Escape and Finite-Size Scaling in Diffusion-Controlled Annihilation

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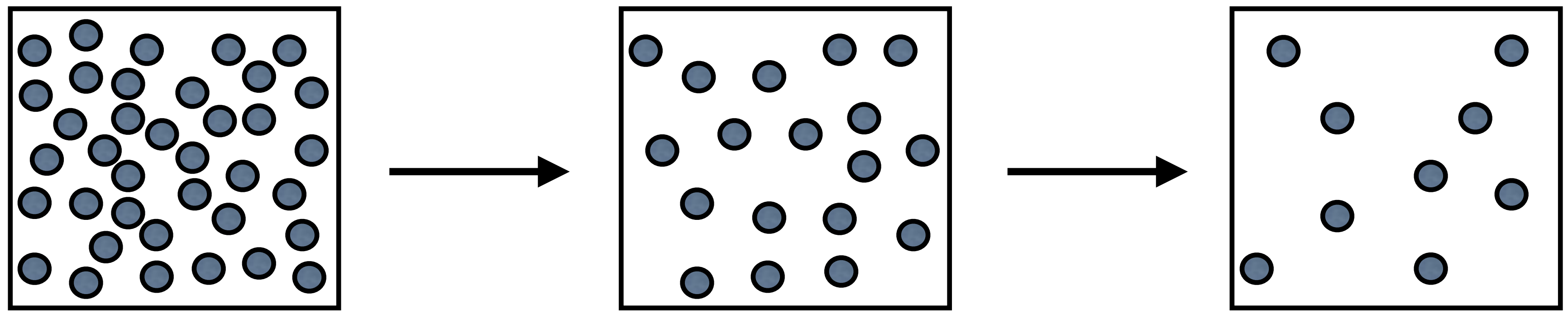
Talk, publications available from: http://cnls.lanl.gov/~ebn

Kinetic Descriptions of Chemical and Biological Systems
Ames IA, March 23, 2017

Plan

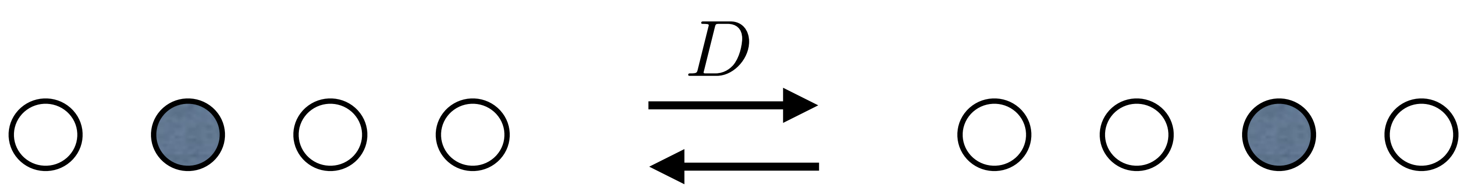
1. Reaction-diffusion with compact initial conditions
    - Finite number of particles
2. Reaction-diffusion with sparse initial conditions
    - Reaction kinetics

Diffusion-Controlled Annihilation



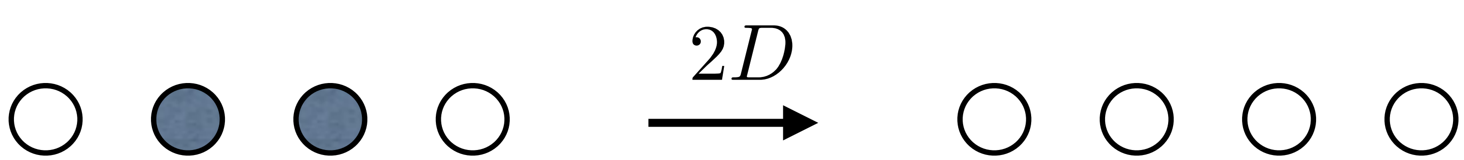
de gennes 82
wilczek 83
Racz 85
Spouge 88

- **Diffusion**: particles move randomly



reversible

- **Annihilation**: two particles annihilate upon contact



irreversible

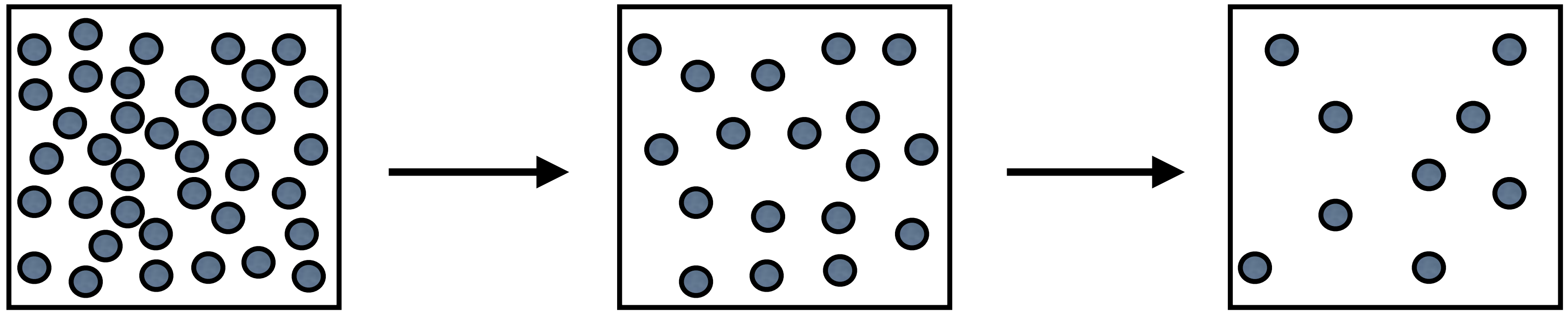
- Theory: role of spatial correlations & fluctuations
- Experiments: photoexcitations in nanotubes

Allam et al
PRB 2013

Textbook model of Nonequilibrium Stat. Phys.

