Escape and Finite-Size Scaling in Diffusion-Controlled Annihilation

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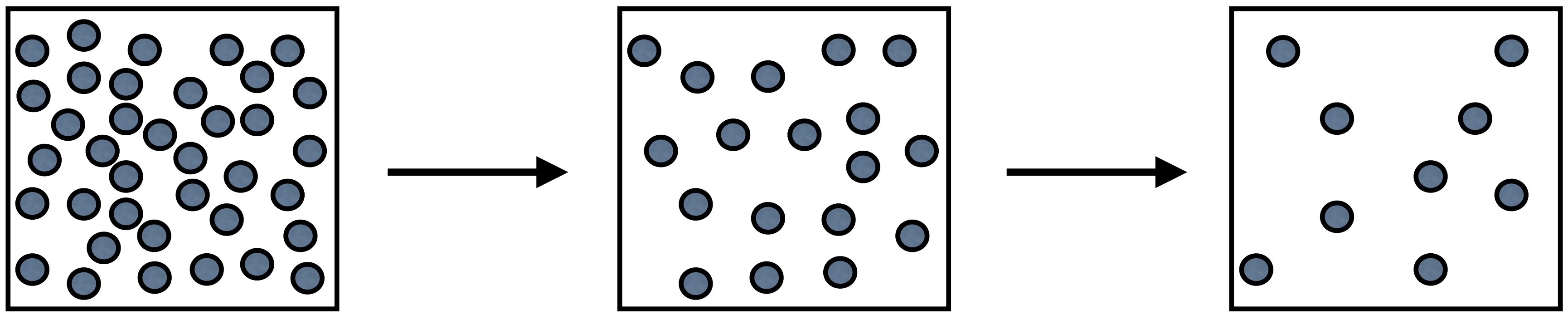
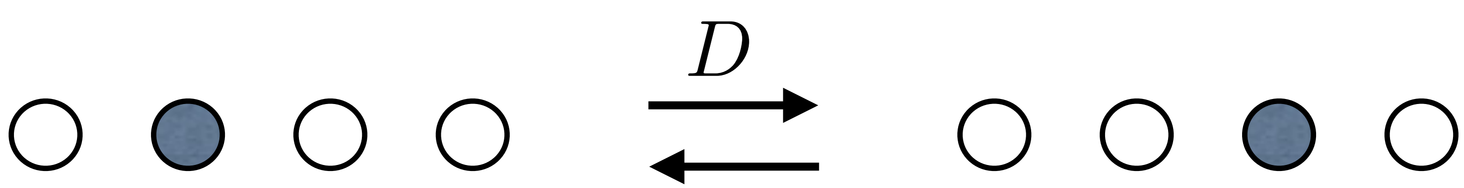
Diffusion-Controlled Annihilation



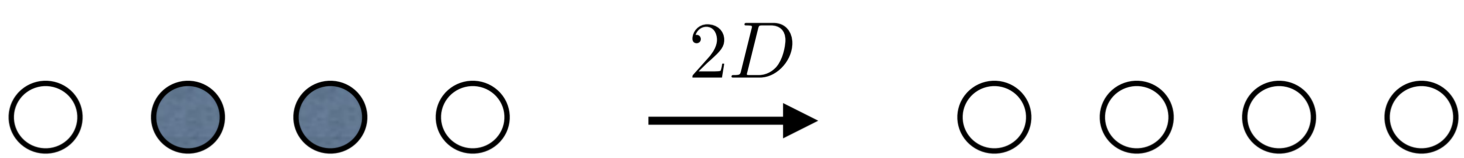
de gennes 82
wilczek 83
Racz 85
Spouge 88

