Effective rates in dilute advection-reaction systems

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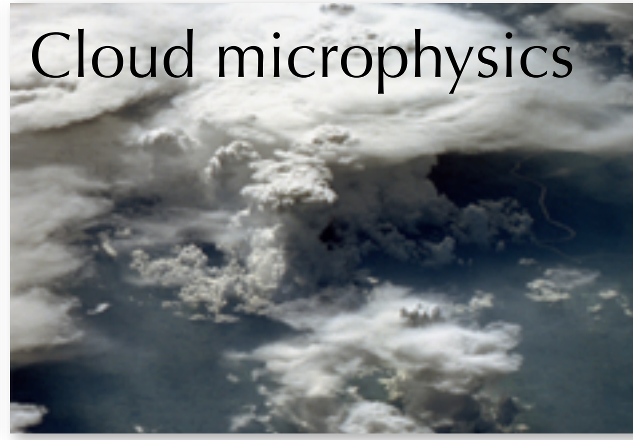
Dilute reactive systems

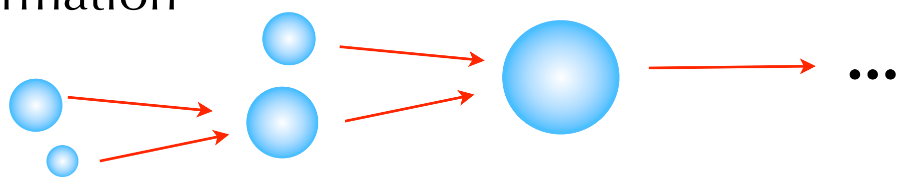


- Transport + reactions modeled by (mean-field) kinetic equations
  $\partial_t \rho + \nabla \cdot (\rho\, \boldsymbol{v}) = R[\rho] + \kappa \nabla^2 \rho$
  Does this apply to very dilute settings?
  (very few particles at the scales of the variations of $\boldsymbol{v}$)

Example: warm-cloud droplets

- Size distribution of droplets?

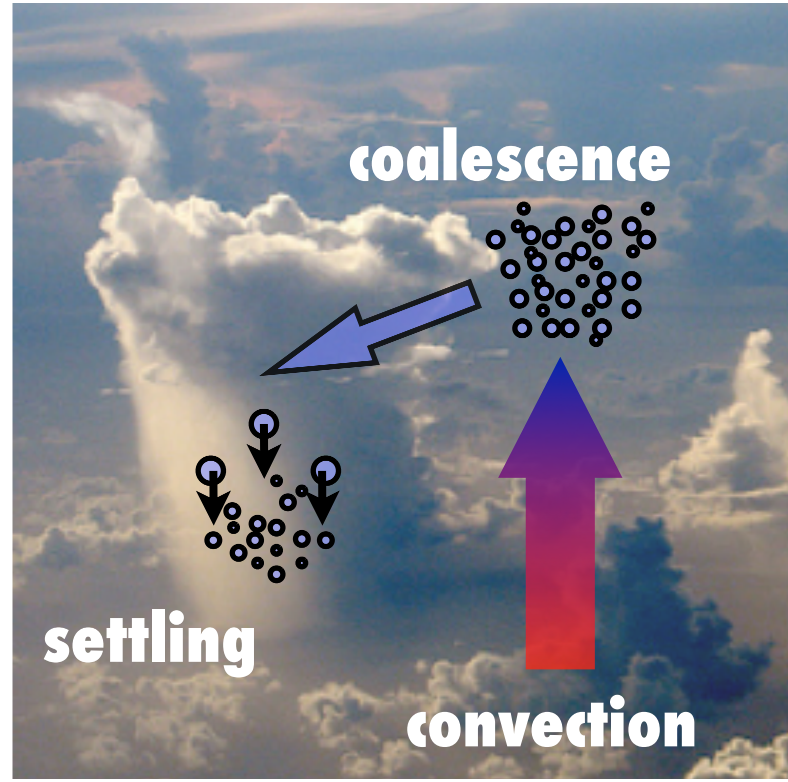
Quantifying the growth by coalescence is required to understand timescales of rain formation



- Traditional (mean-field) approach

Smoluchowski coagulation

$$\partial_t N(m,t) = \frac{1}{2}\int_0^m Q(m', m-m')N(m',t)N(m-m',t)\mathrm{d}m' - \int_0^\infty Q(m',m)N(m',t)N(m,t)\mathrm{d}m'$$



Effects of turbulence and diluteness?