A Kinetic View of Statistical Physics, Krapivsky, Redner, EB

Infinite system: uniform density



- Hydrodynamic approach

$$\frac{d\rho}{dt} = -K\rho^2$$

- Dimensional analysis for reaction rate

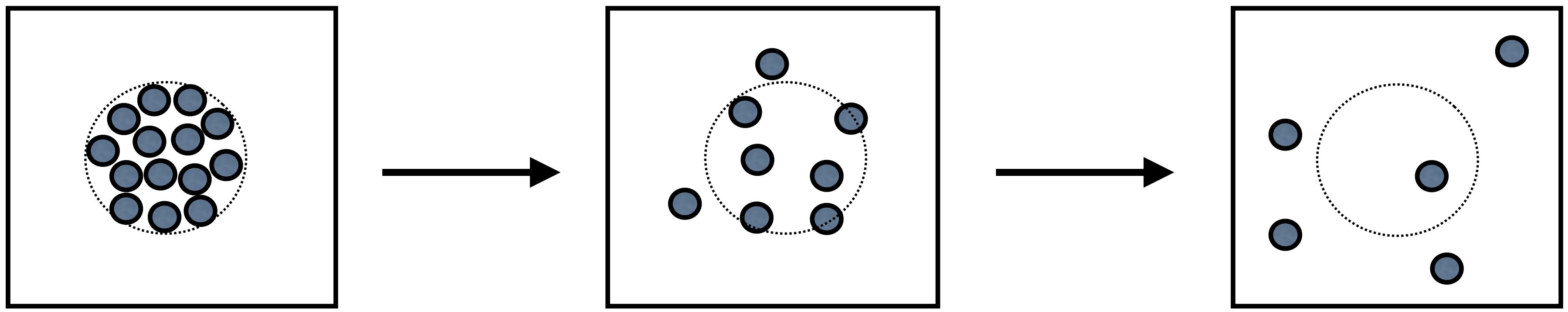
$$[K] = \frac{L^d}{T} \quad \longrightarrow \quad K \propto \begin{cases} D\rho^{2-d} & d < 2 \\ DR^{d-2} & d > 2 \end{cases}$$

- Fluctuations dominate below critical dimension

$$\rho \sim \begin{cases} (Dt)^{-d/2} & d < 2 \\ R^{2-d}(Dt)^{-1} & d > 2 \end{cases}$$

Reaction rate reduced in low spatial dimensions

Infinite system: finite number of particles



- Initial condition: uniform density in compact domain
- Initial number of particles is N
- Final state: average number of particles is M
- Scaling law for final number of surviving particles

$$M \sim \begin{cases} 0 & d < 2 \\ N^{(d-2)/d} & d > 2 \end{cases}$$

Number of reaction events reduced in high spatial dimensions!

Below critical dimension: no escape

- Probability a random walk returns to origin

$$P = 1 \quad \text{when} \quad d \leq 2$$

- The separation between two random walks itself performs a random walk

- Two diffusing particles are guaranteed to meet

All particles eventually disappear

Above critical dimension: escape feasible

- Probability a random walk at distance r returns to origin

$$P \sim r^{-(d-2)} \quad \text{when} \quad d > 2$$

- Two diffusing particles may or may not meet

Uniform-density approximation

- Concentration obeys reaction-diffusion equation

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = D\,\nabla^2 c(\mathbf{r},t) - K\,c^2(\mathbf{r},t)$$

- Dimensionless form $D = K = a = c_0 = 1$

- Total number of particles obeys rate equation

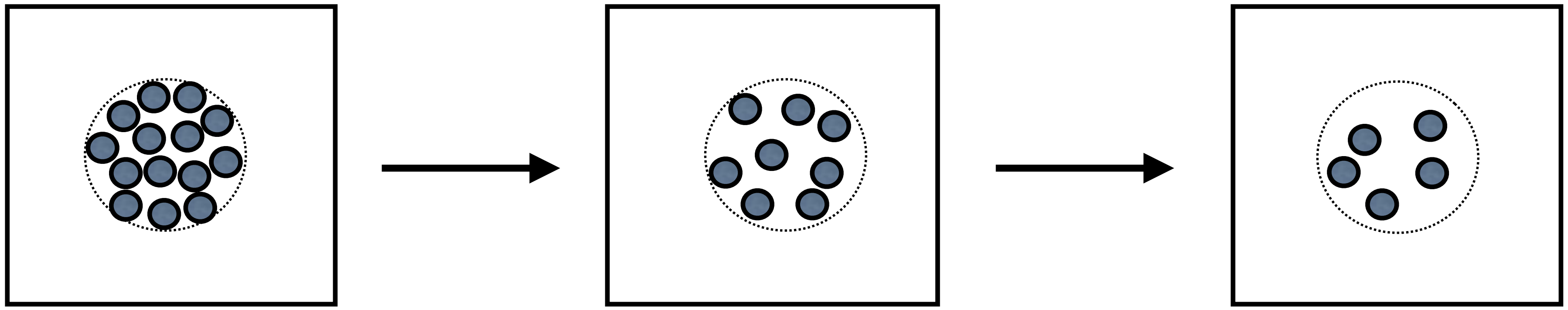
$$n(t) = \int d\mathbf{r}\, c(\mathbf{r},t) \quad \Longrightarrow \quad \frac{dn(t)}{dt} = -\int d\mathbf{r}\, c^2(\mathbf{r},t)$$

- Two simplifying assumptions
    1. Particles confined to volume V
    2. Spatial distribution remains uniform