- **Diffusion**: particles move randomly



reversible

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



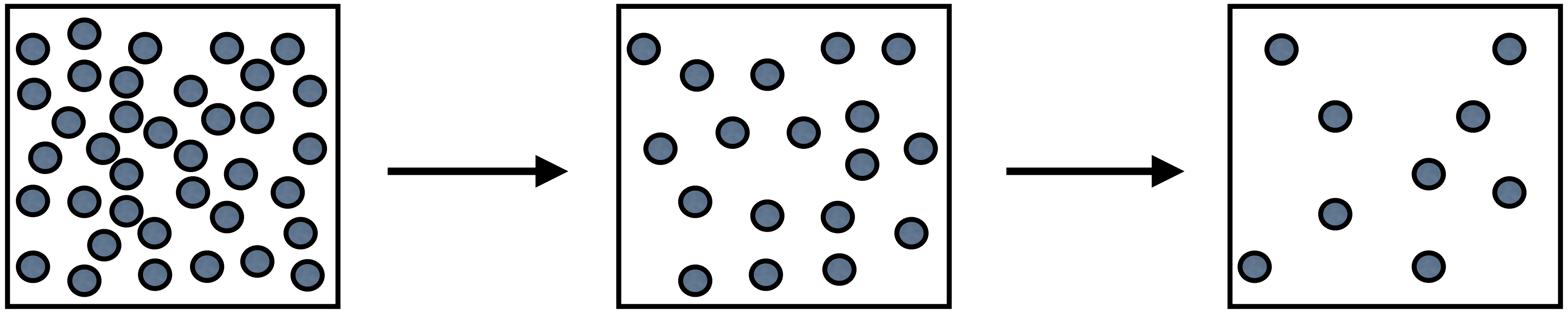
irreversible

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

Allam et al
PRB 2013

Paradigmatic model of Nonequilibrium Stat. Phys.

Infinite system: uniform density



- Hydrodynamic approach

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

- Dimensional analysis for reaction rate

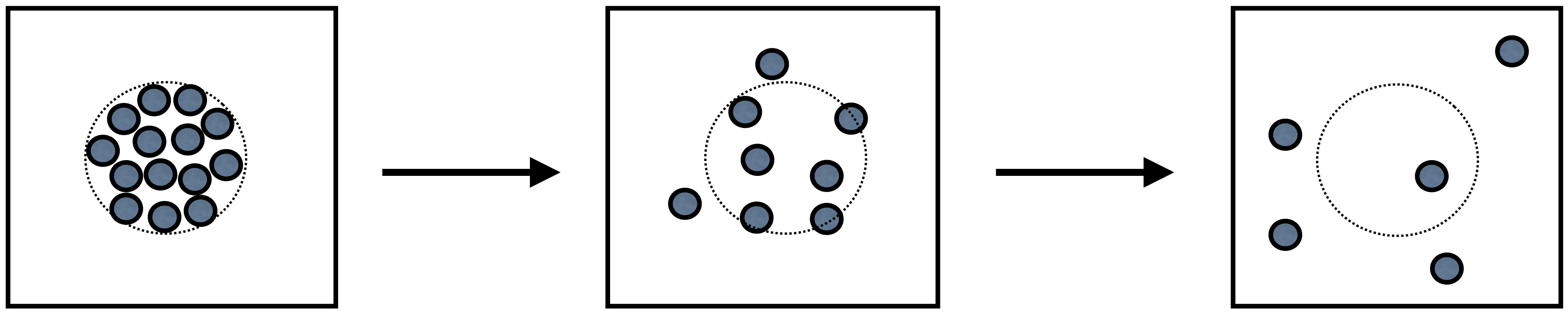
$$[K] = \frac{L^d}{T} \quad \longrightarrow \quad K \propto \begin{cases} D\rho^{2-d} & d < 2 \\ DR^{d-2} & d > 2 \end{cases}$$

