Diffusion-Controlled Processes

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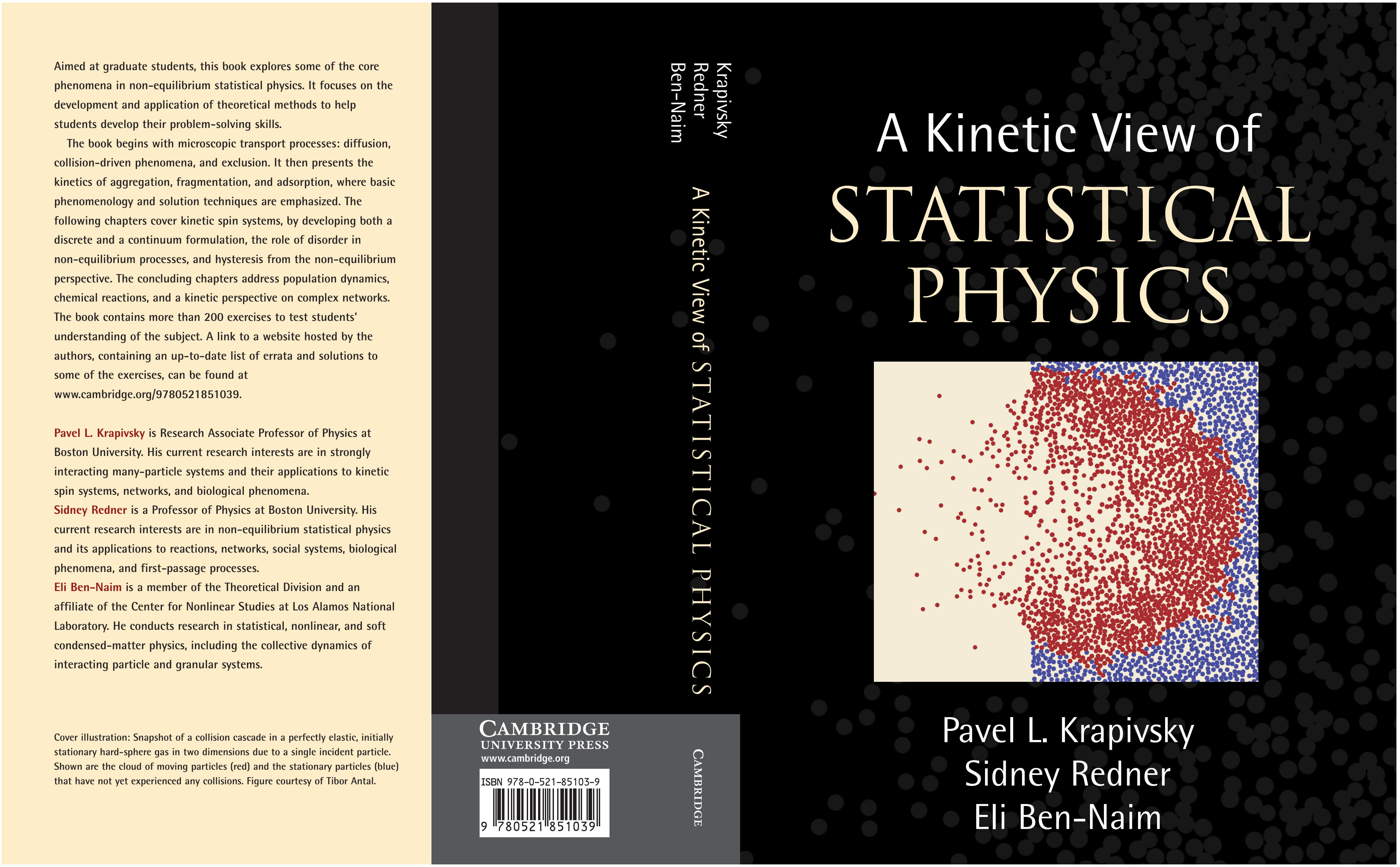
Goals

- Give a flavor of non-equilibrium statistical physics: Not so much the study of specific subjects, but rather a collection of ideas and tools that work for an incredibly wide range of problems.
- Exemplify key insights that have emerged from the analysis of far-from-equilibrium behaviors.
- Diffusion-reaction systems (major lessons, a couple of long-standing challenges).



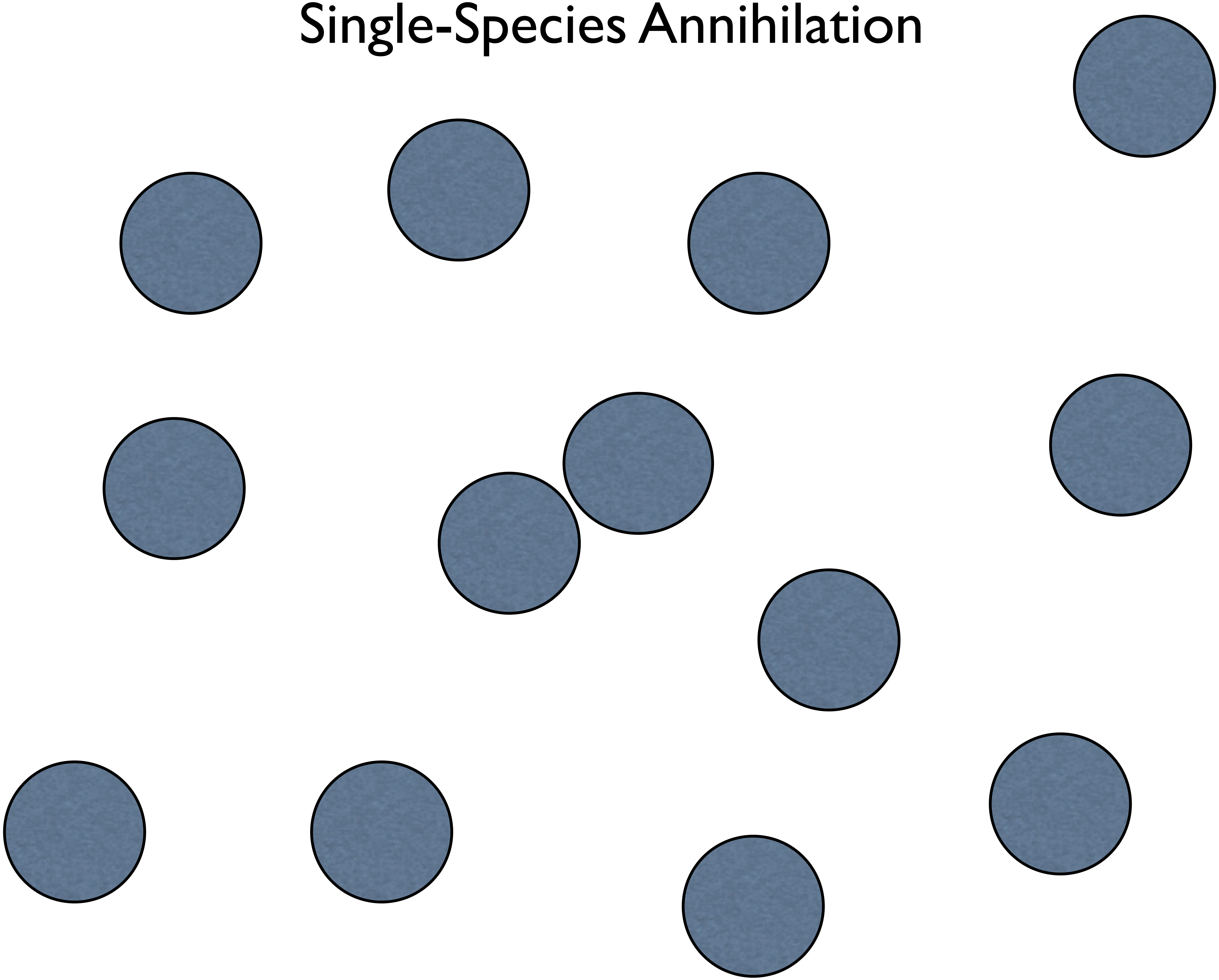
1. Aperitifs
2. Diffusion
3. Collisions
4. Exclusion
5. Aggregation
6. Fragmentation
7. Adsorption
8. Spin Dynamics
9. Coarsening
10. Disorder
11. Hysteresis
12. Population Dynamics
13. Diffusive Reactions
14. Complex Networks

