

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).

Aimed at graduate students, this book explores some of the core phenomena in non-equilibrium statistical physics. It focuses on the development and application of theoretical methods to help students develop their problem-solving skills.

The book begins with microscopic transport processes: diffusion, collision-driven phenomena, and exclusion. It then presents the kinetics of aggregation, fragmentation, and adsorption, where basic phenomenology and solution techniques are emphasized. The following chapters cover kinetic spin systems, by developing both a discrete and a continuum formulation, the role of disorder in non-equilibrium processes, and hysteresis from the non-equilibrium perspective. The concluding chapters address population dynamics, chemical reactions, and a kinetic perspective on complex networks. The book contains more than 200 exercises to test students' understanding of the subject. A link to a website hosted by the authors, containing an up-to-date list of errata and solutions to some of the exercises, can be found at www.cambridge.org/9780521851039.

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Sidney Redner is a Professor of Physics at Boston University. His current research interests are in non-equilibrium statistical physics and its applications to reactions, networks, social systems, biological phenomena, and first-passage processes.

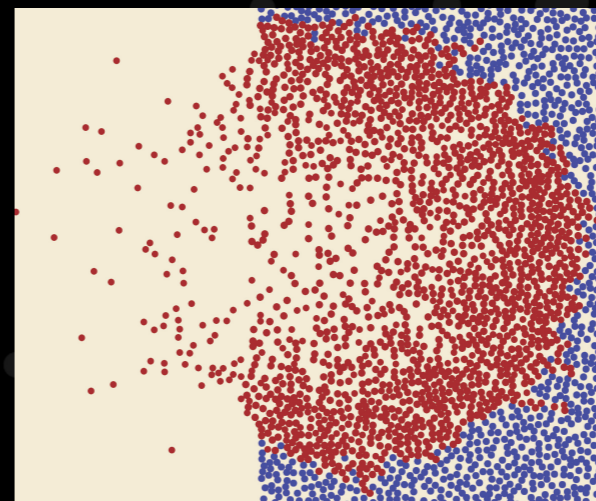
Eli Ben-Naim is a member of the Theoretical Division and an affiliate of the Center for Nonlinear Studies at Los Alamos National Laboratory. He conducts research in statistical, nonlinear, and soft condensed-matter physics, including the collective dynamics of interacting particle and granular systems.

Cover illustration: Snapshot of a collision cascade in a perfectly elastic, initially stationary hard-sphere gas in two dimensions due to a single incident particle. Shown are the cloud of moving particles (red) and the stationary particles (blue) that have not yet experienced any collisions. Figure courtesy of Tibor Antal.

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Redner
Ben-Naim

A Kinetic View of STATISTICAL PHYSICS

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1. Aperitifs
2. Diffusion
3. Collisions
4. Exclusion
5. Aggregation

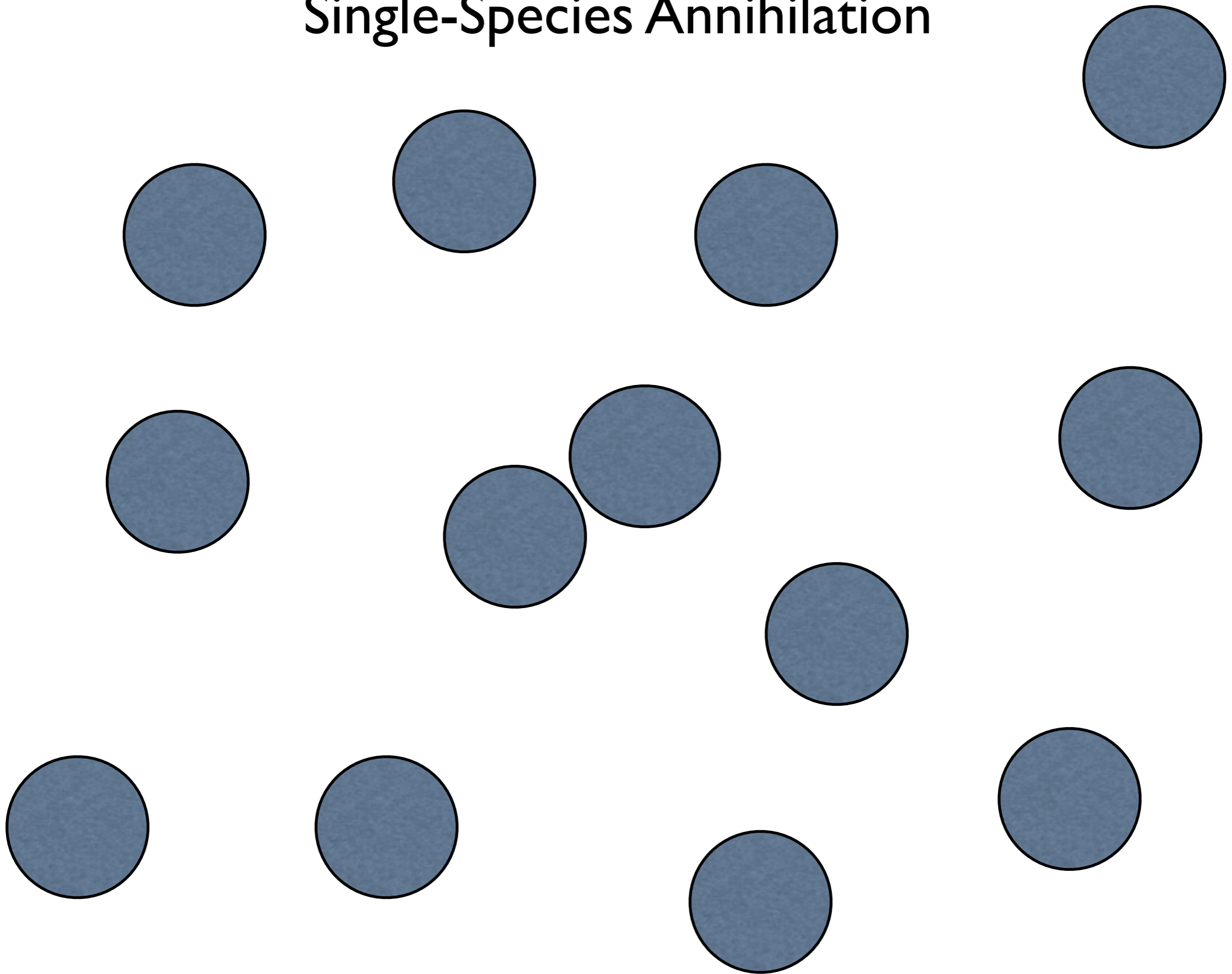
6. Fragmentation
7. Adsorption
8. Spin Dynamics
9. Coarsening
10. Disorder