- Closed equation for number of remaining particles

$$\frac{dn}{dt} = -\frac{n^2}{V}$$

Early phase: fast reactions



- Particles still inside initial-occupied domain

$$V \sim N \quad \Longrightarrow \quad \frac{dn}{dt} = -\frac{n^2}{N}$$

- Mean-field like decay

$$n(t) \sim N\, t^{-1}$$

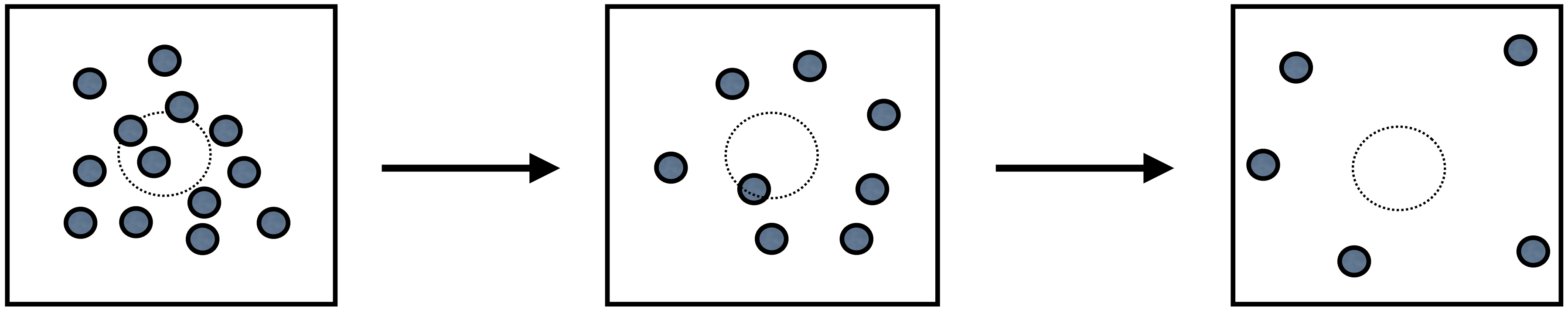
- Valid until particles exit initially-occupied domain

$$\ell^d \sim t^{d/2} \sim N \quad \Longrightarrow \quad T \sim N^{2/d}$$

- Diffusion time scale gives number of particles

$$n(T) \sim N^{(d-2)/d}$$

Intermediate phase: slow reactions



- Particles confined to a growing volume

$$V \sim t^{d/2} \qquad \Longrightarrow \qquad \frac{dn}{dt} = -\frac{n^2}{t^{d/2}}$$

- Slower decay of the density

$$n(t) - n(\infty) \sim N^{2(d-2)/d}\, t^{-(d-2)/2}$$

- Recover scaling law for final number of particles

$$M \sim N^{(d-2)/d}$$

- Reaction rate gives "escape time" for final reaction

$$n(t) - n(\infty) \sim 1 \qquad \Longrightarrow \qquad \tau \sim N^{4/d}$$

Three phases

- Most reactions

$$t \ll N^{2/d}$$

- Few reactions

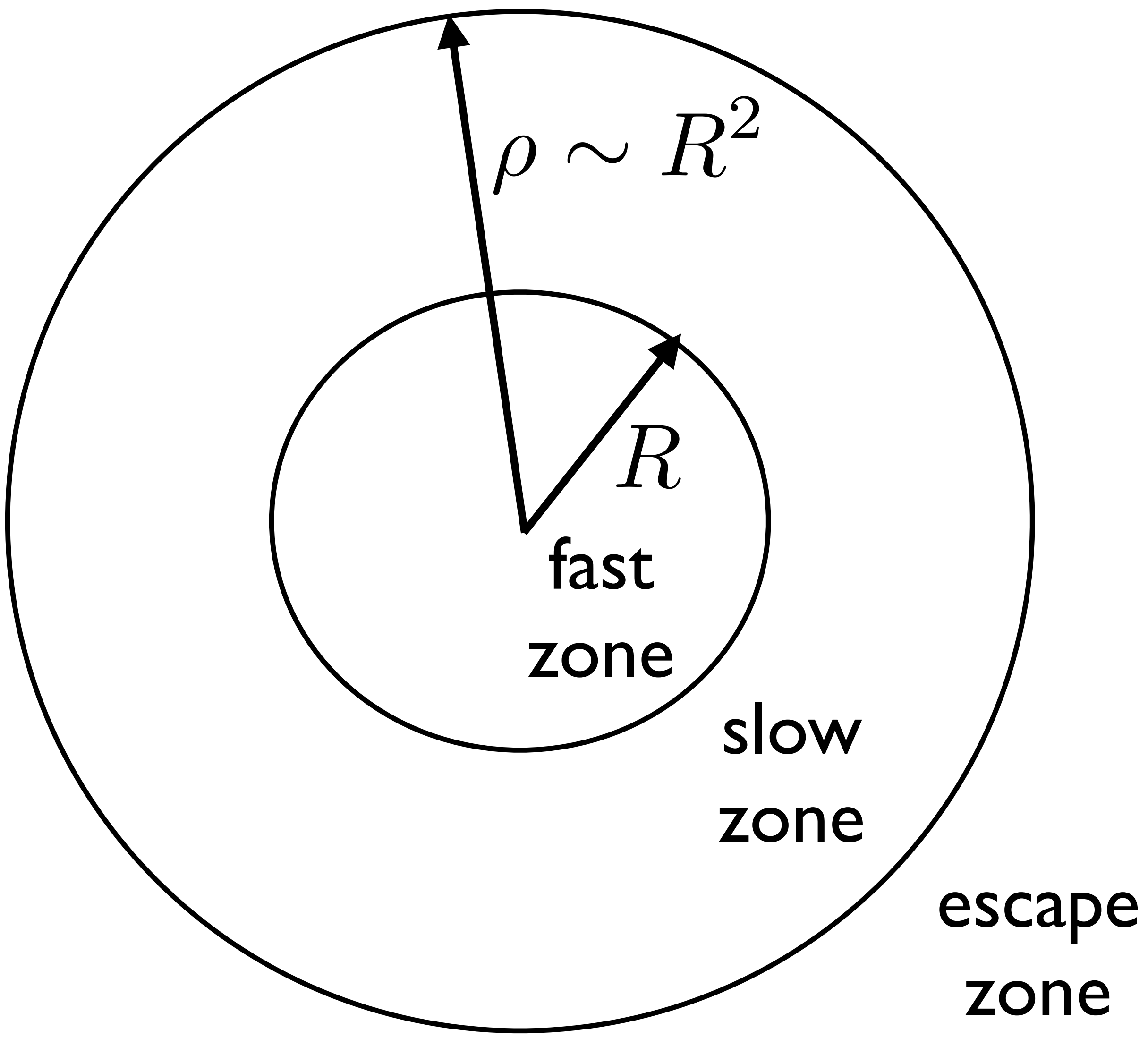
$$N^{2/d} \ll t \ll N^{4/d}$$

- No reactions at all

$$N^{4/d} \ll t$$

- Two length scales

$$R \sim N^{1/d} \quad \text{and} \quad \rho \sim N^{2/d}$$



Two time and length scales

Finite-size scaling

- Universal behavior, independent of system size

$$n(t) \simeq N^{(d-2)/d}\, F\left(t/N^{2/d}\right)$$

- Scaling function

$$F(x) \sim \begin{cases} x^{-1} & x \ll 1; \\ 1 + \text{const.} \times x^{(2-d)/2} & x \gg 1 \end{cases}$$

