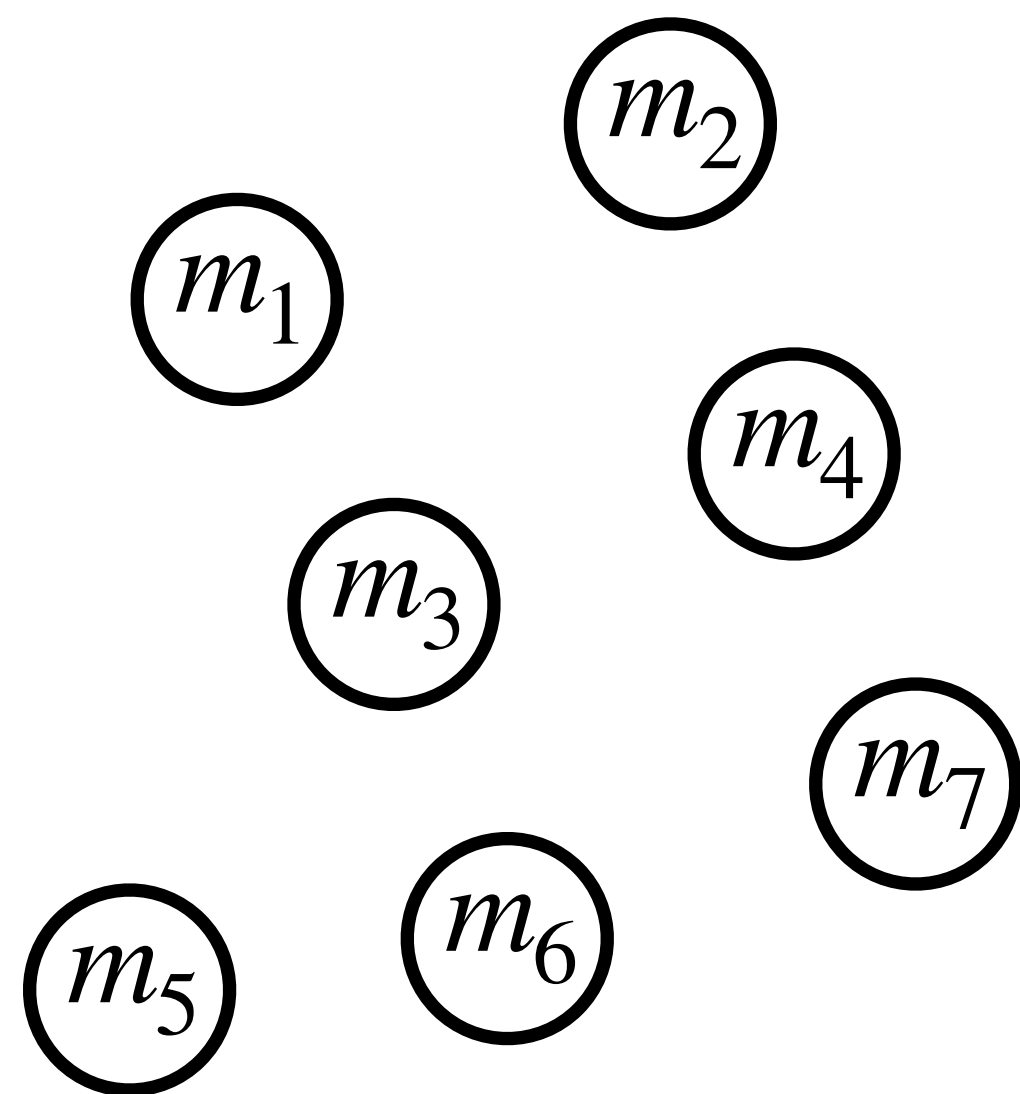
Zhang et al, J. Quant Spect Radiative Transfer, 2020

Liu et al, Phys. Rev. Res, 2021

Bone marrow cancer cells

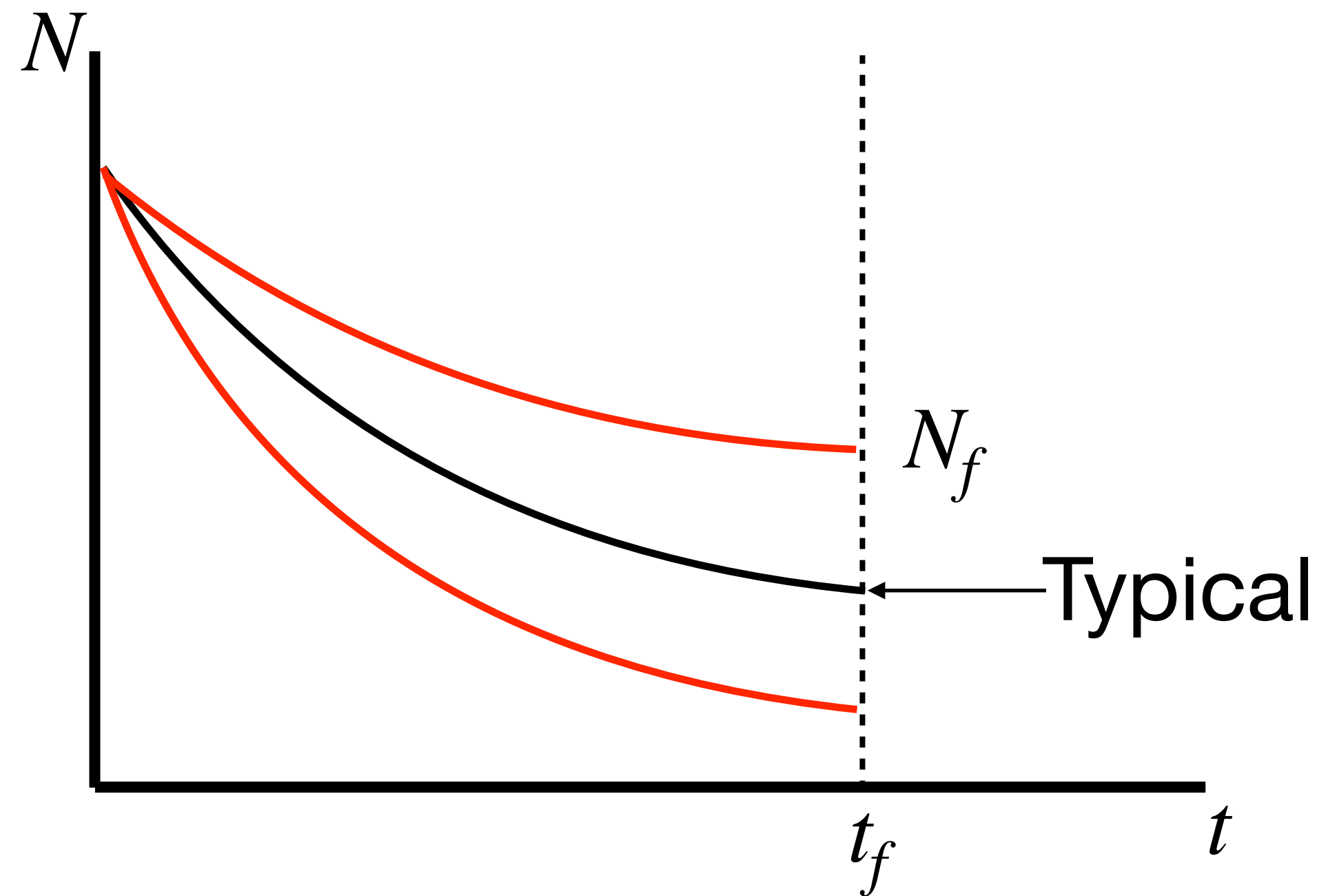
Model (Marcus Lushnikov Model)

A collection of particles labeled by mass



- A pair (m_1, m_2) coagulate with rate $K(m_1, m_2) = m_1 m_2$
- Initial condition: M particles of mass 1
- In a collision/aggregation
 - Mass **conserved**
 - Number decreases by one

