5. Chemical Reactions and Population Dynamics

5.1. Chemical reaction kinetics, rate equations

consider individual "particles" that undergo species transformations, spontaneously or upon encountering others: "chemical reactions"

→ chemistry, biochemistry, nuclear and particle physics, population dynamics

also: kinetics of effective degrees of freedom, e.g. Ising spin chain: view domain walls as "particles" A, spin flip kinetics → reactions

$\ldots\uparrow\uparrow\uparrow\uparrow\ldots \to \ldots\uparrow\uparrow\downarrow\uparrow\ldots$ (flip)   reverse: $\ldots\uparrow\uparrow\downarrow\uparrow\ldots \to \ldots\uparrow\uparrow\uparrow\uparrow\ldots$ etc.

$\emptyset \to 2A$ $2A \to \emptyset$

reversible reaction scheme: $kA + \ell B \underset{\sigma}{\overset{\lambda}{\rightleftharpoons}} mC$; $k, \ell, m = 0, 1, 2 \ldots$ integers

note: system fully characterized by (local) particle numbers $n_\alpha = 0, 1, 2 \ldots$; $\alpha = A, B, C$

→ master equation for configurational probability $P(\{n_\alpha\}; t)$:

$$\frac{\partial P(n_A, n_B, n_C; t)}{\partial t} = \lambda \frac{(n_A+k)!}{n_A!} \frac{(n_B+\ell)!}{n_B!} P(n_A+k, n_B+\ell, n_C-m; t) + \sigma \frac{(n_C+m)!}{n_C!} P(n_A-k, n_B-\ell, n_C+m; t)$$

gain ↗

loss →
$$- \left[\lambda \underbrace{\frac{n_A!}{(n_A-k)!}} \frac{n_B!}{(n_B-\ell)!} + \sigma \frac{n_C!}{(n_C-m)!} \right] P(n_A, n_B, n_C; t)$$

number of possibilities to pick k reactants in given order from n_A particles

(different convention: independent of reactant ordering: $\frac{n_A!}{(n_A-k)!} \to \binom{n_A}{k}$, then just rescale $\lambda \to \frac{\lambda}{k!\ell!}$, $\sigma \to \frac{\sigma}{m!}$)

any $n_\alpha < 0$: set $P(\{n_\alpha\}; t) = 0$

temporal evolution of mean particle numbers $\langle n_\alpha(t) \rangle = \sum_{n_A, n_B, n_C = 0}^{\infty} n_\alpha P(n_A, n_B, n_C; t)$

terms $\sim \sigma$:
$$\frac{d\langle n_A(t)\rangle}{dt} = \sigma \sum_{n_A, n_B, n_C} n_A \left[\frac{(n_C+m)!}{n_C!} \underbrace{P(n_A-k, n_B-\ell, n_C+m; t)}_{n_A \geq k,\ n_B \geq \ell \text{ here}} - \underbrace{\frac{n_C!}{(n_C-m)!} P(n_A, n_B, n_C; t)}_{n_C \geq m \text{ here}} \right]$$

shift $n_A \to n_A + k$, $n_B \to n_B + \ell$, $n_C \to n_C - m$

$$= k\sigma \left\langle [n_C(n_C-1) \ldots (n_C-m+1)](t) \right\rangle$$

in the same way:
$$\frac{d\langle n_C(t)\rangle}{dt} = \sigma \sum_{n_A, n_B, n_C} (n_C - m - n_C) \frac{n_C!}{(n_C-m)!} P(n_A, n_B, n_C; t)$$

$$= -m\sigma \left\langle [n_C(n_C-1) \ldots (n_C-m+1)](t) \right\rangle$$

$$\rightarrow\ -\frac{1}{k}\frac{d\langle n_A(t)\rangle}{dt} = -\frac{1}{l}\frac{d\langle n_B(t)\rangle}{dt} = \frac{1}{m}\frac{d\langle n_C(t)\rangle}{dt} = R(t)$$

reactivity (rate of reactions)

$$= \lambda\langle[n_A(n_A-1)\dots(n_A-k+1)\,n_B(n_B-1)\dots(n_B-l+1)](t)\rangle$$
$$- \sigma\langle[n_C(n_C-1)\dots(n_C-m+1)](t)\rangle$$

yields exact conservation laws (for $k, l, m > 0$):

$l\langle n_A(t)\rangle - k\langle n_B(t)\rangle = \text{const.}$, $m\langle n_A(t)\rangle + k\langle n_C(t)\rangle = \text{const.}$, $m\langle n_B(t)\rangle + l\langle n_C(t)\rangle = \text{co}$

stationary state: $R(t) = 0$

further analysis requires time dependence of higher moments, correlations

→ yields infinite hierarchy of coupled differential equations

for large average particle numbers $\langle n_\alpha(t)\rangle = \alpha(t) \gg k, l, m$

relative fluctuations small → mean-field type factorization

$R(t) \approx \lambda\, a(t)^k\, b(t)^l - \sigma\, c(t)^m \rightarrow 0$ as $t \to \infty$ yields

stoichiometric product $\frac{c_\infty^m}{a_\infty^k\, b_\infty^l} = \frac{\lambda}{\sigma}$ reaction rate ratio → law of mass action

increase forward rate λ, decrease σ → shift stationary state towards larger c_∞

increase backward rate σ, decrease λ → shift towards larger a_∞ and b_∞

irreversible limit scenarios: $\lambda = 0 \rightarrow c_\infty = 0$; $\sigma = 0 \rightarrow a_\infty b_\infty = 0$

