4. Scale invariance and phase transitions in reaction-diffusion systems

"chemical" reactions: particle species (identity) transformations

→ (bio-)chemistry, nuclear and particle physics, also: population dynamics

could also be effective dynamical degrees of freedom:

Ising spin chain: domain walls ↔ particles A, spin flips ↔ reactions

$\ldots\uparrow\uparrow\uparrow\uparrow\ldots \to \ldots\uparrow\uparrow\downarrow\uparrow\ldots$ reverse: $\ldots\uparrow\uparrow\downarrow\uparrow\ldots \to \ldots\uparrow\uparrow\uparrow\uparrow\ldots$

flip: $\emptyset \to 2A$ $\qquad$ $2A \to \emptyset$

$\ldots\uparrow\uparrow\uparrow\downarrow\ldots \to \ldots\uparrow\uparrow\downarrow\downarrow\ldots$ corresponds to particle hopping to left

→ diffusing particles undergoing reactions

- irreversible single-species annihilation: $kA \xrightarrow{\lambda_k} \ell A$, $0 \leq \ell < k$

mean-field description: assume well-mixed system, spatially homogeneous

→ neglect spatial correlations → "law of mass action" factorization

$$\langle a(\vec{x},t)^k \rangle \to \langle a(\vec{x},t)\rangle^k = a(t)^k$$

yields mean-field rate equation $\dfrac{da(t)}{dt} = -\lambda_k\, a(t)^k$

$k=1$, $\ell=0$: "radioactive" decay: $a(t) = a_0\, e^{-\lambda_1 t}$, $a_0 = a(0)$

$k \geqq 2$, $\ell \geqq 0$: integrate $\lambda_k t = -\displaystyle\int_{a_0}^{a(t)} \frac{da}{a^k} = \frac{1}{k-1}\left[a(t)^{1-k} - a_0^{1-k}\right]$

$$\to a(t) = \frac{1}{\left[a_0^{1-k} + (k-1)\lambda_k t\right]^{1/(k-1)}} \xrightarrow[t \gg \frac{1}{\lambda_k a_0^{k-1}}]{} \left[(k-1)\lambda_k t\right]^{-\frac{1}{k-1}}$$

algebraic decay independent of a_0

diffusion-limited pair annihilation: $A + A \xrightarrow{\lambda} \emptyset$ $\quad (k=2, \ell=0)$

in one dimension: random walk recurrence probability 1

→ particles remain in "neighborhood", carve out depletion zone

reactions generate particle anti-correlations at low density, long time: reactions limited by chance of encounter of spatially separated survivors

diffusion time scale for separation ℓ_D: $t = \frac{\ell_D^2}{2D}$, $\ell_D = \sqrt{2Dt}$

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

slower than reaction-limited mean-field decay $\sim \frac{1}{t}$ for $d<2$

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

$$\to \quad a(t) \sim \begin{cases} \frac{1}{\lambda t} & d>2 \\ \frac{\ln Dt}{Dt} & d=d_c=2 \\ \frac{1}{(Dt)^{d/2}} & d<2 \end{cases}$$

diffusion-limited → upper critical dimension $d_c = 2$

→ Fig. 9.8

more generally: $d_c(k) = \frac{2}{k-1}$

triplet reactions $k=3$: $d_c = 1$, so $a(t) \sim \begin{cases} \frac{1}{(\lambda_3 t)^{1/2}} & d>1 \\ \left(\frac{\ln Dt}{Dt}\right)^{1/2} & d=d_c(3)=1 \end{cases}$

$d_c(k \geq 4) < 1$ → fluctuations/correlations not important for decay exponents

- two-species pair annihilation: $A + B \xrightarrow{\lambda} \emptyset$

note: important here is the absence of reactions among same species

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

crucial: conservation law, even local! $c(t) = a(t) - b(t) = c_0$

$c_0 = a_0 - b_0 > 0$: $a(t\to\infty) = a_\infty = c_0 > 0$, $b(t\to\infty) = 0$

rate equations → exponential approach, **decay rate λc_0**

$$a(t) - a_\infty \sim b(t) \sim e^{-\lambda c_0 t}$$

$d \leqq 2$: expect depletion zone anti-correlations

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

stretched exponential decay

$a_0 = b_0$, $c_0 = 0$: rate equations → $a(t) = b(t) = \frac{a_0}{1 + a_0 \lambda t}$ as for $A + A \to \emptyset$

like "critical point"

study spatial correlations: note that $\frac{\partial c(\vec{x},t)}{\partial t} = D\nabla^2 c(\vec{x},t)$ satisfies diffusion equation