A Quantity of Interest



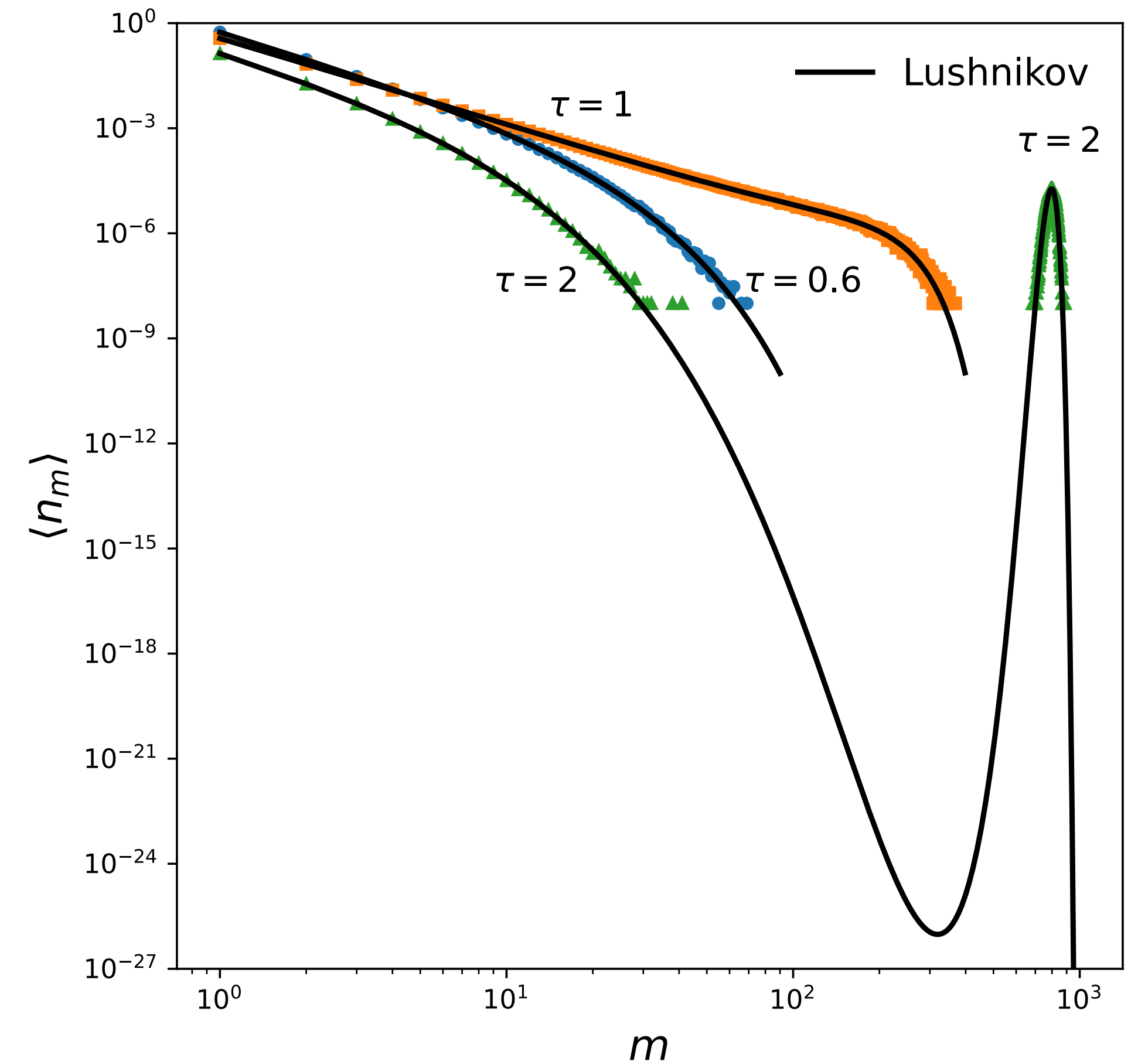
- $P_M(N_f, t_f)$ = Probability of $N_f = 1, 2, \dots, M$ particles at time t_f ?

- We can show $\lim_{M \rightarrow \infty} \frac{-1}{M} \ln P_M(M\phi_f, \tau_f/M) = f(\phi_f, \tau_f)$

$$\tau = Mt; \phi = N/M$$

Product Kernel Aggregation

- $K(m_1, m_2) = m_1 m_2$
- Why study?
 - The canonical model for studying sol-gel transition
 - At scaled time $\tau = Mt = 1$, a macroscopic gel cluster emerges ($\phi = 1/2$).
- $\langle n(m, \tau) \rangle = \frac{m^{m-2} \tau^{m-1} e^{-m\tau}}{m!}$
- $\langle n(m, 1) \rangle \sim m^{-5/2}$; $\langle m^2 \rangle$ diverges

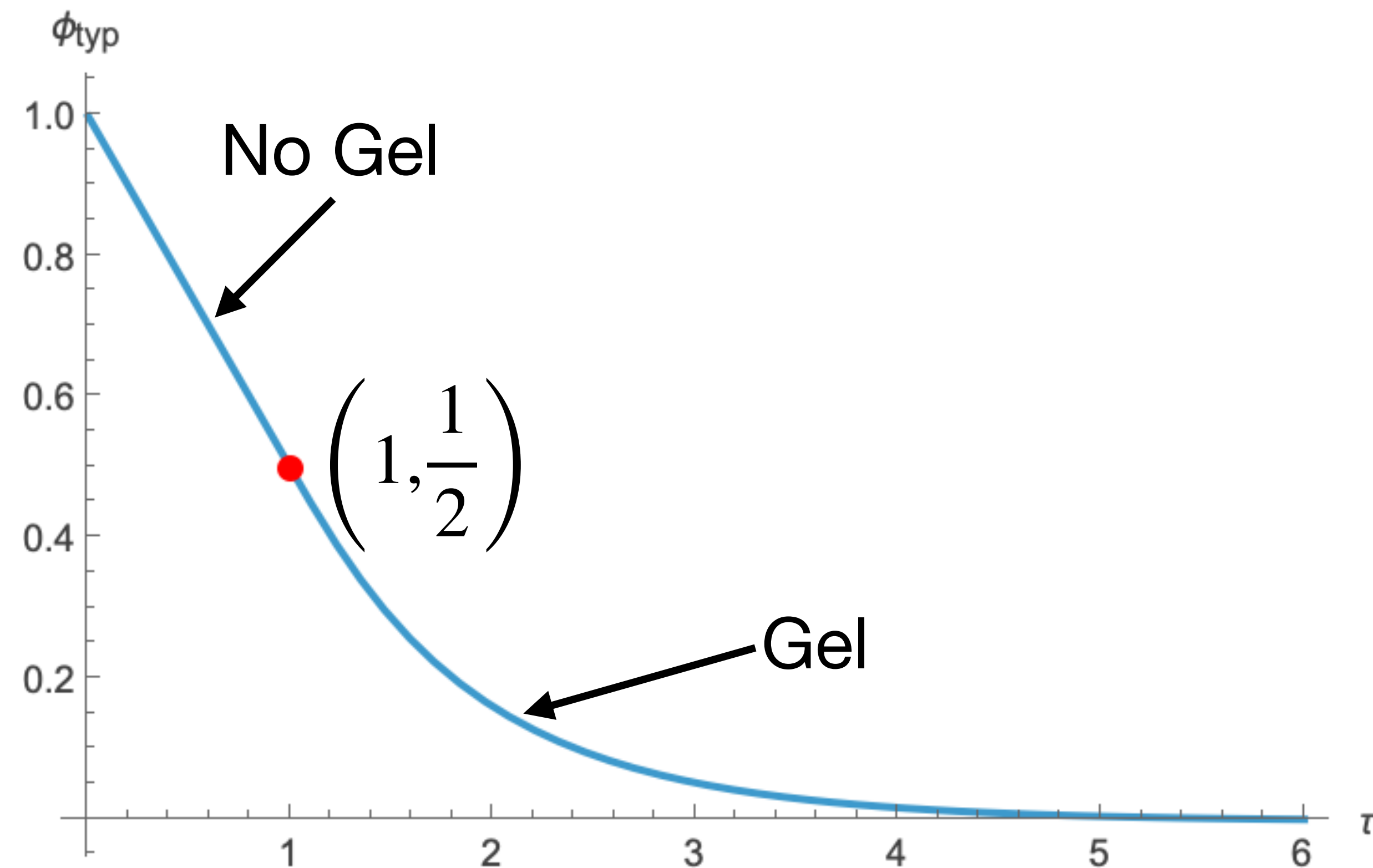


Mapping to Other Models

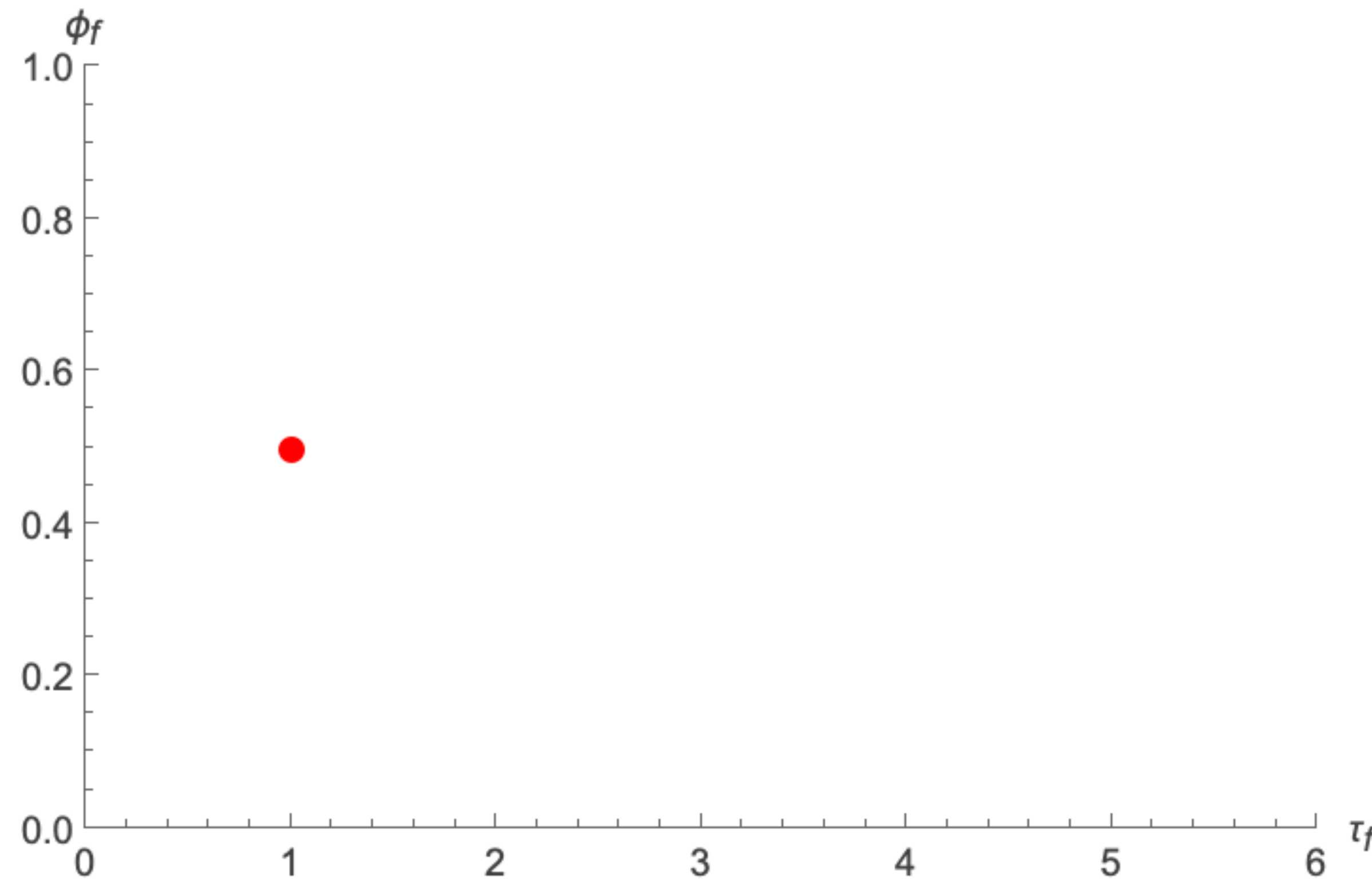
- Product kernel aggregations maps onto
 - Evolution of connected components in Erdős–Rényi random graph (emergence of the giant component).
 - The partition function of the Fortuin–Kasteleyn model on complete graph (or Potts model) [*only for monodisperse initial condition and $P_M(N, t)$*]
 - The random average process (RAP) in one dimension [*in the non-gelling regime*]

Information from Typical trajectory

$$\phi_{typ} = \frac{-1}{\tau} \left(W(-e^{-\tau}\tau) + \frac{1}{2}W(-e^{-\tau}\tau)^2 \right)$$



Information from Typical trajectory



What is the rest of the phase diagram?