Stratocumulus cloud: droplet diameter ≃ few μm

≲ 1 droplet / mm^3

ℓ_K ≃ 1 mm (Kolmogorov turbulent dissipative scale)

L ≃ 100-1000 m (largest scale of turbulence)

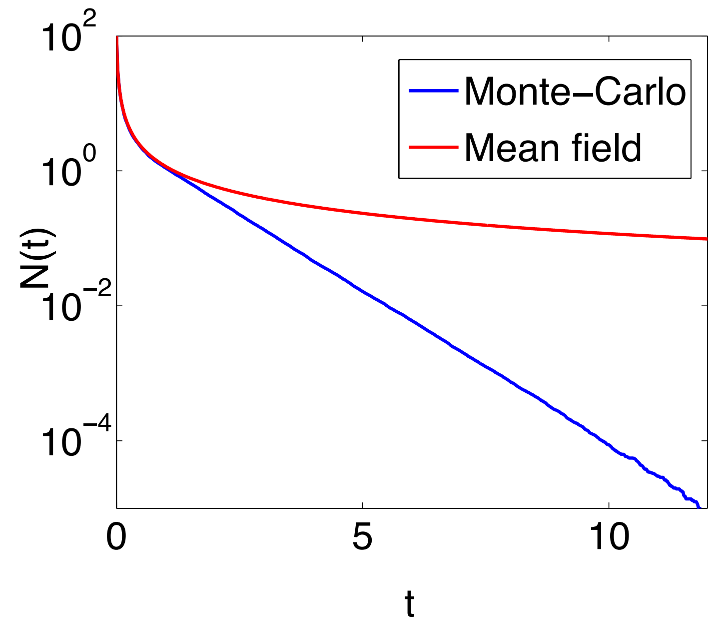
Finite-number effects

- **Annihilation process** $A + A \xrightarrow{\mu} \varnothing$

Mean field: $$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mu\,\rho^2$$

$$\Rightarrow\ \rho(t) = \frac{\rho_0}{1 + \mu\,\rho_0\,t}$$

Does not work predict the large-time behavior



- **Reaction-diffusion** [cf. works of Cardy, Doi, Gardiner, Glauber, Peliti...]

Fluctuations due to diluteness can be modeled by a multiplicative (imaginary) noise:

$$\partial_t \rho = R[\rho] + \kappa \nabla^2 \rho + G[\rho]\xi(t)$$

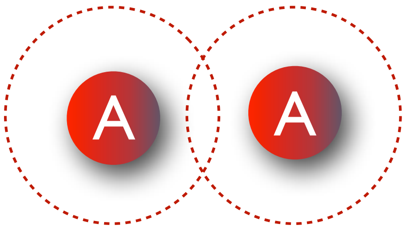
Deal with the full master equations on the lattice, make use of Poisson representation/coherent states decomposition...

Advection-reaction

- Previous approach does not straightforwardly extend

$$\frac{\mathrm{d}\boldsymbol{X}_j}{\mathrm{d}t} = \boldsymbol{v}(\boldsymbol{X}_j, t) + \sqrt{2\kappa}\,\boldsymbol{\eta}_j(t)$$

$\boldsymbol{v}$ prescribed



$\xrightarrow{\mu} \varnothing$ when $|\boldsymbol{X}_j - \boldsymbol{X}_k| < a$

Mean field: $\partial_t \rho + \nabla\cdot(\rho\,\boldsymbol{v}) = -\gamma\rho^2 + \kappa\nabla^2\rho$ $\qquad \gamma \propto \mu\, a^d$

- Underlying assumptions:
  - very large number of particles at the coarse-graining scale $\bar{r}$
  - well-mixing: at that scale, all particles react together, i.e. $\bar{r} \ll a$
  - the flow does not vary at such a scale $\bar{r} \ll \ell_{\mathrm{K}}$

- Here we neglect diffusion (transport is dominant at reaction scales)

$a \gg \ell_{\mathrm{B}}$ $\longleftarrow$ Batchelor scale $\ell_{\mathrm{B}} = (\kappa/\nu)^{1/2}\ell_{\mathrm{K}}$