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examples: • single-species annihilation $kA \xrightarrow{\lambda} lA$, $k > l \geq 0$

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mean-field rate equation ($k \to k-l$ above): $\frac{da(t)}{dt} = -(k-l)\lambda\, a(t)^k$

solution for $k = 1$ ("radioactive" decay) ($l = 0$): $a(t) = a_0\, e^{-\lambda t}$, $a_0 = a(0)$

$k \geq 2$ ($l \geq 1$): $(k-l)\lambda t = -\int_{a_0}^{a(t)} \frac{da}{a^k} = \frac{1}{k-1}\left[a(t)^{1-k} - a_0^{1-k}\right]$

yields $a(t) = \frac{1}{\left[a_0^{1-k} + (k-l)(k-1)\lambda t\right]^{\frac{1}{k-1}}} \xrightarrow{t \gg \frac{1}{\lambda a_0^{k-1}}} \left[(k-l)(k-1)\lambda t\right]^{-\frac{1}{k-1}}$

algebraic decay independent of a_0

- two-species pair annihilation $A + B \xrightarrow{\lambda} \emptyset$ (no reactions among just the A or B species)

rate equations: $\frac{da(t)}{dt} = \frac{db(t)}{dt} = -\lambda\, a(t)\, b(t)$

note conservation law (even local): $c(t) = a(t) - b(t) = c_0 = \text{const}$

– equal $a_0 = b_0 \to c_0 = 0$: $a(t) = b(t) = \frac{a_0}{1 + a_0 \lambda t}$ (as for $A + A \to$ power law

– $c_0 = a_0 - b_0 > 0$: $a_\infty = c_0$, $b_\infty = 0$

exponential approach : $a(t) - c_0 \sim b(t) \sim e^{-\lambda c_0 t}$

$\to c_0 = 0$ resembles critical point with algebraic replacing exponential decay

- competing particle decay and production processes $A \xrightarrow{\mu} \emptyset$; $A \underset{\lambda}{\overset{\sigma}{\rightleftharpoons}} A + A$

rate equation: $\frac{da(t)}{dt} = (\sigma - \mu)\, a(t) - \lambda\, a(t)^2$

– $\sigma < \mu$: $a(t) \xrightarrow{t \to \infty} e^{-(\mu - \sigma) t} \to 0$ empty, absorbing state (reactions cease when $a = 0$)

note: absorbing state is unique stationary state in finite system

– $\sigma > \mu$: $a(t) \xrightarrow{t \to \infty} a_\infty = \frac{\sigma - \mu}{\lambda}$, approached exponentially, with characteristic rate $\sim \sigma - \mu$

in infinite system (i.e. spatially extended): $\sigma_c = \mu$ is genuine critical point, continuous non-equilibrium active-absorbing phase transition (requires thermodynamic limit first, then $t \to \infty$)

define critical exponents: $a_\infty \sim (\sigma - \sigma_c)^\beta$, $\sigma > \sigma_c$; here $\beta = 1$

$a_c(t) \sim t^{-\alpha}$, $\sigma = \sigma_c$; here $\alpha = 1$

add diffusive spreading $\to$ mean-field reaction-diffusion model

local particle density : $\frac{\partial a(\vec{x}, t)}{\partial t} = (\sigma - \mu + D \nabla^2)\, a(\vec{x}, t) - \lambda\, a(\vec{x}, t)^2$

note : still **mass-action** factorization, correlations neglected

in population dynamics: Fisher-Kolmogorov equation characteristic correlation length: $\xi = \sqrt{\frac{D}{|\sigma - \mu|}}$

diffusive relaxation time: $t = \frac{1}{|\sigma-\mu|} = \xi^2 / D$

define generally: $\xi \sim |\sigma - \sigma_c|^{-\nu}$; here $\nu = \frac{1}{2}$

dynamic scaling exponent: $t_c \sim \xi^z$; here $z = 2$ (diffusion)

near critical point: fluctuations strong, correlations crucial, $a \approx 0$

$\rightarrow$ expect modified critical exponents ($d < d_c$)

- Lotka-Volterra predator-prey competition and coexistence

"predators" $A \xrightarrow{\mu} \emptyset$, "prey" $B \xrightarrow{\sigma} B + B$, "predation" $A + B \xrightarrow{\lambda} A + A$

coupled mean-field rate equations:

$$\left.\begin{aligned} \frac{da(t)}{dt} &= -\mu a(t) + \lambda a(t) b(t) \\ \frac{db(t)}{dt} &= \sigma b(t) - \lambda a(t) b(t) \end{aligned}\right\}$$

eliminate time: $\frac{da}{db} = \frac{(\lambda b - \mu) a}{(\sigma - \lambda a) b}$

separate variables:

$\left(\frac{\sigma}{a} - \lambda\right) da = \left(\lambda - \frac{\mu}{b}\right) db$

integrate: $K(t) = \lambda [a(t) + b(t)] - \sigma \ln a(t) - \mu \ln b(t) = K_0 = \text{const.}$

conserved first integral

$\rightarrow$ regular nonlinear population oscillations, fixed by initial densities

stationary states: – $a = b = 0$ empty, absorbing; complete extinction

– $a = 0$, $b \to \infty$ Malthusian prey explosion

– $a_c = \frac{\sigma}{\lambda}$, $b_c = \frac{\mu}{\lambda}$ species coexistence, yet never reached

linearize $a(t) = a_c + \delta a(t)$, $b(t) = b_c + \delta b(t)$

$\rightarrow \frac{d\,\delta a(t)}{dt} = \sigma\, \delta b(t)$, $\frac{d\,\delta b(t)}{dt} = -\mu\, \delta a(t)$

gives $\frac{d^2 \delta a(t)}{dt} = -\sigma\mu\, \delta a(t)$ harmonic oscillator, frequency $\omega = \sqrt{\sigma\mu}$

stochastic simulations: erratic oscillations about a_c, b_c

on lattice: spreading activity fronts (prey followed by predators)

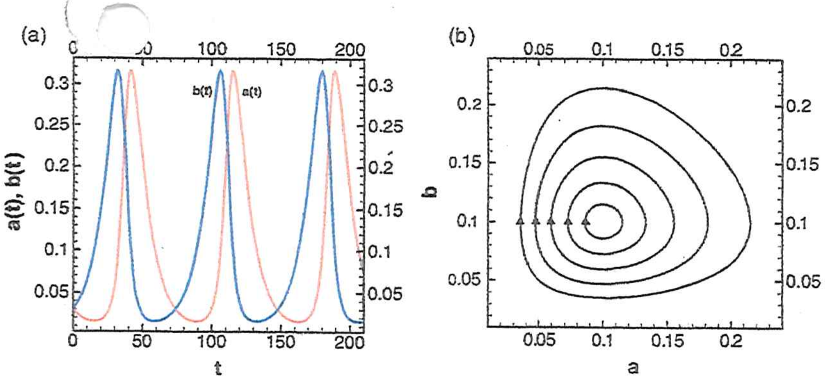


Figure 1. (a) Predator $a(t)$ (red) and prey $b(t)$ (blue) population oscillations resulting from the deterministic Lotka–Volterra equations (2), all computed with rates $\sigma = 0.1$, $\mu = 0.1$, and $\lambda = 1$. (b) Several periodic orbits in the a–b phase plane. The oscillatory kinetics is determined by the initial conditions.

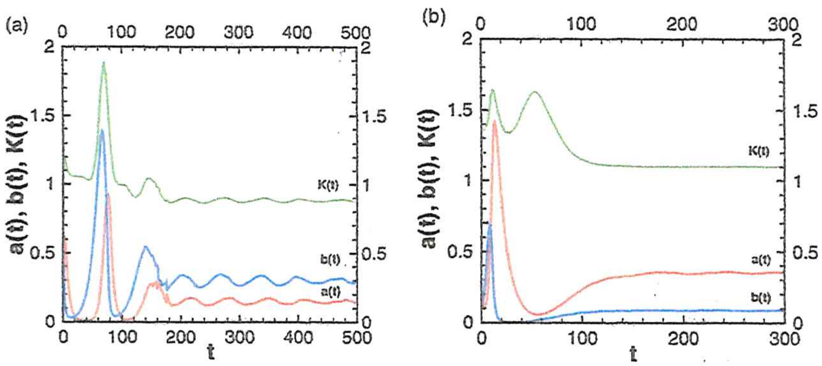


Figure 4. Early time evolution for the population density of predators $a(t)$ (red), prey $b(t)$ (blue), and the quantity $K(t)$ (green) defined in (3) from two single runs on a 1024×1024 lattice, both starting with a random distribution with rates (a) $\sigma = 0.1$, $\mu = 0.2$, and $\lambda = 1.0$, and (b) $\sigma = 0.4$, $\mu = 0.1$, and $\lambda = 1.0$.

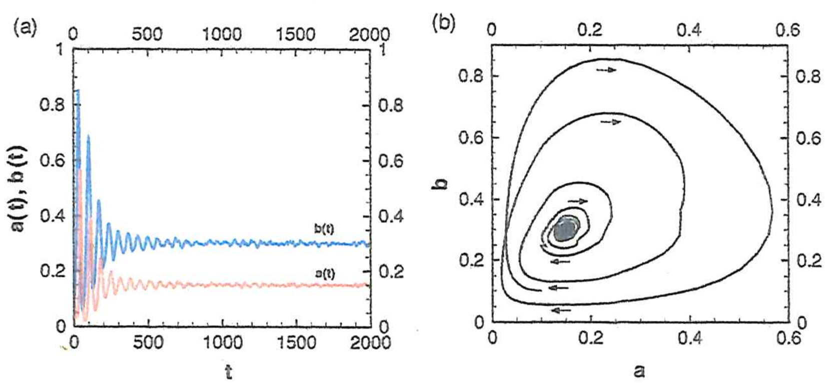


Figure 5. (a) Predator $a(t)$ (red) and prey $b(t)$ (blue) densities versus time in a simulation run on a 1024×1024 lattice, with random initial distribution, and rates $\sigma = 0.1$, $\mu = 0.2$, $\lambda = 1.0$, and