Green function to solve general initial density problem:

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

since $G(\vec{x}, t\to 0) \to \delta(\vec{x})$

assume initially random Poisson distributions: $\overline{}$ average over initial conditions

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

$$\to \overline{c(\vec{x},0)} = 0\,, \qquad \text{and } \overline{a(\vec{x},0)\,b(\vec{x}',0)} = a_0^2$$

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

$$\to \overline{c(\vec{x},t)^2} = \int d^dx'\, G(\vec{x}-\vec{x}',t) \int d^dx''\, G(\vec{x}-\vec{x}'',t)\, 2a_0\,\delta(\vec{x}-\vec{x}') = 2a_0 \int G(\vec{x}-\vec{x}',t)^2\, d^dx'$$

$$= \frac{2a_0}{(4\pi D t)^d}\,(2\pi D t)^{d/2} = \frac{2a_0}{(8\pi D t)^{d/2}}$$

$c(\vec{x},t)$ will be Gaussian-distributed, width $\sqrt{\overline{c^2}}$: $P(c) = \frac{1}{\sqrt{2\pi\overline{c^2}}}\, e^{-\frac{c^2}{2\overline{c^2}}}$

$$\to \overline{|c|} = \frac{2}{\sqrt{2\pi\overline{c^2}}} \underbrace{\int_0^\infty c\, e^{-\frac{c^2}{2\overline{c^2}}}\, dc}_{=\overline{c^2}} = \sqrt{\frac{2}{\pi}\,\overline{c^2}} \quad \to \overline{|c(\vec{x},t)|} = 2\sqrt{\frac{a_0}{\pi}}\,(8\pi D t)^{-d/4}$$

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

$\to$ uniform, well-mixed spatial distribution, $a(t) = b(t) \sim \frac{1}{\lambda}$

$d < d_c = 4$: local density excess decays slower, governs kinetics

$\to$ species segregation in A/B-rich domains   A   B

separated by reaction fronts $\to a(t) = b(t) \sim \frac{1}{(Dt)^{d/4}}$

note: special initial condition in one dimension: $\ldots AB\cancel{A}BA\cancel{BA}B\ldots$

reactions preserve ordering

$\to$ A/B distinction meaningless, $a(t) \sim (Dt)^{-1/2}$ as for $A + A \to \emptyset$

q-species generalization: $A_i + A_j \to \emptyset$, $1 \le i < j \le q$ ($q \to \infty$: all species coincide)

special symmetric situation: equal D, λ, $a_i(0)$

$d \ge 2$: no conservation laws for $q \ge 3$, $d_c(q) = \frac{4}{q-1}$ $\to$ decay $\sim \frac{1}{\lambda t}$

$d = 1$: species segregation $a_i(t) \sim \underbrace{t^{-\alpha(q)}}_{\text{segregation}} + \underbrace{C\,t^{-1/2}}_{\text{depletion}}$, $\alpha(q) = \frac{q-1}{2q}$: $\alpha(2) = \frac{1}{4}$, $\alpha(\infty) = \frac{1}{2}$

- population dynamics: competing decay and offspring production processes

$A \xrightarrow{\mu} \emptyset$, $A \underset{\lambda}{\overset{\sigma}{\rightleftharpoons}} A+A$ (coagulation limits total particle number)

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

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

(stochastic processes in finite systems: absorbing state stable)

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

in infinite system, spatially extended: genuine continuous non-equilibrium phase transition at $\sigma_c = \mu$

critical exponents: $a_\infty \sim (\sigma-\sigma_c)^\beta$, $\sigma > \sigma_c$ mean-field: $\beta = 1$

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

add diffusive spreading, $a(t) \to a(\vec{x},t)$ coarse-grained density

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

note: still mass action factorization, correlations not properly accounted for

Fisher-Kolmogorov-~~Piskunov~~-Petrovskii (FKPP) equation

correlation length: $\xi \sim \sqrt{\frac{D}{|\sigma-\mu|}}$ $\to \nu = \frac{1}{2}$

diffusive relaxation time: $t_c \sim \frac{1}{|\sigma-\mu|} \sim \xi^2 \Rightarrow z\nu = 1$, $z = 2$

note scaling relation $\alpha = \frac{\beta}{z\nu}$ holds

- more general setup: use language of epidemics

simple epidemic process:

- susceptible medium, locally infected, recovery possible
  infection $\sim n(\vec{x},t)$ local infected density
- diffusive spreading of infection: adjacent sites can be infected
- $n = 0$ extinction of infection: absorbing state
- Markovian dynamics, local in time, also local noise

→ coarse-grained Langevin-type description:

$$\frac{\partial n(\vec{x},t)}{\partial t} = D\vec{\nabla}^2 n(\vec{x},t) - \underbrace{R[n(\vec{x},t)]}_{\text{reaction functional, vanishes for } n=0} n(\vec{x},t) + \eta(\vec{x},t) \, , \quad \langle \eta \rangle = 0$$

$$\langle \eta(\vec{x},t)\eta(\vec{x}',t')\rangle = 2\underbrace{N[n(\vec{x},t)]\, n(\vec{x},t)}_{\text{noise functional, multiplicative, vanishes for } n=0} \delta(\vec{x}-\vec{x}')\delta(t-t')$$

expand in the spirit of Landau theory:

$R[n] = D\tau + u'n + \dots$, $N[n] = v + \dots$ and rescale:

$$\frac{\partial S(\vec{x},t)}{\partial t} = -D(\tau - \vec{\nabla}^2)\, S(\vec{x},t) - u\, S(\vec{x},t)^2 + \zeta(\vec{x},t) \, , \quad \langle \zeta \rangle = 0$$

$$\langle \zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = 2u\, S(\vec{x},t)\, \delta(\vec{x}-\vec{x}')\delta(t-t')$$

or use "square-root" noise: $\zeta(\vec{x},t) = \sqrt{S(\vec{x},t)}\, \tilde{\zeta}(\vec{x},t)$

→ FKPP equation with multiplicative noise, adequate for absorbing state

equivalent basic reaction processes generate directed percolation clusters in space-time

critical properties: scaling exponents of critical directed percolation (Reggeon field theory)

→ generic universality class for active-to-absorbing phase transitions

upper critical dimension $d_c = 4$

$\epsilon = d_c - d$ expansion: $\frac{1}{\nu} = 2 - \frac{\epsilon}{4} + O(\epsilon^2)$, $\eta = -\frac{\epsilon}{12} + O(\epsilon^2)$

$z = 2 - \frac{\epsilon}{12} + O(\epsilon^2)$, $\beta = \frac{\nu}{2}(d + z - 2 + \eta) = 1 - \frac{\epsilon}{6} + O(\epsilon^2)$

$\alpha = \frac{\beta}{z\nu} = 1 - \frac{\epsilon}{4} + O(\epsilon^2)$

general epidemic process: also "debris" of previously infected sites can be infectious → history dependence, non-Markovian