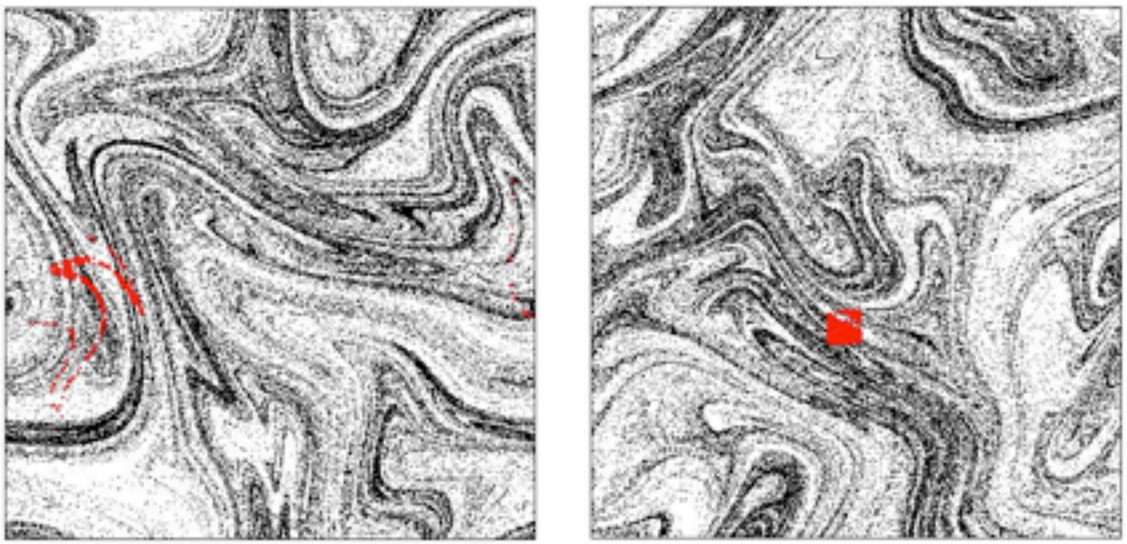
For 1μm water droplet in air $\ell_{\mathrm{B}} \simeq 1\mu m$

Compressible transport

Particles with a small inertia $\boldsymbol{v} \simeq \boldsymbol{u} - \tau_{\rm p} \frac{{\rm D}\boldsymbol{u}}{{\rm D}t}$

Surface flows $\boldsymbol{v}(x,y) = \boldsymbol{u}(x,y,h)$

⇒ characterized by clustering properties



Tracers in a random Gaussian compressible flow

Compressibility

$$\wp = \frac{\overline{(\nabla \cdot \boldsymbol{v})^2}}{\overline{\|\nabla \boldsymbol{v}\|^2}}$$

$\wp = 0$ incompressible

$\wp = 1$ potential

$$\mathrm{Prob}\,\{|\boldsymbol{X}_1 - \boldsymbol{X}_2| < r\} \propto r^{\mathcal{D}_2} \ll r^d$$

- **Combined effects of concentration and diluteness on the reaction rates?**

  How do the correlations in the particle trajectories induced by $\boldsymbol{v}$ enter the game ?

Master equations

- Joint n-point number density

$$\mathcal{F}_n(\boldsymbol{x}_1,\dots,\boldsymbol{x}_n,t) = \left\langle \sum_{i_1\neq\ldots\neq i_n} \delta\left(\boldsymbol{X}_{i_1}(t)-\boldsymbol{x}_1\right)\cdots\delta\left(\boldsymbol{X}_{i_n}(t)-\boldsymbol{x}_n\right)\right\rangle_\mu$$

$\langle\,\cdot\,\rangle_\mu$ $\Rightarrow$ ensemble average with respect to the reactions

$$\mathsf{F}_1(t) = \int \mathcal{F}_1(\boldsymbol{x},t)\mathrm{d}^d x = \langle N(t)\rangle_\mu$$

$$\mathsf{F}_n(t) = \int \mathcal{F}_n(\boldsymbol{x}_1,\dots,\boldsymbol{x}_n,t)\,\mathrm{d}^d x_1\cdots\mathrm{d}x_n = \left\langle \frac{N(t)!}{(N(t)-n)!}\right\rangle_\mu$$

transport

$$\partial_t\mathcal{F}_n + \sum_{i=1}^n \nabla_{\boldsymbol{x}_i}\cdot\left[\boldsymbol{v}(\boldsymbol{x}_i,t)\,\mathcal{F}_n\right] = -\mu\,\mathcal{F}_n\sum_{i<j}\theta(a-|\boldsymbol{x}_i-\boldsymbol{x}_j|)$$