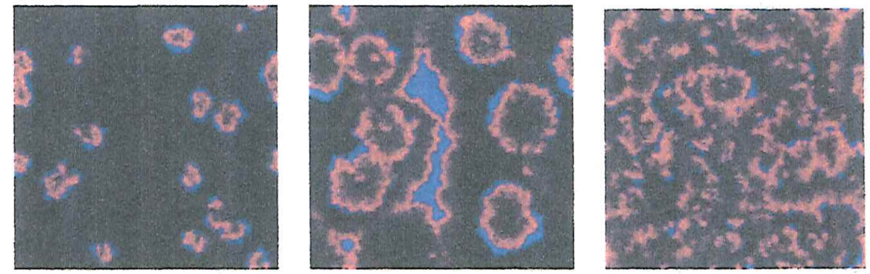


Fig. 2. (Color online.) Snapshots of the time evolution (time increases from left to right) of the two-dimensional SLLVM model in the species coexistence phase, when the fixed point is a focus. The red, blue, and dark dots respectively represent the prey, predators, and empty lattice sites. The rates here are $D = 0$, $\sigma = 4.0$, $\mu = 0.1$, and $\lambda = 2.2$. The system is initially homogeneous with densities $a(0) = b(0) = 1/3$ and the lattice size is 512×512.

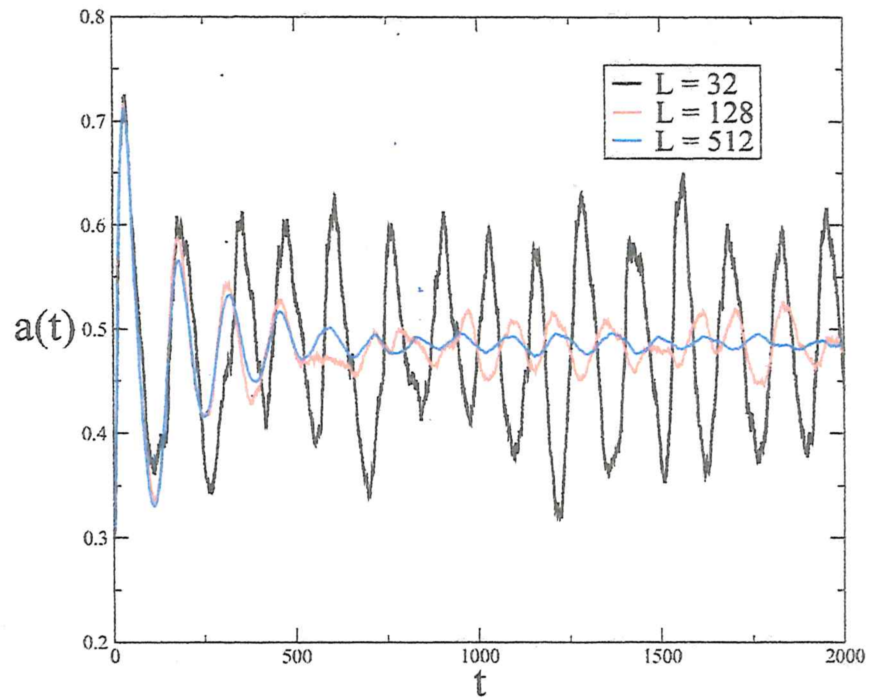


Fig. 7. (Color online.) The density of the predators $a(t)$ vs. t on two-dimensional lattices (measured for single realizations) with $L = 32$, 128 and 512. The values of the stochastic parameters are $D = 0$, $\lambda = 1$, $\sigma = 4$, and $\mu = 0.1$. Initially the particles are homogeneously distributed with densities $a(0) = b(0) = 0.3$.

5.2. Pair annihilation: depletion zones and particle segregation

so far: system well-mixed, reactions just limited by reaction rates

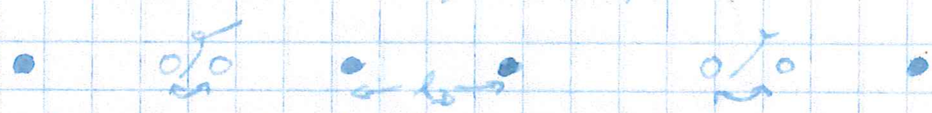
in spatial setting: particles may need to reach each other to enable reactions upon encounter

consider diffusive particle spreading and simplest single-species binary reaction process: pair annihilation $A + A \to \emptyset$

recall recurrence properties of random walks:

- dimension $d < 2$: recurrence probability to origin is 1

  → particles remain in neighborhood, reactions carve out "depletion zones"



reactions eventually become diffusion-limited at low density

moreover, annihilations generate particle anti-correlations:

closeby neighbors quickly annihilate, remaining survivors well separated

characteristic length scale: diffusion length $\ell_D = \sqrt{2Dt}$

associated particle density: $a(t) \sim \frac{1}{\ell_D^{\,d}} \sim (2Dt)^{-d/2}$