11. Hysteresis
 12. Population Dynamics
 13. Diffusive Reactions
 14. Complex Networks
- + >200 problems & soln manual

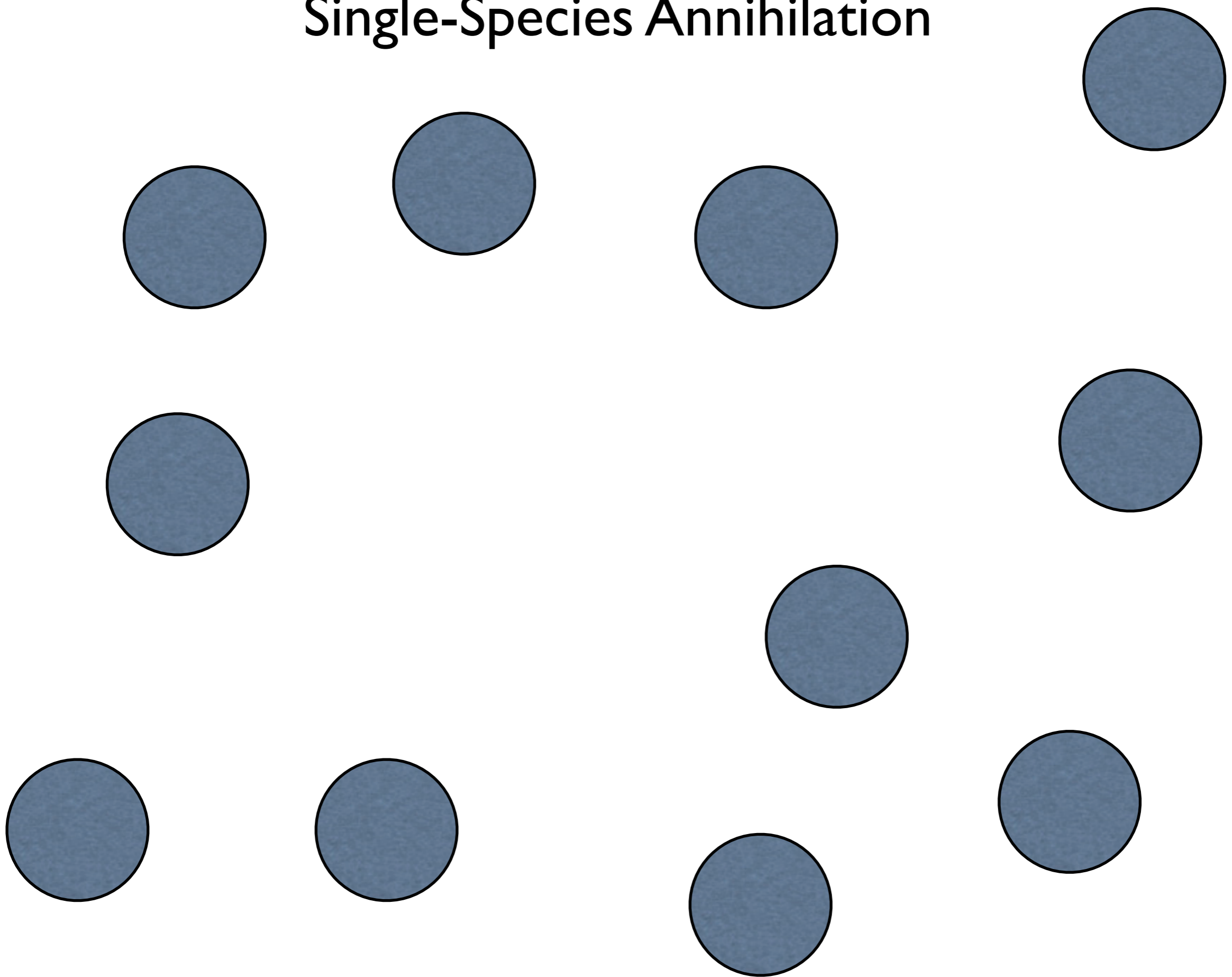
Simplified Reactions

- Coalescence: $A + A \Rightarrow A$
- Single-Species Annihilation: $A + A \Rightarrow 0$
- Two-Species Annihilation: $A + B \Rightarrow 0$

Single-Species Annihilation



Single-Species Annihilation



Hydrodynamic description

n particle density

K reaction rate

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

Hydrodynamic description

n particle density

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

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

Dimensional analysis

$$K = K(D, R) \sim DR^{d-2}$$

$$n \sim \frac{1}{DR^{d-2} t}$$

$$n = n(D, t) \sim \frac{1}{\sqrt{Dt}} \quad \text{when } d = 1$$

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

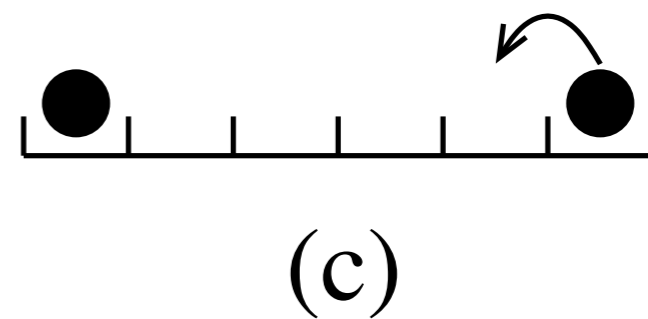
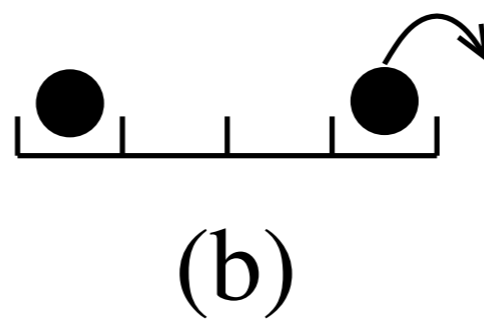
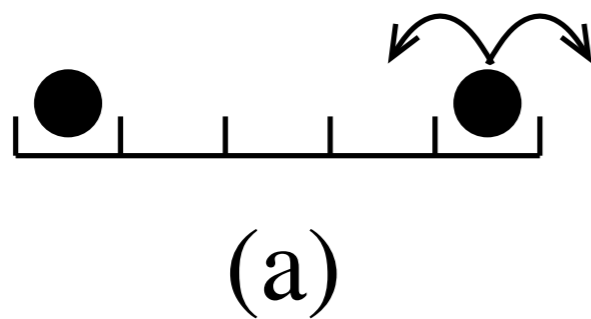
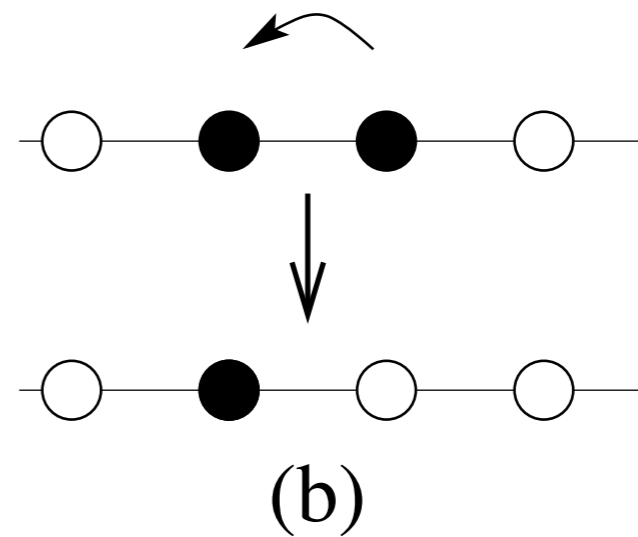
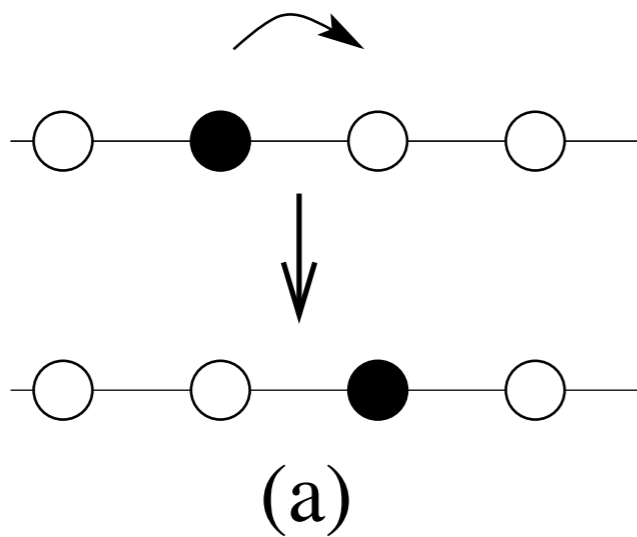
There is a critical dimension d_c that separates different kinetic behaviors. (For single-species annihilation, $d_c = 2$.)

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



V_n : density of voids of length n .

Evolution of 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

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

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

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

$c(t)$: Density of particles

$I_n(2t)$: Modified Bessel function

A bit of wisdom

In non-equilibrium statistical physics the

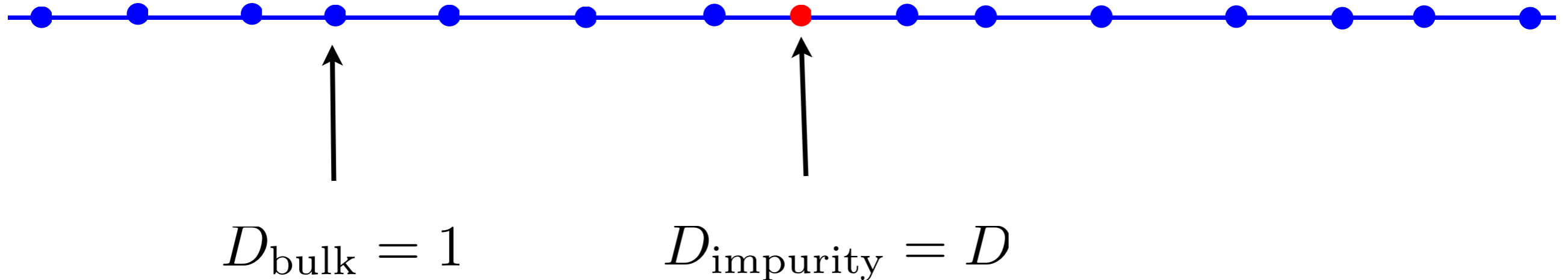
Diffusion Equation plays a role of the

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 ?