← reaction among the n particles

$$-\mu\sum_{i=1}^n\int\theta(a-|\boldsymbol{x}_i-\boldsymbol{x}_{n+1}|)\mathcal{F}_{n+1}\,\mathrm{d}^d x_{n+1}$$

← one of the n particles react with another

Lagrangian approach

Closed hierarchy if the initial number of particles N_0 is fixed

$$\partial_t \mathcal{F}_{N_0} + \sum_{i=1}^{N_0} \nabla_{\boldsymbol{x}_i} \cdot [\boldsymbol{v}(\boldsymbol{x}_i, t)\, \mathcal{F}_{N_0}] = -\mu\, \mathcal{F}_{N_0} \sum_{i<j} \theta(a - |\boldsymbol{x}_i - \boldsymbol{x}_j|)$$

Characteristics: $\begin{cases} \dfrac{\mathrm{d}}{\mathrm{d}s} \boldsymbol{Y}(s; \boldsymbol{x}_j) = \boldsymbol{v}(\boldsymbol{Y}(s; \boldsymbol{x}_j), s) \\ \boldsymbol{Y}_j(t; \boldsymbol{x}_j) = \boldsymbol{x}_j \end{cases}$ [no reactions]

$$\mathcal{F}_{N_0}(\boldsymbol{x}_1, \dots, \boldsymbol{x}_{N_0}, t) = \left\langle \mathcal{F}^0_{N_0} \mathrm{e}^{-\mu \sum_{i<j} \int_0^t \theta(a - |\boldsymbol{Y}(s, \boldsymbol{x}_i) - \boldsymbol{Y}(s, \boldsymbol{x}_j)|) \mathrm{d}s} \right\rangle_{N_0}$$

$\langle \cdot \rangle_{N_0}$ = average over sets of tracer trajectories satisfying the final condition

⇒ recurrence to solve at an arbitrary order $n \le N_0$

$$\mathcal{F}_n(\boldsymbol{x}_1, \dots, \boldsymbol{x}_n, t) = \left\langle \mathcal{F}^0_n \,\mathrm{e}^{-\Lambda_n(t)} \right\rangle_n$$

$$- \mu \int \left\langle \mathcal{F}^0_{n+1}\, \mathrm{e}^{-\Lambda_n(t)} \sum_{i=1}^{n} \int_0^t \theta(a - |\boldsymbol{Y}(s; \boldsymbol{x}_i) - \boldsymbol{Y}(s; \boldsymbol{x}_{n+1})|)\, \mathrm{e}^{\Lambda_n(s) - \Lambda_{n+1}(s)} \mathrm{d}s \right\rangle_{n+1} \mathrm{d}^d x_{n+1}$$

with $\Lambda_n(t) = \mu \sum_{i<j\le n} \int_0^t \theta(a - |\boldsymbol{Y}(s; \boldsymbol{x}_i) - \boldsymbol{Y}(s; \boldsymbol{x}_j)|)\, \mathrm{d}s.$