- 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

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

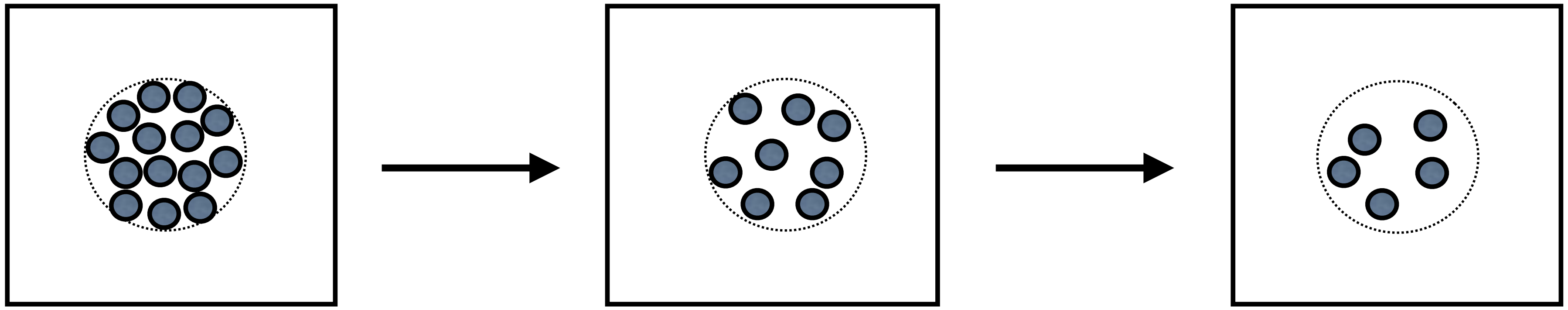
- Dimensionless form $D = K = a = c_0 = 1$
- Total number of particles obeys rate equation

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

- 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

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

- Mean-field like decay

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

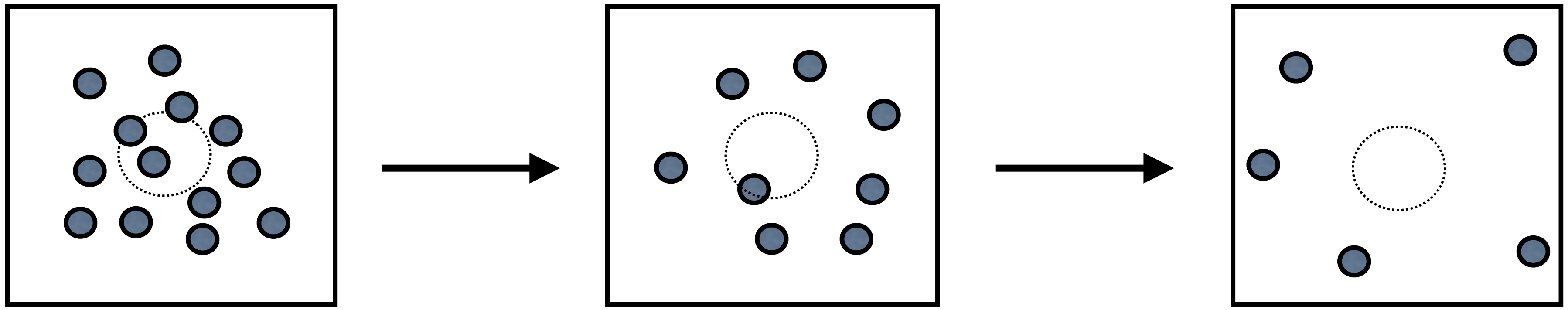
- Valid until particles exit initially-occupied domain