\+ *>200 problems & soln manual*

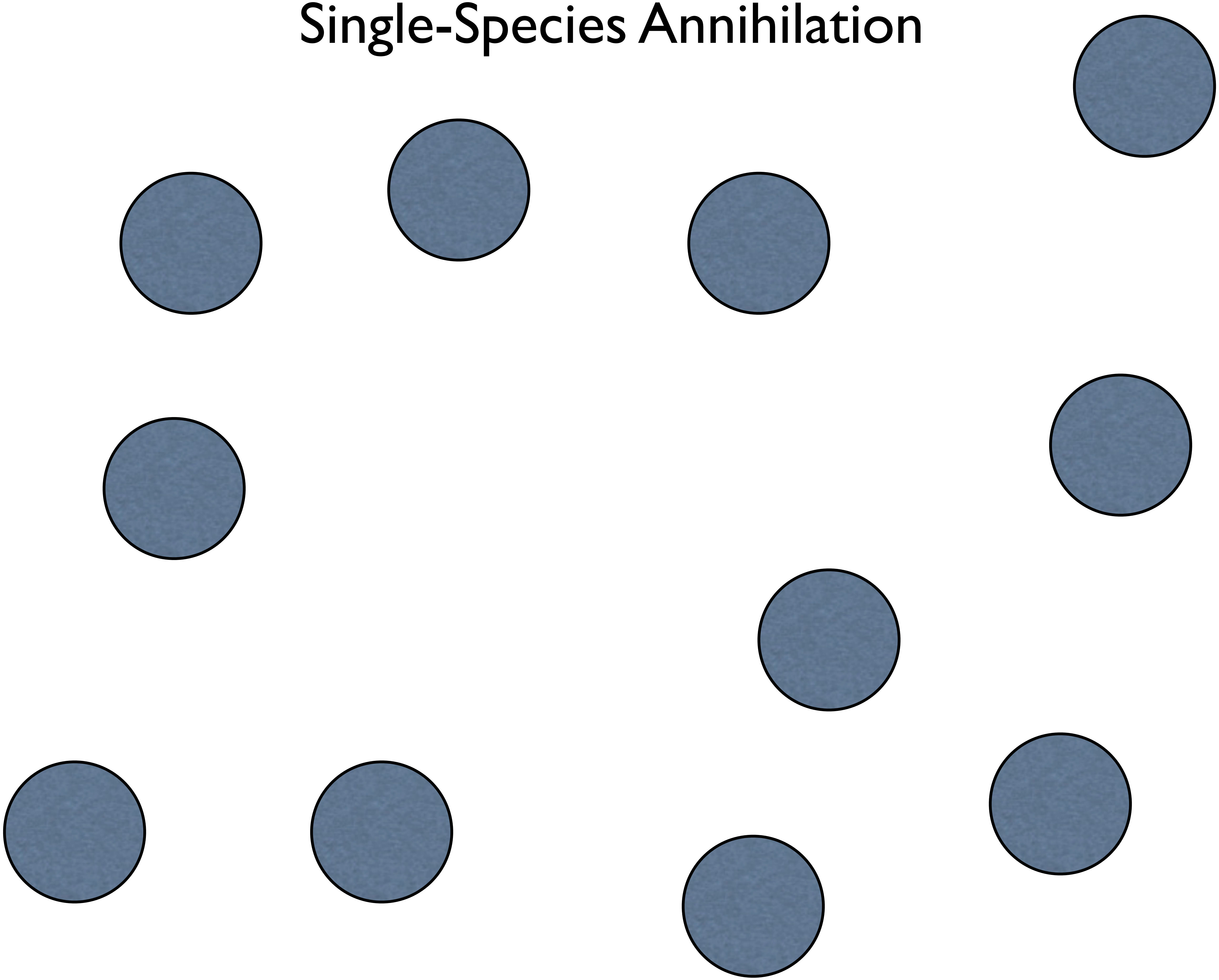
Simplified Reactions

- Coalescence: A + A => A
- Single-Species Annihilation: A + A => 0
- Two-Species Annihilation: A + B => 0

Single-Species Annihilation



Single-Species Annihilation



Hydrodynamic description

n particle density

K reaction rate

$$\frac{dn}{dt} = -Kn^2, \qquad n = \frac{n_0}{1 + n_0 K t} \simeq \frac{1}{Kt}$$

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$$n(t) \sim \begin{cases} t^{-1/2} & d = 1 \\ t^{-1} \ln t & d = 2 \\ t^{-1} & d > 2 \end{cases}$$

Dimensional analysis

$$
\begin{aligned}
K &= K(D,R) \sim D R^{d-2} \\
n &\sim \frac{1}{D R^{d-2}\, t} \\
n &= n(D,t) \sim \frac{1}{\sqrt{Dt}} \qquad \text{when} \quad d = 1
\end{aligned}
$$

Polya Theorem

If you need more than five lines to prove something,
then you are on the wrong track. *Anonymous*.

$$\#(\text{sites visited by RW}) \sim \begin{cases} \sqrt{t} & d = 1 \\ t/\ln t & d = 2 \\ t & d \geq 3 \end{cases}$$

Polya theorem 'explains' the asymptotic behavior in the single-species annihilation process.

Lessons

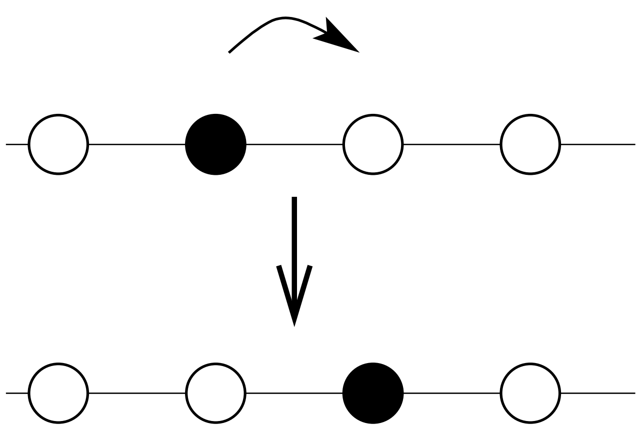
There is a critical dimension d_c that separates different kinetic behaviors. (For single-species annihilation, $d_c = 2$.)

Above d_c, the rate equation description is OK.

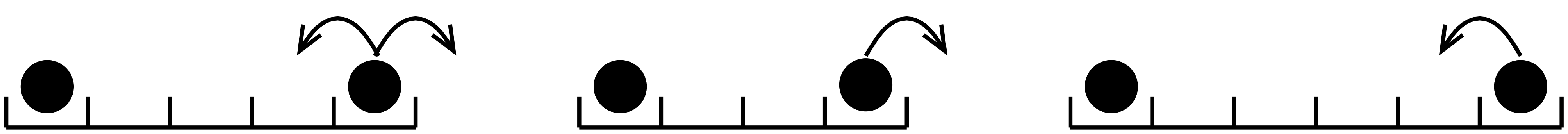
Below d_c, it is wrong.

At d_c, at most logarithmically wrong.

Coalescence in 1D



(a) (b)



(a) (b) (c)

$\mathbf{V_n}$: density of voids of length $\mathbf{n}$.

Evolution of $\mathbf{V_3}$ is exemplified.

Coalescence in 1D: Equations

$$\frac{dV_n}{dt} = V_{n+1} - 2V_n + V_{n-1}$$

$$V_n(0) = \delta_{n,0} \quad \text{fully occupied lattice}$$

Coalescence in 1D: Equations and Solutions

$$\frac{dV_n}{dt} = V_{n+1} - 2V_n + V_{n-1}$$

$$V_n(t) = e^{-2t}\ \left[I_n(2t) - I_{n+2}(2t)\right]$$

$$c(t) = \sum_{n\geq 0} V_n(t) = e^{-2t}\ \left[I_0(2t) + I_1(2t)\right]$$

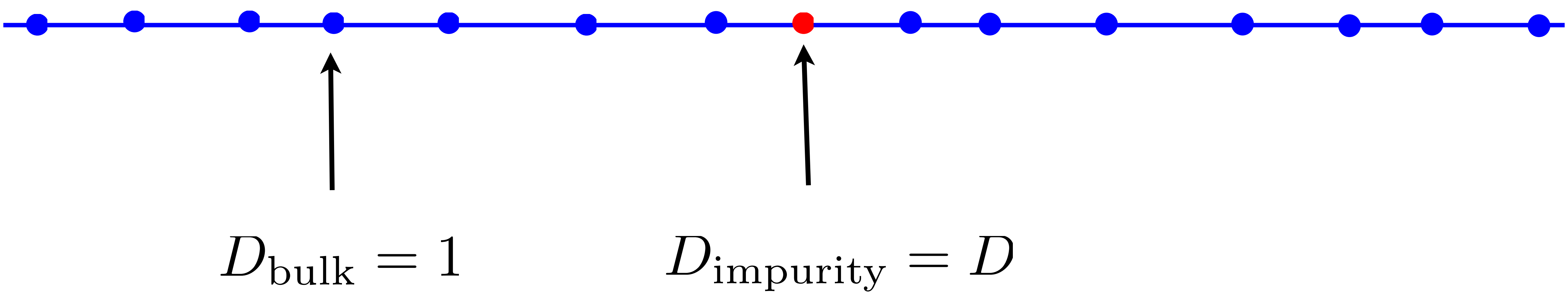
$c(t)$: Density of particles

$I_n(2t)$: Modified Bessel function

A bit of wisdom

In non-equilibrium statistical physics the **Diffusion Equation** plays a role of the **Harmonic Oscillator**. One must express some characteristics of a strongly interacting many-particle system via the diffusion equation.