- Average lifetime of particles logarithmic in N

$$\int^{N^{2/d}} dt\, t\, t^{-2} \quad \Longrightarrow \quad \langle t \rangle \sim \ln N$$

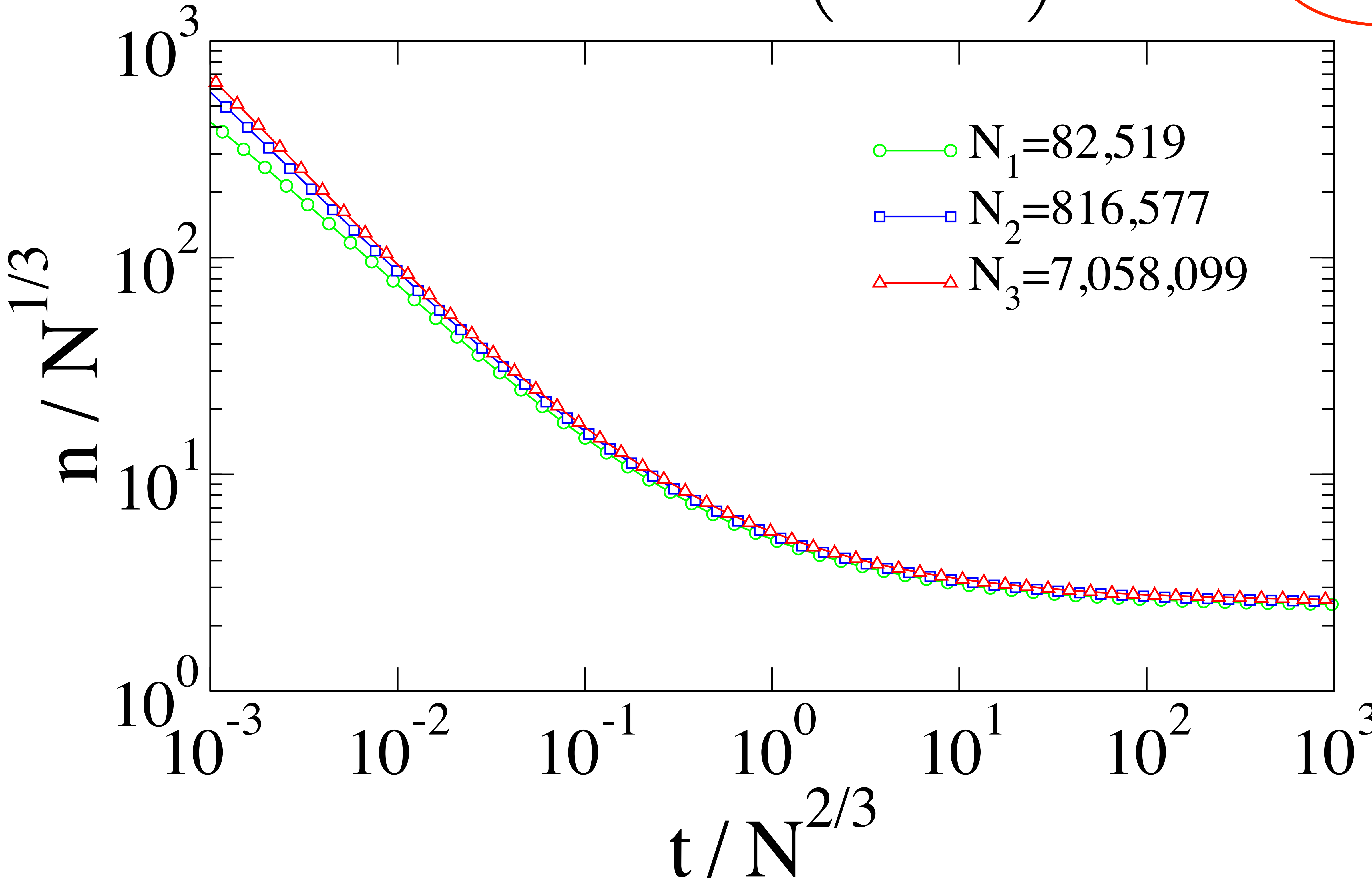
- Numerical simulations can not measure M directly
- Confirm finite-size scaling, extrapolation for M
- Brute-force Monte Carlo (keep track of sites, not particles)