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

Half-filled line: Mostly unsolved for annihilation



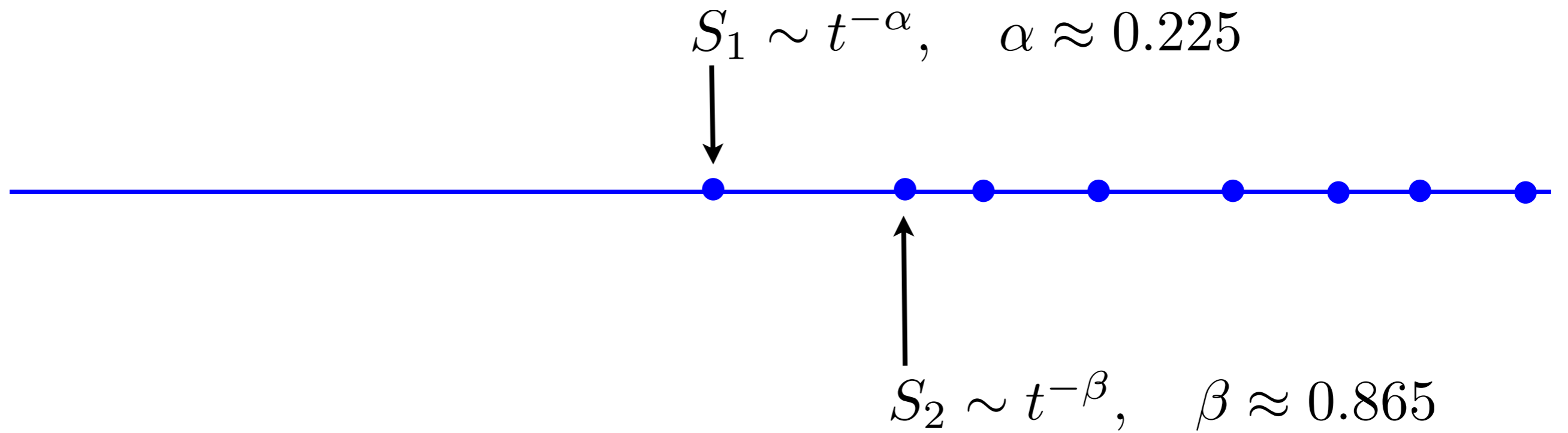
The survival probability $S_n(t)$ is the probability that the n^{th} particle is alive at time t . How $S_n(t)$ decays ?

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



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





Just two (non-trivial!) exponents.

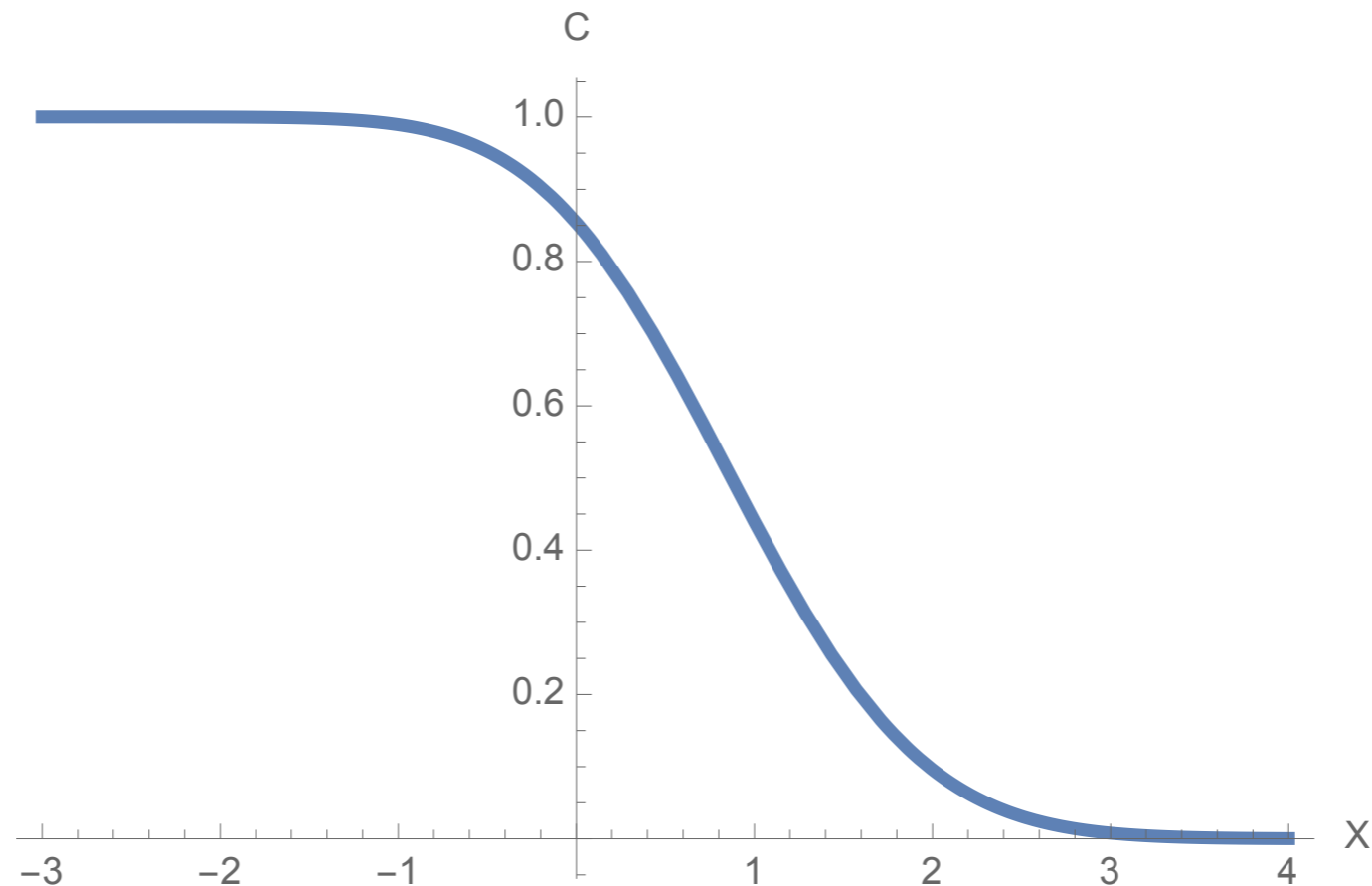
$$S_{77} \sim t^{-0.225}, \quad S_{666} \sim t^{-0.865}$$

Never $t^{-1/2}$

Average Density

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

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



Number of particles in the initially empty half-line

$$\langle N \rangle_c = \frac{3}{8} + \frac{1}{2\pi} = 0.53415494309 \dots$$

$$\langle N \rangle_a = \frac{1}{2} \langle N \rangle_c = \frac{3}{16} + \frac{1}{4\pi} = 0.2670774715 \dots$$

