Reaction/Aggregation Processes

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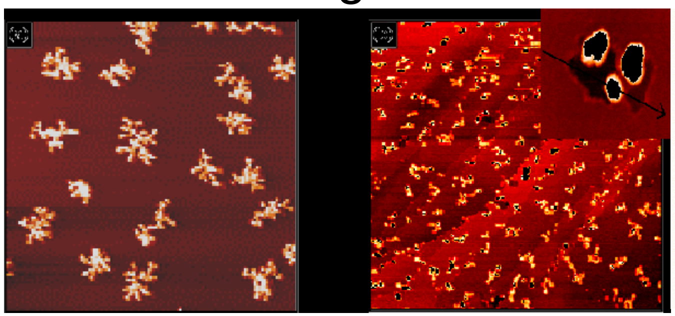
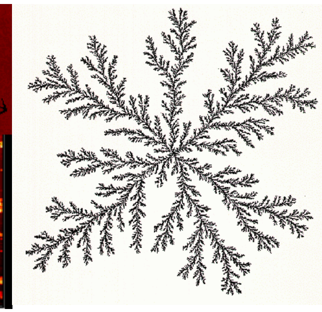
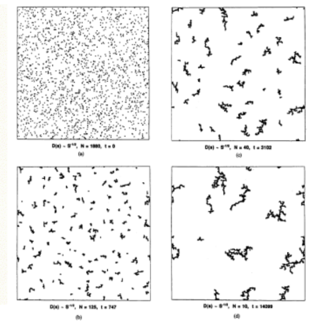
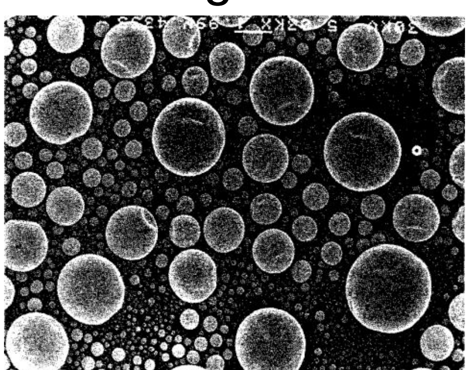
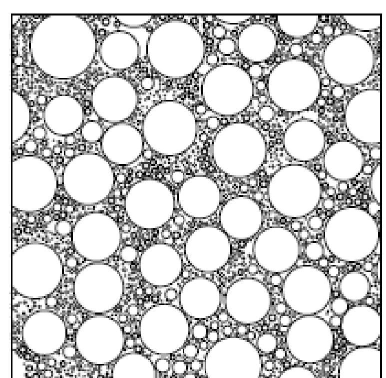
A Few Classical Examples

- Ubiquitous in **physics** and **chemistry**
  - Atoms diffusing on a surface and Diffusion Limited Aggregation

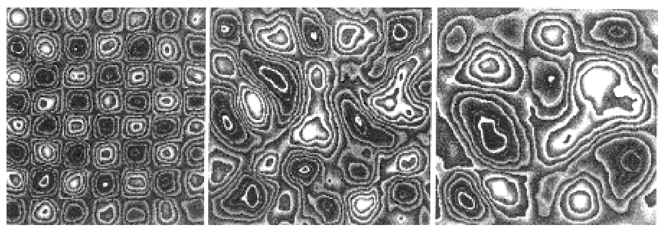




  - Atomic clusters
  - Chemical reactions (A+B $\rightarrow$ C)
  - Smoke in air/latex particles at the surface of water
  - Breath figures