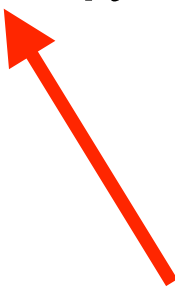
What is the instanton trajectory for general (τ_f, ϕ_f)

Results (an exact formula)

- An exact formula valid for any $M = 1, 2, \dots$ and $N_f = 1, 2, \dots, M$ and all t

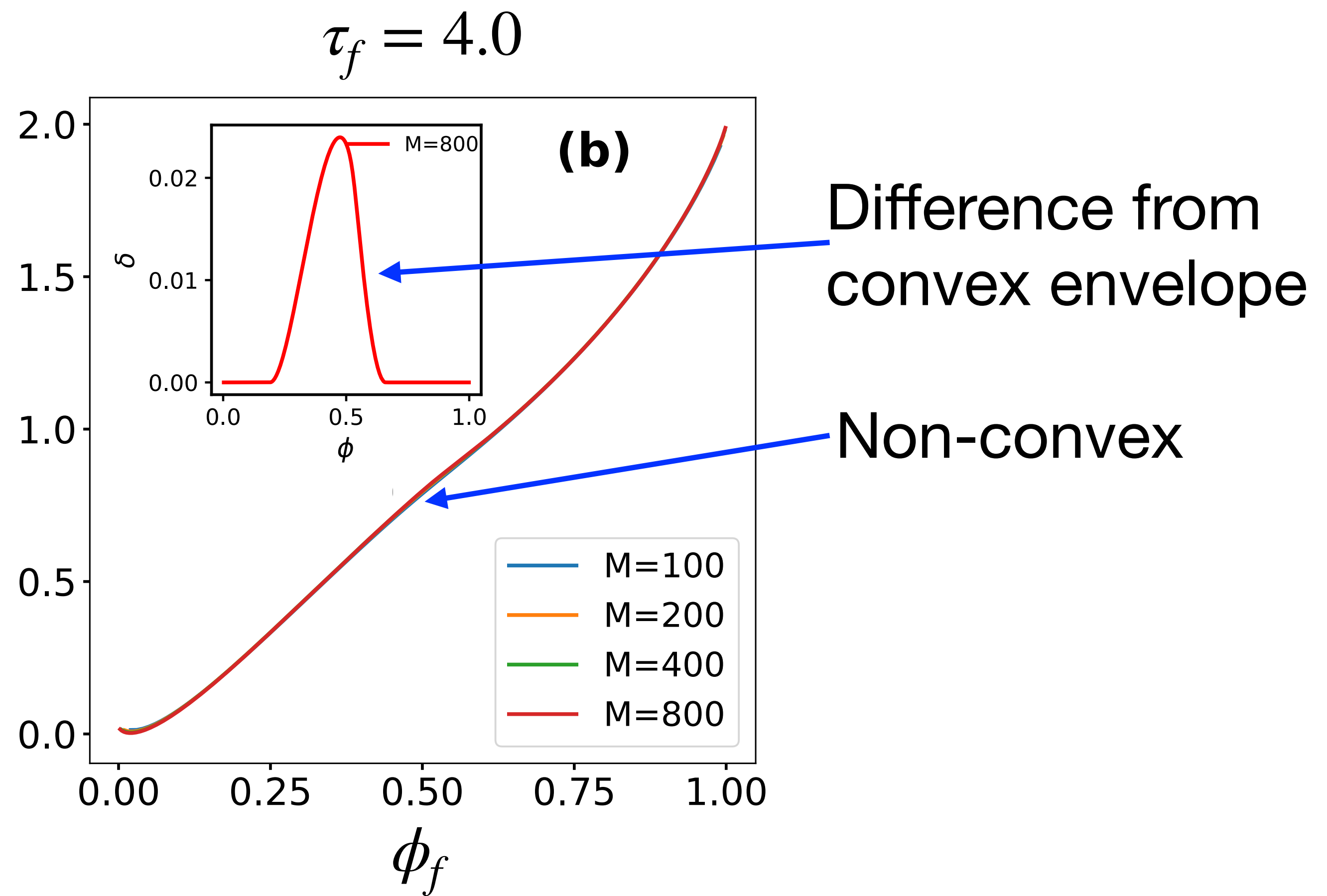
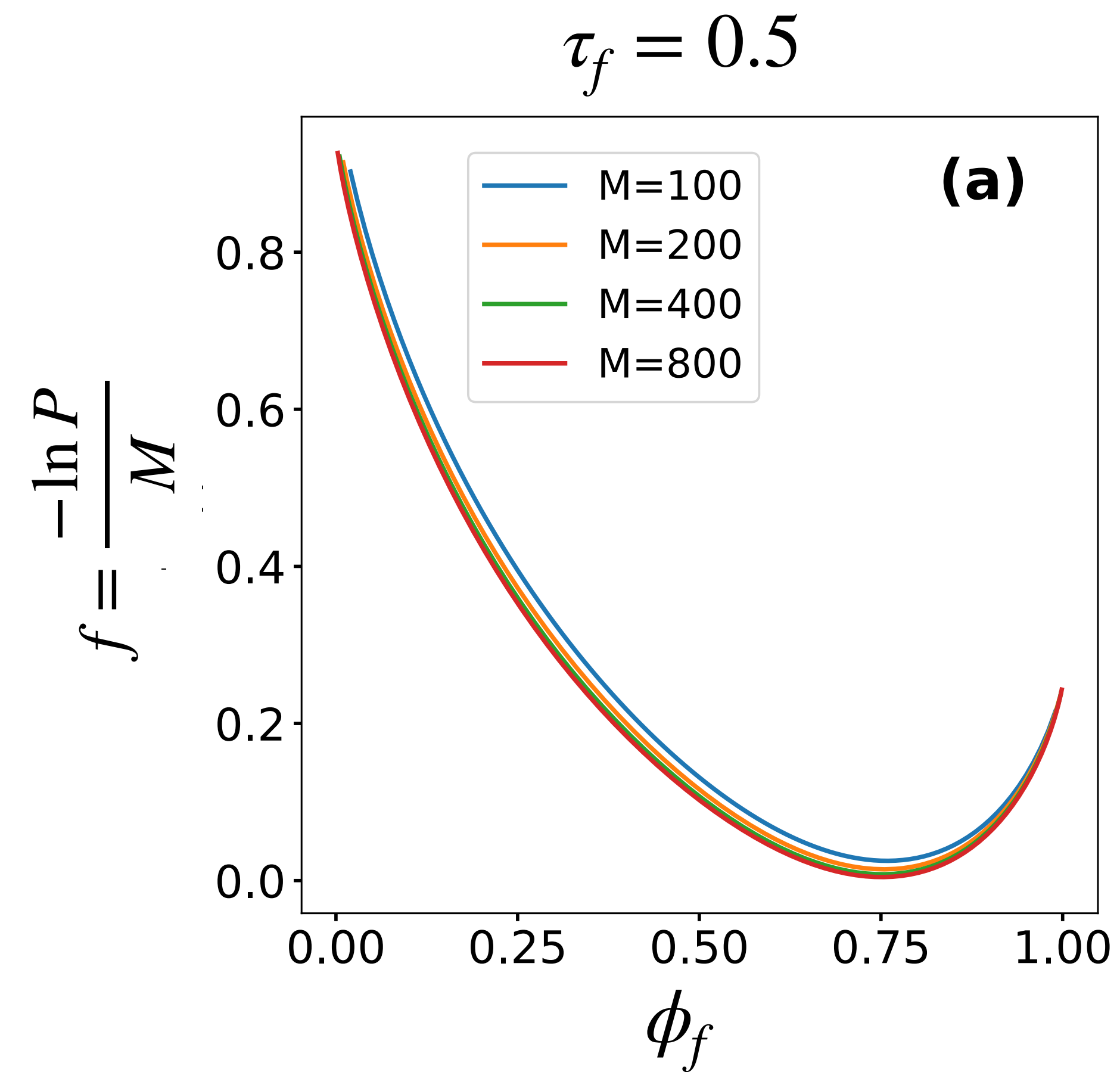
$$P_M(N_f, t_f) = \frac{e^{-\frac{1}{2}M^2 t_f} M!}{N_f!} \oint \frac{d\mu}{2\pi i \mu^{1+M}} \left[\sum_{n=1}^{\infty} (e^{t_f} - 1)^{n-1} e^{n t_f / 2} F_{n-1}(e^{t_f}) \frac{\mu^n}{n!} \right]^{N_f}$$