Long-time behavior

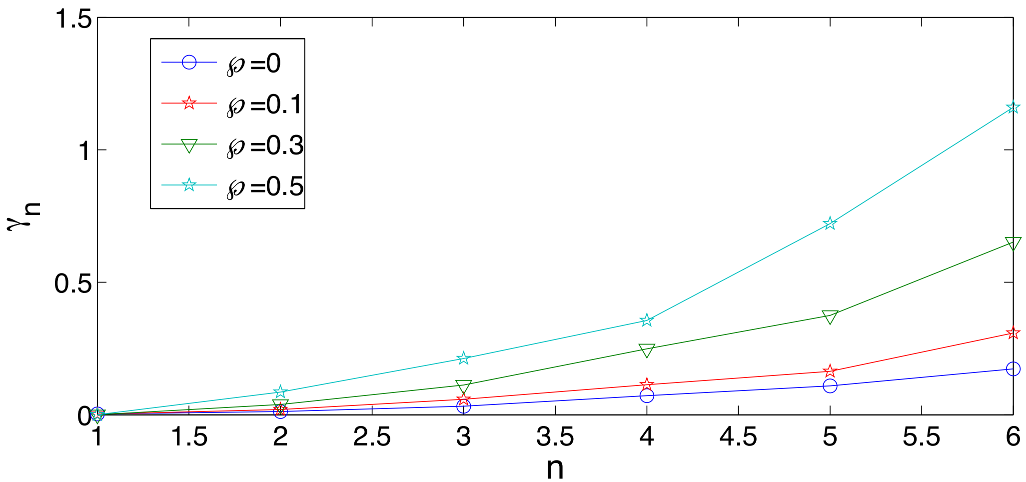
- At large times $\mathcal{F}_n(\boldsymbol{x}_1,\dots,\boldsymbol{x}_n,t) \simeq \left\langle \mathcal{F}_n^0\, \mathrm{e}^{-\mu \sum_{i<j\leq n} \int_0^t \theta(a-|\boldsymbol{Y}(s,\boldsymbol{x}_i)-\boldsymbol{Y}(s,\boldsymbol{x}_j)|\mathrm{d}s} \right\rangle_n$

$$\mathsf{F}_n(t) = \left\langle \frac{N(t)!}{(N(t)-n)!} \right\rangle_\mu \simeq \int \left\langle \mathcal{F}_n^0\, \mathrm{e}^{-\mu \sum_{i<j\leq n} \int_0^t \theta(a-|\boldsymbol{Y}(s,\boldsymbol{x}_i)-\boldsymbol{Y}(s,\boldsymbol{x}_j)|\mathrm{d}s} \right\rangle_n \mathrm{d}^d x_1 \cdots \mathrm{d}^d x_n$$

+ average with respect to the velocity field realizations

$$\overline{\mathsf{F}}_n(t) \simeq \overline{\mathsf{F}}_n(0)\, \mathrm{e}^{-\gamma_n\, t}$$

effective rate γ_n depends on the order
$n \mapsto \gamma_n$ increasing function



← numerics in a random Gaussian velocity field

- Moments are dominated by $n=2$: $\langle N^p(t)\rangle \propto \mathrm{e}^{-\gamma_2\, t}$

Long-time closure

- Long-time behavior dominated by two-particle dynamics

all moments decay with exponential rate $\gamma_2 = \gamma$ $\Rightarrow$ closure $N_0 = 2$

$$n_1(t) \equiv \overline{\langle N(t) \rangle_\mu} = \overline{\mathsf{F}_1(t)}, \qquad n_2(t) \equiv \frac{1}{2}\overline{\langle N(t)\,[N(t)-1] \rangle_\mu} = \frac{1}{2}\overline{\mathsf{F}_2(t)}.$$

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\gamma\, n_2, \qquad \frac{\mathrm{d}n_2}{\mathrm{d}t} = -\gamma\, n_2$$

- Lagrangian approach: $n_2(t) = \overline{\mathrm{e}^{-\mu \int_0^t \theta(a-R(s))\,\mathrm{d}s}}$

$R(t) = |\boldsymbol{Y}_1(t) - \boldsymbol{Y}_2(t)|$ $\qquad \overline{(\cdot)}$ = average over all pairs + velocity realizations

Ergodicity $\Rightarrow$ $\displaystyle \lim_{t\to\infty} \frac{1}{t}\int_0^t \theta(a - R(s))\,\mathrm{d}s = \mathrm{Prob}\,(R(s) < a) = P_2^<(a)$

Heuristically $\gamma_{\mathrm{naive}} = \mu\, P_2^<(a)$ ($\Leftrightarrow$ quenched disorder)