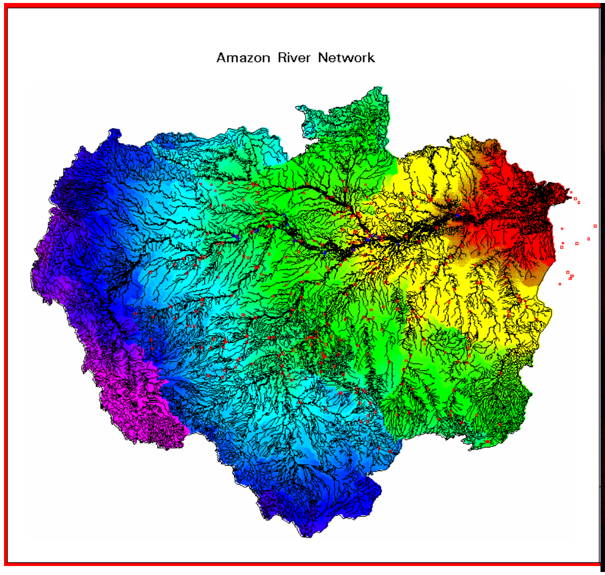



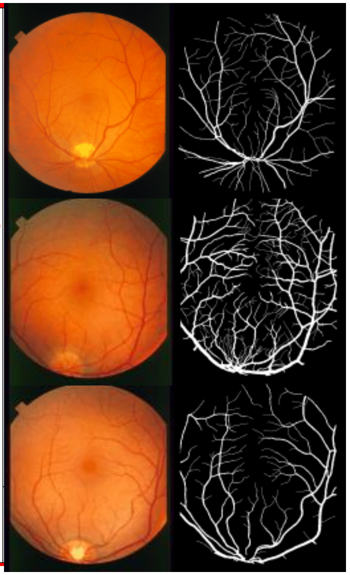
But Also…

- Two-dimensional decaying turbulence



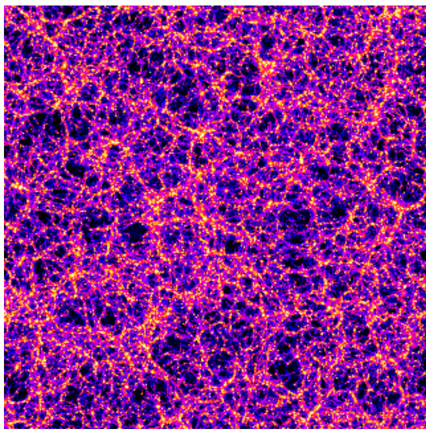
- Epidemics spreading (S+H → S+S, S → H, or S → Ø…)
- Formation of river and vascular networks

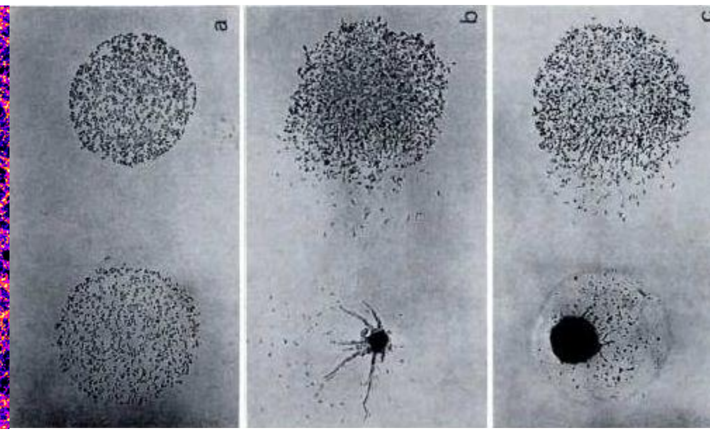


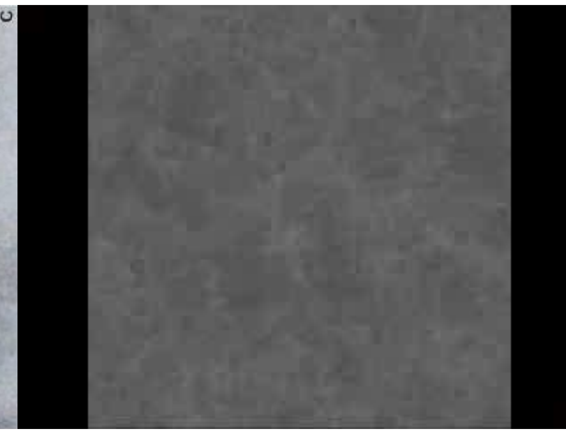


And Even…

- Galaxy… or bacteria clusters





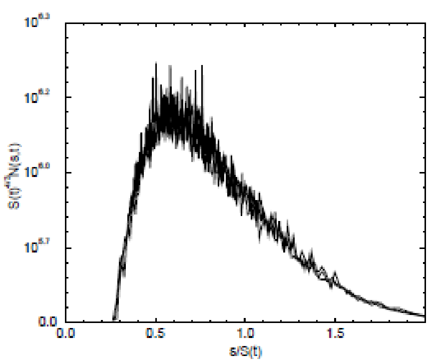


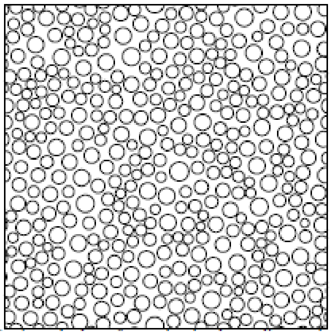
- Poker tournaments (players "aggregate", chips are conserved…)

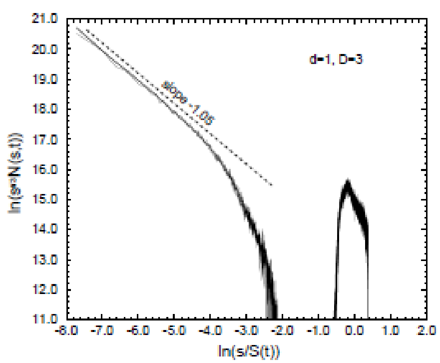
- … and the reverse and similar problem of **fracture** (A → A+A)

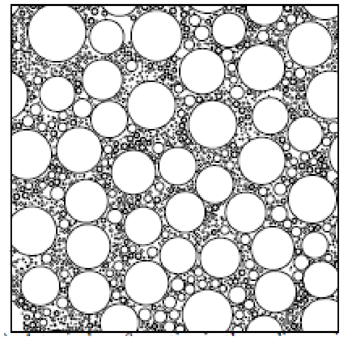
Important Features

- Importance of **conservation laws**: mass, energy, momentum, or more exotic quantities (flow of a river, chips in a poker tournament…)
- Important quantities: **distribution of cluster masses** (or joint distribution of conserved quantities), number of remaining clusters…
- This distribution of "mass" can be **mono or polydisperse** and is often **scale invariant**: $P(m,t) = t^{-\beta} f(m/t^{z})$