Mallows–Riordan polynomials



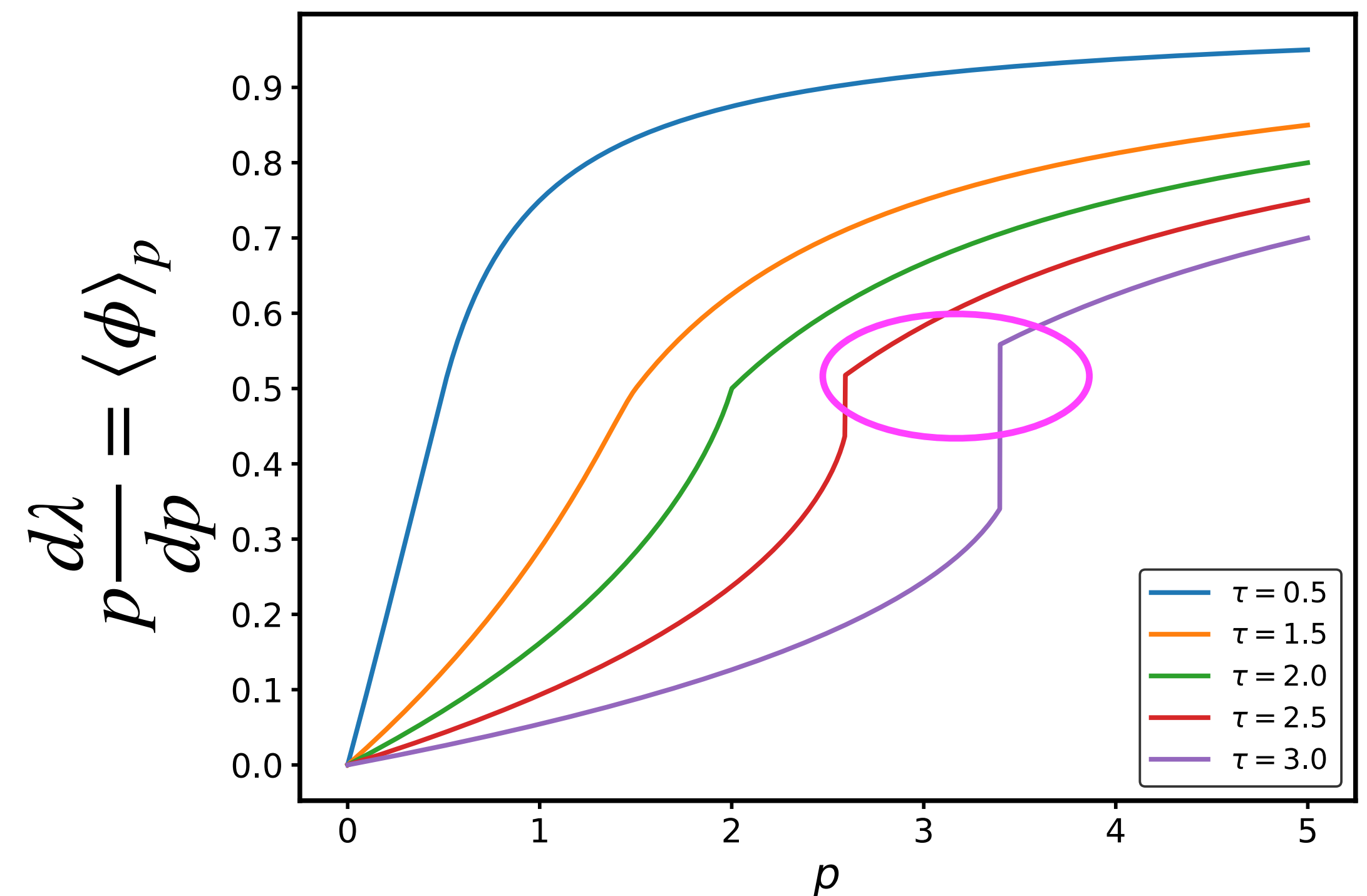
- An easy result
 - Probability of **full gelation** $\equiv P_M(1, t_f) = e^{-\frac{1}{2}M^2 t_f} (e^{t_f} - 1)^{M-1} e^{M t_f / 2} F_{M-1}(e^{t_f})$
 - Scaling $t, N_f \implies f(0, \tau) = -\ln(1 - e^{-\tau})$

LDF from the exact formula



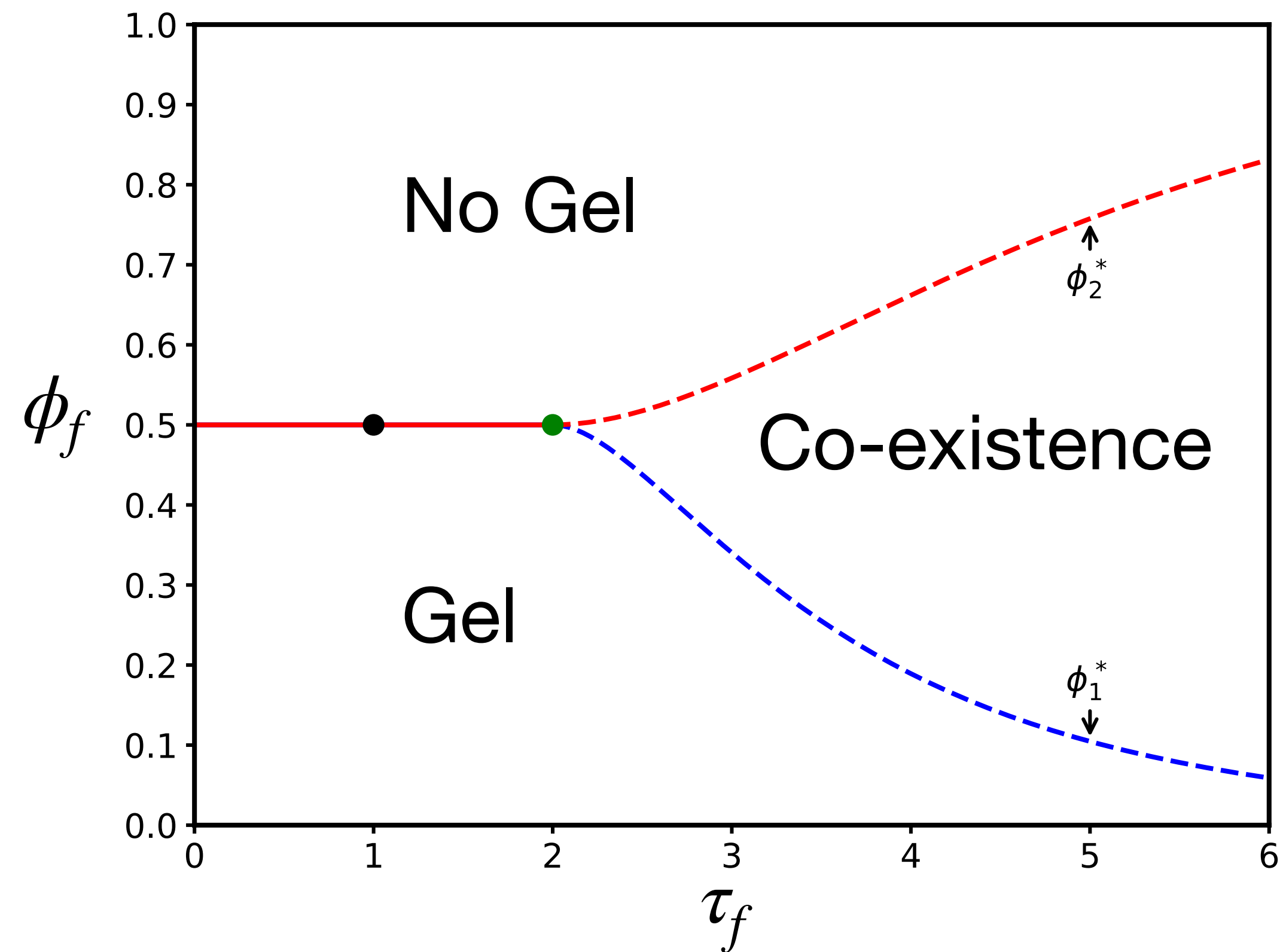
Results (Exponential Moments)

- $\langle p^{N_f} \rangle$ evaluated exactly for integer p ; saddle-point yields
$$\lambda(p, \tau_f) = \lim_{M \rightarrow \infty} M^{-1} \ln \langle p^{N_f} \rangle$$
- Analytically continue integer $p \rightarrow$ real, $p \geq 0$ (validated by finite- M scaling)
- For $p > 2$, $\lambda(p, \tau_f)$ develops a kink at τ_c and is not differentiable
- Legendre transform gives convex envelope of LDF (CELDF)



Exponential Moment

- The CELDF phase diagram reveals:
 - A tricritical point at $(\tau_f, \phi_f) = (2, 1/2)$
 - Continuous transitions for $\tau \leq 2$
 - Discontinuous transitions for $\tau > 2$
- But
 - It hides the non-convex part
 - No information about instantons
 - To go further, we must work strictly in the canonical ensemble (fixed N_f)



Methodology (summary)

- Doi-Peliti-Zeldovich-Ovchinnikov

- Master equation → Schrödinger-like equation with effective Hamiltonian H → coherent states → effective action → Euler Lagrange equations

- Product kernel simplification: $H = H_0 + \hat{M}^2/2$, where $[H_0, \hat{M}] = 0$

- $$P_M(N_f, t_f) = \frac{e^{-\frac{M^2 t_f}{2}}}{N_f!} \langle 0 | \left(\sum_{k=1}^M a_k \right)^{N_f} e^{-H_0 t_f} a_1^{\dagger M} | 0 \rangle,$$