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

- Diffusion time scale gives number of particles

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

Intermediate phase: slow reactions



- Particles confined to a growing volume

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

- 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

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

Three Phases

- Most reactions

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

- Few reactions

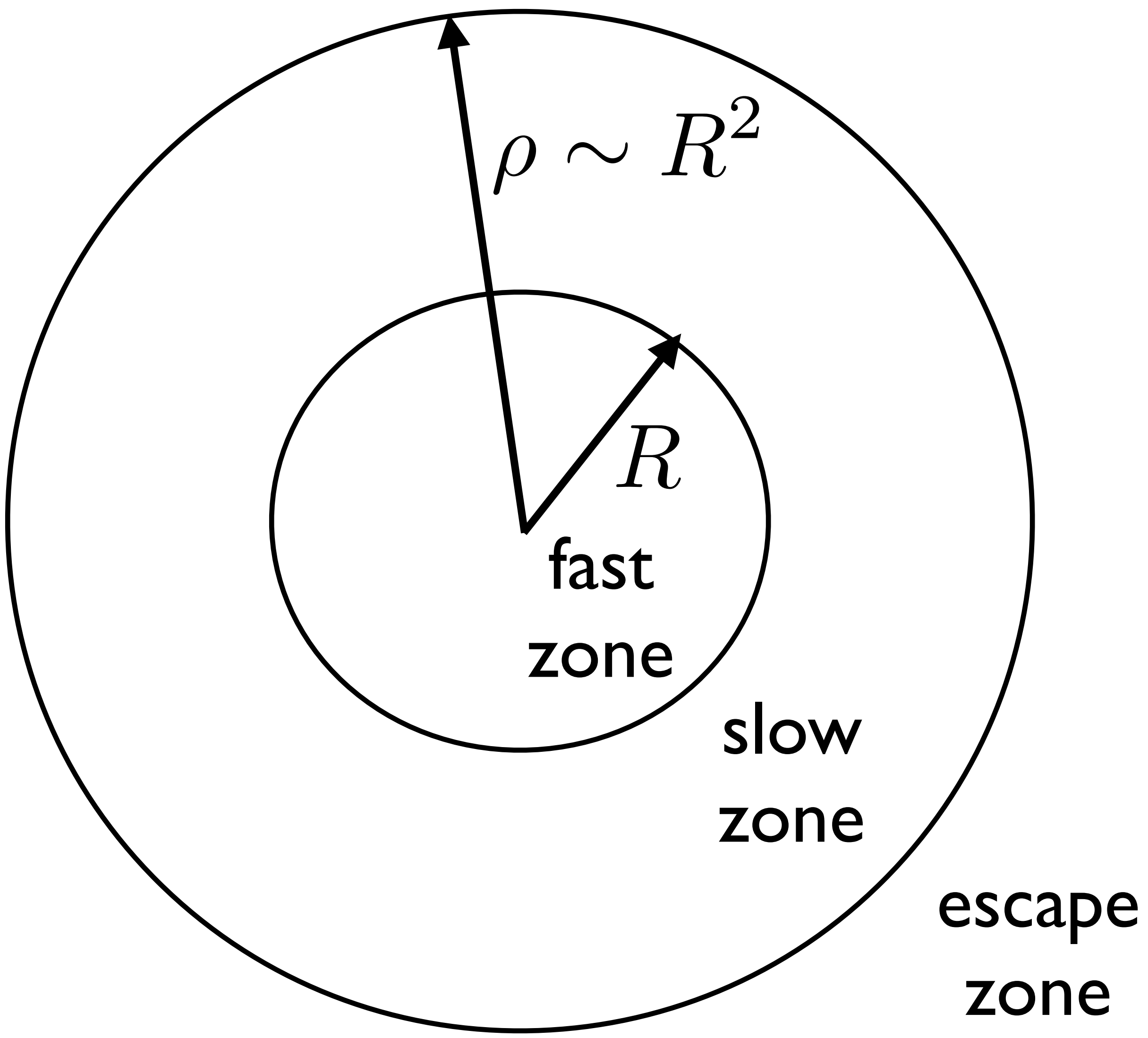
$$N^{2/d} \ll t \ll N^{4/d}$$

- 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

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

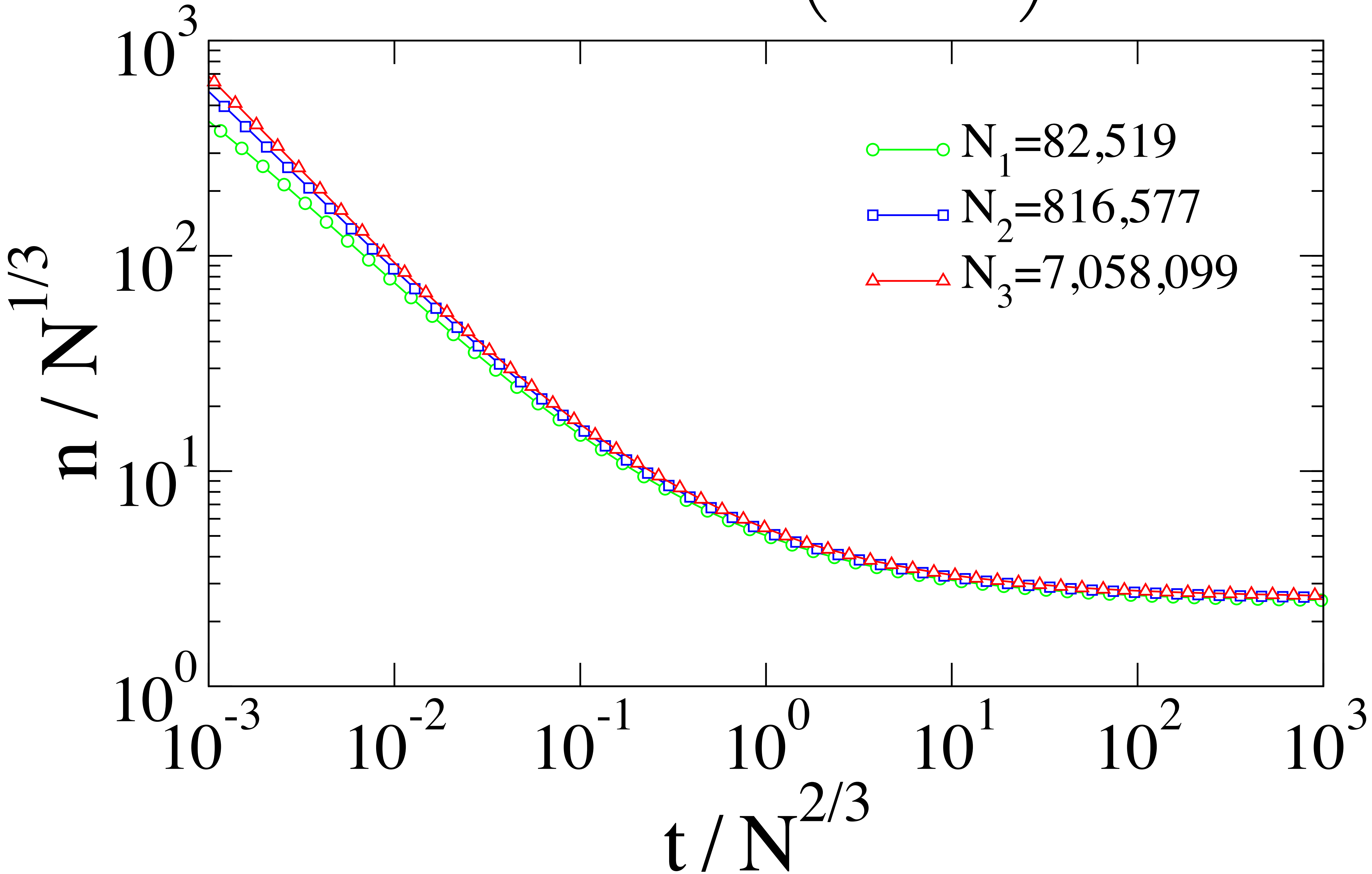
- Numerical simulations can not measure M directly
- Confirm finite-size scaling, extrapolate M
- Brute-force Monte Carlo (keep track of sites, not particles)