$$\mathcal{O}(N \times N \times \ln N)$$

Numerical Simulations: Finite-Size Scaling

$$n(t) \simeq N^{1/3}\, F\left(t/N^{2/3}\right)$$

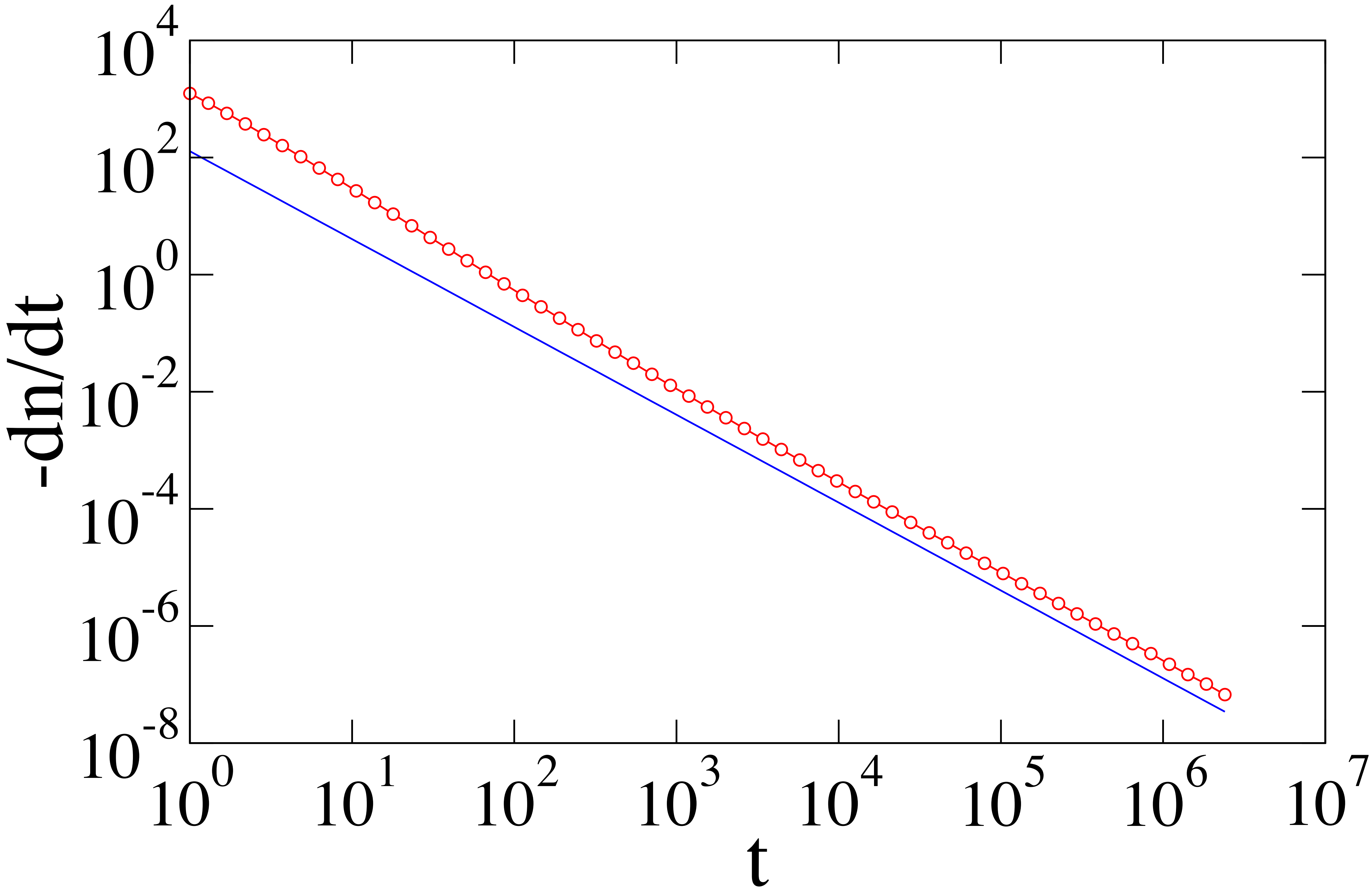
$d = 3$



Numerical Simulations: Slow Kinetics

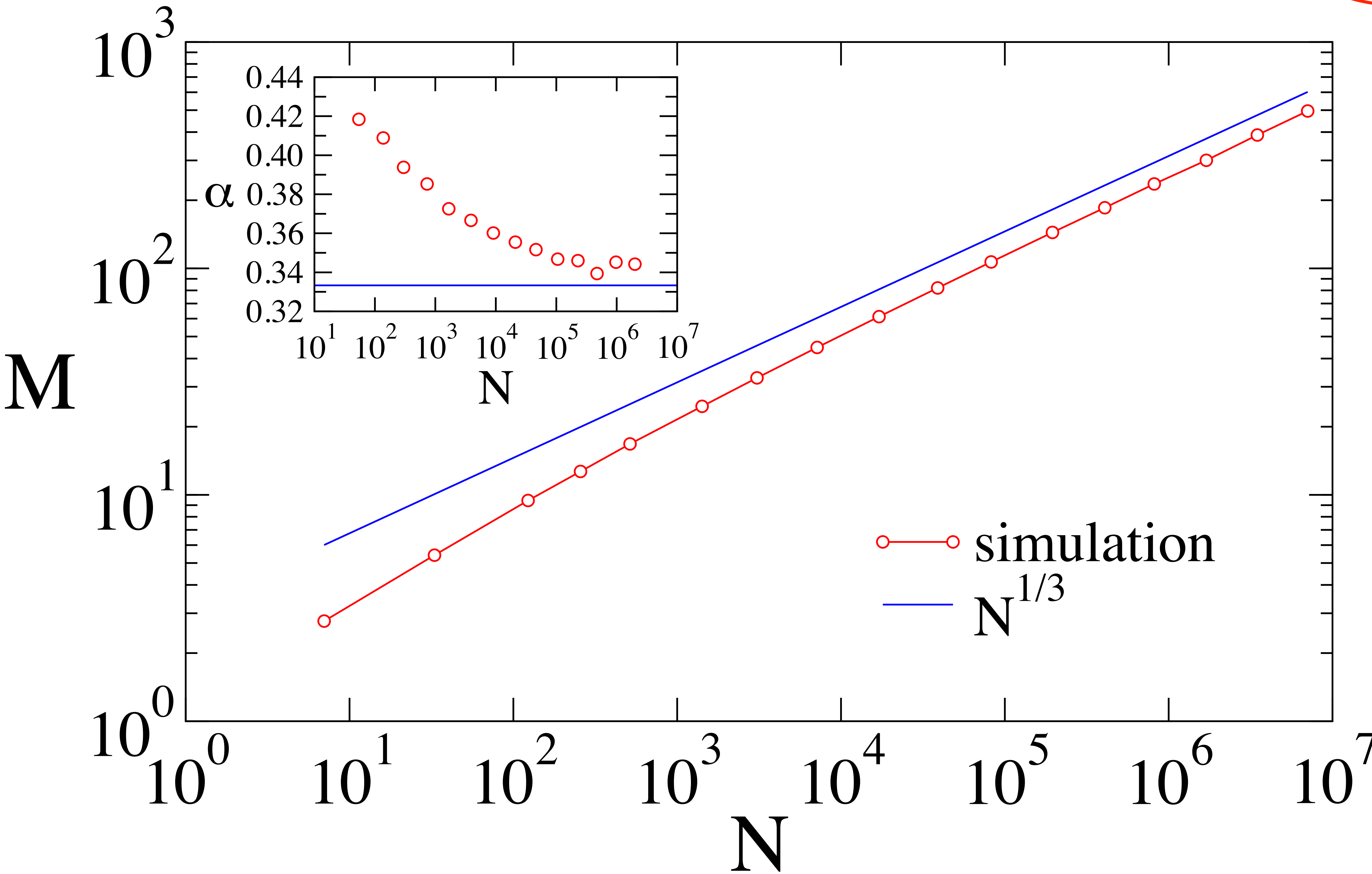
$$n(t) - n(\infty) \sim t^{-1/2}$$

$d = 3$



Numerical Simulations: Final Number

$$n(t) - M \sim t^{-1/2} \qquad M \sim N^{1/3} \qquad d = 3$$



Reaction-diffusion equations

- Concentration obeys reaction-diffusion equation

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = D\,\nabla^2 c(\mathbf{r},t) - K\,c^2(\mathbf{r},t)$$

- Initial state: compact initial conditions with N particles

$$c(\mathbf{r},t) = \begin{cases} 1 & \frac{4\pi r^3}{3} < N \\ 0 & \frac{4\pi r^3}{3} > N \end{cases}$$

- Final state: "Gaussian cloud" with $N^{1/3}$ particles

$$c(\mathbf{r},t) \to \frac{a\,N^{1/3}}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{2Dt}\right)$$

Nonlinear "selection" problem for constant a

Probabilistic derivation

- Initial state: many particles uniformly pack a sphere

$$\text{spacing} = 1 \quad \Longrightarrow N \sim L^d$$

- Late state: few surviving particles uniformly spaced

$$\text{spacing} = \ell \quad \Longrightarrow M \sim (L/\ell)^d$$

- Survival probability of test particle at the origin