- $$H_0 = -\frac{1}{2} \sum_{k,l=1}^{\infty} k l a_{k+l}^{\dagger} a_k a_l - \frac{1}{2} \sum_{k=1}^{\infty} k^2 a_k^{\dagger} a_k \quad (\text{linear in } a^{\dagger} / \text{ action linear in response field})$$

- A key step: rewrite measurement operator as

- $$\left(\sum_{k=1}^M a_k \right)^{N_f} = \left(\sum_{k \sim M^0} a_k + \sum_{k \sim M} a_k \right)^{N_f} = \text{sum over 0-gel} + \text{1-gel} + \text{2-gel} + \dots$$

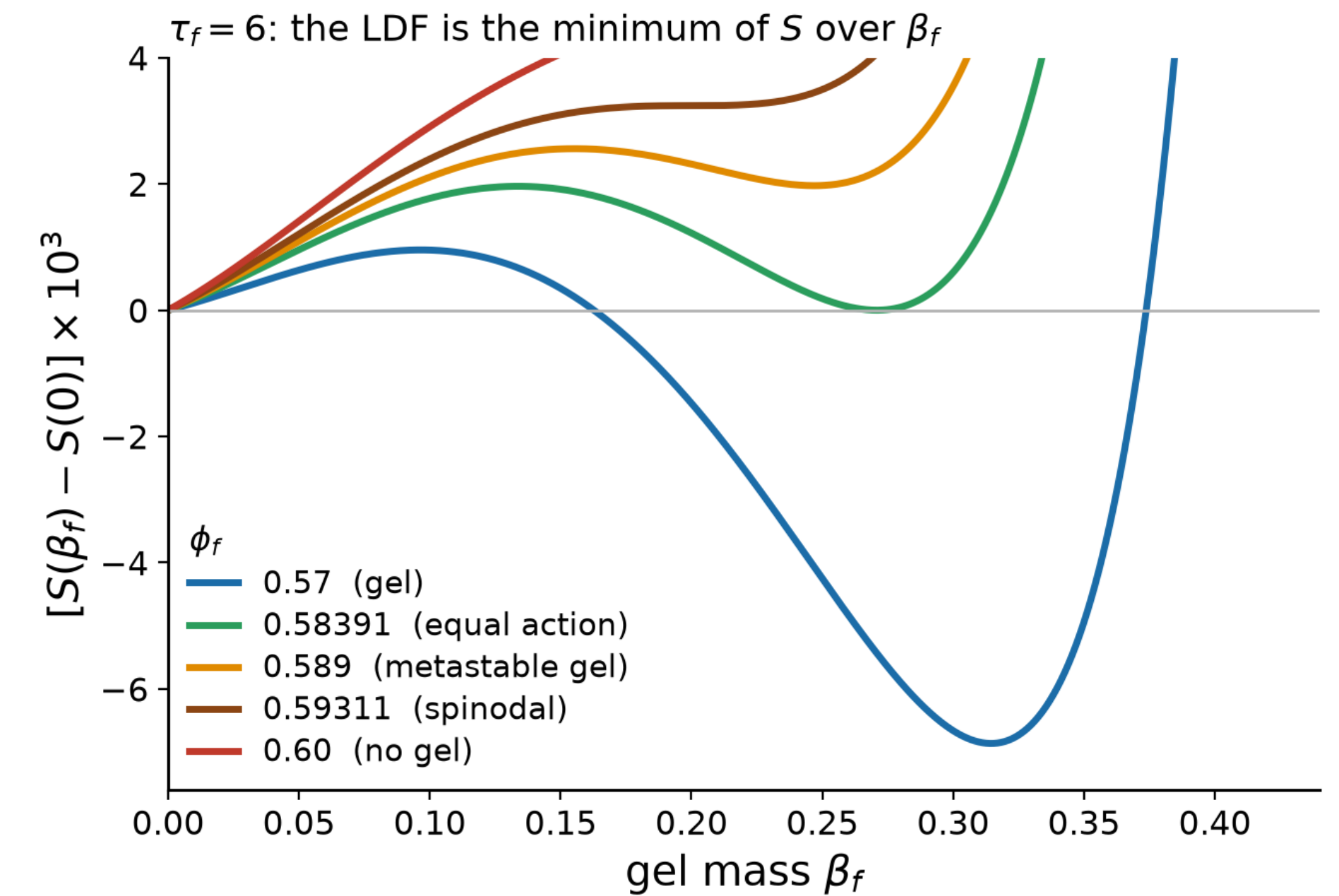
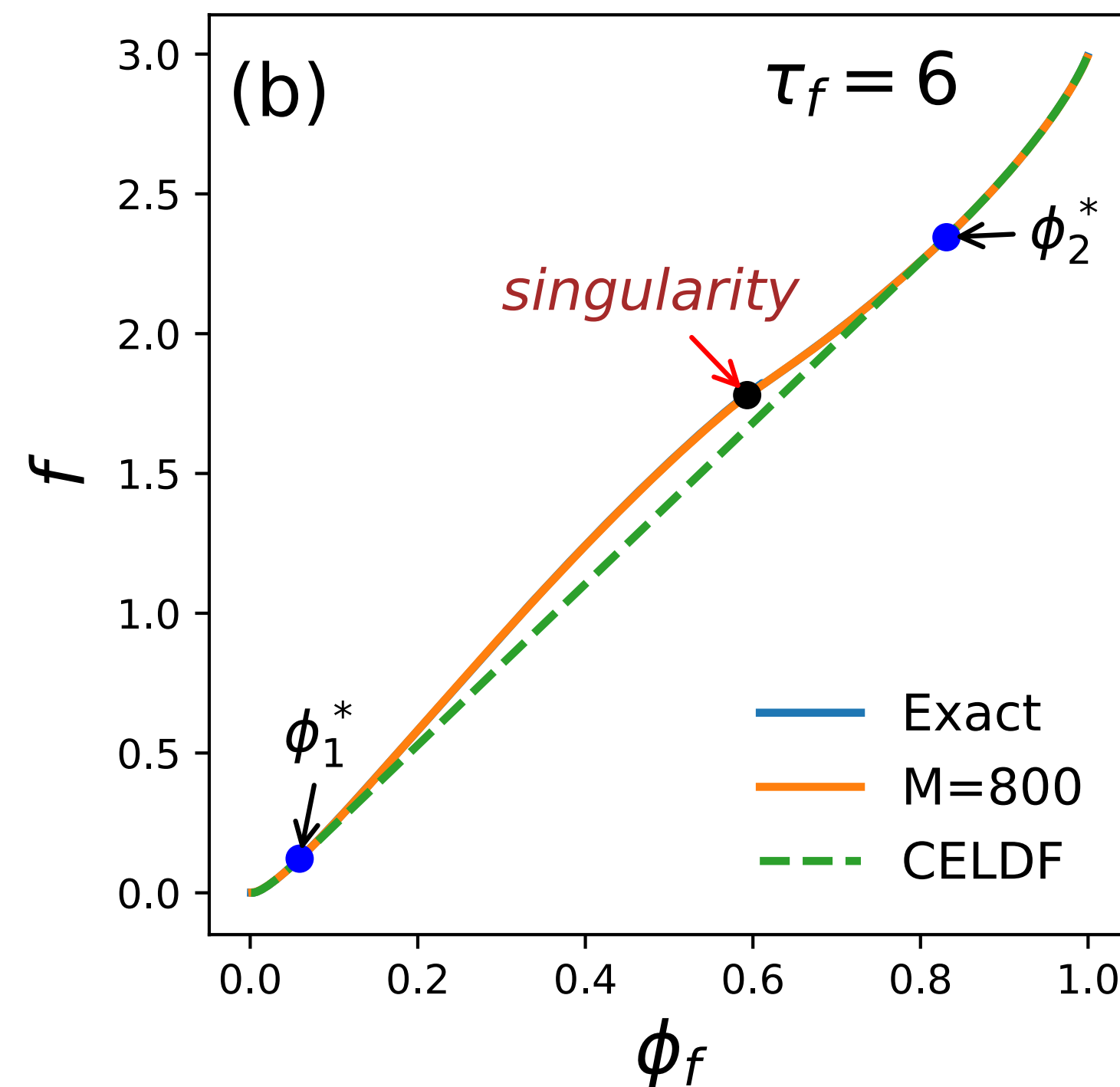
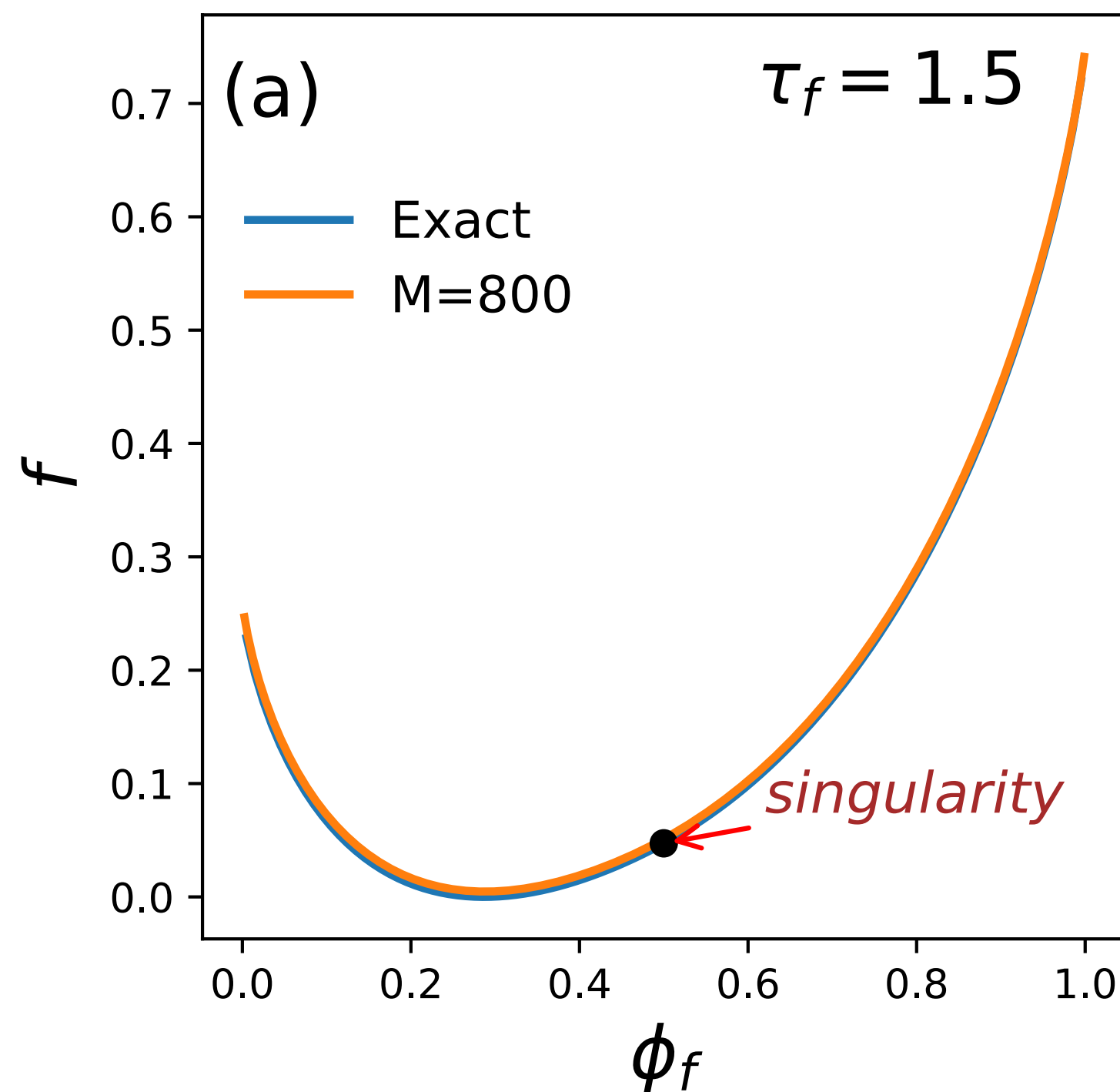
Action and Euler Lagrange Eqs