Important Features

- Importance of the **diffusive** or **ballistic** motion of clusters
- Possibility of obtaining **compact** or **fractal** clusters
- The **mean-field approach** (neglecting spatial correlations) is often incorrect in low effective dimensions (typically $d \leq 2$ or even $d \leq 4$ for diffusion processes)
- Out of equilibrium reaction/aggregation processes can lead to **dynamical phase transitions** (directed percolation…)

A Few Selected Topics

- **Simple reaction-diffusion processes:**
  A+A $\longrightarrow$ Ø; A+B $\longrightarrow$ Ø; A+A $\longrightarrow$ A
  (application to a river network, in the latter case)

- **Monodispersity (bell-shaped mass distribution)**
  & polydispersity (power-law mass distribution)
  in the framework of Smoluchowsky's approach
  (application to breath figures and… poker tournaments)

- **Dynamical phase transitions:**
  A+A $\longrightarrow$ Ø, A $\longrightarrow$ (n+1)A
  (n odd: directed percolation; n even: parity conserving)

Reaction-Diffusion Processes

- **The reaction** $\mathrm{A}+\mathrm{A} \rightarrow \varnothing$

  Mean-field approach:

$$\frac{d\rho}{dt} = -2\times k\times \rho^2, \quad \rho(t) = \frac{1}{\frac{1}{\rho(0)}+2kt} \sim \frac{1}{2kt}$$

In fact, there is a strong **depletion effect** near surviving particles:

$$\rho(t) \sim L^{-d}(t) \sim t^{-d/2}, \quad d \leq 2$$

$$\rho(t) \sim \frac{\ln t}{t}, \quad d = 2$$

And the mean-field approximation is **exact** in $d > d_c = 2$

The mean-field decay is the **fastest** and can be realized by stirring the solution (hence eliminating **spatial correlations**)

Reaction-Diffusion Processes

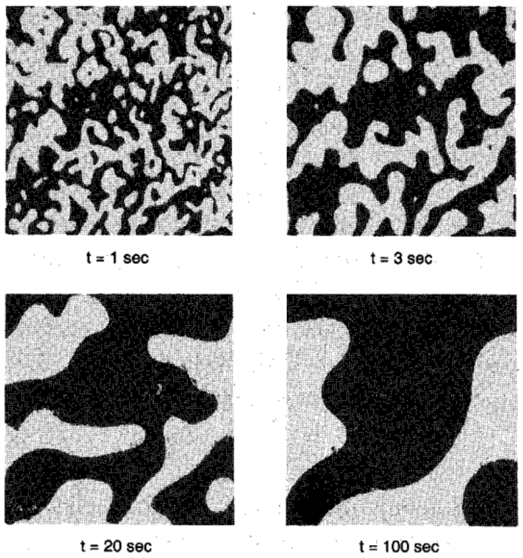
- **The reaction** A+B $\rightarrow \varnothing$

  Mean-field approach: $\dfrac{d\rho_A}{dt} = -k \times \rho_A \times \rho_B,$

$$\rho_A(t) \approx \rho_A(0)\exp\left(-kt\left[\rho_B(0)-\rho_A(0)\right]\right), \text{ if } \rho_A(0) < \rho_B(0)$$

$$\rho_A(t) = \frac{1}{\frac{1}{\rho_A(0)}+kt} \sim \frac{1}{kt}, \text{ if } \rho_A(0) = \rho_B(0)$$

In fact, when $\rho_A(t) = \rho_B(t)$ there is again a very strong **depletion effect** giving rise to **segregation** of the particles



Reaction-Diffusion Processes

- **The reaction** A+B $\rightarrow$ Ø, for $\rho_A(0) = \rho_B(0)$

A physical argument:

Initially, in a region of linear size L, $|\rho_A(0) - \rho_B(0)| \sim L^{-d/2}$

The species in excess will **dominate** in this region, and L is ultimately the **diffusion length**, $L(t) \sim t^{1/2}$. Hence,

$$\rho(t) \sim t^{-d/4}, \quad d \leq 4$$

$$\rho(t) \sim \frac{\ln t}{t}, \quad d = 4$$

And the mean-field approximation is **exact** in $d > d_c = 4$

Reaction-Diffusion Processes

- **The reaction** $\mathrm{A}+\mathrm{A} \rightarrow \mathrm{A}$

  Mean-field approach:

$$\frac{d\rho}{dt} = -k \times \rho^2, \quad \rho(t) = \frac{1}{\frac{1}{\rho(0)} + kt} \sim \frac{1}{kt}$$