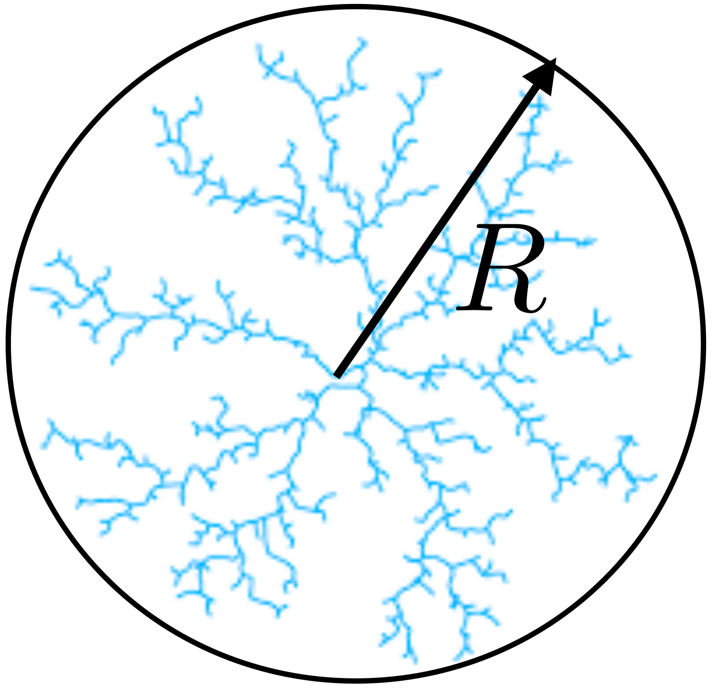
spherical shells
radius $n\ell$
$n = 1, 2, \ldots, L/\ell$

$$\prod_{\ell=1}^{L/\ell} \left(1 - \frac{1}{(n\ell)^{d-2}}\right)^{n^{d-1}}$$

- Probability finite iff log of product is finite

$$\frac{1}{\ell^{d-2}} \sum_{\ell=1}^{L/\ell} n \sim \frac{L^2}{\ell^d} \sim 1 \quad \Longrightarrow \quad \ell \sim L^{1/d} \quad \Longrightarrow \quad M \sim N^{(d-2)/d}$$

Sparse & compact initial conditions



- Particles occupy a fractal region

$$N \sim R^{\delta}$$

- Co-dimension controls the behavior

$$\Delta = d - \delta$$

- Scaling law for the number of escaping particles

$$M \sim \begin{cases} N^{(d-2)/\delta} & \Delta < 2, \\ N(\ln N)^{-1} & \Delta = 2, \\ N & \Delta > 2. \end{cases}$$

- Example: two-dimensional disk in three dimensions

$$M \sim N^{1/2}$$

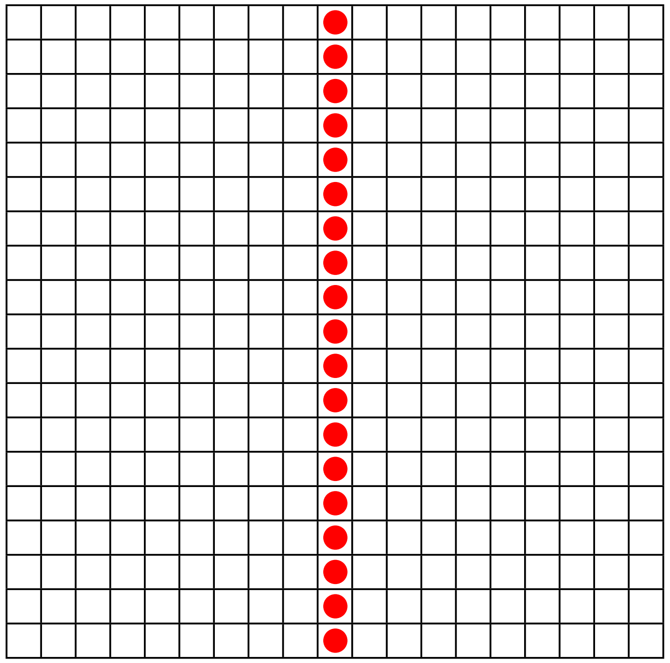
Conclusions I

- Diffusion-controlled annihilation, starting with finite number of particles
- Finite number of particles escape annihilation
- Two time scales control the kinetics
- Escape time scale is nontrivial
- Average lifetime is logarithmic
- Scaling law for time-dependence
- Scaling law for final number of particles
- Finite-size scaling allows for numerical verification
- Beyond scaling arguments?
- Other reaction schemes: two-species annihilation?