- Action: $P_M(\phi_f, \tau_f) = \frac{e^{-M\tau_f/2}}{N_f!} \int \mathcal{D}[z] \mathcal{D}[\tilde{z}] \left[e^{-MS_0} + \int d\beta_f e^{-MS_1} \right]$
- Euler Lagrange equations
 - Forward field: $\frac{dz_m}{d\tau} = \frac{1}{2} \sum_{k=1}^{m-1} k(m-k) z_k z_{m-k} + \frac{m^2 z_m}{2M}$
 - Response field: $\frac{d\tilde{z}_m}{d\tau} = - \sum_{k=1}^{\infty} mk \tilde{z}_{m+k} z_k - \frac{m^2 \tilde{z}_m}{2M}$
 - Boundary conditions: $z_m(0) \tilde{z}_m(0) = \delta_{m,1}$, $\tilde{z}_m(\tau_f) = \frac{\phi_f}{\sum_{k \sim M^0} z_k(\tau_f)}$
- Solve the optimal trajectory for fixed gel mass β_f , find the action and then minimise over β_f

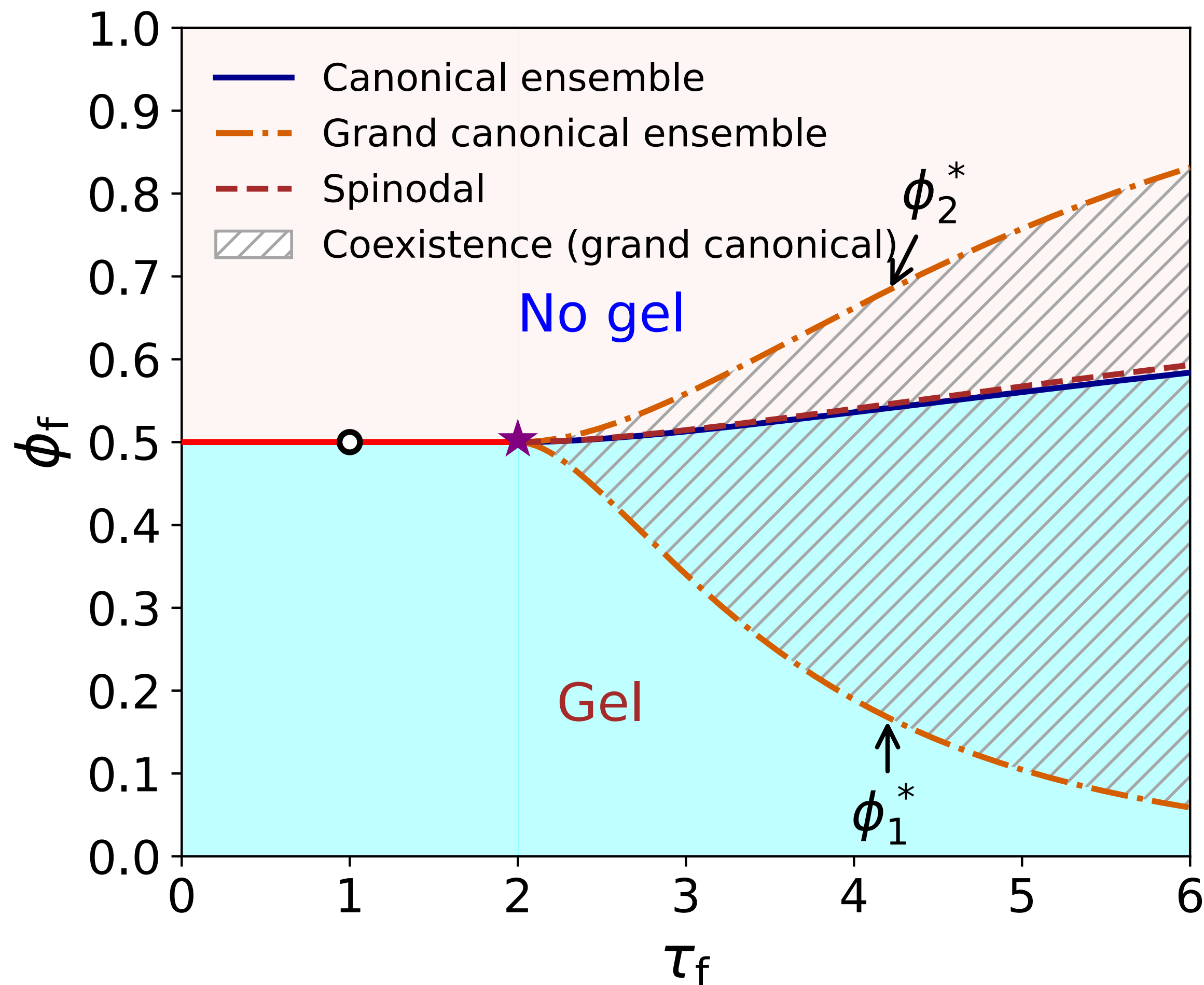
LDF (Results)

$$f(\phi_f, \tau_f) = 1 + \frac{\tau_f}{2} - \phi_f \ln \left[\frac{2e(1 - \phi_f - \beta_f^*)}{\tau_f(1 - \beta_f^*)^2} \right] - \frac{\beta_f^{*2}\tau_f}{2} - \beta_f^* + \frac{\beta_f^*\tau_f(\beta_f^* - 1)}{1 - e^{-\beta_f^*\tau_f}} + \ln \left[\frac{\beta_f^*}{1 - e^{-\beta_f^*\tau_f}} \right] \quad \beta_f^*: \text{gel mass at } \tau_f$$

$$\frac{2(1 - \phi_f - \beta_f^*)}{(1 - \beta_f^*)} \exp \left[-\frac{2(1 - \phi_f - \beta_f^*)}{(1 - \beta_f^*)} \right] - \frac{\beta_f^*\tau_f}{1 - e^{-\beta_f^*\tau_f}} \exp \left[-\frac{\beta_f^*\tau_f}{1 - e^{-\beta_f^*\tau_f}} \right] = 0$$