  Same **depletion effect** as for $\mathrm{A}+\mathrm{A} \rightarrow \varnothing$:

$$\rho(t) \sim L^{-d}(t) \sim t^{-d/2}, \quad d \leq 2$$

$$\rho(t) \sim \frac{\ln t}{t}, \quad d = 2$$

And the mean-field approximation is again **exact** in $d > d_c = 2$

Reaction-Diffusion Processes

- **The reaction** $\mathrm{A}+\mathrm{A} \rightarrow \mathrm{A}$ **with conservation of "mass"**

  Mean-field approach (Smoluchowsky's equation):

$$\frac{d\rho}{dt}(m,t)=k\int_0^m \rho(m-s,t)\rho(s,t)\,ds-2k\rho(m,t)\rho(t),$$

with $\rho(t)=\int_0^{+\infty}\rho(m,t)\,dm, \quad and \quad m_{tot}=\int_0^{+\infty}m\rho(m,t)\,dm$

Mean-field solution: $$\rho(m,t)=\frac{\exp\left(-\frac{m}{m_{tot}kt}\right)}{m_{tot}(kt)^2}$$

Only correct in $d>d_c=2$

Reaction-Diffusion Processes

- **The reaction $A + A \to A$ with conservation of "charge" and constant injection of particles (mass distribution $I(m)$)**

Mean-field approach (Smoluchowsky's equation):

$$\frac{d\rho}{dt}(m,t) = k\int_{-\infty}^{+\infty} \rho(m-s,t)\rho(s,t)\, ds - 2k\rho(m,t)\rho(t) + I(m),$$

with $m_{tot} = \int_{-\infty}^{+\infty} m\rho(m,t)\, dm + \langle I \rangle t$

General *scaling solution:* $\rho(m,t) = m^{-\tau} f(m/t^z),$

with $f(0) \underset{x\to 0}{\sim} 1,$ and $f(x) \underset{x\to +\infty}{\sim} \exp(-x)$

$$\langle I \rangle > 0: \; z_{\text{MF}} = 2, \; z_{d=1} = \frac{3}{2}, \text{ and } \tau = 2 - \frac{1}{z}$$

$$\langle I \rangle = 0: \; z_{\text{MF}} = 1, \; z_{d=1} = \frac{3}{4}, \text{ and } \tau = 3 - \frac{2}{z}$$

Polydispersity

$(d_c = 2)$

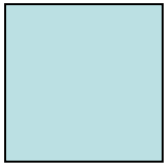
Reaction-Diffusion Processes

➢ Application to the formation of a river network

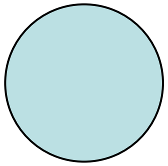
- **Fractal** dimension:

$$d_f = \frac{4}{3}$$

- The "next" river is **~ 3 x longer** than the previous one

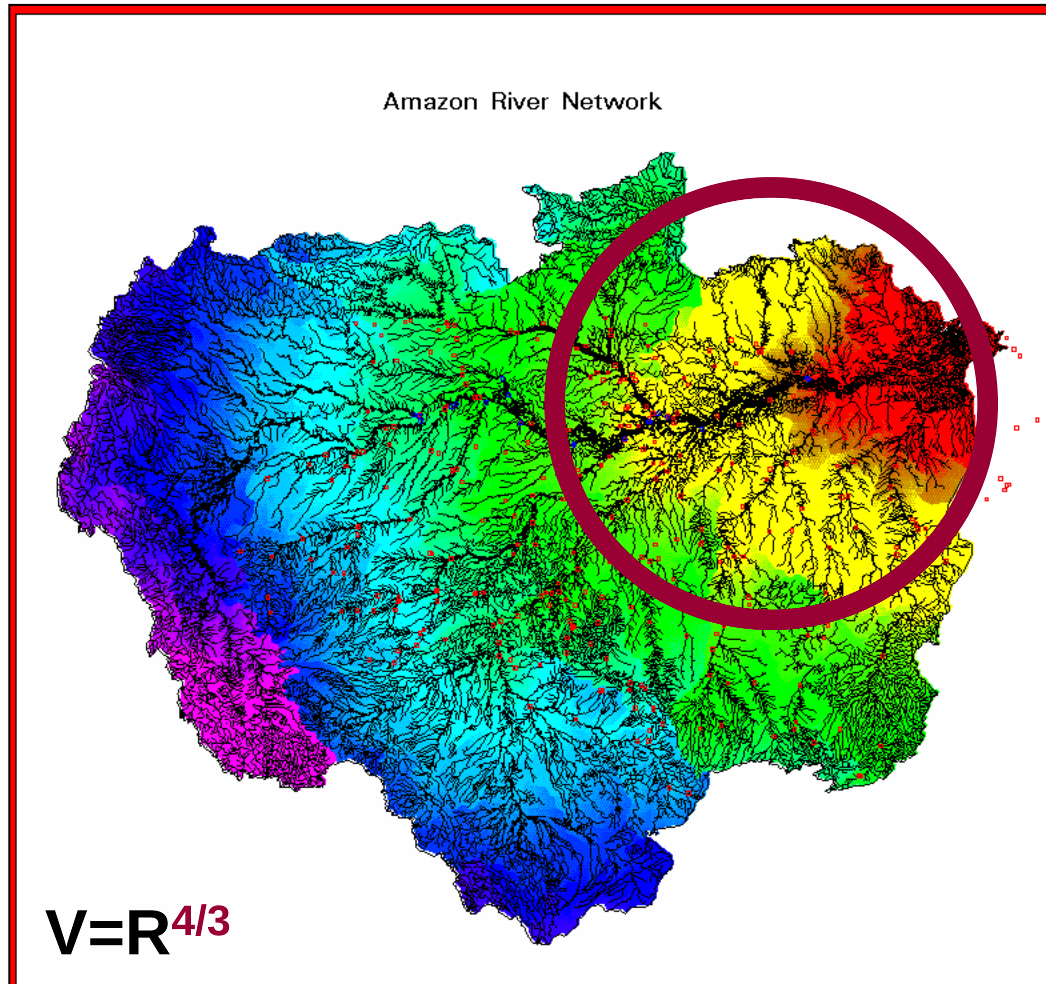


$V=R^2$



$V=\pi R^2$

$V=R^3$



General Mean-Field Approach

A general physical aggregation process is described by:

- Conservation law(s): $m = m_1 + m_2$
- Nature of the collision/aggregation physical process: the merging Kernel, $K(m_1, m_2)$

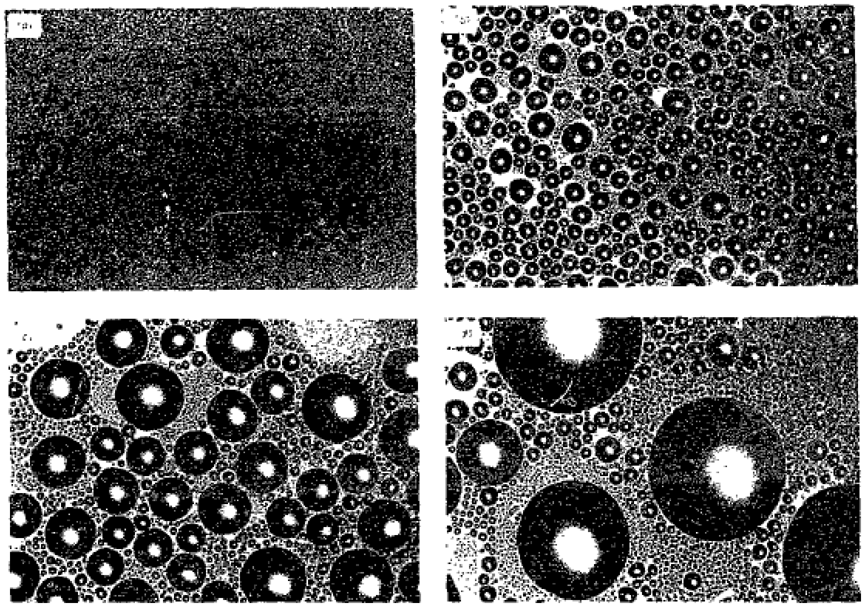
  Ex: d-dimensional "cross-section" $\sigma \sim R^d$ and $m \sim R^D$

$$K(m_1, m_2) = \left(m_1^{1/D} + m_2^{1/D}\right)^d$$

- Intrinsic growth of clusters

$$\dot{m} = v(m,t)$$

- Deposition: $+I(m,t)$
- Fracture Kernel $m \to m_1 + m_2$
- …



General Mean-Field Approach

A general physical aggregation process is described by:

$$\frac{\partial \rho}{\partial t}(m,t) + \frac{\partial}{\partial m}\left[v(m,t)\rho(m,t)\right] = \int_{-\infty}^{+\infty} K(m-s,s)\rho(m-s,t)\rho(s,t)\,ds$$

$$-2\rho(m,t)\int_{-\infty}^{+\infty} K(m,s)\rho(s,t)\,ds$$

$$+I(m,t) + \text{Fracture} + \ldots$$

Can describe many physical situations and can lead to mono and polydispersity and even gelation…

General Mean-Field Approach

The general case of pure aggregation $(v(m,t)=0,\ I(m,t)=0)$

- Assume that the collision Kernel satisfies

$$K(\alpha m_1,\alpha m_2)=\alpha^{\lambda}K(m_1,m_2)$$

$$K(m_1,m_2)\sim m_1^{\mu}m_2^{\lambda-\mu},\ \text{for } m_2 \gg m_1$$

Ex: $K(m_1,m_2)=\left(m_1^{1/D}+m_2^{1/D}\right)^d$

$$\lambda=d/D,\ \mu=0$$

- Then (Van Dongen and Ernst), there is a precise **mono/polydispersity criterion**: $\rho(m,t)=m^{-\tau}f(m/t^{z});\ f(0)\sim 1$
  - $\mu<0$: the mass distribution is **monodisperse** $(\tau\le 0)$
  - $\mu>0$: the mass distribution is **polydisperse** with $\tau=1+\lambda$
  - $\mu=0$: the mass distribution is **polydisperse** with $\tau<1+\lambda$