- $d > 2$: finite escape probability, system effectively well-mixed

  → expect mean-field rate equation prediction $a(t) \sim (2\lambda t)^{-1}$

- $d = d_c = 2$: "critical dimension" same power law predicted

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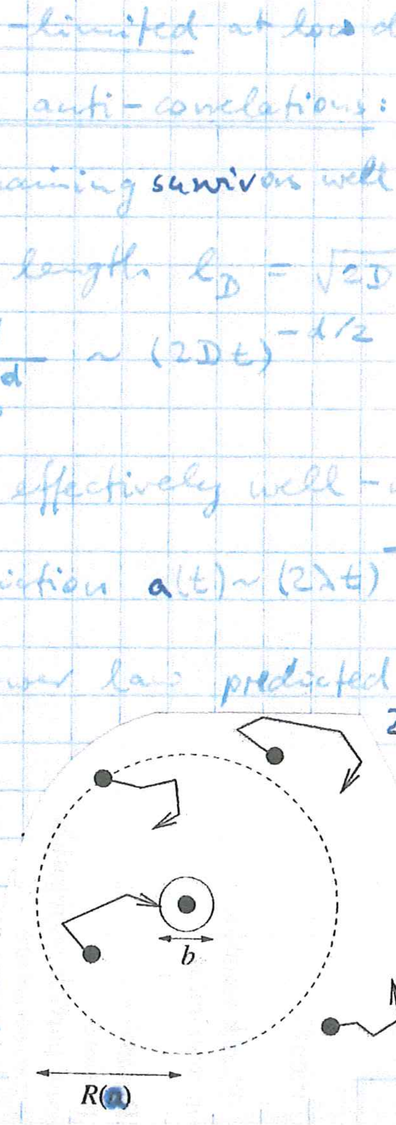
refined self-consistent treatment:

Smoluchowski theory:



continuum diffusion model, relative diffusivity for two particles: $2D$

distance $R < b$: "reaction radius"

→ annihilation with probability 1

solve stationary, radial diffusion equation; i.e. Laplace's equation:

$$0 = \nabla^2 a(r) = \frac{d^2 a(r)}{dr^2} + \frac{d-1}{r}\,\frac{da(r)}{dr}$$

with boundary conditions $a(r=b) = 0$, $a(r) \xrightarrow{r\to\infty} a_\infty$

• $d > 2$: try $a(r) \sim r^{\varrho}$ → $\varrho(\varrho-1) + (d-1)\varrho = 0$ → $\varrho = 0,\ 2-d$

$$\rightarrow\ a(r) = a_\infty \left[1 - \left(\frac{b}{r}\right)^{d-2}\right]$$

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flux at reaction sphere, with $K_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$ (surface area of unit sphere in d dimensions)

$$2 D K_d \frac{b^{d-1}}{a_\infty} \frac{da(r)}{dr}\Big|_{r=b} = 2 D K_d (d-2) b^{d-2} = 2\lambda_{eff}$$

effective reaction rate

→ self-consistent rate equation: $\frac{da(t)}{dt} = -2\lambda_{eff}\, a(t)^2$

yields $a(t) = \frac{a_0}{1 + 2\lambda_{eff} a_0 t}$ mean-field power law but $\lambda_{eff} \sim D$, vanishes as $d \to 2$

• $d < 2$: at typical particle spacing: $a(R) = \frac{1}{V(R)} = \frac{1}{\frac{K_d}{d} R^d} \rightarrow R(a) = \left(\frac{d}{K_d a}\right)^{\frac{1}{d}}$

need new boundary condition: $a(r=R) = a_\infty$

$$\rightarrow\ a(r) = a_\infty \frac{\left(\frac{r}{b}\right)^{2-d} - 1}{\left(\frac{R(a)}{b}\right)^{2-d} - 1}$$

reaction sphere flux: $2 D K_d \frac{b^{d-1}}{a_\infty} \frac{da(r)}{dr}\Big|_{r=b} = 2 D K_d (2-d) b^{d-2} \frac{1}{\left(\frac{R(a)}{b}\right)^{2-d} - 1}$

dilute, low density: $R(a) \gg b$ $\longrightarrow 2 D K_d (2-d) R(a)^{d-2}$

$$= 2 D K_d^{2/d} (2-d) \left(\frac{a}{d}\right)^{\frac{2}{d}-1} = 2\lambda_{eff}(a)$$

effective reaction rate depends on density: $\lambda_{eff}(a) = \lambda_R\, a^{\frac{2}{d}-1}$, $\lambda_R \to 0$ as $d \to 2$

→ "renormalized" rate equation: $\frac{da(t)}{dt} = -2\lambda_R\, a(t)^{1+\frac{2}{d}}$

solution: $a(t) = \frac{a_0}{\left(1 + \frac{4}{d}\lambda_R a_0^{\frac{2}{d}} t\right)^{d/2}} \xrightarrow{t \gg \frac{1}{\lambda_R a_0^{2/d}}} \left(\frac{4}{d}\lambda_R t\right)^{-\frac{d}{2}}$

thus $\lambda_{eff}(t) \sim (Dt)^{\frac{d}{2}-1}$ decreases with time

• at $d_c = 2$: $a(t) \sim \frac{1}{16\pi D t} \ln \frac{8Dt}{b^2}$ logarithmic correction to mean-field power law