Annihilation process with impurity: Unsolved



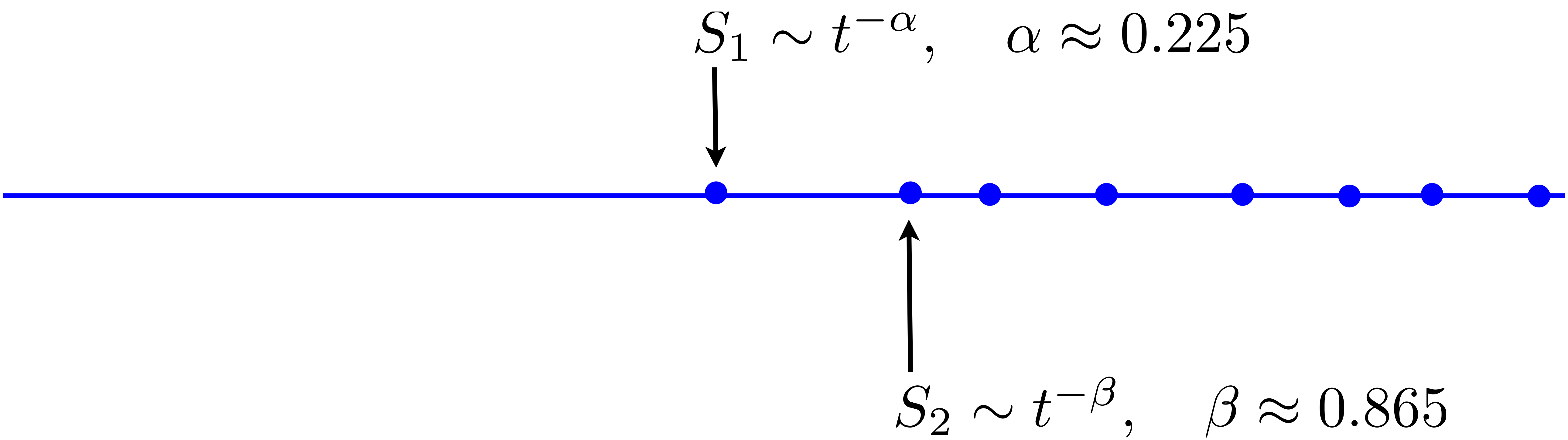
What is the survival probability $S(t)$ of the impurity particle ?

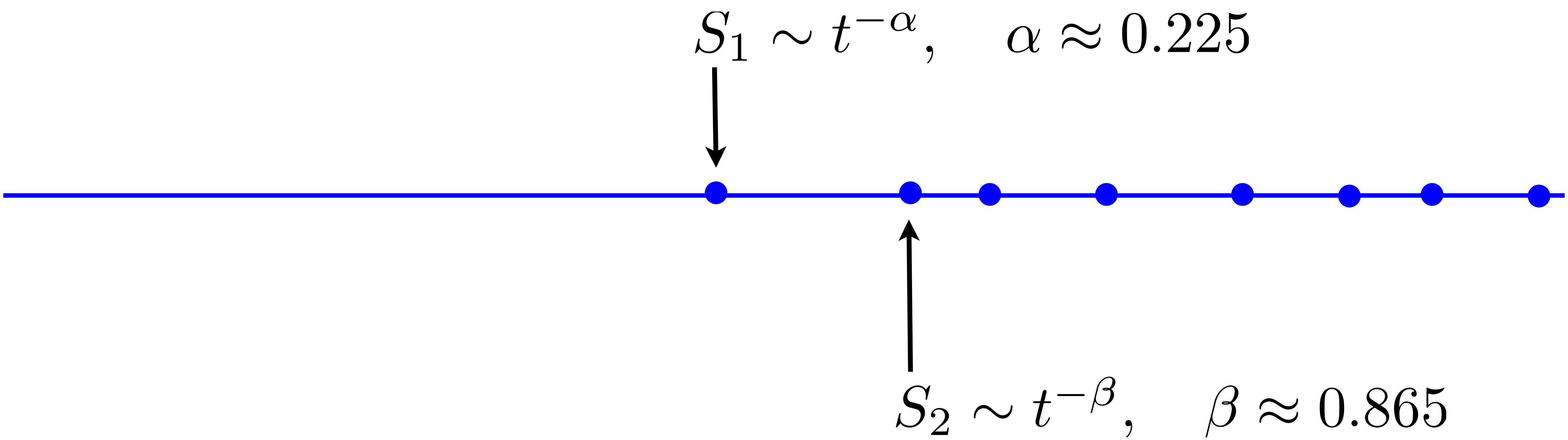
$$S \sim t^{-\theta(D)}, \qquad \theta(1) = \frac{1}{2}, \quad \theta(0) = \frac{3}{8}, \quad \theta(D) \approx \sqrt{\frac{1+D}{8}}$$

Half-filled line: Mostly unsolved for annihilation

The survival probability $S_n(t)$ is the probability that

the n^{th} particle is alive at time t. How $S_n(t)$ decays ?


$S_1 \sim t^{-\alpha}, \quad \alpha \approx 0.225$
$S_2 \sim t^{-\beta}, \quad \beta \approx 0.865$



Just two (non-trivial!) exponents.

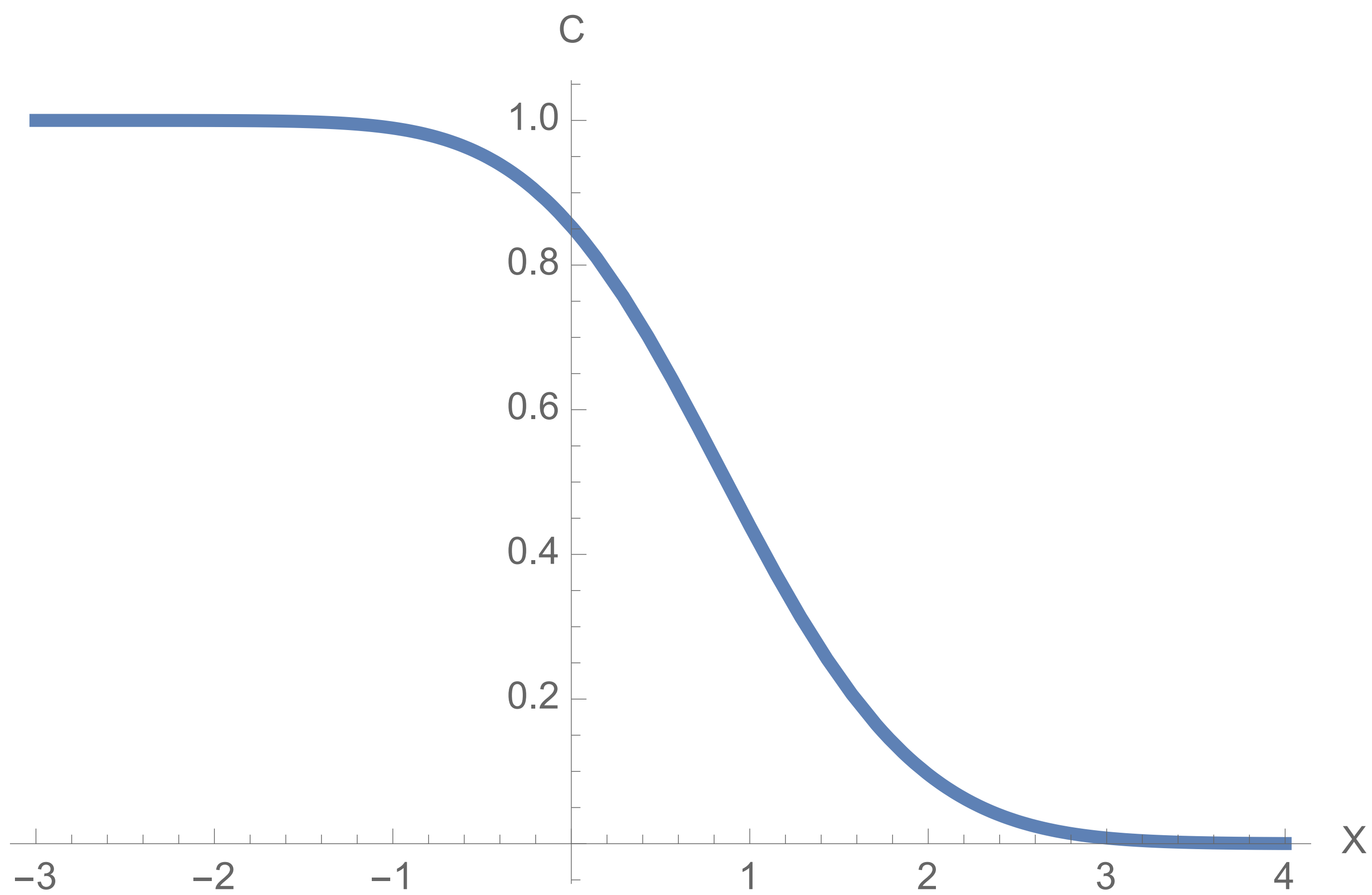
$S_{77} \sim t^{-0.225}, \qquad S_{666} \sim t^{-0.865}$

Never $\quad t^{-1/2}$

Average Density

$$c(x,t) = \frac{1}{\sqrt{2\pi D t}}\, C(X), \qquad X = \frac{x}{\sqrt{2Dt}}$$

$$C(X) = \frac{1}{2}\mathrm{Erfc}(X) + \frac{1}{\sqrt{8}}\, e^{-X^2/2}\,\mathrm{Erfc}\left(-\frac{X}{\sqrt{2}}\right)$$



Number of particles in the initially empty half-line

$$\langle N \rangle_{\mathrm{c}} = \frac{3}{8} + \frac{1}{2\pi} = 0.53415494309\ldots$$

$$\langle N \rangle_{\mathrm{a}} = \frac{1}{2}\,\langle N \rangle_{\mathrm{c}} = \frac{3}{16} + \frac{1}{4\pi} = 0.2670774715\ldots$$

$\langle N \rangle$ is finite, so we need the full distribution $P(N)$.