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

$d = 3$

Numerical Simulations I

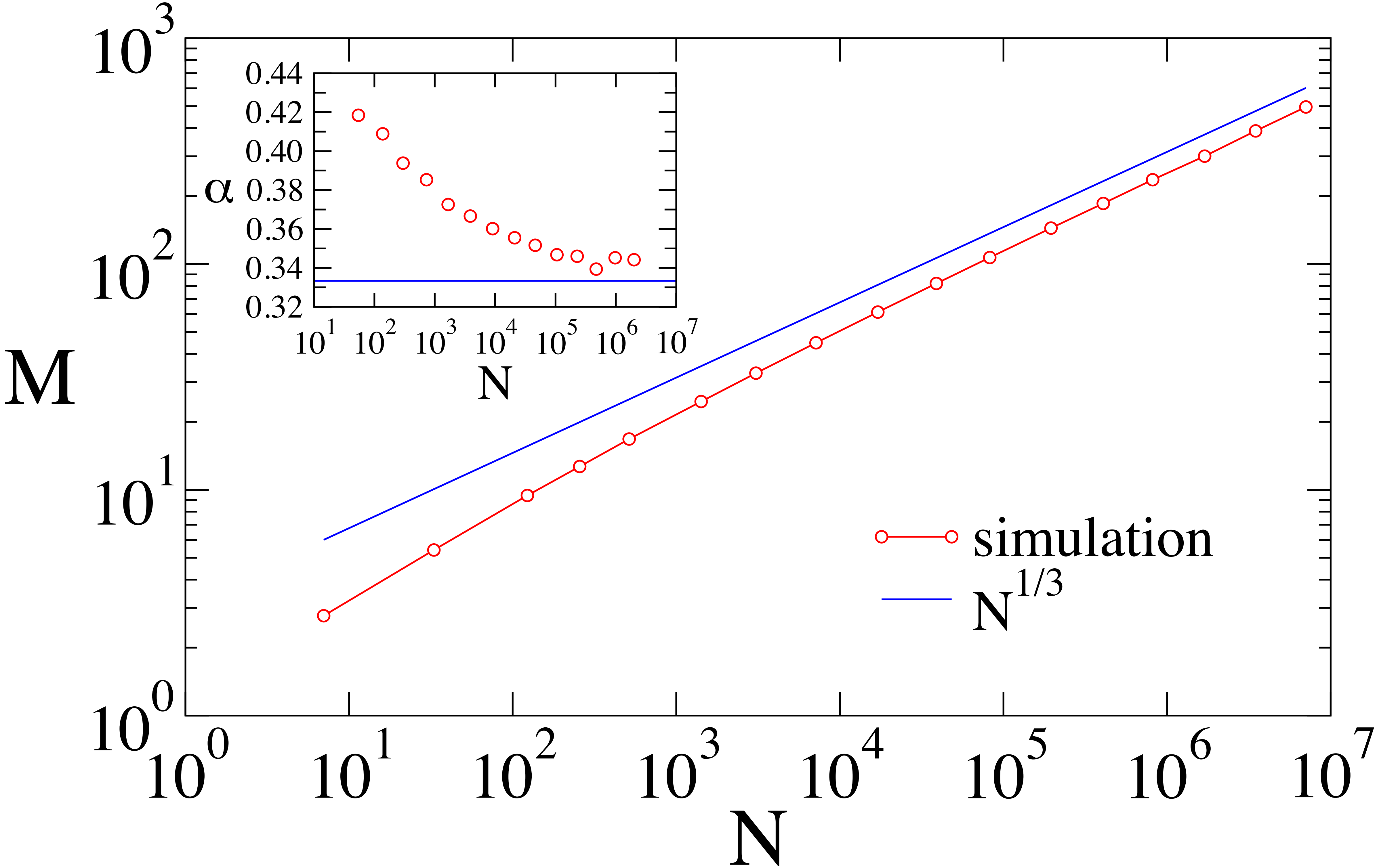
$$n(t) \simeq N^{1/3} F\left(t/N^{2/3}\right)$$



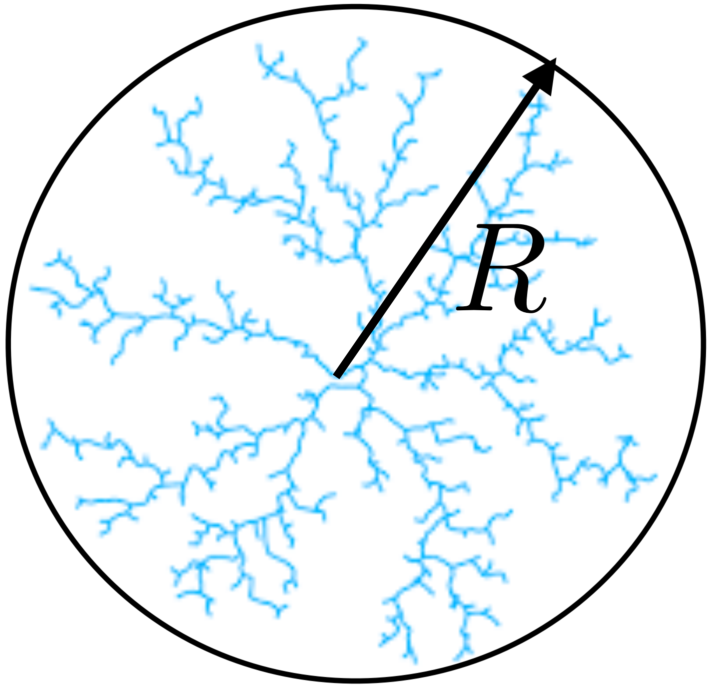
$d = 3$

Numerical Simulations II

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



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

- 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?