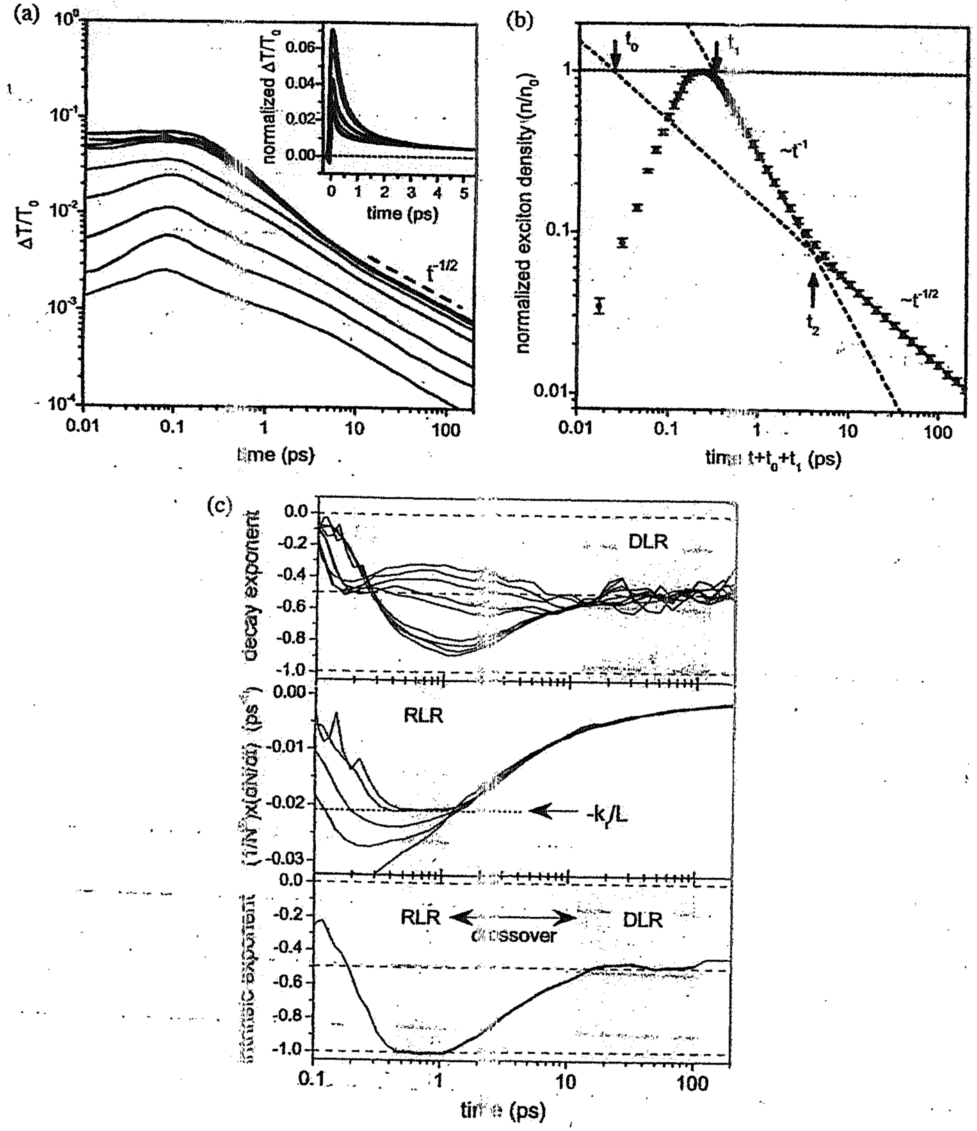


Fig. 9.8 Experimental data for exciton recombination in single-walled carbon nanotubes showing the crossover from reaction- to diffusion-limited scaling: (a) decay of the exciton density, proportional to the differential transmission $\Delta T/T_0$ at various laser pulse energies (bottom to top: 0.19, 0.48, 1.1, 4.0, 12, 40, 60, 80, and 104 nJ; inset: same data normalized to the amplitude at long time); (b) normalized exciton concentration n/n_0 plotted against the scaling time $t + t_0 + t_1$; and (c) upper panel: evolution of the effective decay exponent (for the same pulse energies as in (a) from top to bottom); middle panel: $n(t)^{-2}dn(t)/dt$ for the highest excitation levels (decreasing from top to bottom); lower panel: intrinsic exponent given by the measured exponent multiplied by $(t + t_0 + t_1)/t$, with the heavy line indicating the experimentally determined crossover function [Figures adapted with permission from: J. Allam, M. T. Sajjad, R. Sutton, *et al.*, *Phys. Rev. Lett.* **111**, 197401 (2013).]