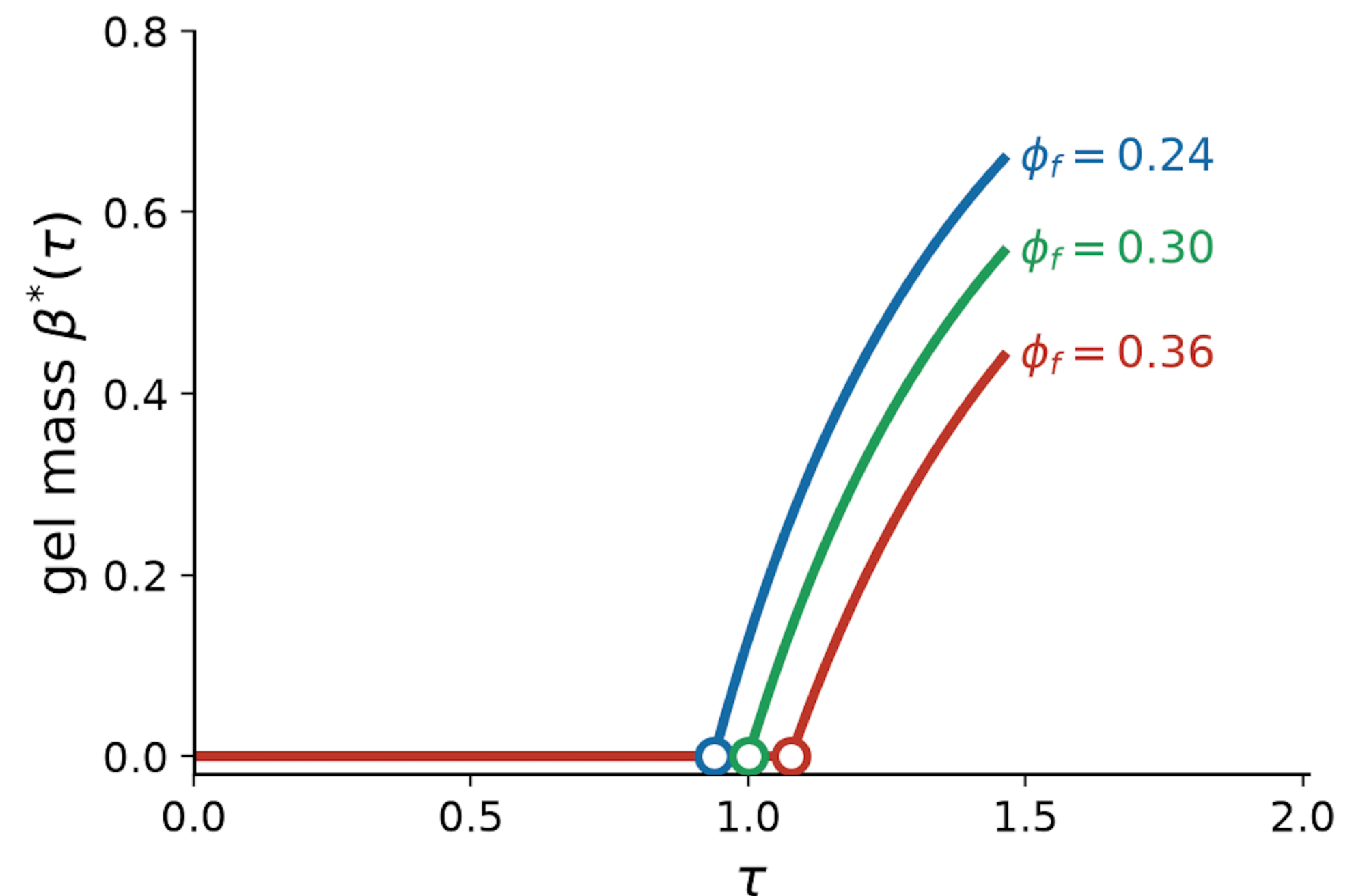
Phase Diagram (Results)