Number of particles in the initially empty half-line

$$P_{\mathrm{c}}(0) = \frac{1}{2} \qquad \text{(elementary)}$$

$$P_{\mathrm{a}}(0) \approx 0.74 \qquad (\textbf{unknown})$$

$$P_{\mathrm{a}}(0) + P_{\mathrm{a}}(2) + P_{\mathrm{a}}(4) + \ldots = \frac{3}{4} \quad (\textbf{duality})$$

$$P_{\mathrm{c}}(1) = 0.4660959764\ldots \qquad \text{(very involved derivation)}$$

$$P_{\mathrm{c}}(1) = \frac{11\pi - 4}{16\pi} + \frac{1}{2\pi}\left[\arctan\left(\tfrac{1}{\sqrt{8}}\right) - 2\arctan\left(\tfrac{1}{\sqrt{2}}\right)\right]$$

Localized Input

$$\frac{\partial n}{\partial t} = D\nabla^2 n - Kn^2 + J\delta(\mathbf{r})$$

$$n \sim \begin{cases} \frac{1}{r^{d-2}} & d > 4 \\ \frac{1}{r^2 \ln r} & d = 4 \\ \frac{1}{r^2} & 4 > d > 2 \\ \frac{\ln r}{r^2} & d = 2 \\ \frac{1}{r^d} & 2 > d \end{cases} \qquad N \sim \begin{cases} t & d > 4 \\ \frac{t}{\ln t} & d = 4 \\ \sqrt{t} & d = 3 \\ (\ln t)^2 & d = 2 \\ \ln t & d = 1 \end{cases}$$

$$N \sim \int^{\sqrt{t}} dr\, r^{d-1}\, n(r)$$

The specialist knows more and more about less and less and finally knows everything about nothing. *Konrad Lorenz*

$$c_1 \sim r^{-(\sqrt{17}+1)/2} \qquad \text{in} \quad 3d$$

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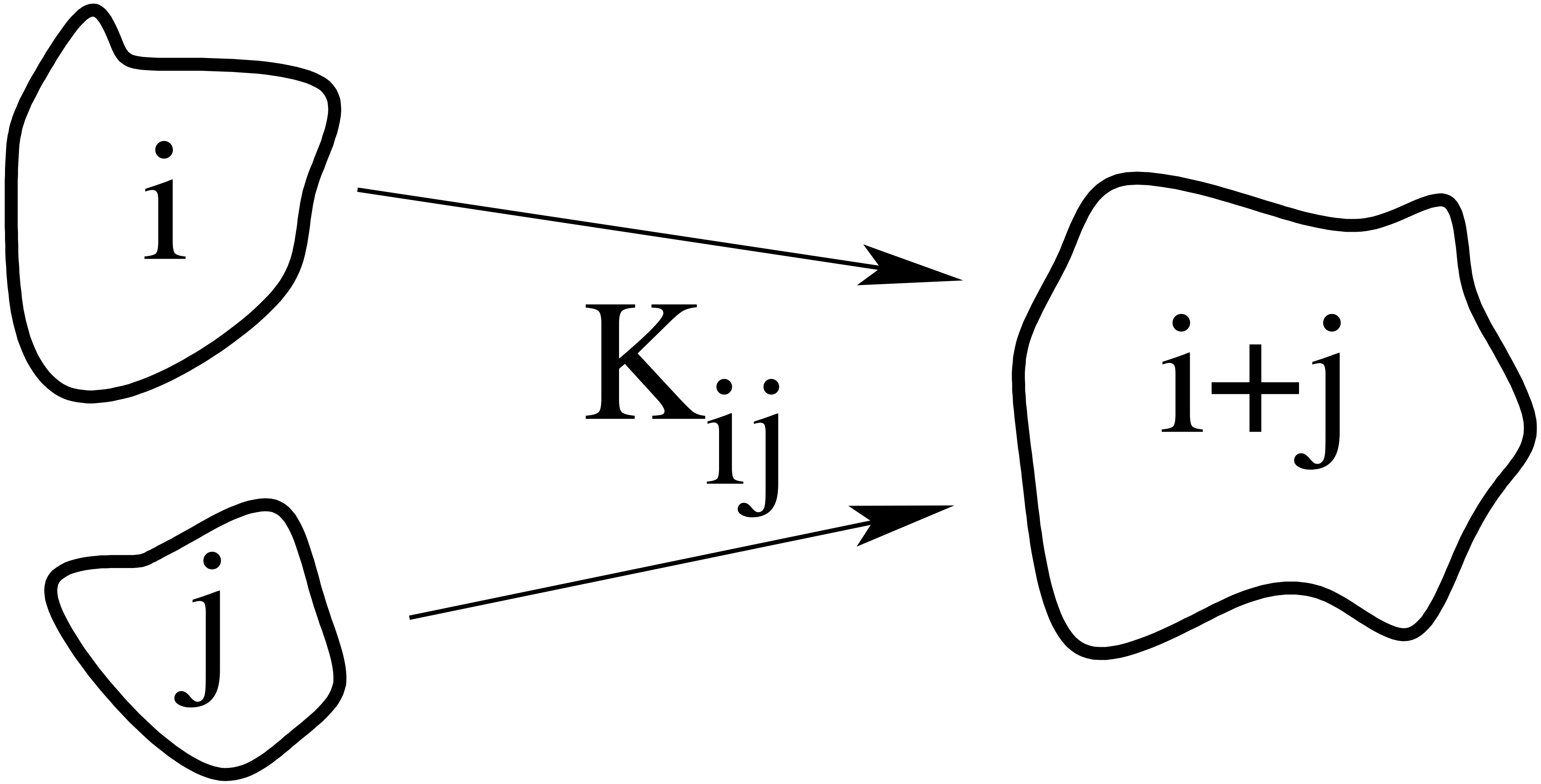
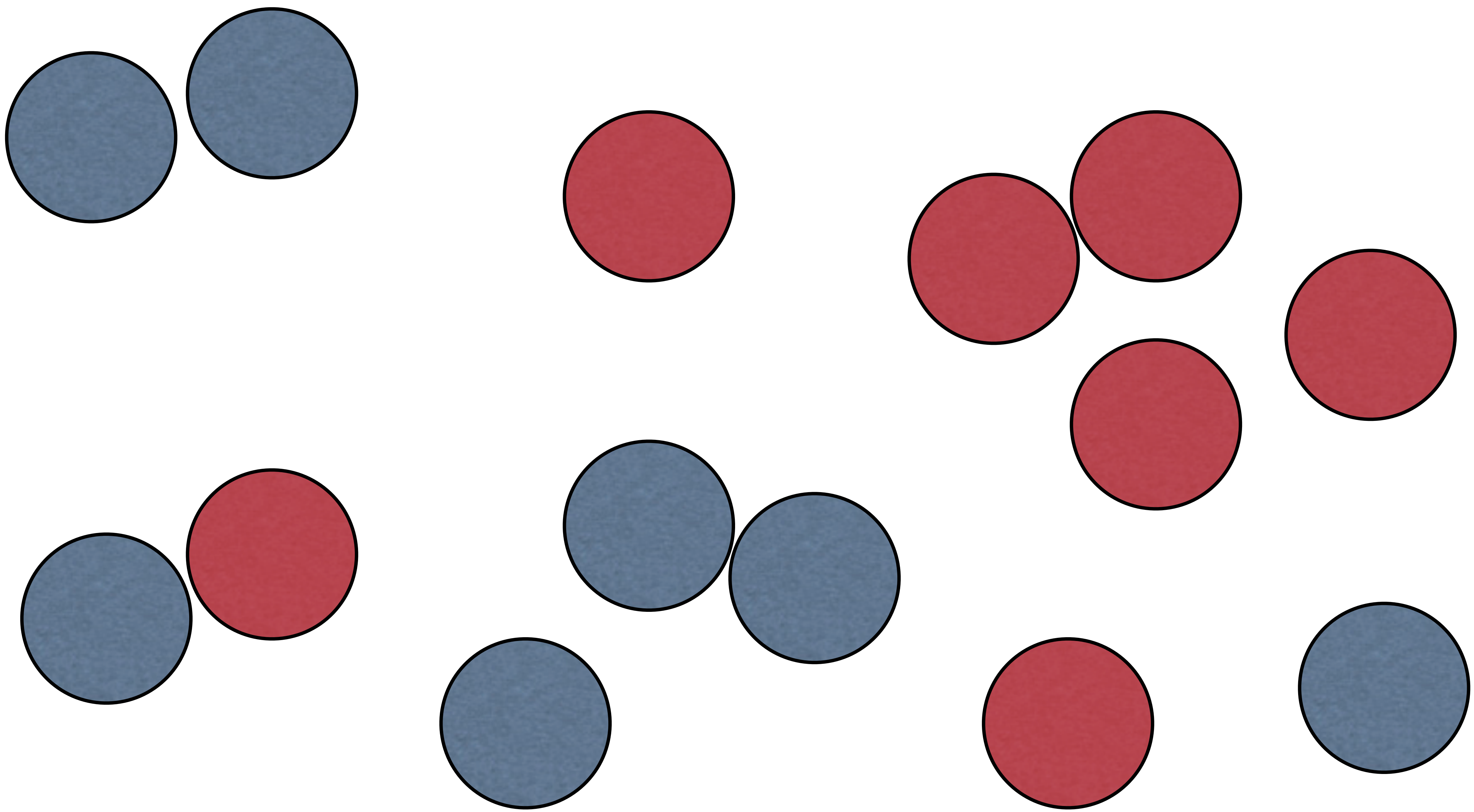
Reaction