Large deviations

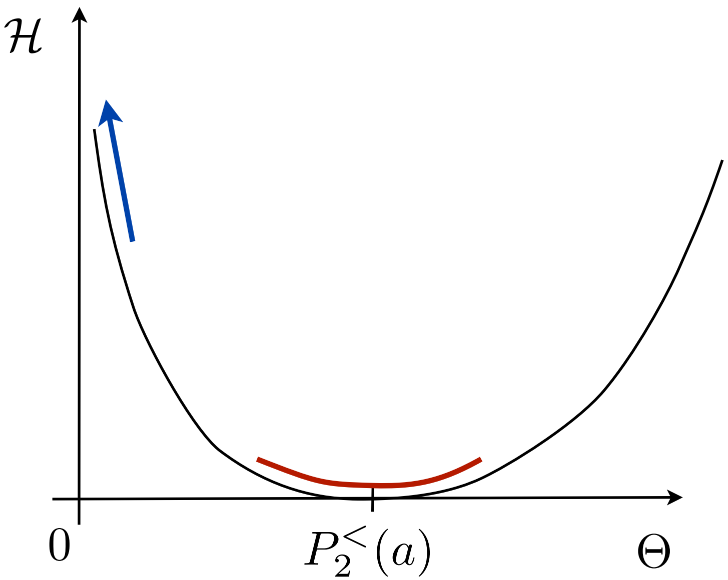
$$\gamma = \lim_{t\to\infty} \frac{1}{t} \ln \left(\overline{e^{-\mu\,\Theta\,t}} \right) \qquad \Theta = \frac{1}{t}\int_0^t \theta(a - R(s))\,\mathrm{d}s$$

fraction of time spent at a distance $\leq a$

- Large deviations of the local time $-\lim_{t\to\infty} \frac{1}{t} \ln p(\Theta) = \mathcal{H}(\Theta)$

Rate function $\mathcal{H} \geq 0$, convex, attaining its minimum equal to 0 for $\Theta = P_2^<(a)$

$$n_2(t) \propto \int_0^\infty e^{-t\,(\mu\,\Theta + \mathcal{H}(\Theta))}\mathrm{d}\Theta \quad \Rightarrow \quad \gamma = \inf_{\Theta \geq 0} [\mu\,\Theta + \mathcal{H}(\Theta)]$$



Central-limit $\mathcal{H}(\Theta) \simeq (\Theta - P_2^<(a))^2/(2\sigma^2)$

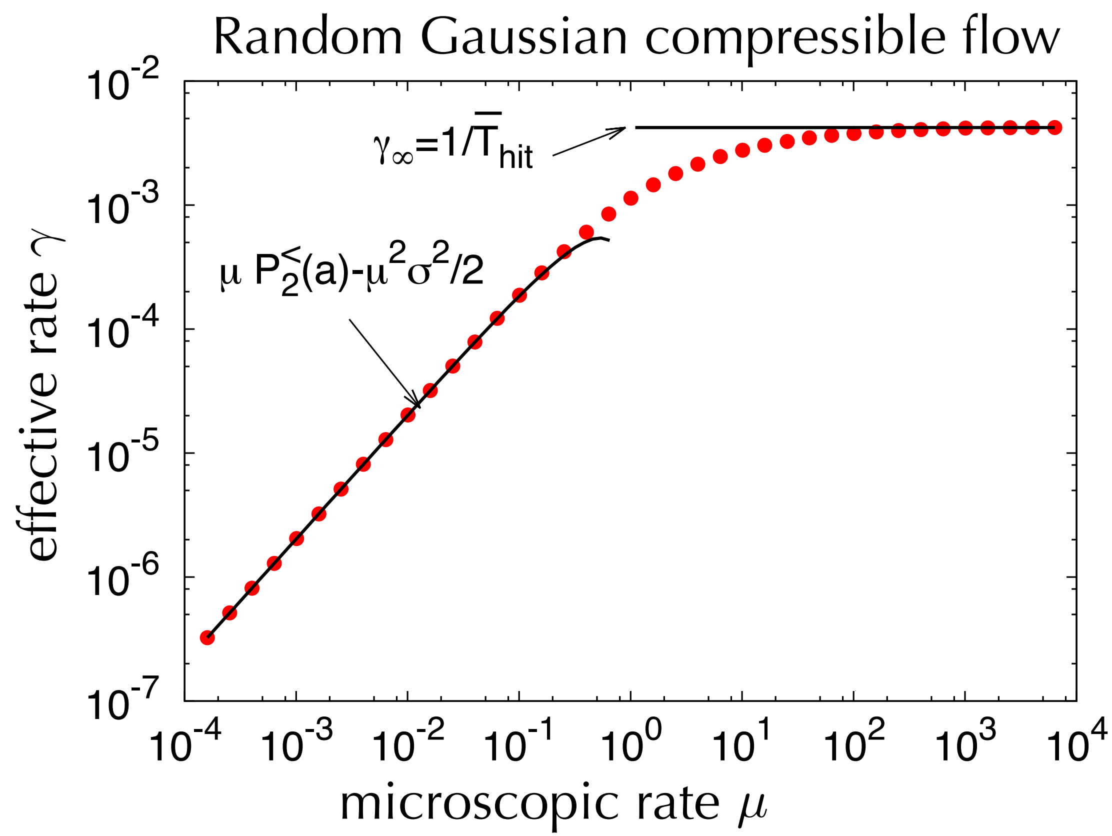
$$\gamma \simeq \mu\, P_2^<(a) - \mu^2\,\frac{\sigma^2}{2} \qquad \mu \to 0$$