Sparse initial conditions

- Particles occupy a sub-space with dimension δ
- Embedded in space with dimension $d > 2$
- Number of particle is unbounded
- Co-dimension controls behavior

$d = 2,\ \delta = 1$



$$\Delta = d - \delta$$

- Survival probability of a test particle

$$S(t) \sim \begin{cases} t^{-(2-\Delta)/2} & \Delta < 2, \\ (\ln t)^{-1} & \Delta = 2, \\ S_\infty + \text{const.} \times t^{-(\Delta-2)/2} & \Delta > 2. \end{cases}$$

Finite survival probability when $\delta < d - 2$

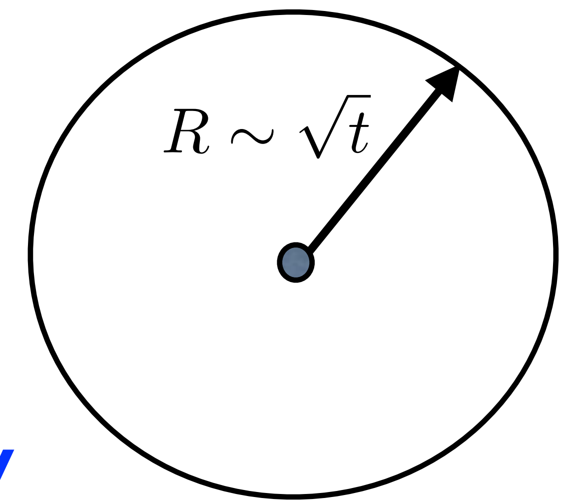
A filament in three dimensions

$$\delta = 1$$
$$d = 3$$

- Concentration obeys reaction-diffusion equation

$$\frac{\partial c(x,y,z,t)}{\partial t} = \nabla^2 c(x,y,z,t) - c^2(x,y,z,t)$$

- Problem is effectively two dimensional



$$\partial_z = 0 \quad \Longrightarrow \quad \nabla^2 \equiv \partial_x^2 + \partial_y^2$$

- Rate equation for the survival probability

$$S(t) = \iint dx\, dy\, c(x,y,t) \quad \Longrightarrow \quad \frac{dS}{dt} = -\iint dx\, dy\, c^2$$

- Assume uniform distribution inside circle with

$$c(r,t) \sim \frac{S(t)}{t} \times \begin{cases} 1 & r < \sqrt{t} \\ 0 & r > \sqrt{t} \end{cases} \quad \Longrightarrow \quad \frac{dS}{dt} \sim -\frac{S^2}{t}$$

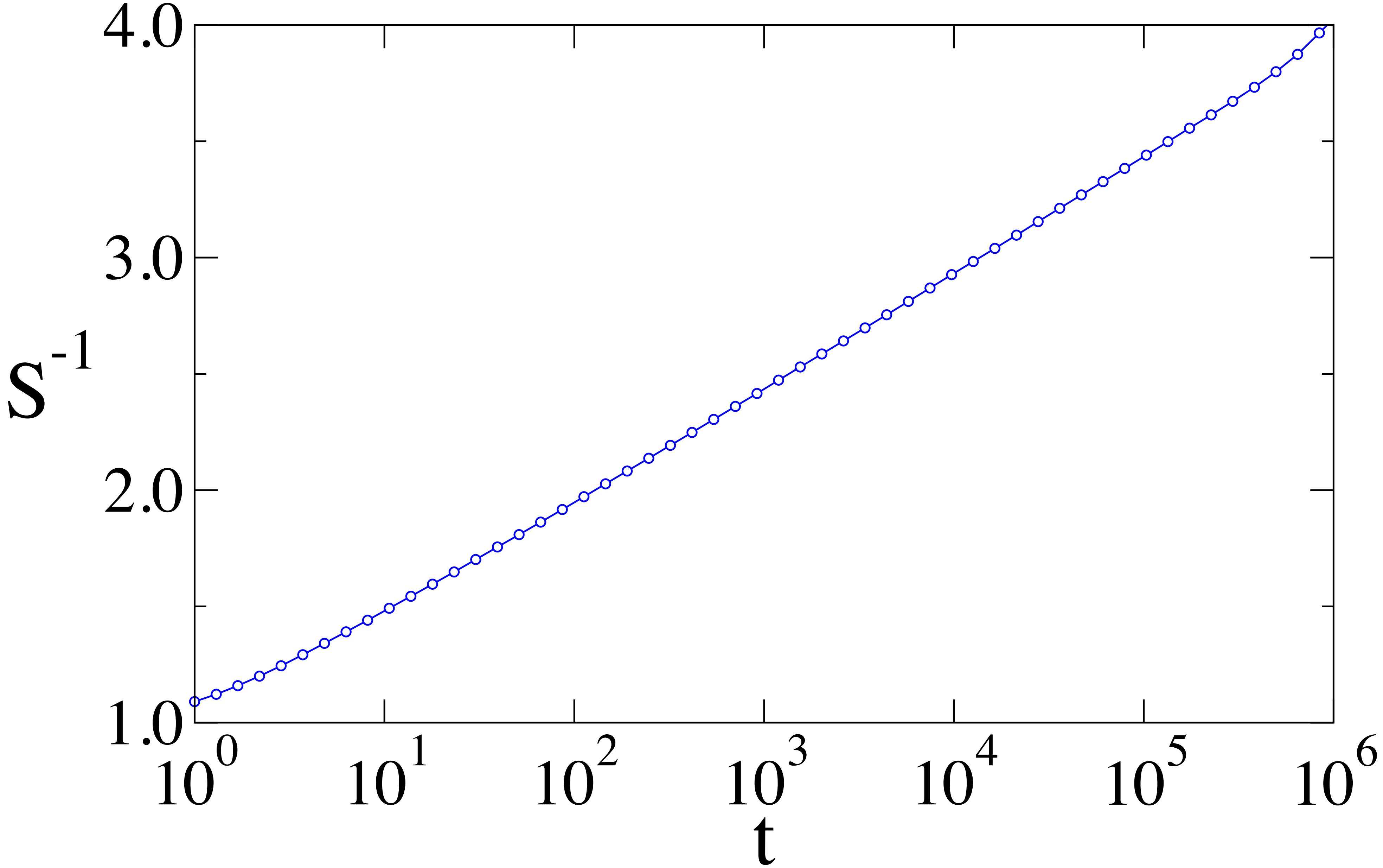
Uniform density approximation, again

Numerical simulations:
Filament in three dimensions

$\delta = 1$

$d = 3$

$$\frac{dS}{dt} \sim -\frac{S^2}{t} \quad \Longrightarrow \quad S \sim (\ln t)^{-1}$$