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

Number of particles in the initially empty half-line

$$P_c(0) = \frac{1}{2} \quad (\text{elementary})$$

$$P_a(0) \approx 0.74 \quad (\text{unknown})$$

$$P_a(0) + P_a(2) + P_a(4) + \dots = \frac{3}{4} \quad (\text{duality})$$

$$P_c(1) = 0.4660959764\dots \quad (\text{very involved derivation})$$

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

Localized Input

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

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

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

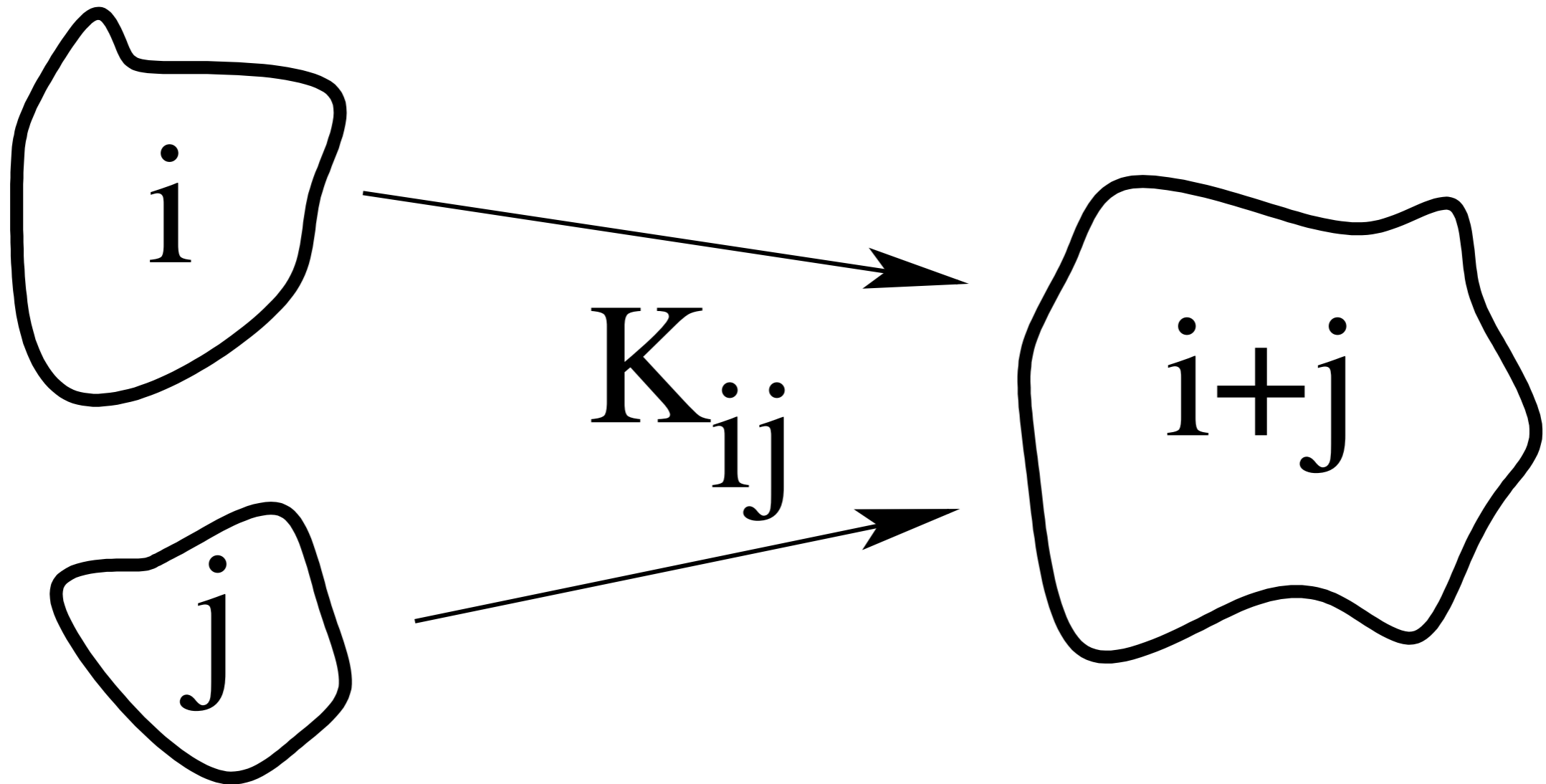
The specialist knows more and more about less and less
and finally knows everything about nothing. *Konrad Lorenz*

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

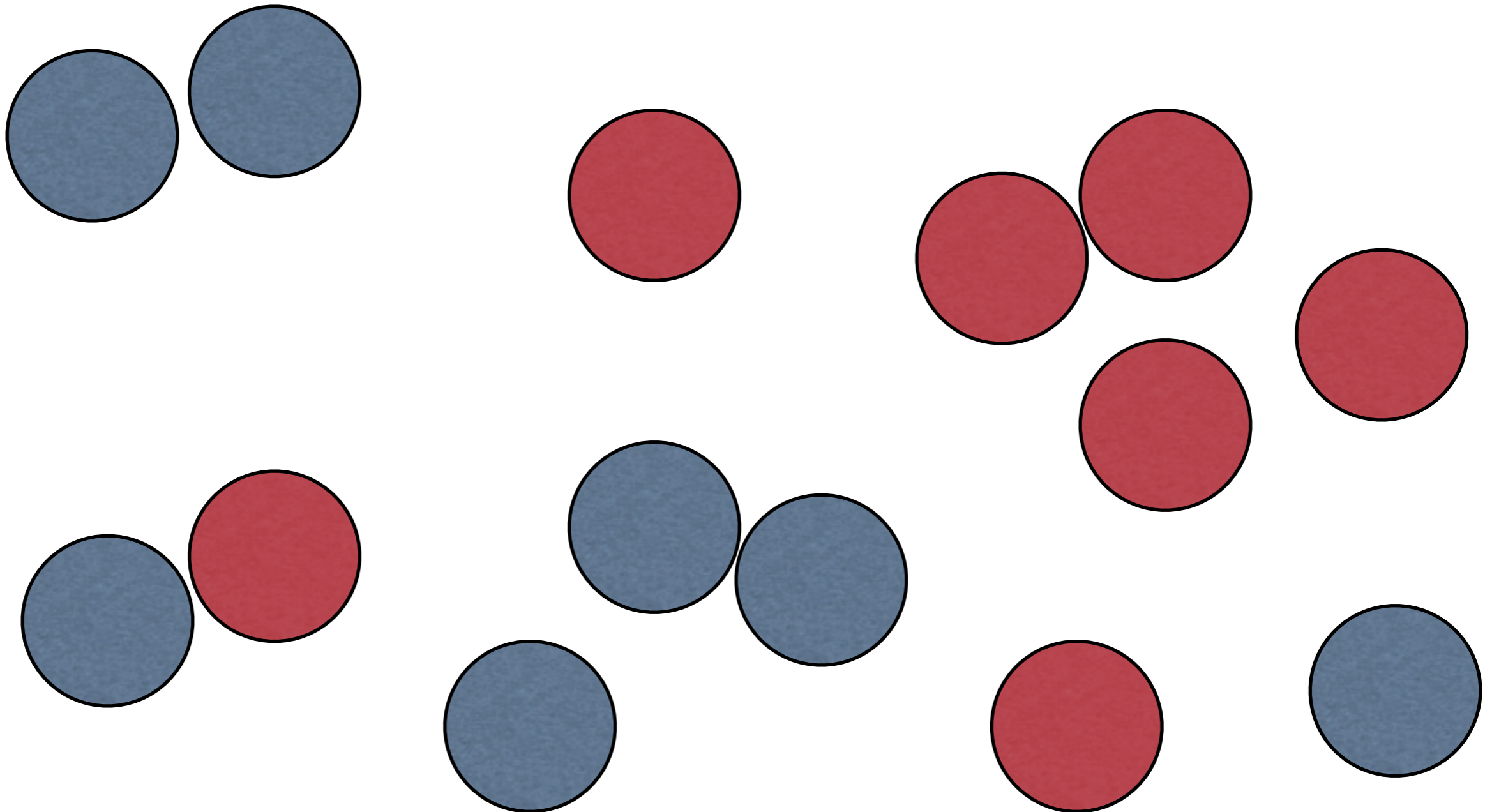
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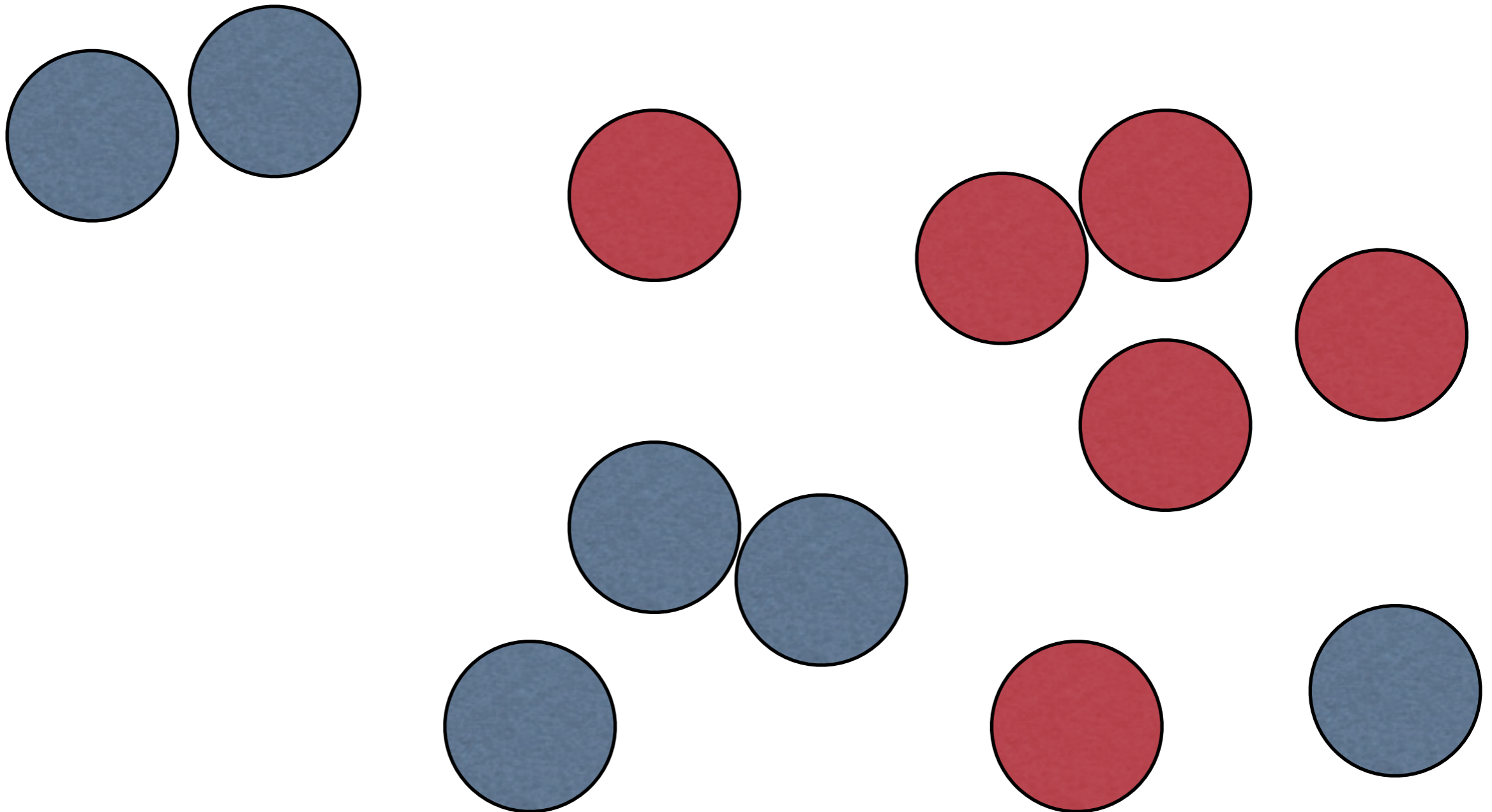
Reaction