→ static critical exponents of isotropic percolation, $d_c = 6$

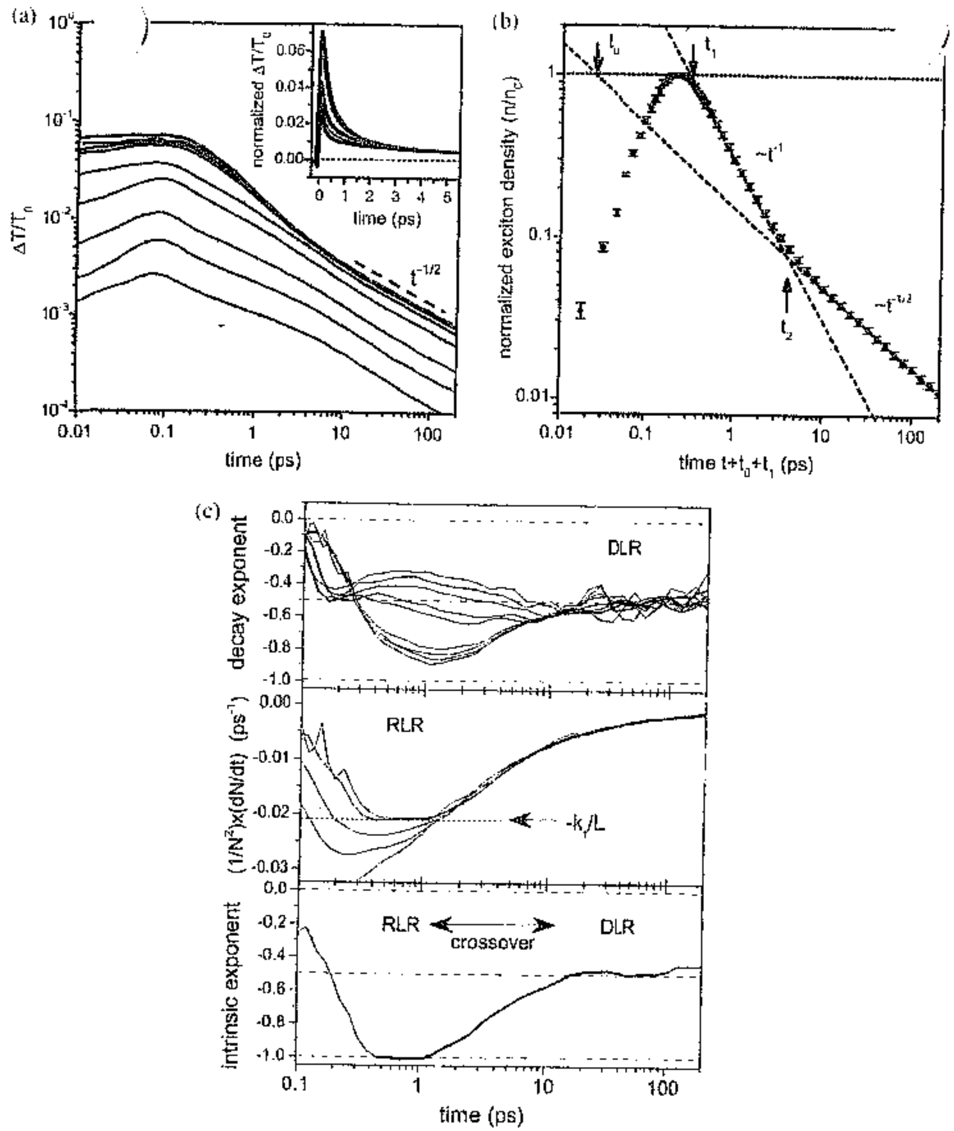

Fig. 9.8 Experimental data for exciton recombination in single-walled carbon nanotubes showing the crossover from reaction- to diffusion-limited scaling: (a) decay of the exciton density, proportional to the differential transmission $\Delta T / T_0$ at various laser pulse energies (bottom to top: 0.19, 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: $n(t)^{-2}\mathrm{d}n(t)/\mathrm{d}t$ 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).]

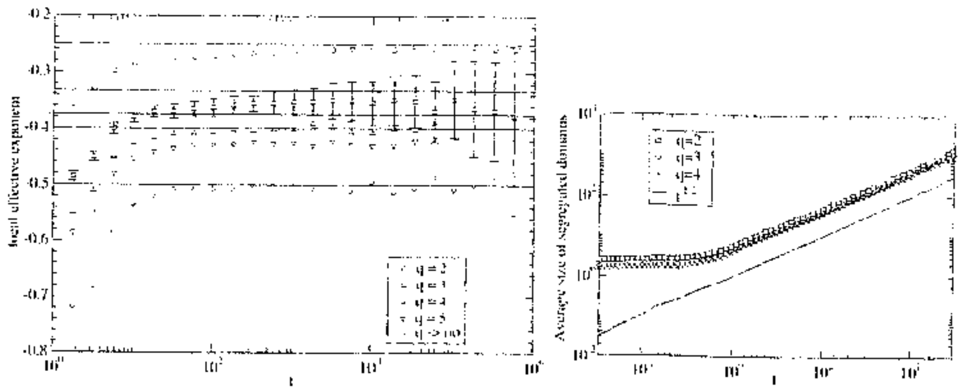

Fig. 9.12 Monte Carlo results for q-species pair annihilation reactions, obtained with random initial conditions on one-dimensional lattices with 10^5 sites, averaged over 50 simulation runs. (a) Local effective density decay exponent $-\alpha_{\rm eff}(q, t)$ for $q = 2, 3, 4, 5$ different species, 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.]