Two-Species Annihilation



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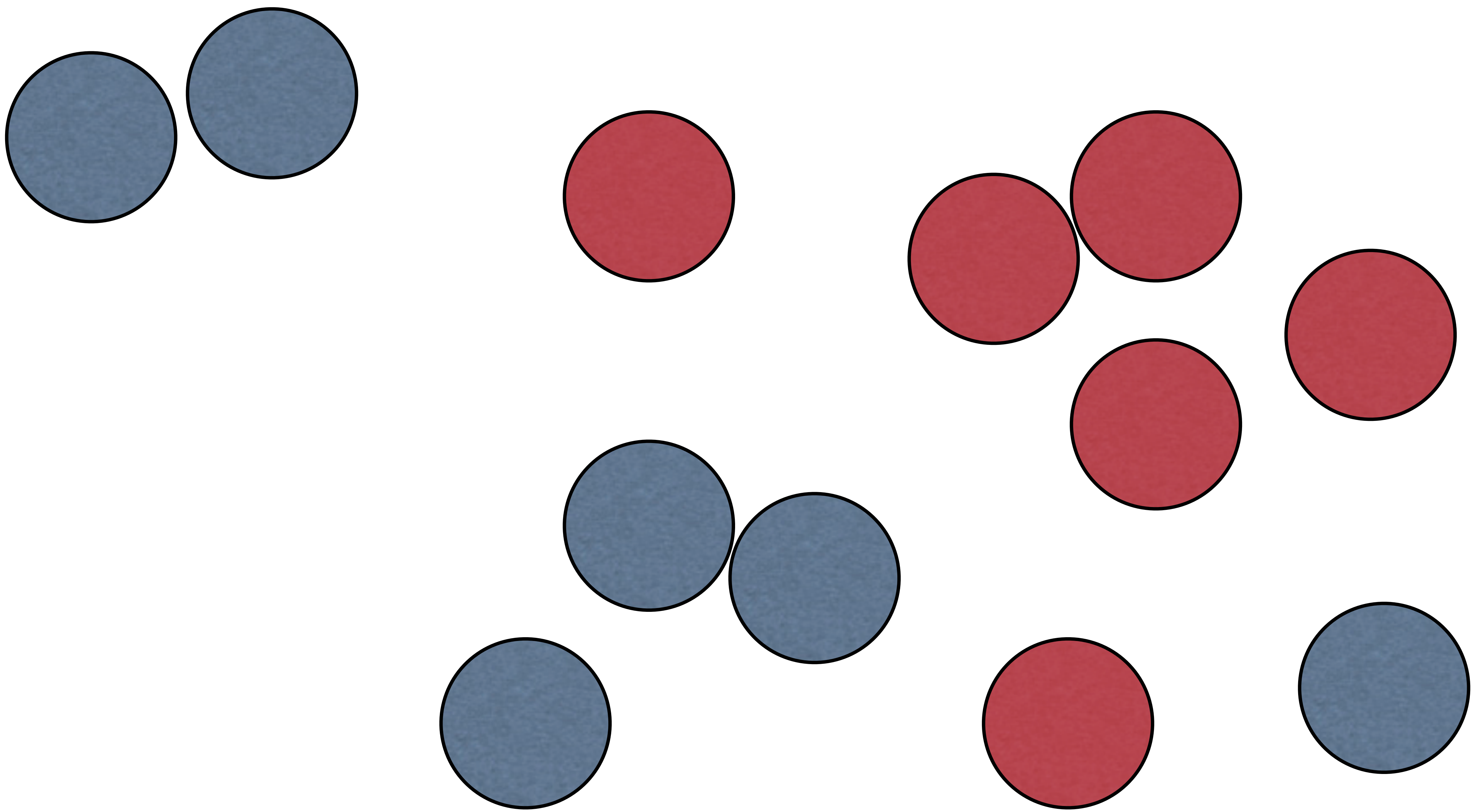

Rate Equation Description

Suppose densities are equal: $n_A = n_B = n$

$$\frac{dn}{dt} = -Kn^2, \qquad n \sim t^{-1}$$

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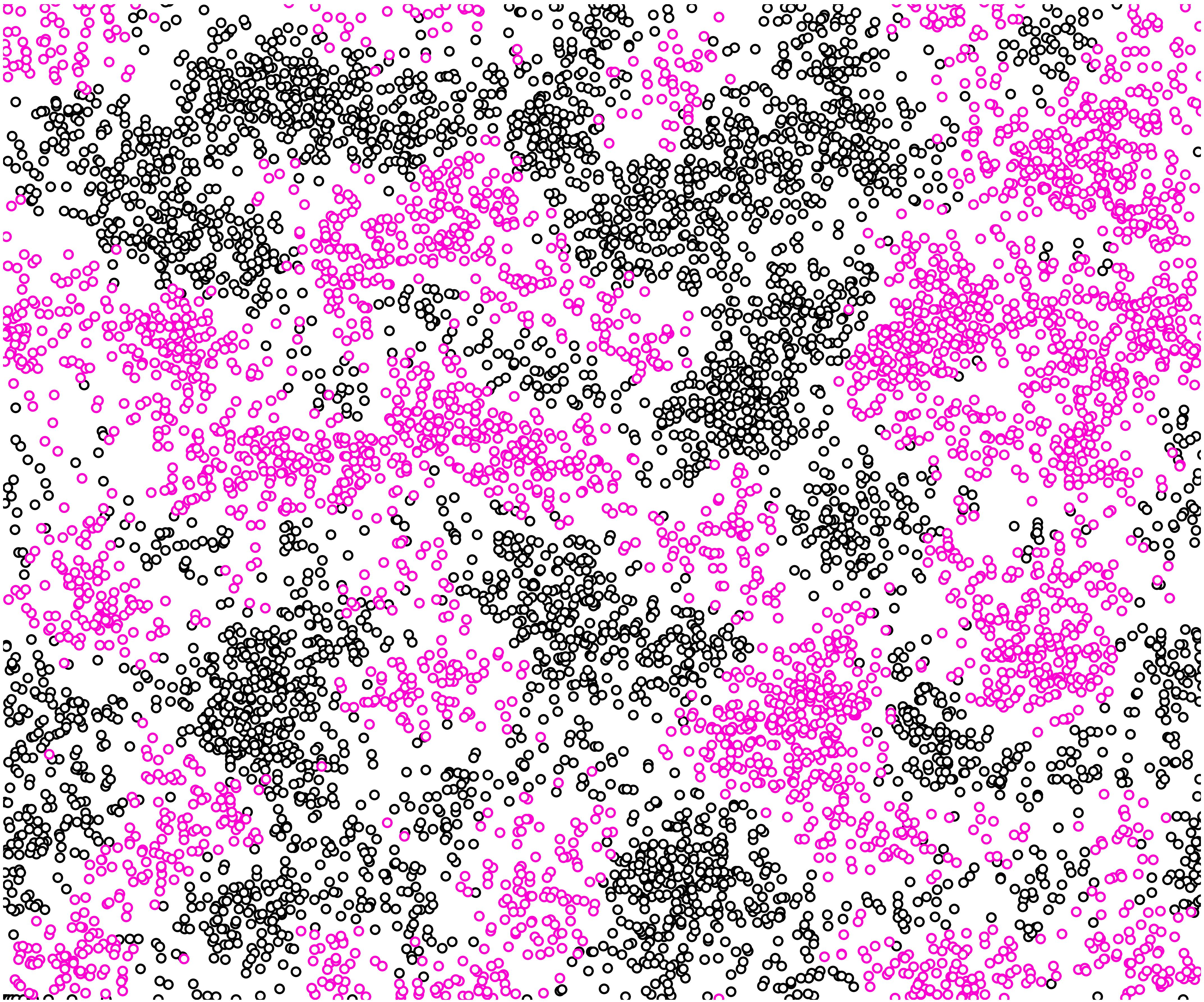
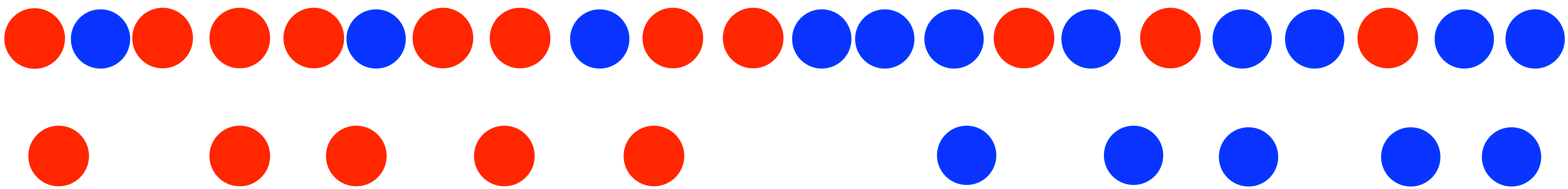
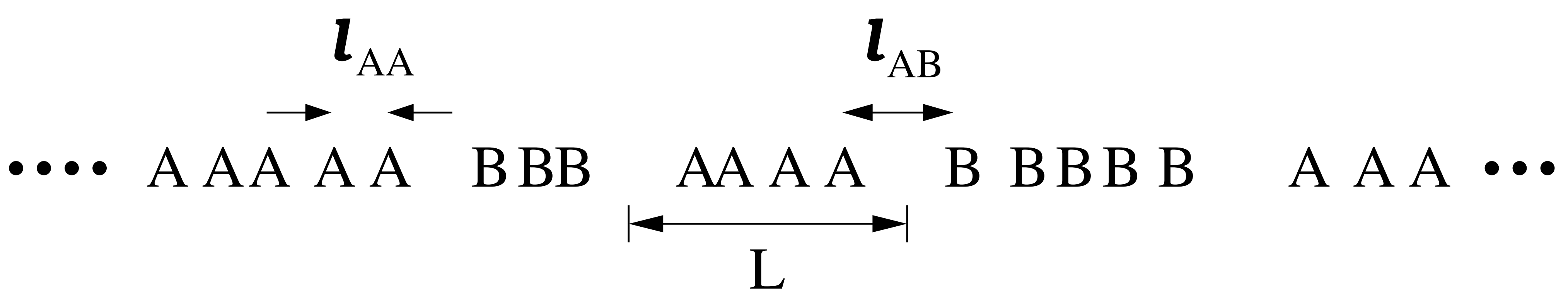
Correct answer: $$n \sim \begin{cases} t^{-1/4} & d = 1 \\ t^{-1/2} & d = 2 \\ t^{-3/4} & d = 3 \\ t^{-1} & d \geq 4 \end{cases}$$