Two-Species Annihilation



Two-Species Annihilation



Rate Equation Description

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

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

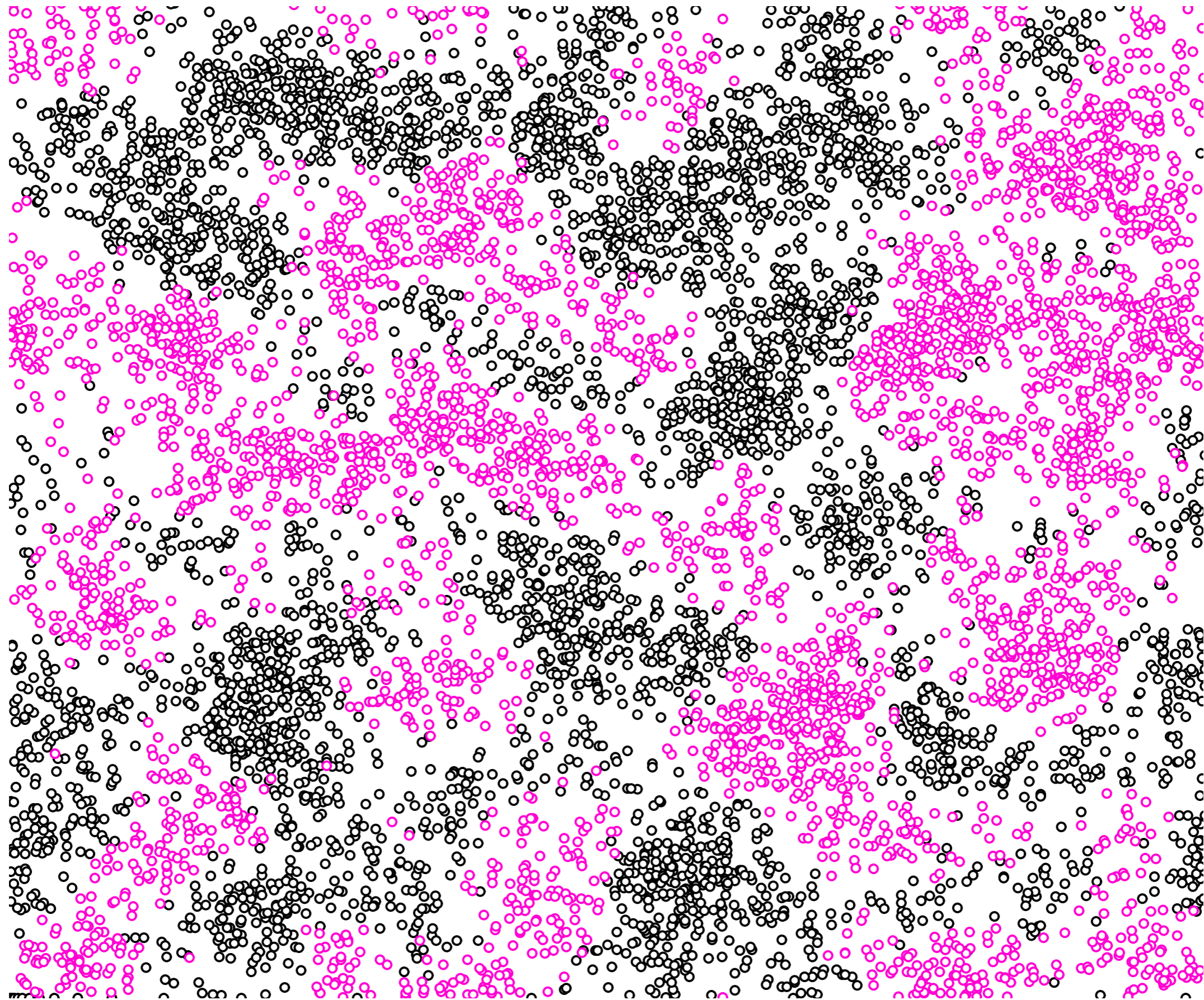
Rate Equation Description

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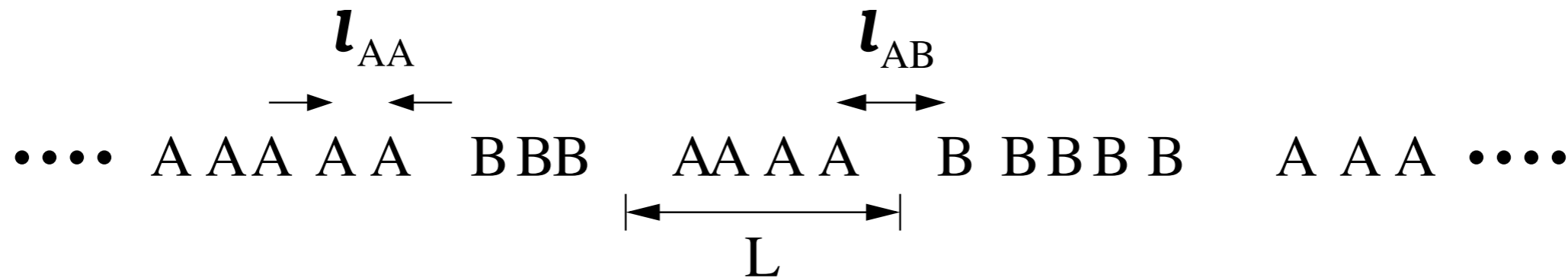
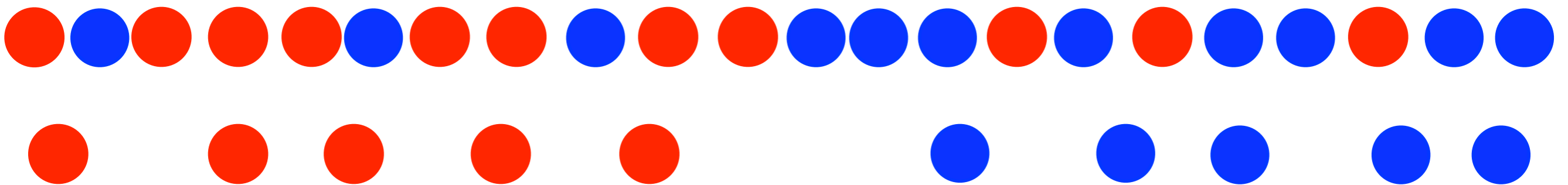
$$\frac{dn}{dt} = -Kn^2, \quad n \sim t^{-1}$$

