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
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Plan

1. Reaction-diffusion with compact initial conditions
   • Finite number of particles

2. Reaction-diffusion with sparse initial conditions
   • Reaction kinetics
Diffusion-Controlled Annihilation

- **Diffusion**: particles move randomly

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

- **Theory**: role of spatial correlations & fluctuations

- **Experiments**: photoexcitations in nanotubes

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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**

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

• **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

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

• Dimensionless form \( D = K = a = c_0 = 1 \)

• Total number of particles obeys rate equation

\[ n(t) = \int dr \, c(r, t) \iff \frac{dn(t)}{dt} = -\int dr \, c^2(r, t) \]

• 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

\[ V \sim N \quad \Rightarrow \quad \frac{dn}{dt} = -\frac{n^2}{N} \]

- Mean-field like decay

\[ n(t) \sim N t^{-1} \]

- Valid until particles exit initially-occupied domain

\[ \ell^d \sim t^{d/2} \sim N \quad \Rightarrow \quad T \sim N^{2/d} \]

- Diffusion time scale gives number of particles

\[ n(T) \sim N^{(d-2)/d} \]
Intermediate phase: slow reactions

- Particles confined to a growing volume
  \[ V \sim t^{d/2} \implies \frac{dn}{dt} = -\frac{n^2}{t^{d/2}} \]

- 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
  \[ n(t) - n(\infty) \sim 1 \implies \tau \sim N^{4/d} \]
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
  \[ n(t) \sim N^{(d-2)/d} F \left( \frac{t}{N^{2/d}} \right) \]

- 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 \( N \)
  \[ \int_{N^{2/d}}^{\infty} dt \, t \, t^{-2} \quad \Longrightarrow \quad \langle t \rangle \sim \ln N \]

- 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

\[ n(t) \approx N^{1/3} F \left( \frac{t}{N^{2/3}} \right) \]

d = 3

\[ N_1 = 82,519 \]
\[ N_2 = 816,577 \]
\[ N_3 = 7,058,099 \]
Numerical Simulations: Slow Kinetics

\[ n(t) - n(\infty) \sim t^{-1/2} \]
Numerical Simulations: Final Number

\[ n(t) - M \sim t^{-1/2} \]

\[ M \sim N^{1/3} \]

\[ d = 3 \]
Reaction-diffusion equations

- Concentration obeys reaction-diffusion equation

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

- Initial state: compact initial conditions with \(N\) particles

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

- Final state: “Gaussian cloud” with \(N^{1/3}\) particles

\[
c(r, t) \rightarrow \frac{a N^{1/3}}{(4\pi D t)^{3/2}} \exp \left( -\frac{r^2}{2D t} \right)
\]

Nonlinear “selection” problem for constant \(a\)
Probabilistic derivation

• Initial state: many particles uniformly pack a sphere
  \[ \text{spacing} = 1 \implies N \sim L^d \]

• Late state: few surviving particles uniformly spaced
  \[ \text{spacing} = \ell \implies M \sim (L/\ell)^d \]

• Survival probability of test particle at the origin
  \[
  \text{spherical shells} \quad \text{radius } n\ell \\
  n = 1, 2, \ldots, L/\ell \\
  \frac{L/\ell}{\prod_{\ell=1}^{L/\ell} \left(1 - \frac{1}{(n\ell)^{d-2}}\right)^{n^{d-1}}}
  \]

• Probability finite iff log of product is finite
  \[
  \frac{1}{\ell^{d-2}} \sum_{\ell=1}^{L/\ell} n \sim \frac{L^2}{\ell^d} \sim 1 \implies \ell \sim L^{1/d} \implies M \sim N^{(d-2)/d}
  \]
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 $\delta$
- Embedded in space with dimension $d > 2$
- Number of particle is unbounded
- Co-dimension controls behavior
  \[ \Delta = d - \delta \]
- 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

- 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

\[
\partial_z = 0 \quad \implies \quad \nabla^2 \equiv \partial_x^2 + \partial_y^2
\]

- Rate equation for the survival probability

\[
S(t) = \int \int dx \, dy \, c(x, y, t) \quad \implies \quad \frac{dS}{dt} = - \int \int dx \, dy \, c^2
\]

- Assume uniform distribution inside circle with

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

Uniform density approximation, again
Numerical simulations:
Filament in three dimensions

\[ \frac{dS}{dt} \sim - \frac{S^2}{t} \implies S \sim (\ln t)^{-1} \]

Very slow decay: inverse logarithmic
Filament in three dimensions

\[
\frac{dS}{dt} \sim -\frac{S^2}{\sqrt{t}} \quad \Rightarrow \quad S \sim t^{-1/2}
\]

\[\delta = 2\]
\[d = 3\]
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
  
  \[
  \frac{dS}{dt} \sim -\frac{S^2}{t^{\Delta/2} \ln(t^{1/2}/S)} \quad \Rightarrow \quad S \sim (\ln t) t^{-\delta/2}
  \]
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