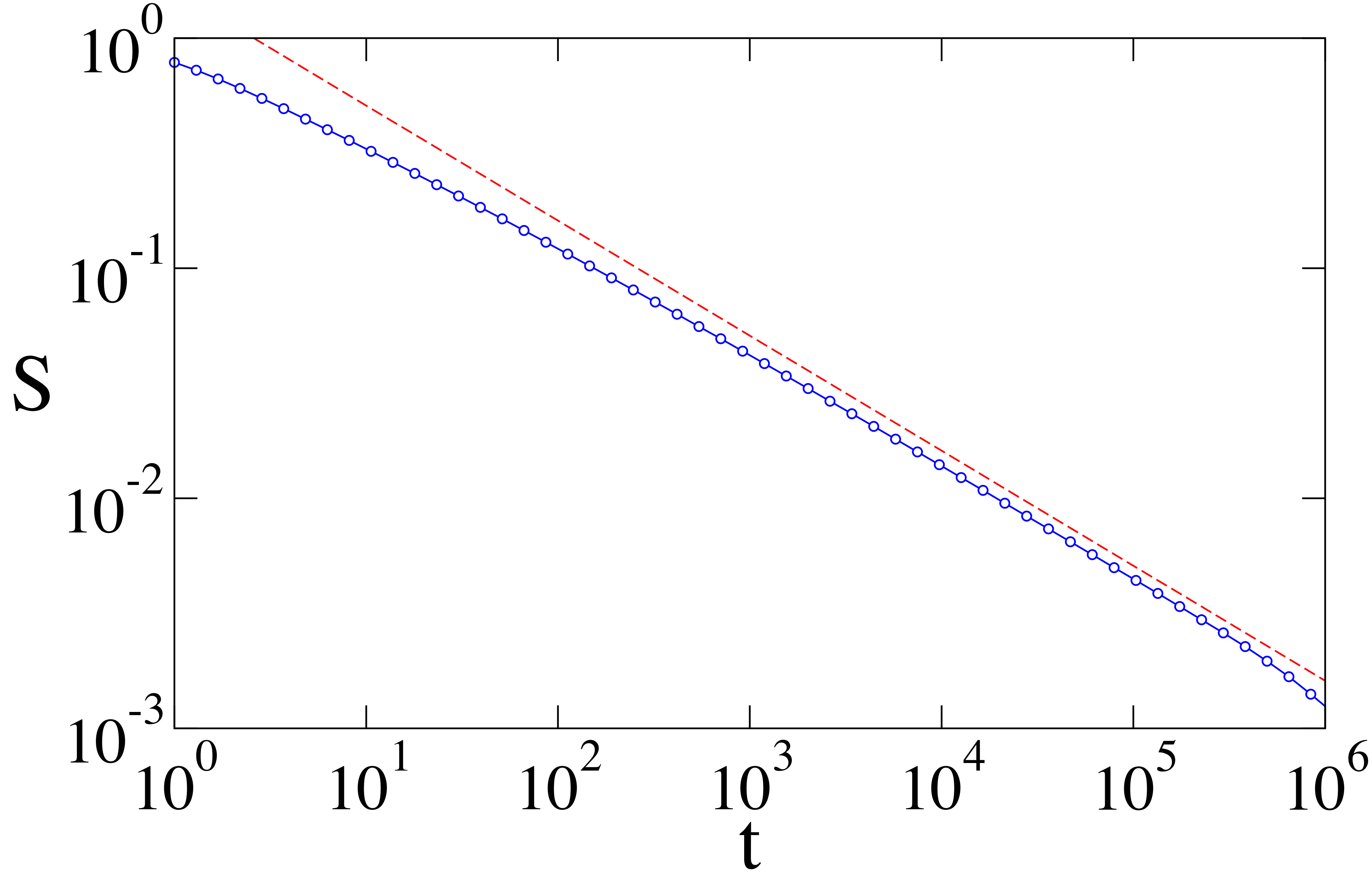
Very slow decay: inverse logarithmic

Filament in three dimensions

$\delta = 2$

$d = 3$

$$\frac{dS}{dt} \sim -\frac{S^2}{\sqrt{t}} \quad \Longrightarrow \quad S \sim t^{-1/2}$$



General behavior ($d>2$)

- Dimension of Laplace operator = co-dimension

$$\frac{dS}{dt} \sim -\frac{S^2}{t^{\Delta/2}}$$

- Three regimes of behavior

$$S(t) \sim \begin{cases} t^{-(2-\Delta)/2} & \Delta < 2, \\ (\ln t)^{-1} & \Delta = 2, \\ S_\infty + \text{const.} \times t^{-(\Delta-2)/2} & \Delta > 2. \end{cases}$$

Critical dimension ($d=2$)

- Logarithmic correction to reaction rate

$$\frac{dS}{dt} \sim -\frac{S^2}{t^{\Delta/2}\ln(t^{1/2}/S)} \quad \Longrightarrow S \sim (\ln t)\, t^{-\delta/2}$$

Conclusions II

- Diffusion-controlled annihilation with sparse initial conditions
- Used same uniform volume approximation
- Co-dimension controls the behavior
- Slow kinetics below critical co-dimension
- Extremely slow (inverse logarithmic) kinetics at the critical co-dimension
- Finite survival probability above the critical co-dimension