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



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

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*

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

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

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

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

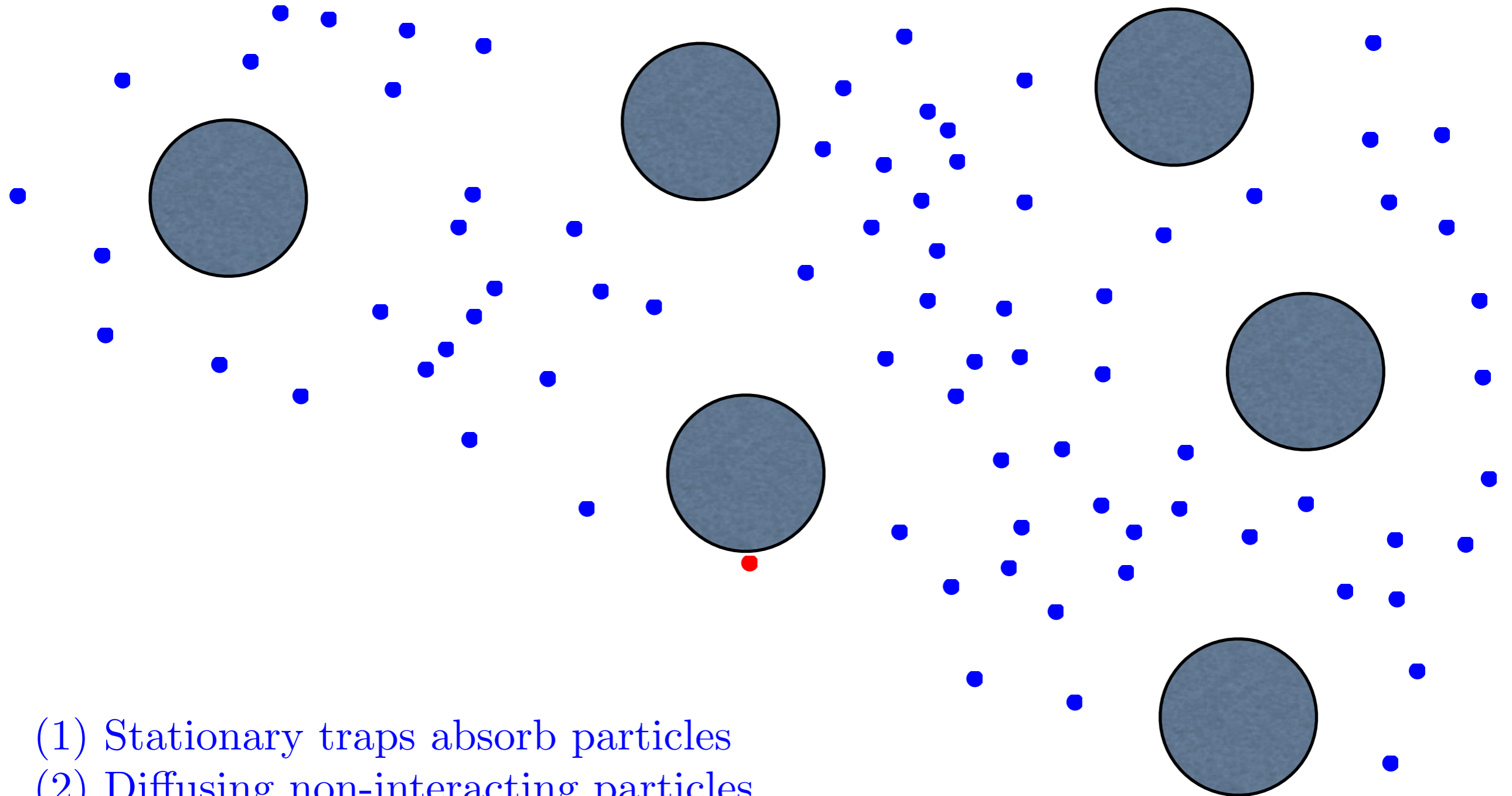
$$\frac{dn}{dt} \sim \frac{\Delta n}{\Delta t} \sim -\frac{(Dt)^{-1/2}}{\ell_{AB}^2/D} \quad \text{leads to} \quad \ell_{AB} \sim t^{3/8}$$

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

Lessons

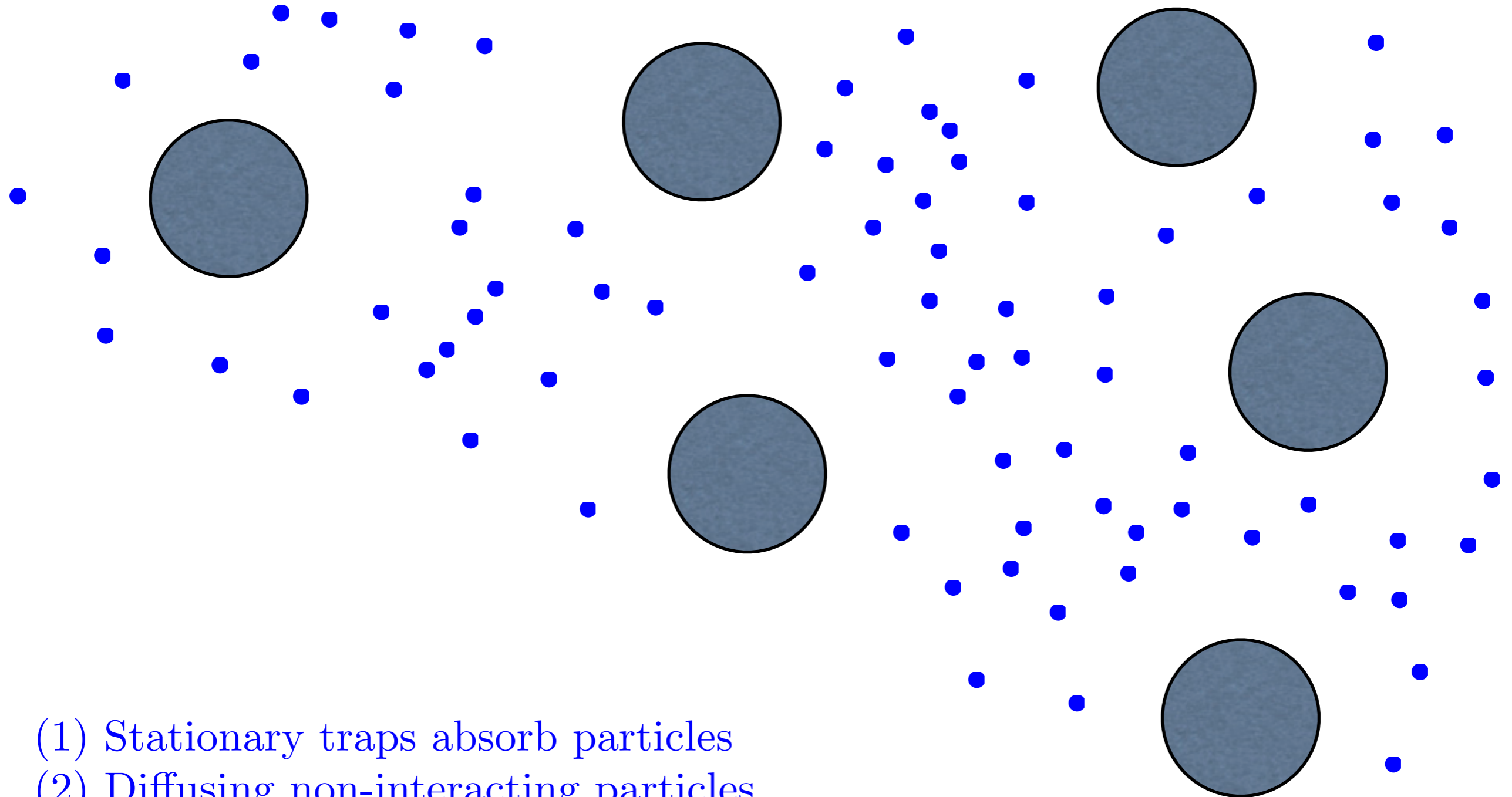
- (1) $d_c = 4$ for two-species annihilation
- (2) Three characteristic length scales
- (3) Exact solution is lacking even in one dimension
- (4) The $t^{-3/4}$ asymptotic in $d = 3$ is beyond the reach in simulations (but maybe not in Nature)
- (5) No log-correction at $d = d_c = 4$