Asymptotic Spatial Arrangement





$$\begin{cases} L \sim t^{1/2} & \text{domain size} \\ \ell_{AA} = \ell_{BB} \sim t^{1/4} & \text{inter-particle spacing} \\ \ell_{AB} \sim t^{3/8} & \text{depletion zone} \end{cases}$$

Heuristic Derivation

In physics, your solution should convince a reasonable person. In math, you have to convince a person who's trying to make trouble. *Frank Wilczek*

$$L \sim (Dt)^{1/2} \quad \text{typical mixing scale}$$

$$\#(A \;\; \text{particles}) = n_0 L + \sqrt{n_0 L}$$

$$\#(B \;\; \text{particles}) = n_0 L - \sqrt{n_0 L}$$

$$n_A \sim \frac{\#(A)-\#(B)}{L} \sim \sqrt{n_0}\,(Dt)^{-1/4}$$

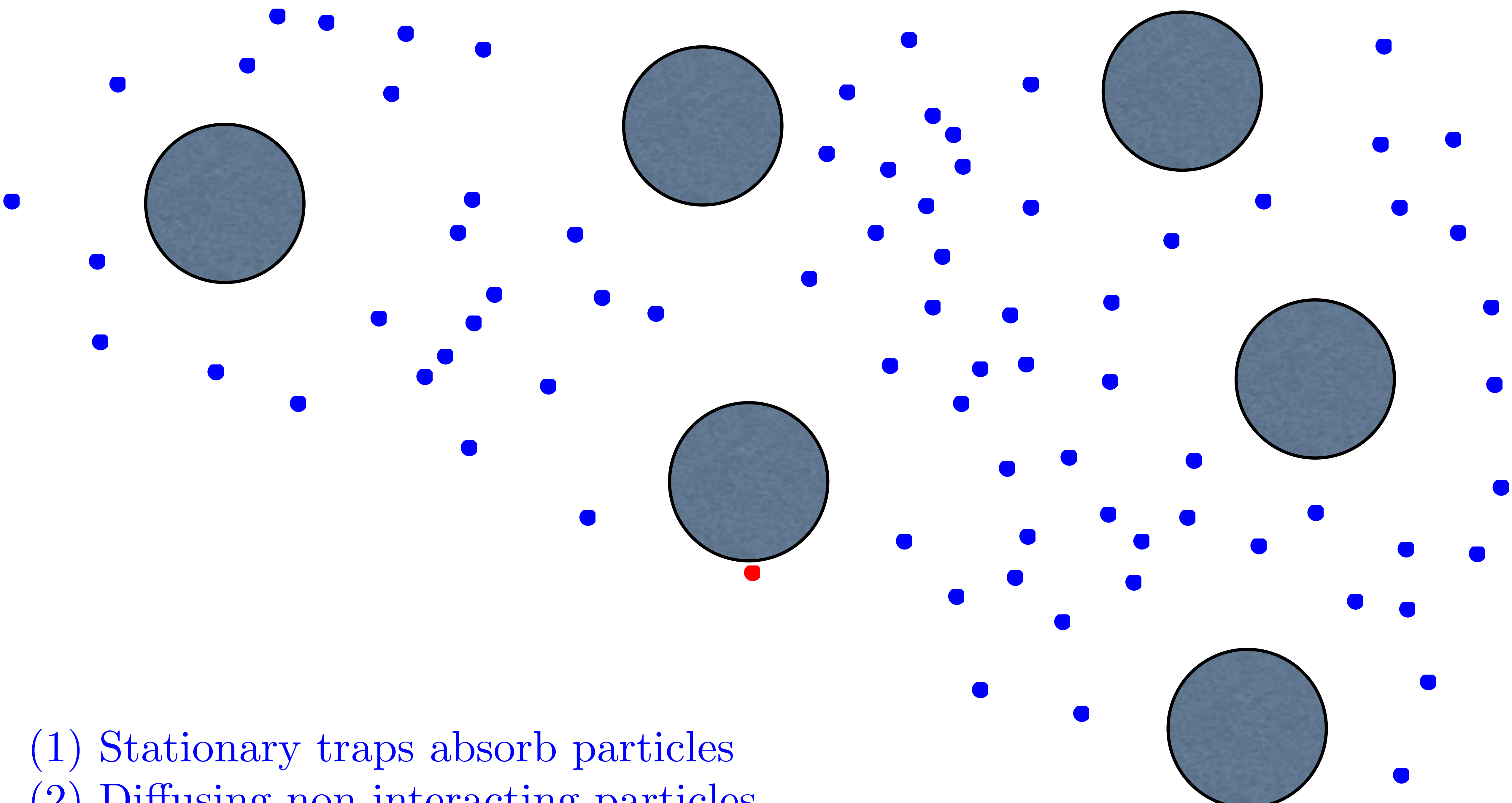
$$\frac{dn}{dt} \sim \frac{\Delta n}{\Delta t} \sim -\frac{(Dt)^{-1/2}}{\ell_{AB}^2/D} \qquad \text{leads to} \quad \ell_{AB} \sim t^{3/8}$$

In d dimensions $n \sim \frac{\sqrt{n_0 L^d}}{L^d} \sim L^{-d/2} \sim t^{-d/4}$

Lessons

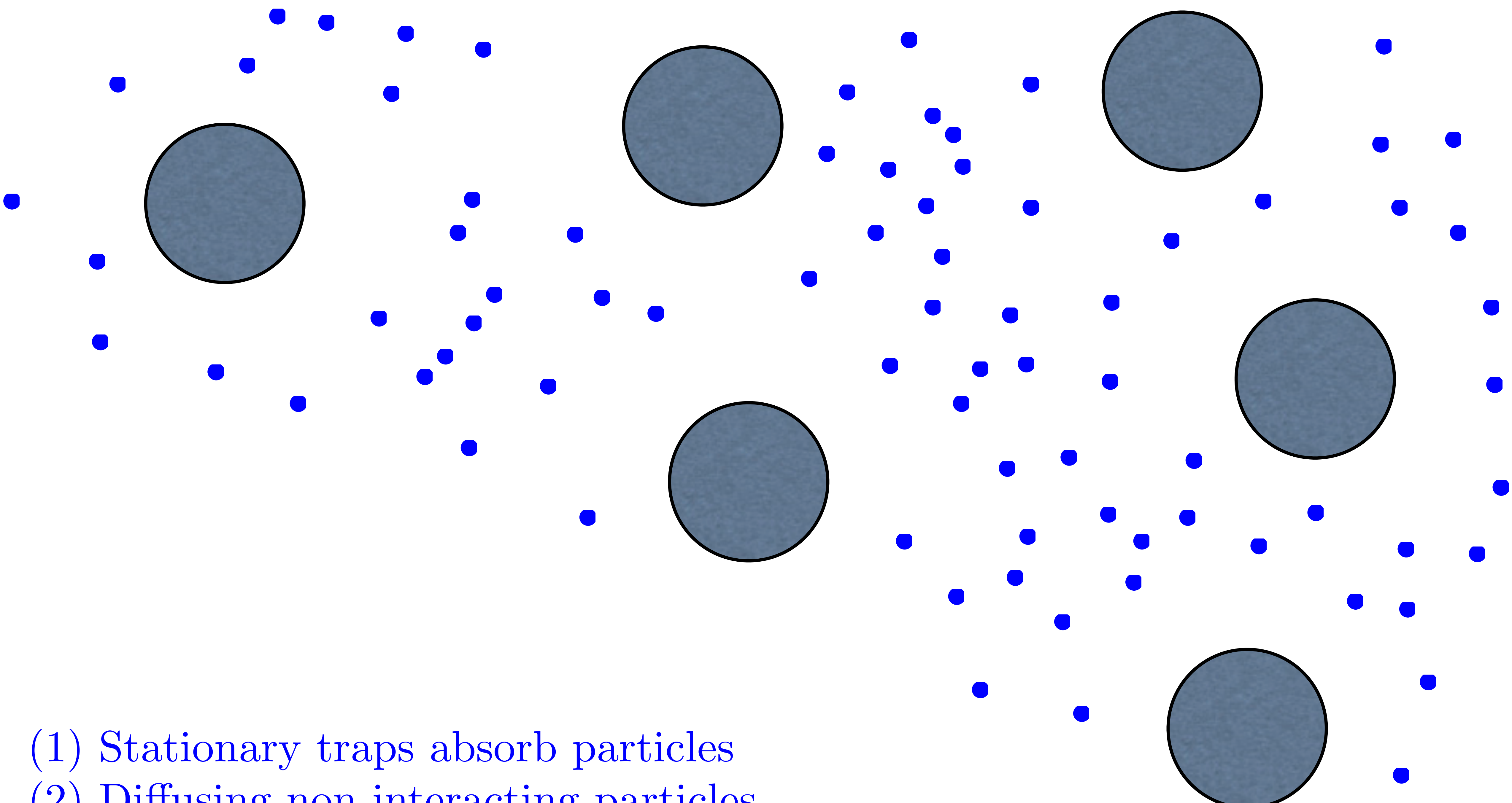
(1) $d_c = 4$ for two-species annihilation
(2) Three characteristic length scales
(3) Exact solution is lacking even in one dimension
(4) The $t^{-3/4}$ asymptotic in $d = 3$ is beyond the reach in simulations (but maybe not in Nature)
(5) No log-correction at $d = d_c = 4$