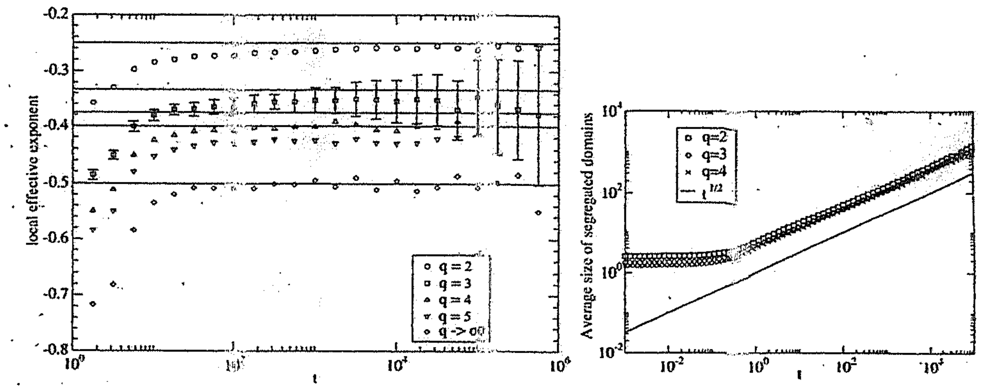


Fig. 9.12 Monte Carlo results for q-species pair annihilation reactions, obtained with random initial conditions on one-dimensional lattices with 10^5 sites, averaged over 50 simulation runs. (a) Local effective density decay exponent $-\alpha_{\text{eff}}(q, t)$ for $q = 2, 3, 4, 5$ different species, and for $q \to \infty$ (i.e., $A + A \to \emptyset$); (statistical) error bars are indicated for $q = 3$. Note the rather slow approach to the asymptotic predictions (9.104), shown as straight lines, except for the single-species annihilation reaction. (b) Growth $\sim t^{1/2}$ of the average domain size of the single-species segregated regions for $q = 2, 3$, and 4 in one dimension. [Figures reproduced with permission from: H. J. Hilhorst, O. Deloubrière, M. J. Washenberger, and U. C. Täuber, *J. Phys. A: Math. Gen.* **37**, 7063 (2004); DOI: 10.1088/0305-4470/37/28/001; copyright (2004) by Inst. of Physics Publ.]

$$\alpha_{eff}(t) = \frac{\partial \ln a(t)}{\partial \ln t}$$

- <u>two-species pair annihilation</u> $A+B \xrightarrow{\lambda} \emptyset$

  - unequal initial densities $a_0 \neq b_0$, $c_0 = a_0 - b_0 = a(t) - b(t)$ conserved

    depletion zones should modify exponential relaxation for $d \leq 2$:

$$\ln[a(t) - c_0] \sim \ln b(t) \sim \begin{cases} -\lambda c_0 t & d>2 \\ -(Dt)^{d/2}, & d<2 \\ -\frac{Dt}{\ln(Dt)}, & d=2 \end{cases}$$

    anticorrelations produced by reaction kinetics slow relaxation down

    $\rightarrow$ "<u>stretched **exponential**</u>" <u>diffusion-limited decay</u>

  - equal initial densities $a_0 = b_0$, $c_0 = 0$

    local density difference obeys diffusion equation $\frac{\partial c(\vec{x},t)}{\partial t} = D \nabla^2 c(\vec{x},t)$

    solution of general initial value problem: **use Green's function**

$$c(\vec{x},t) = \int d^d x' \, G(\vec{x}-\vec{x}',t)\, c(\vec{x}',0) \quad , \quad G(\vec{x},t) = \frac{\Theta(t)}{(4\pi D t)^{d/2}} e^{-\frac{\vec{x}^2}{4Dt}}$$

    (straightforward extension of our one-dimensional analysis)

    assume initially random, Poisson distribution for A and B particles:

$$\overline{a(\vec{x},0)} = a_0 = \overline{b(\vec{x},0)} \qquad \overline{} : \text{average over initial conditions}$$

$$\overline{a(\vec{x},0)\,a(\vec{x}',0)} = a_0^2 + a_0\,\delta(\vec{x}-\vec{x}') = \overline{b(\vec{x},0)\,b(\vec{x}',0)} \quad , \quad \overline{a(\vec{x},0)\,b(\vec{x}',0)} = a_0^2$$

$$\rightarrow \quad \overline{c(\vec{x},0)\,c(\vec{x}',0)} = 2a_0^2 + 2a_0\,\delta(\vec{x}-\vec{x}') - 2a_0^2 = 2a_0\,\delta(\vec{x}-\vec{x}')$$

and
$$\overline{c(\vec{x},t)^2} = \int d^d x' \, G(\vec{x}-\vec{x}',t) \int d^d x'' \, G(\vec{x}-\vec{x}'',t)\, \underbrace{\overline{c(\vec{x}',0)\,c(\vec{x}'',0)}}_{=2a_0\,\delta(\vec{x}'-\vec{x}'')}$$

$$= 2a_0 \int G(\vec{x}-\vec{x}',t)^2 \, d^d x' = \frac{2a_0}{(4\pi D t)^d} \underbrace{\int e^{-\frac{(\vec{x}-\vec{x}')^2}{2Dt}} d^d x'}_{=(2\pi D t)^{d/2}} \, \Theta(t) = \frac{2a_0\,\Theta(t)}{(8\pi D t)^{d/2}}$$

    distribution of c will be a Gaussian, with **width** $\sqrt{\overline{c^2}}$:

$$P(c) = \frac{1}{\sqrt{2\pi\,\overline{c^2}}} e^{-c^2/2\overline{c^2}} \quad \rightarrow \quad \overline{|c|} = \frac{2}{\sqrt{2\pi\,\overline{c^2}}} \underbrace{\int_0^\infty c\, e^{-c^2/2\overline{c^2}} dc}_{=\overline{c^2}} = \sqrt{\frac{2}{\pi}\,\overline{c^2}}$$

$\rightarrow$ average local density excess: $\overline{|c(\vec{x},t)|} = 2\sqrt{\frac{a_0}{\pi}}\,(8\pi D t)^{-d/4}\ \Theta(t)$

- dimensions $d > 4$: density excess decays faster than $a(t) \sim b(t) \sim \frac{1}{t}$