Trapping Reaction



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

Trapping Reaction



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- (2) Diffusing non-interacting particles

Mean-Field and Exact Descriptions

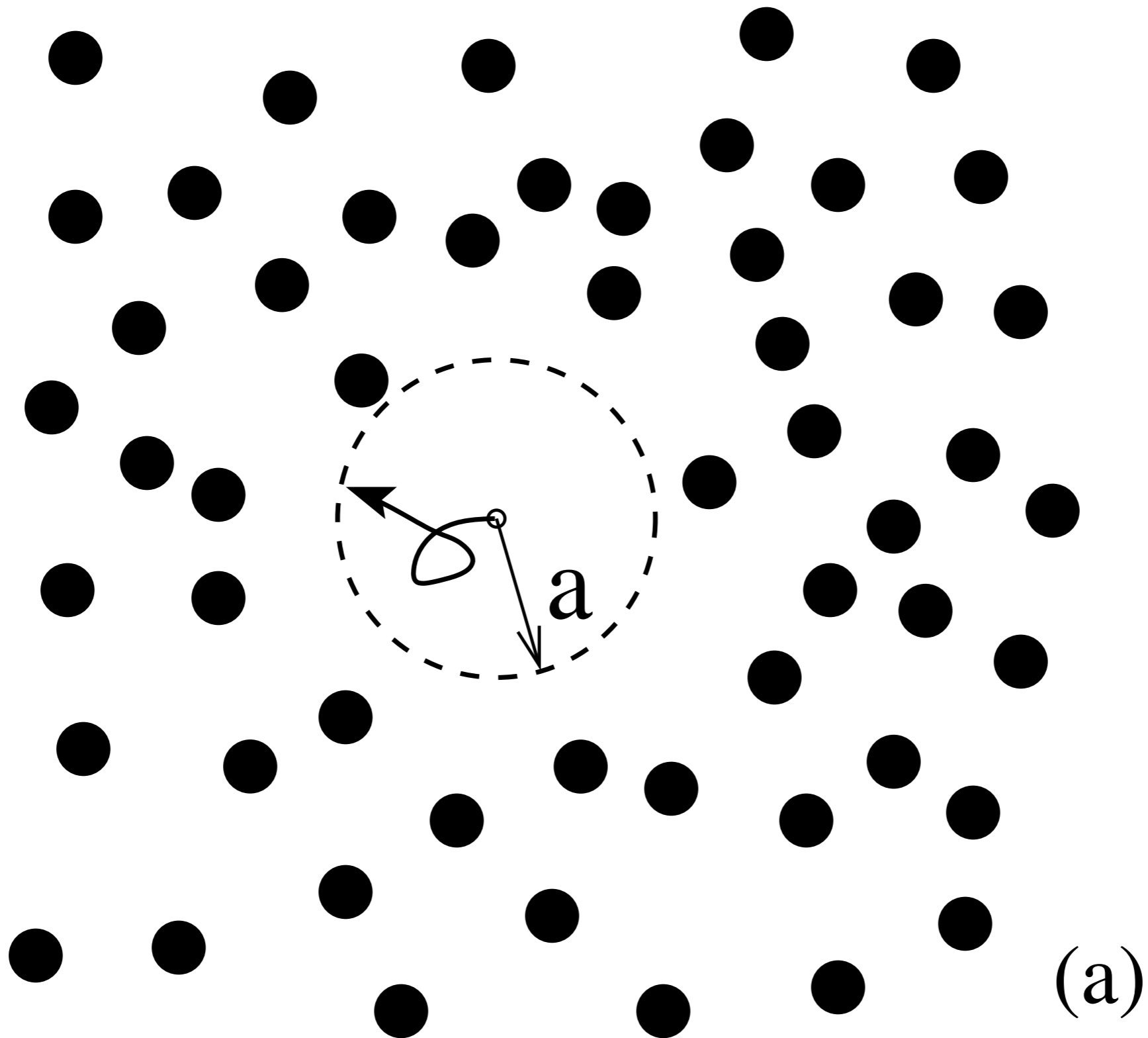
ρ the density of traps
 n the density of particles

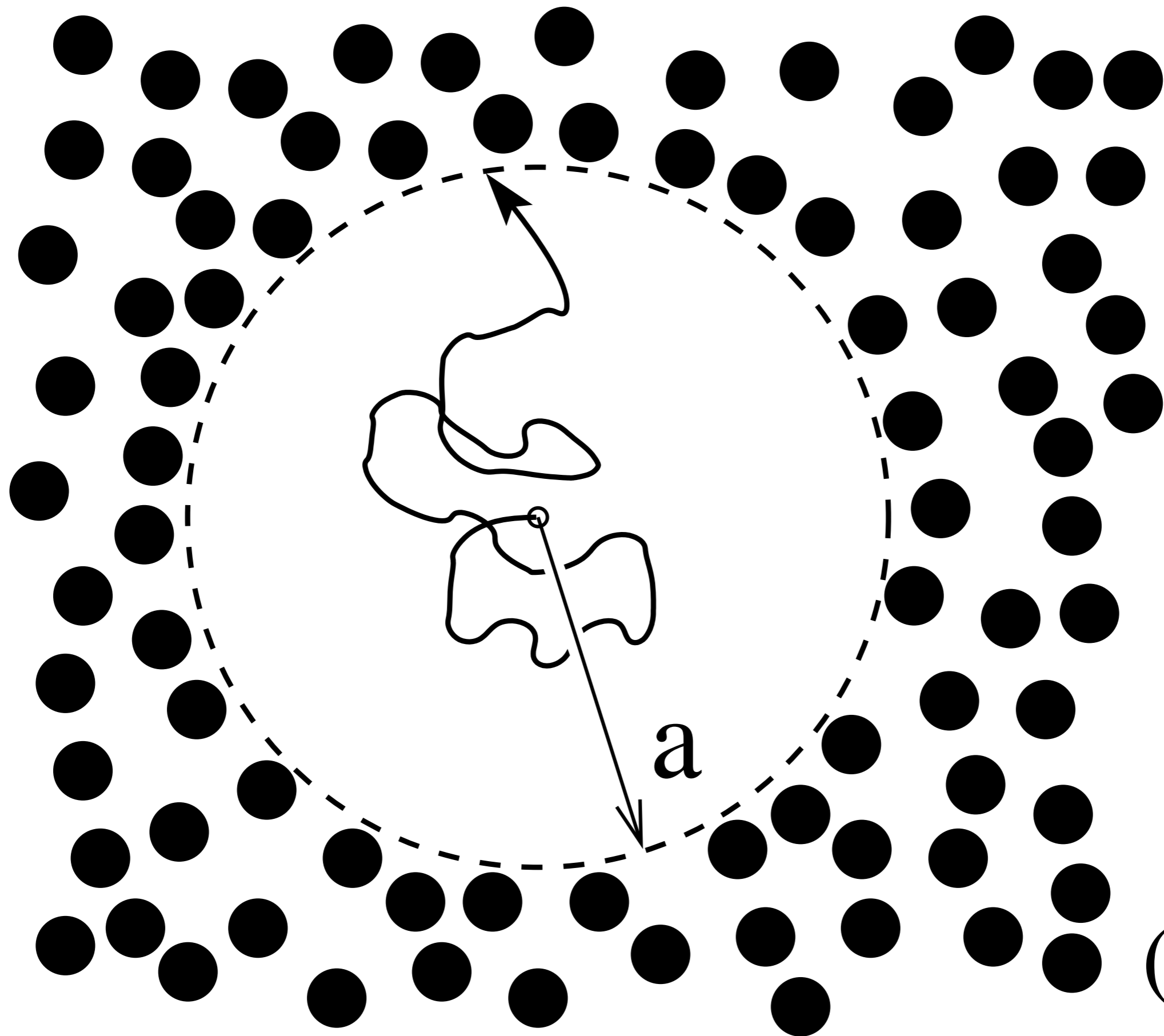
$$\frac{dn}{dt} = -K\rho n, \quad n \sim e^{-K\rho t}$$