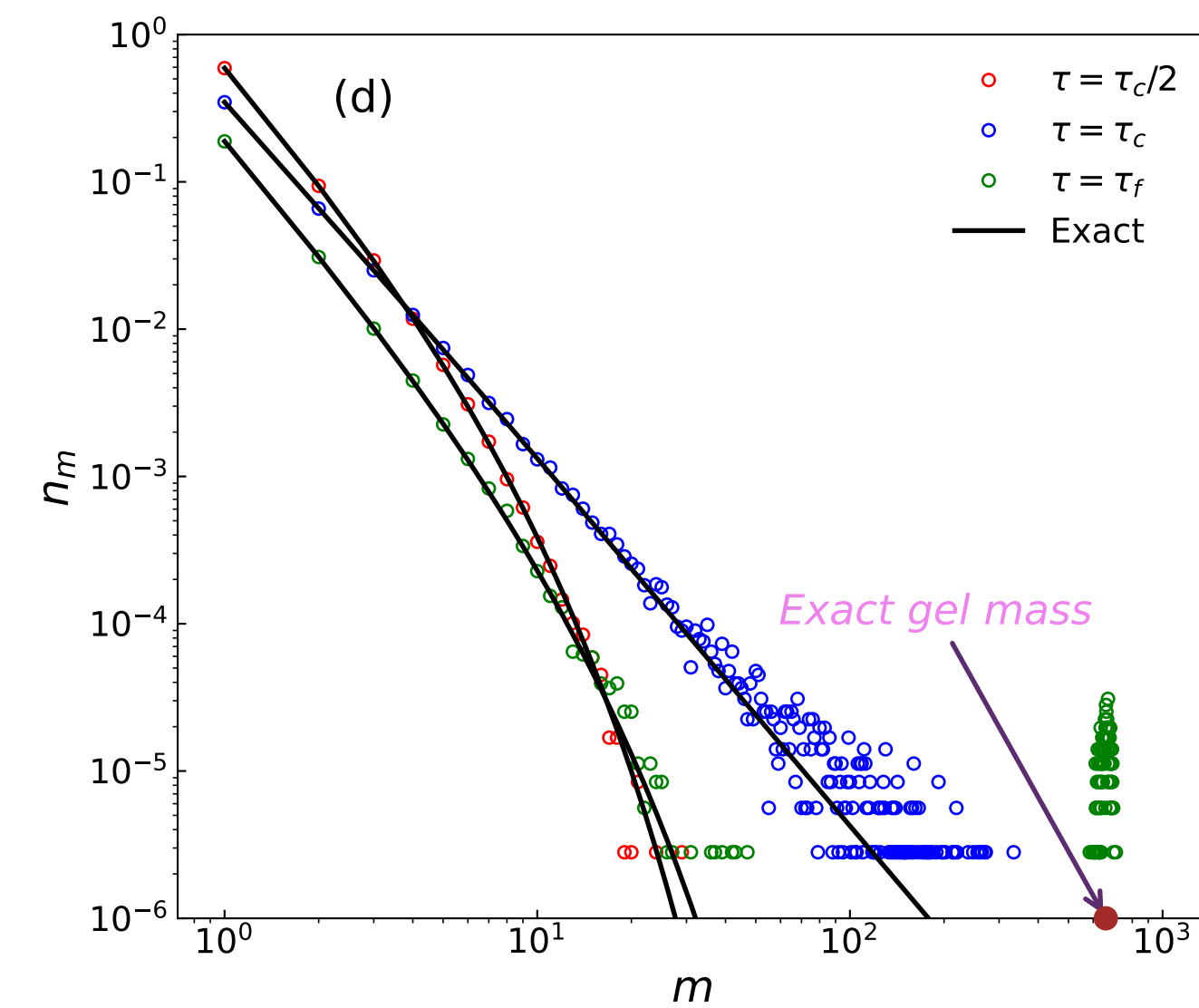
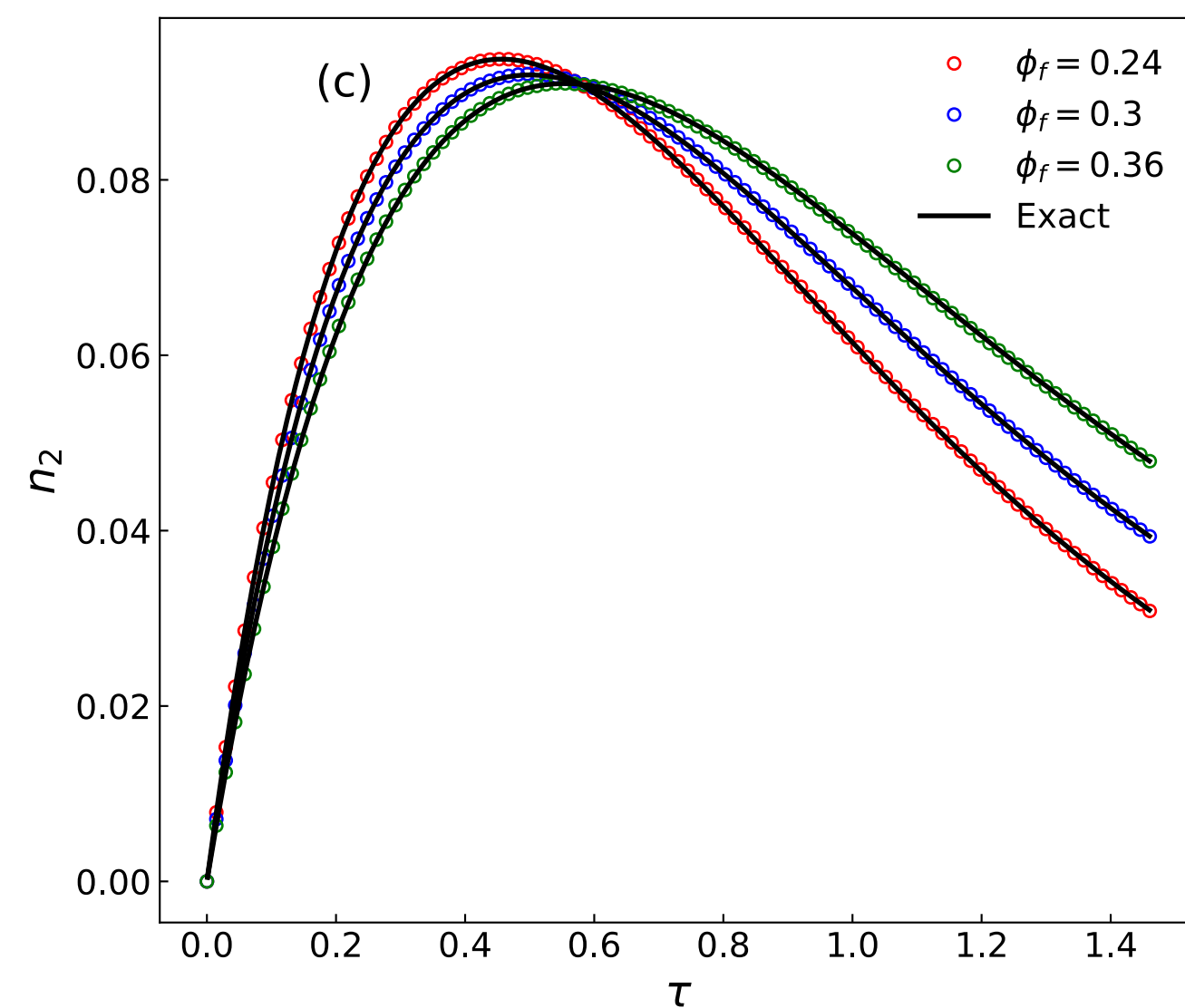
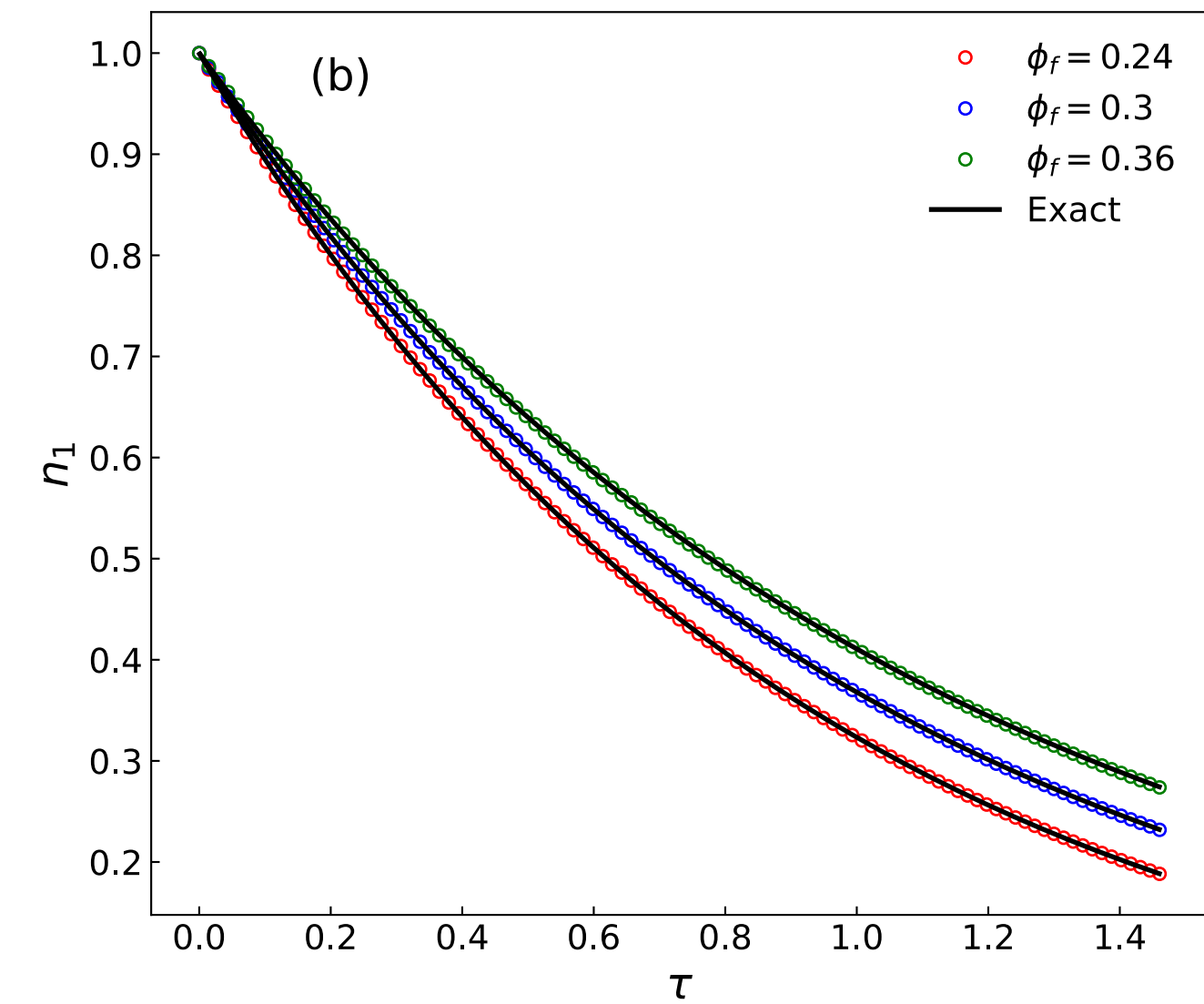
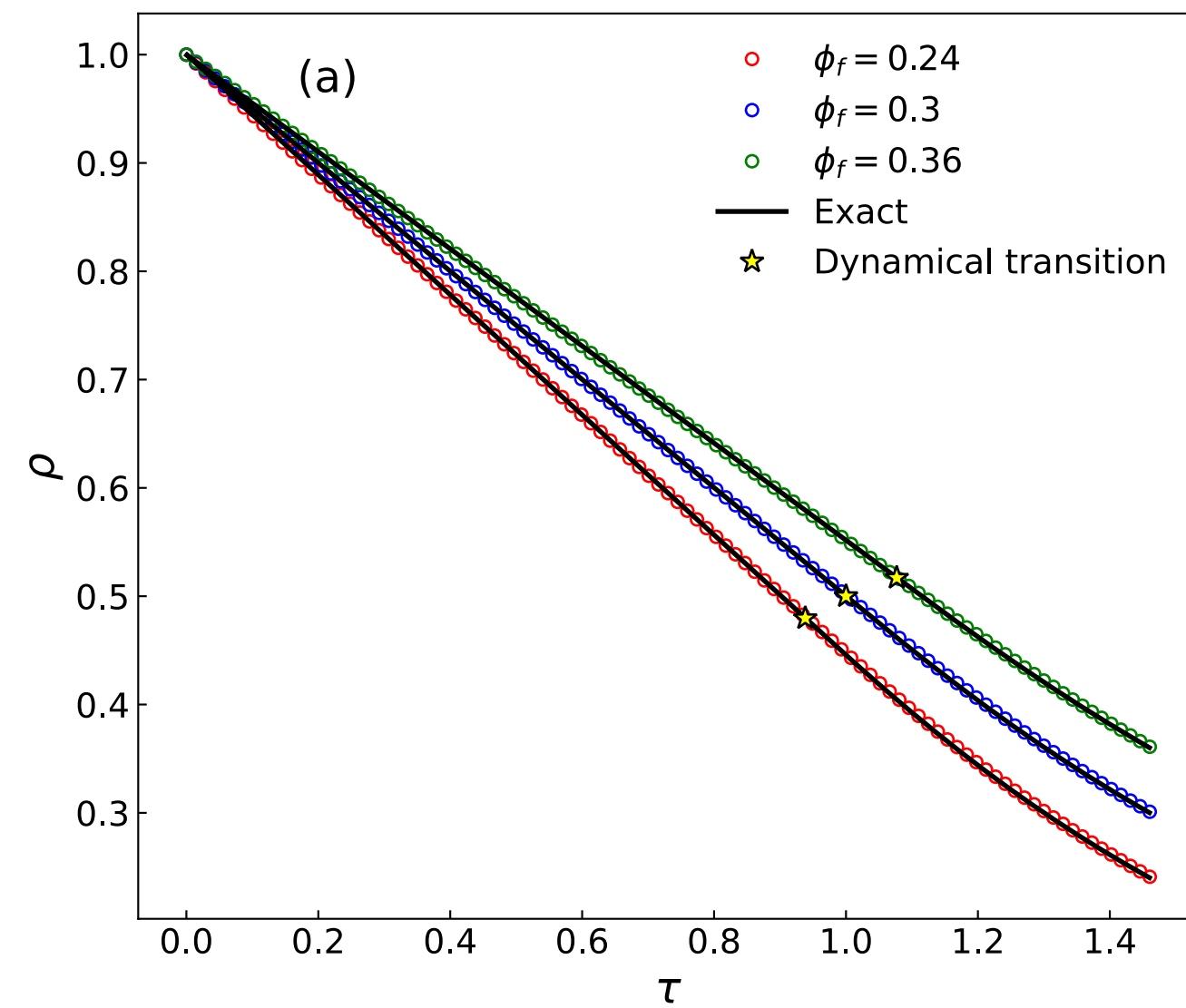
- Same continuous line ($\phi_f = 1/2, \tau_f \leq 2$)
- Different first-order lines (canonical vs grand canonical)
- Equilibrium: ensemble inequivalence results from non-additive long range interactions
- Here: No energy function, no detailed balance

Gel nucleation along the optimal path

- The gel mass $\beta(\tau)$ for a given constraint is a dynamic variable: $\beta^*(\tau) = C + \frac{1}{\tau}W(-C\tau e^{-C\tau})$, where C is fixed by condition at τ_f
- Along trajectory, dynamical phase transition at $\tau_c = 1/C$: gel emerges for $\tau > \tau_c$
- At τ_c , mass distribution develops $m^{-5/2}$ power-law tail and transition is always continuous in time.
- In typical dynamics, gelation is at $(\tau_c, \phi_c) = (1, 1/2)$. Along the instanton, (τ_c, ϕ_c) depends on the final boundary conditions.



Optimal Trajectory (Simulations)



Summary

- We answered three fundamental questions for an interacting stochastic system:
 - **Q1.** Derived the complete, non-convex LDF for product-kernel aggregation.
 - **Q2.** Found the exact instanton trajectories, revealing a dynamical gelation transition along the optimal path.
 - **Q3.** Demonstrated ensemble inequivalence arising purely from nonequilibrium dynamics
- Obtained the detailed phase diagram

Outlook

- Beyond particle number fluctuations
 - $\text{Prob}(N_k)$: probability of there being N_k clusters of mass k
 - Probability of largest mass being m^*
 - Probability of multiple gels, polydispersity, ...
- Other kernels
 - Constant and sum kernels (LDF solvable)
 - Generic kernels
 - Biased Monte Carlo simulations [*Dandekar, Computer Physics Communications (2023)*]
 - Perturbative?

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