  $\rightarrow$ densities largely uniform, mean-field theory applies

- $d < d_c = 4$: density excess decays slower than mean-field density

  $\rightarrow$ fluctuations dictate long-time behavior

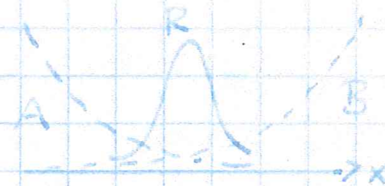
  system segregates into A/B rich domains, separated by reaction fronts, $a(t) \sim b(t) \sim (Dt)^{-d/4}$

  note: special initial conditions, e.g. in one dimension:

  $\ldots AB\cancel{AB}A\cancel{BA}B\ldots \rightarrow \ldots ABAB \ldots$ AB-correlations preserved by dynamics

  $\rightarrow$ A/B distinction meaningless, $a(t) \sim (Dt)^{-1/2}$

- reaction front scaling properties:



  steady-state approximation: fixed particle current J

  i.e. $\left(\frac{\partial a(\vec{x})}{\partial x}, \frac{\partial b(\vec{x})}{\partial x}\right) \longrightarrow \begin{cases} (-J, 0), & x \to -\infty \\ (0, J), & x \to +\infty \end{cases}$ so $c(\vec{x}) = -Jx$

  $d > 2$: use reaction-diffusion equation, $b(\vec{x}) = -c(\vec{x}) + a(\vec{x}) = Jx + a(\vec{x})$

  $0 = D\frac{\partial^2 a(\vec{x})}{\partial x^2} - \lambda J x\, a(\vec{x}) - \lambda\, a(\vec{x})^2$ render dimensionless by

  rescaling $x = \left(\frac{D}{\lambda J}\right)^{1/3} y$, $a(x) = \left(\frac{DJ^2}{\lambda}\right)^{1/3} \varrho(y) \rightarrow \frac{\partial^2 \varrho}{\partial y^2} - y\varrho - \varrho^2 = 0$

  $\rightarrow$ scaling solution: $a(\vec{x}) = \left(\frac{DJ^2}{\lambda}\right)^{1/3} \varrho\left(\left(\frac{\lambda J}{D}\right)^{1/3} x, \vec{x}_\perp\right)$

  front width $w(J) = \left(\frac{D}{\lambda J}\right)^{1/3}$

  reactivity, reaction front density $R(\vec{x}) = \lambda\, a(\vec{x})\, b(\vec{x}) = (\lambda D^2 J^4)^{1/3} \varrho^2\left(\left(\frac{\lambda J}{D}\right)^{1/3} x, \ldots\right)$

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  general scaling form: $R(\vec{x}) = J^{\beta'} \hat{R}(J^{\alpha'} x, \vec{x}_\perp)$, $w(J) \sim J^{-\alpha'}$

  $d > 2$: mean-field exponents $\alpha' = \frac{1}{3}$, $\beta' = \frac{4}{3}$

  $d \leq d_c = 2$: $\alpha' = \frac{1}{d+1}$, $\beta' = \frac{d+2}{d+1}$

Temporal scaling: under time scale separation

front motion much slower than relaxation to quasi-stationary state

$$\to \quad \mathcal{J}(t) \sim \frac{a(t)}{\ell_D(t)} \sim (Dt)^{-\frac{d}{4}-\frac{1}{2}} = (Dt)^{-\lambda'/\alpha'} \quad , \quad \lambda' = \frac{d+2}{4(d+1)}$$

$$w(t) \sim \mathcal{J}(t)^{-\alpha'} = (Dt)^{\lambda'}$$

segregated domains grow as $\ell_D(t) \sim (Dt)^{1/2}$

$\to$ relative front width $\frac{w(t)}{\ell_D(t)} \sim (Dt)^{\lambda' - \frac{1}{2}} = (Dt)^{-\frac{d}{4(d+1)}}$

sharpens as $t \to \infty$

q-species pair annihilation: $A_i + A_j \to \emptyset$, $1 \leq i < j \leq q$

consider all equal initial densities, reaction rates, diffusivities

- dimensions $\underline{d \geq 2}$: no conservation laws for $q \geq 3$

$\to$ decay just as for $A + A \to \emptyset$ since $d_s(q) = \frac{4}{q-1}$

indeed for $q \to \infty$: no alike particles ever meet

$\to$ species distinction irrelevant

- $\underline{d = 1}$: species segregation occurs, algebraic density decay:

$$a_i(t) \sim \underbrace{t^{-\alpha(q)}}_{\text{segregation}} + \underbrace{C\, t^{-1/2}}_{\text{depletion zones}} \quad , \quad \alpha(q) = \frac{q-1}{2q}$$

$\to$ correctly $\alpha(2) = \frac{1}{4}$ with $d_s(2) = 4$, $\alpha(\infty) = \frac{1}{2}$

reaction zone width exponent $\lambda'(q) = \frac{2q-1}{4q}$, $\lambda'(2) = \frac{3}{8}$

again, special initial conditions can be constructed, e.g. $d = 1$, $q = 4$:

... ABCDABCD ... $\to$ no alike particles ever adjacent

$\to$ scaling as for $A + A \to \emptyset$

cyclic variants: $A + B \to \emptyset$, $B + C \to \emptyset$, $C + D \to \emptyset$, $A + D \to \emptyset$

$\to$ identify C with A, D with B $\to$ as for $A + B \to \emptyset$