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

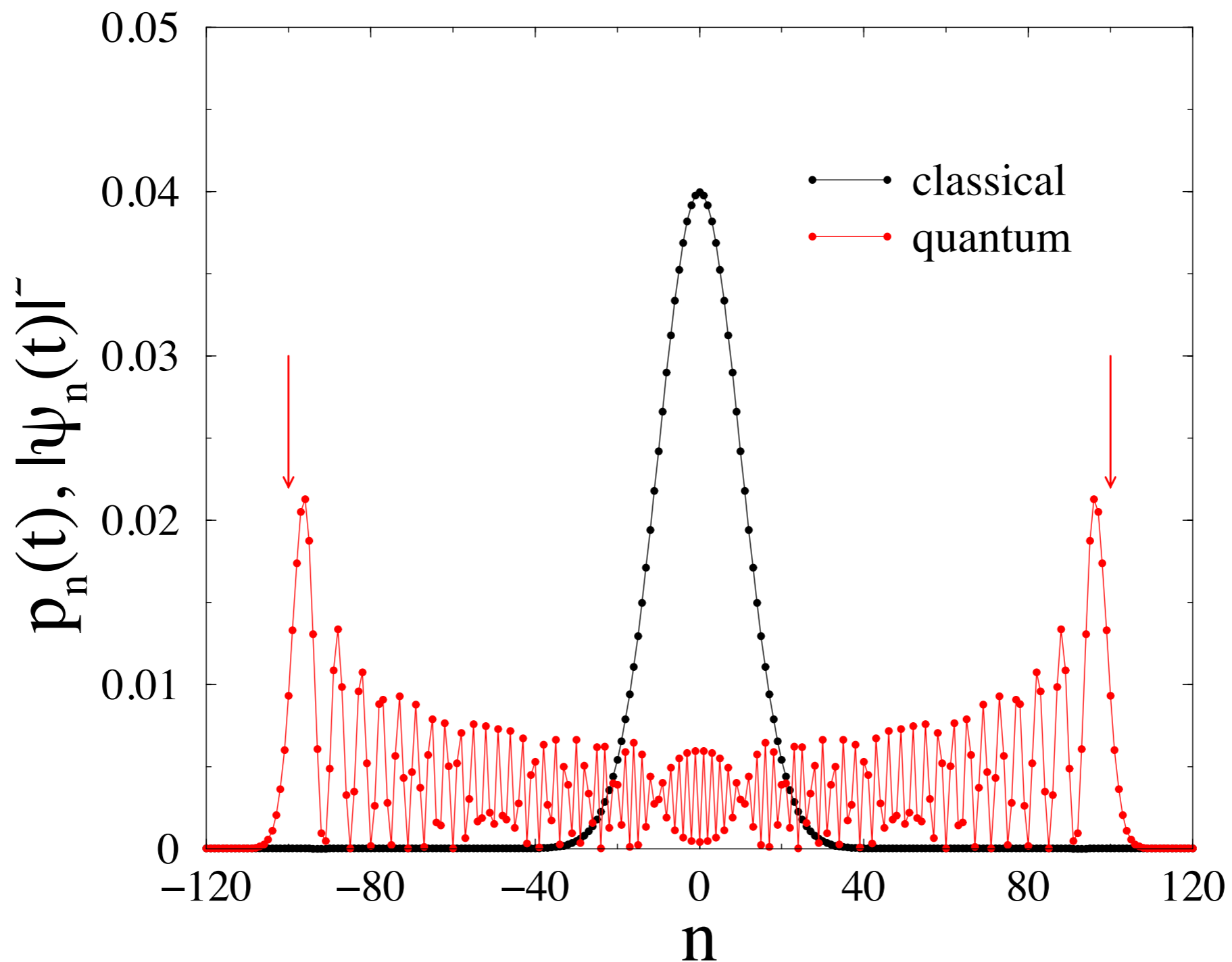
The density decays as $\exp(-A_d t^{d/(d+3)})$

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

Annihilation in Quantum Regime

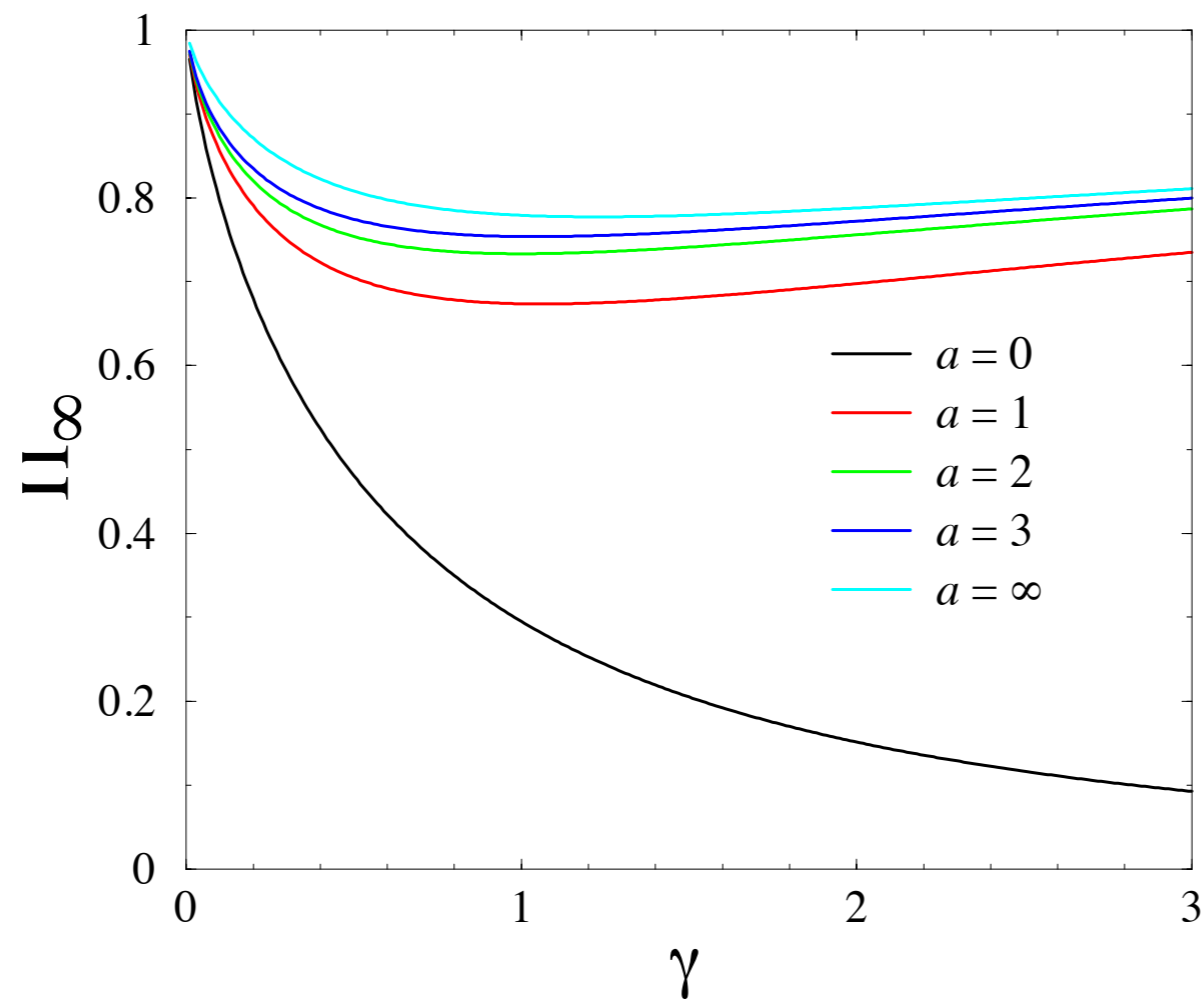
- (1) An ultracold Fermi gas like ${}^6\text{Li}$ is a two-component Fermi gas.
- (2) When two atoms with opposite spin collide, they can form a molecule.
- (3) The energy and momentum conservation makes $A + A \longrightarrow A_2$ impossible.
- (4) The three-body process $A + A + A \longrightarrow A_2 + A$ 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*