Trapping Reaction



(1) Stationary traps absorb particles
(2) Diffusing non-interacting particles

Trapping Reaction



(1) Stationary traps absorb particles
(2) Diffusing non-interacting particles

Mean-Field and Exact Descriptions

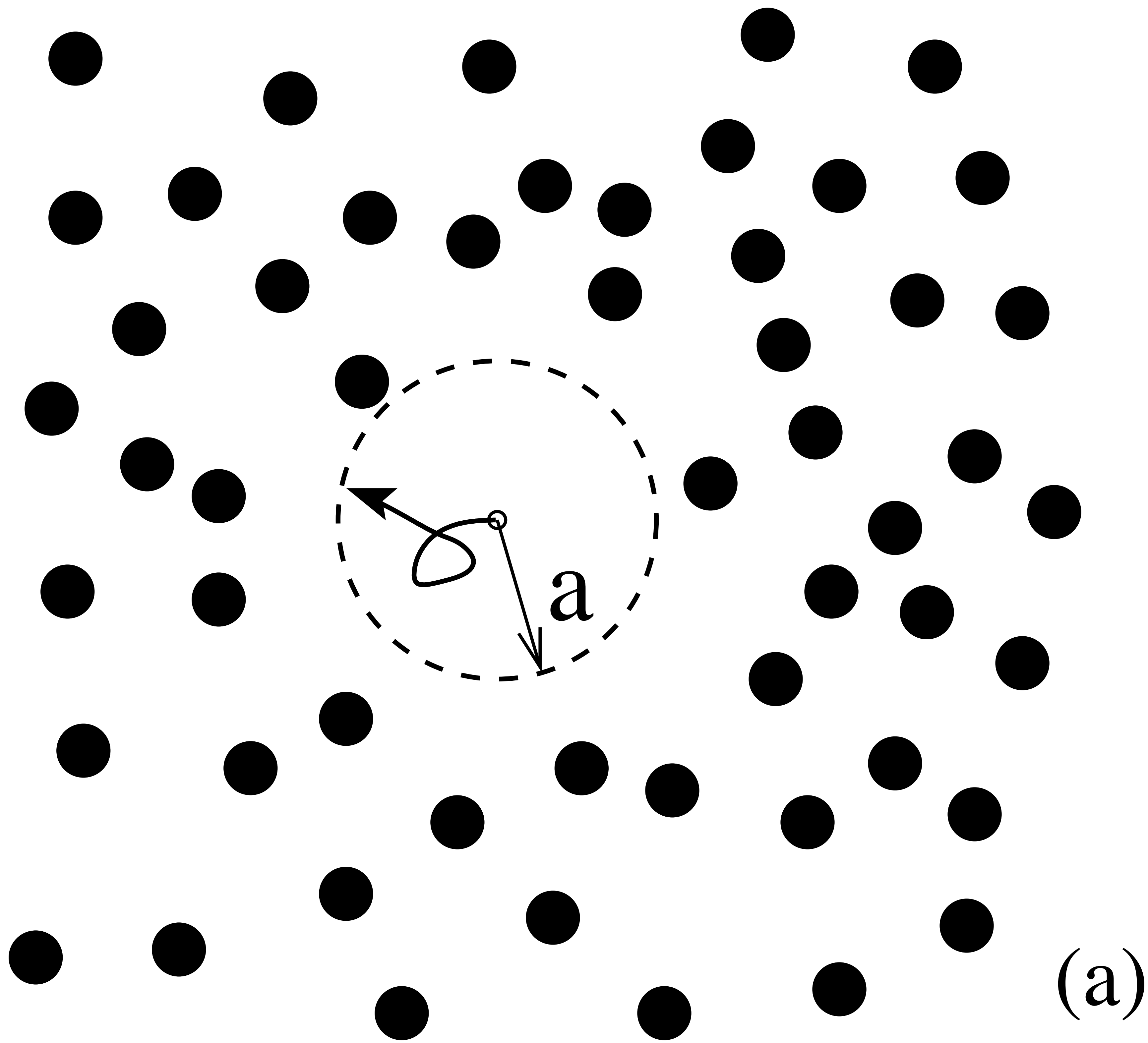
ρ the density of traps
n the density of particles

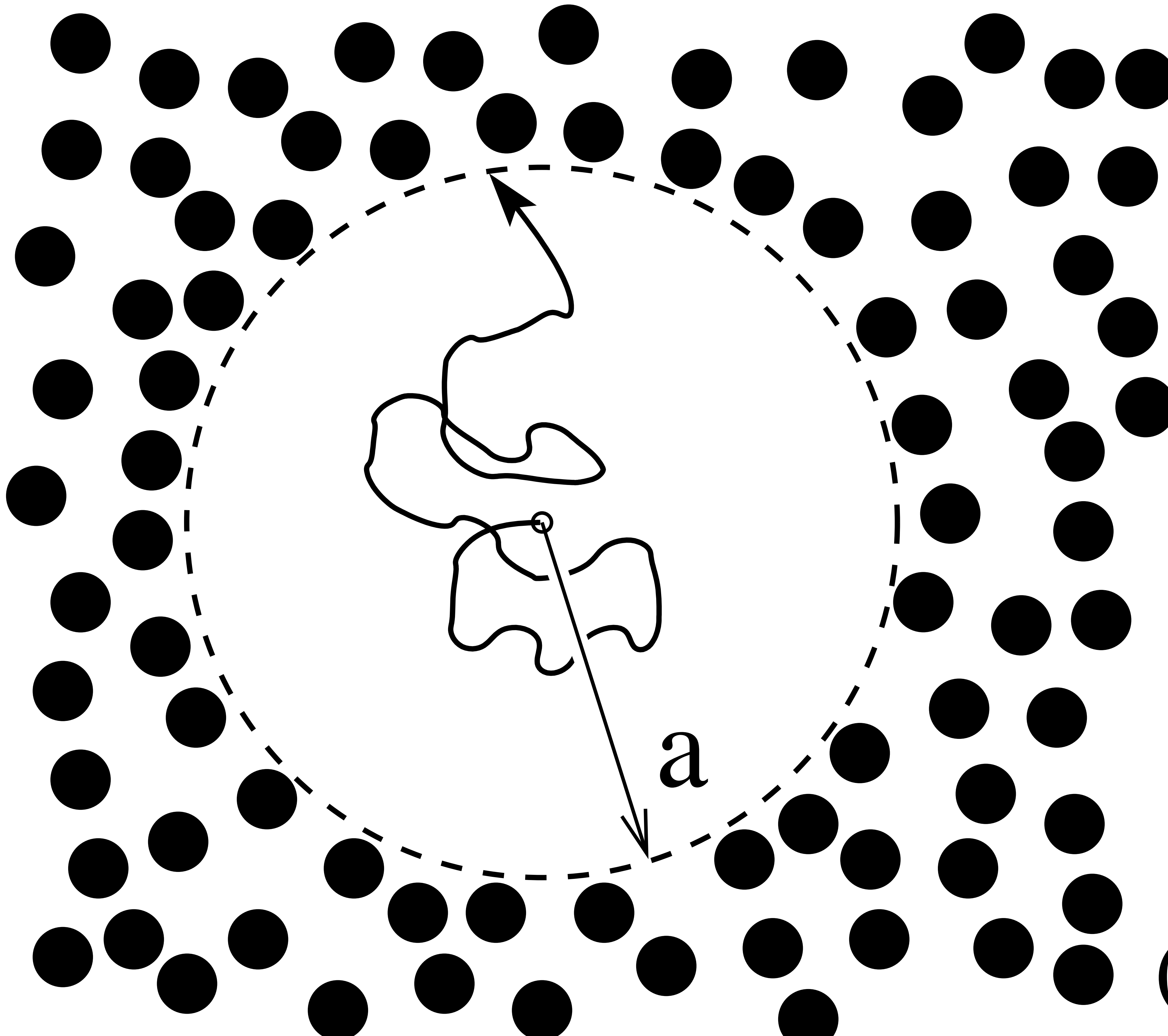
$$\frac{dn}{dt} = -K\rho n, \qquad n \sim e^{-K\rho t}$$

The mean-field description is **wrong** in all dimensions:

$$n \sim \exp\left[-A_d \rho^{2/(d+2)} (Dt)^{d/(d+2)}\right]$$

Higher Dimensions





(b)

Higher Dimensions

Premature optimization is the root of all evil. *Donald E. Knuth*

(1) The best chance to survive is to be in a large void.

(2) The competition between increasing the survival probability

and decreasing the existence probability of a void by increasing its size selects the optimal void.

(3) One can posit the adsorption BC on the 'boundary' of a void.

(4) Asymptotically the density in such a void $\sim \exp(-\Lambda_1^2 Dt)$ (Λ_1^2 is the smallest eigenvalue of the Laplacian).

(5) Overall $n \sim \int \exp\left(-\lambda_1^2 Dt/V^{2/d} - \rho V\right) \rho\, dV$

(6) Minimal λ_1 corresponds to the spherical void. (Rayleigh-Faber-Krahn theorem.)