$\tau=2-\int_0^{+\infty}x^{\lambda-\tau}f(x)\,dx$ can be determined by

perturbative and **non-perturbative** methods

Scaling in Poker Tournaments

- Scaling distribution of fortunes (stacks):

$$P(x,t) = \frac{N(t)}{\bar{x}(t)} f\left(\frac{x}{\bar{x}(t)}\right)$$

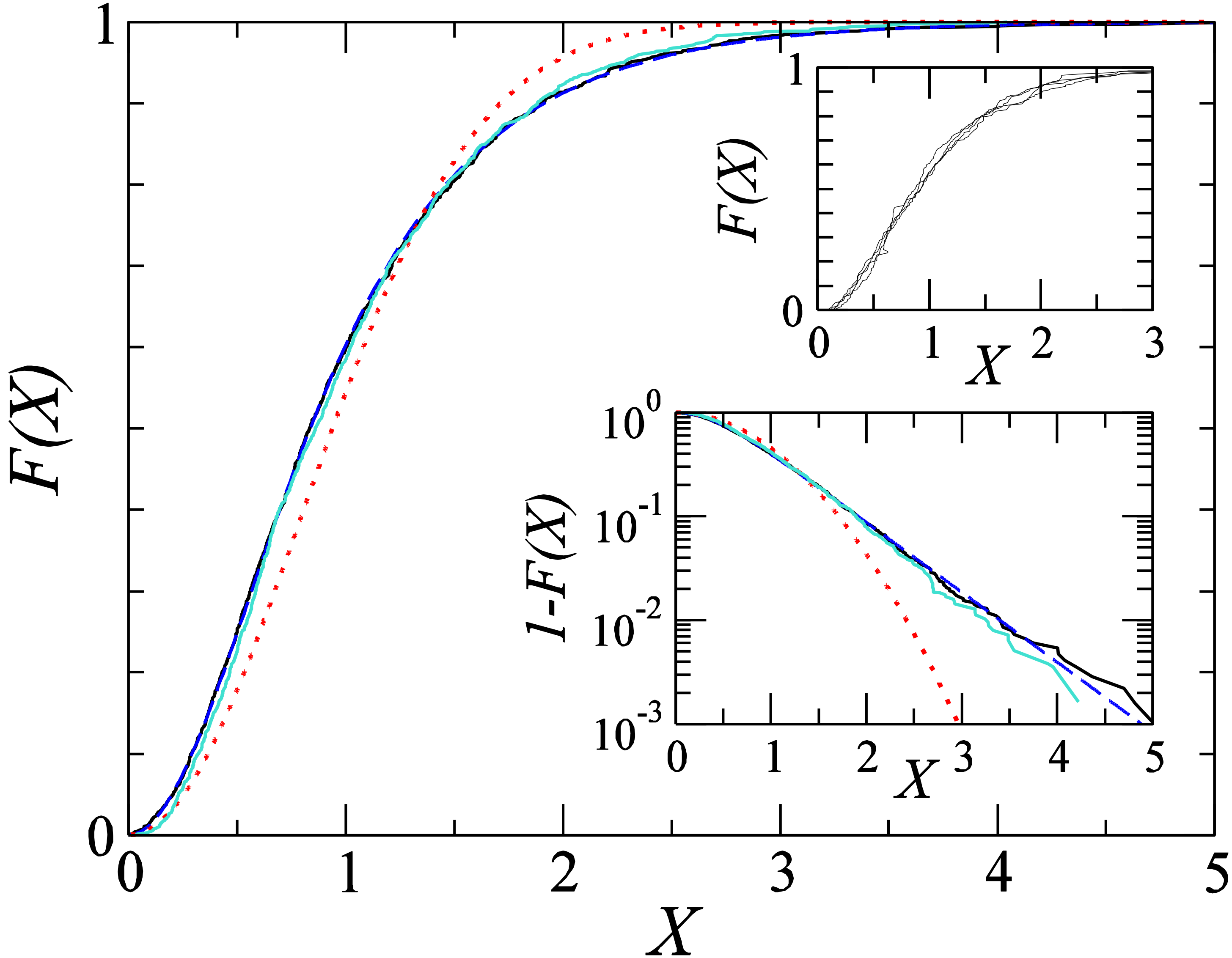
$$N(t) = \frac{\lambda}{\bar{x}(t)} \sim N_0 \exp(-t/t_0)$$

- Scaling equation (integro-differential and non-linear; *no parameter*):

$$f''(X) + Xf'(X) + \tfrac{1}{2} f(X/2) \int_{X/2}^{+\infty} f(Y)\, dY$$
$$+ \int_0^{X/2} f(X-Y) f(Y)\, dY$$
$$+ \tfrac{1}{2} \int_0^{+\infty} f(X+Y) f(Y)\, dY = 0$$

Internet & WPT Data

(20-10000$ buy-in)



Dynamical Phase Transitions

Consider the reaction/breakdown process for diffusing particles: A+A $\longrightarrow$ Ø (rate k), A $\longrightarrow$ (n+1)A (rate p)