Quantum Reactions is a Challenge

The only success (up to now) is with the trapping reaction.

The key is it is essentially a single-particle problem

One associates an imaginary potential energy $-i\Gamma$ with each trap

The density decays as $\exp(-A_d t^{d/(d+3)})$

Recall that in the classical case the decay is $\exp(-B_d t^{d/(d+2)})$

Annihilation in Quantum Regime

(1) An ultracold Fermi gas like ^{6}Li is a two-component Fermi gas.

(2) When two atoms with opposite spin collide, they can form a molecule.

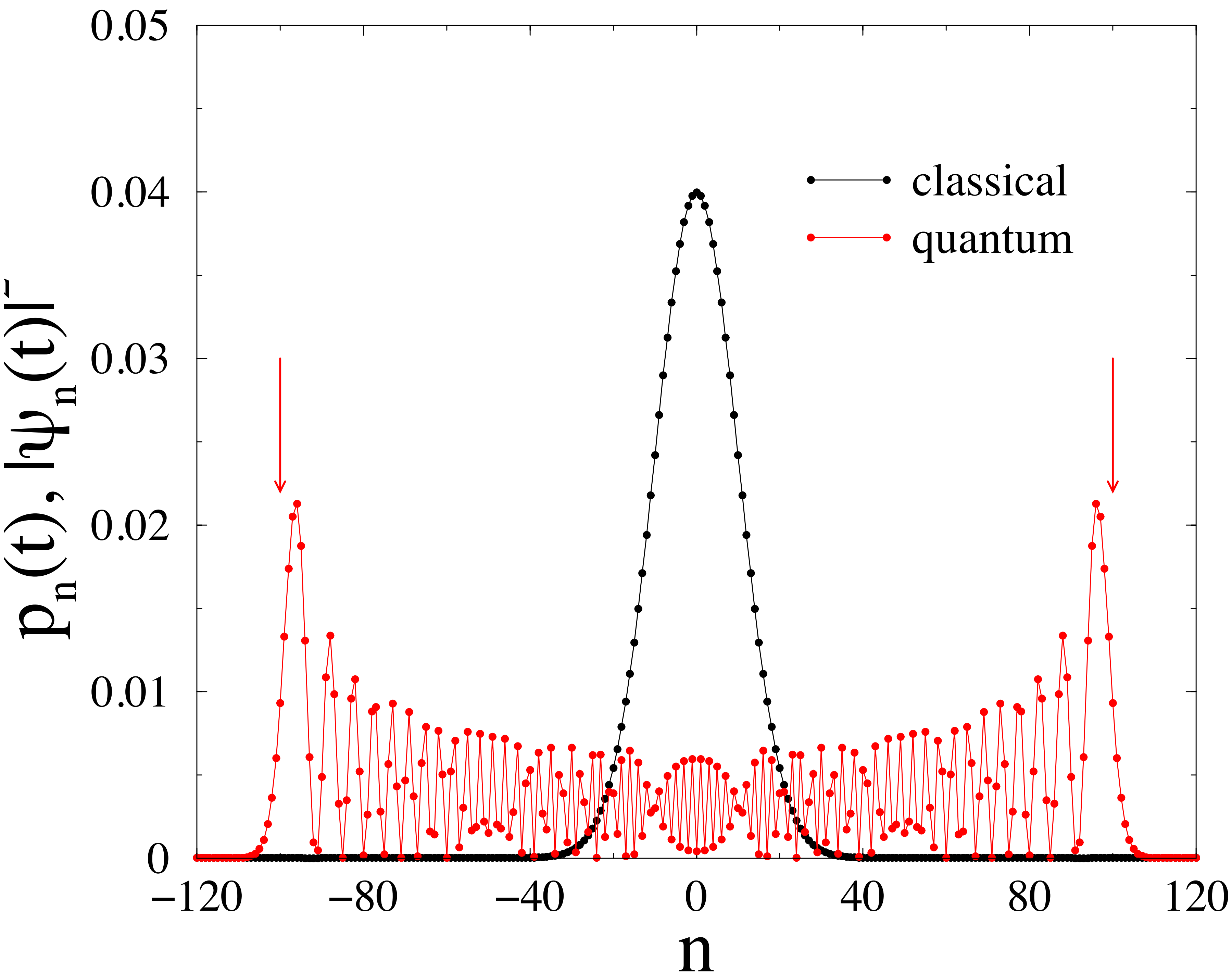
(3) The energy and momentum conservation makes $A + A \longrightarrow A_2$ impossible.

(4) The three-body process $A + A + A \longrightarrow A_2 + A$ is possible.

(5) The energies of the products are so large that they overcome a trapping potential and leave the system.

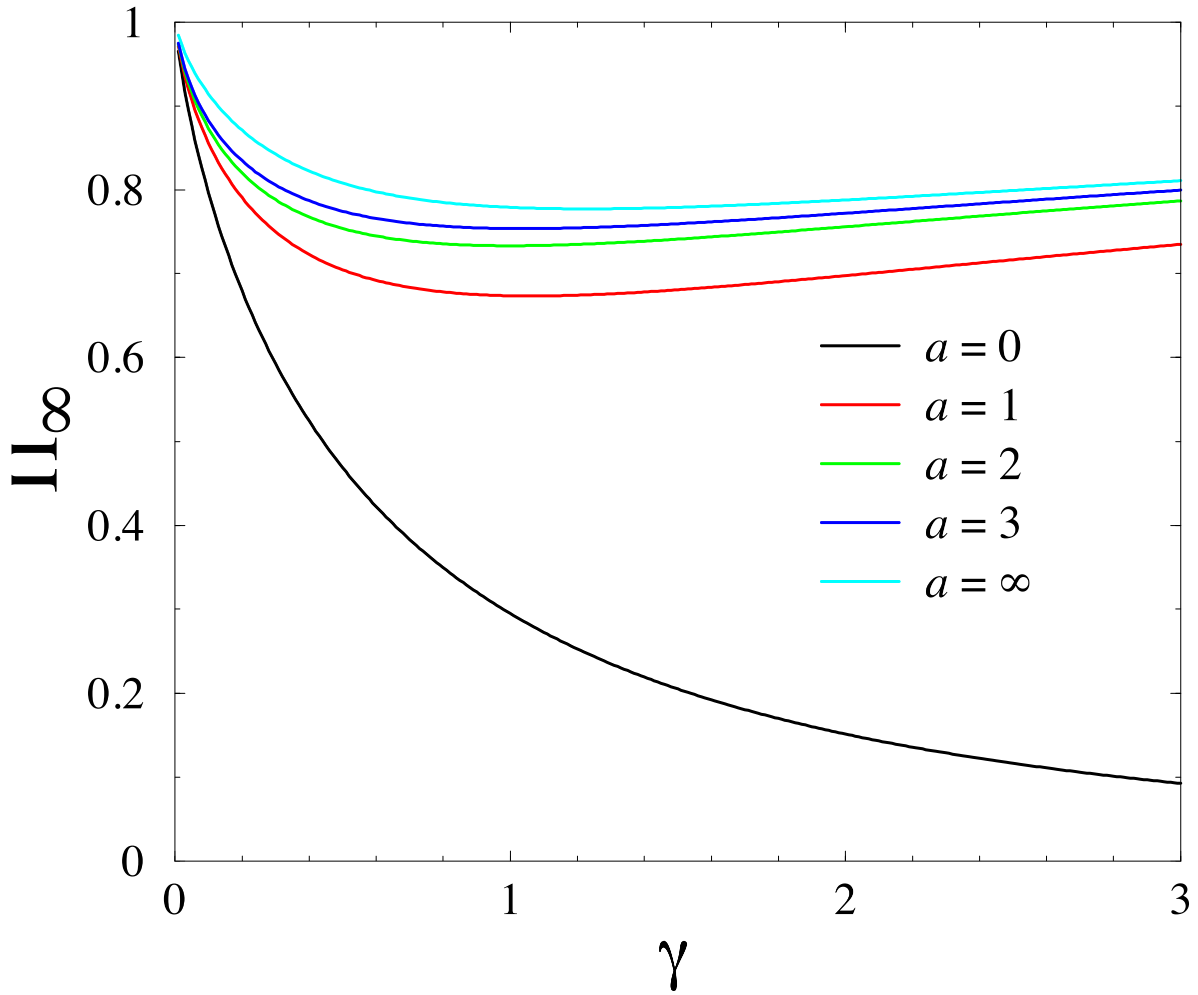
(6) Thus essentially $A + A + A \longrightarrow \emptyset$

Classical vs. Quantum Particle on a lattice



Infinite chain with a single trap

$$i\,\frac{d\psi_n}{dt} = \psi_{n-1} + \psi_{n+1} - i\gamma\delta_{n,0}\psi_0, \quad \psi_n(t=0) = \delta_{n,a}$$



Particle on a finite ring with a single trap

Classical: survival prob decays as $\exp\left(-\frac{\pi^2 t}{N^2}\right)$

Quantum: survives with prob $\frac{1}{2}$

except when it starts at $a = 0$ or $a = N/2$

Why? Thanks to avoiding modes.

Summary

(1) Non-equilibrium statistical physics has traditionally dealt with small deviations from equilibrium.

(2) Far-from-equilibrium systems do not have an underlying master equation, there are no analogs e.g. to the Boltzmann factor or the partition function of equilibrium statistical physics.

(3) Still far-from-equilibrium systems often have simple collective behaviors.

(4) Various tools efficiently work in numerous problems.


The End