Mean-field approach:

$$\frac{d\rho}{dt} = -2k\rho^2 + np\rho,$$

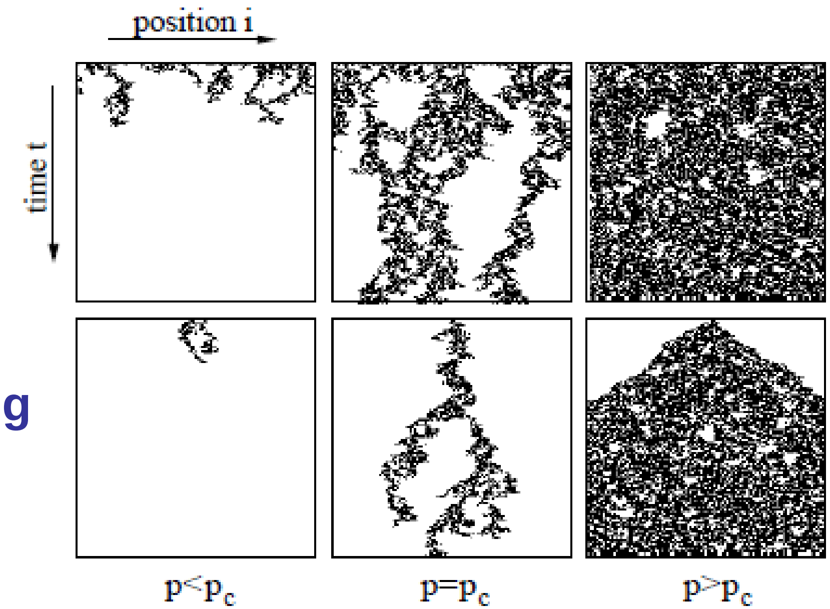
- $\rho(\infty,\lambda) = \frac{n}{2k}(p - p_c)^{\beta}$, with $p_c = 0,$ and $\beta = 1$
- $\rho(t, p_c) \sim t^{-\delta}$, with $\delta = 1$

Mean-field completely fails in describing the fact that for $d<d_c$, one has $p_c>0$, and **different universality classes** depending on the **parity of n**

Dynamical Phase Transitions

Odd n: the directed percolation (DP) universality class

Absorbing State



Active State

$d_c = 4$; for $d = 1$, $\beta \approx 0.276486(6)...$ and $\delta \approx 0.159464(6)...$

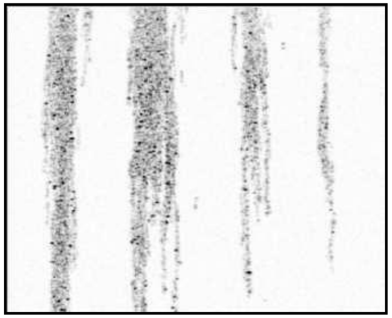
- Best theoretical estimate in $d = 1$: $\beta = \left(1 - 1/\sqrt{5}\right)/2 = 0.276393...!$
- Field theoretical methods available for d close to d_c ($\beta = 1 - \varepsilon/6 - 0.01128\varepsilon^2 ...;\ \varepsilon = 4 - d$)

Dynamical Phase Transitions

Odd n: the directed percolation (DP) universality class

- DP universality class is **ubiquitous** in out of equilibrium physics and is thus **very robust** (adding the reaction A+A $\rightarrow$ A does not change anything…),… except in the presence of **disorder**

- In principle, many possible **experimental realizations**:
  - Catalytic reactions on a surface ($CO+O \rightarrow CO_2$)
  - Growing interfaces
  - Flowing granular matter
  - Porous media
  - **Turbulent liquid crystals**
  - …



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Dynamical Phase Transitions

DP universality class observed in d=2+1 (time) in turbulent liquid crystals

(intermittent regimes between to dynamic scattering modes – DSM)

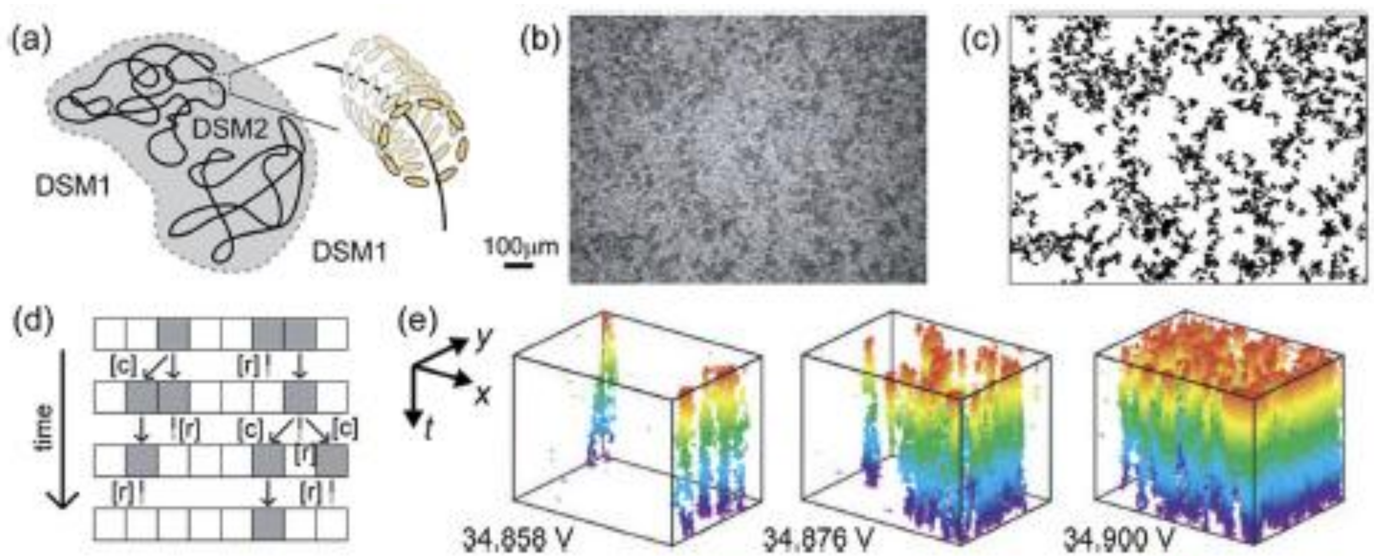
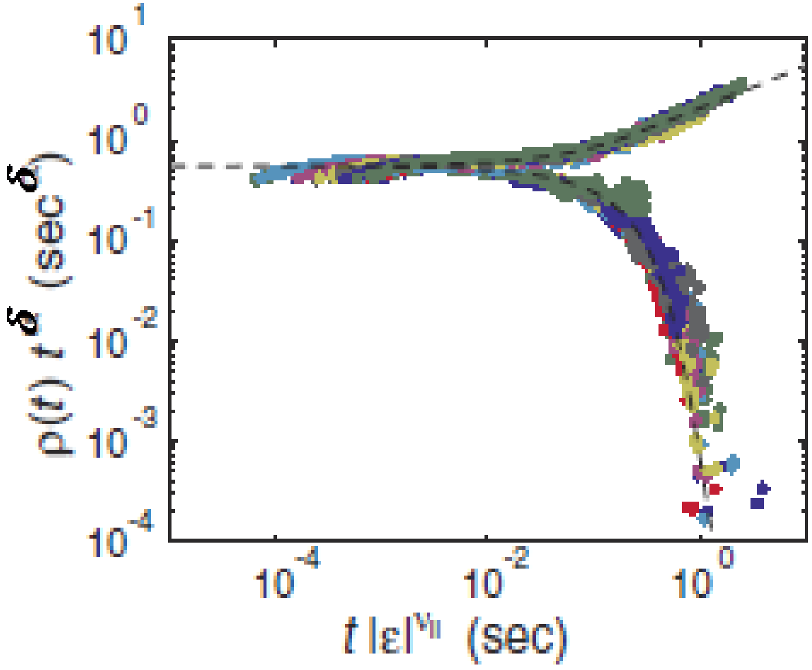


FIG. 1 (color online). Spatiotemporal intermittency between DSM1 and DSM2. (a) Sketch of a DSM2 with its many entangled disclinations, i.e., loops of singularities in orientations of liquid crystals. (b) Snapshot taken at 35.153 V. Active (DSM2) regions appear darker than the absorbing DSM1 background. See also Movie S1 [8]. (c) Binarized image of (b). See also Movie S2 [8]. (d) Sketch of the dynamics: DSM2 domains (gray) stochastically contaminate [c] neighboring DSM1 regions (white) and/or relax [r] into the DSM1 state, but do not nucleate spontaneously within DSM1 regions (DSM1 is absorbing). (e) Spatiotemporal binarized diagrams showing DSM2 regions for three voltages near the critical point, namely, 34.858, 34.876, and 34.900 V. The diagrams are shown in the range of 1206 μm $\times$ 899 μm (the whole observation area) in space and 6.6 s in time.

Dynamical Phase Transitions

DP universality class observed in $d=2+1$ (time) in turbulent liquid crystals (scaling function)



$$\rho(t) \sim t^{-\delta} f\left(\varepsilon t^{1/\nu_\parallel}\right);\ \varepsilon = p - p_c$$

$$\left(f(0) = 1;\ f(x) \underset{x\to+\infty}{\sim} x^{\beta};\ \delta = \beta/\nu_\parallel;\ f(x) \underset{x\to-\infty}{\sim} \exp(-|x|) \right)$$

Dynamical Phase Transitions

Even n: the parity conserving (PC) universality class
(a "theorist's curiosity")

- $d_c > 1$, but $d_c \leq 5/3 < 2$!
- Different critical exponents from DP (in $d = 1$, $\beta \approx 0.4$, $\delta \approx 0.2$)
- Strong numerical corrections to scaling (DP ???)
- No analytical (even approximate) results available

Conclusion

Reaction/aggregation processes:

- Are **ubiquitous** in Nature
- Appear at **all spatial and temporal** scales
- Offer **rich physical properties** (dynamical phase diagram, fractals, dynamical scaling…)
- Involve all the **modern tools of theoretical physics** (field theory, renormalization group, perturbative and non perturbative methods, sophisticated numerical methods…)

Thank you for your attention