Hitting time $\lim_{\mu\to\infty} \gamma = \lim_{\Theta\to 0} \mathcal{H}(\Theta)$

$$= -\lim_{t\to\infty} \frac{1}{t} \ln \mathrm{Prob}\,(T_{\mathrm{hit}} > t)$$

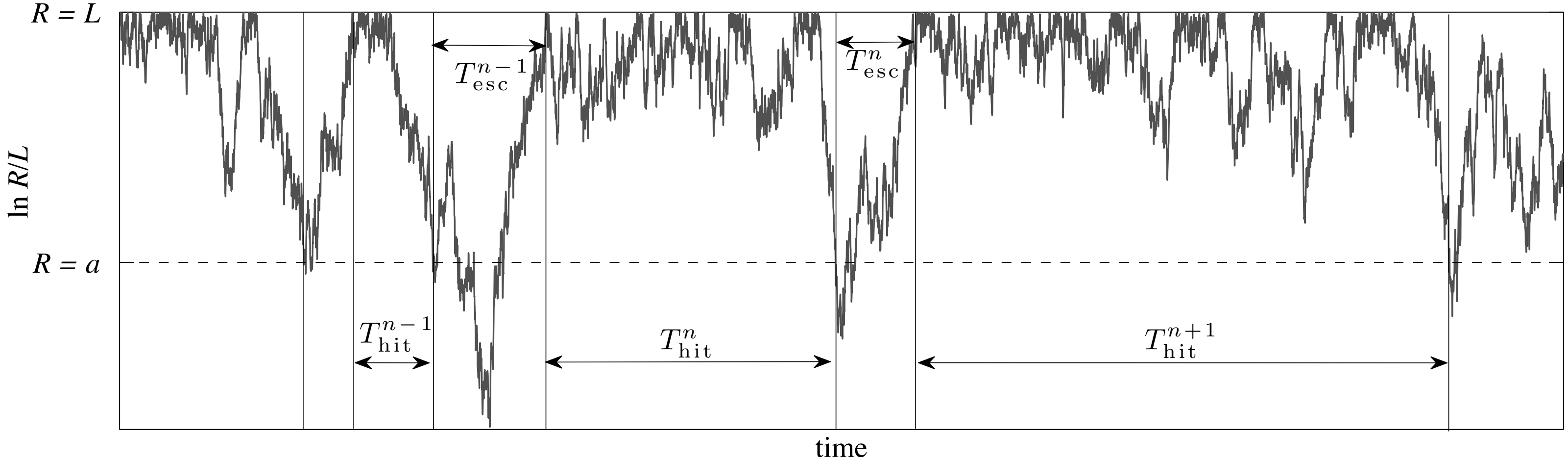
exponential distribution: $\gamma_\infty = \dfrac{1}{\langle T_{\mathrm{hit}} \rangle}$

Effective rate



Phenomenology

- Over-simplification of the dynamics in a bounded domain



$T^n_{\rm hit}$ exponential distribution with average $\overline{T_{\rm hit}}$

$T^n_{\rm esc} \approx T_{\rm esc} = (1/\lambda)\ln(L/a)$ dominated by the exponential separation for $a \ll L$

$$t \approx \sum_{n=1}^{n_{\rm rea}} [T^n_{\rm hit} + T^n_{\rm esc}] \approx \sum_{n=1}^{n_{\rm rea}} T^n_{\rm hit}$$

Time spent below a is assumed $\propto T_{\rm esc}$ $\Rightarrow$ $\Theta = \frac{1}{t}\sum_{n=1}^{n_{\rm rea}} \alpha_n\, T^n_{\rm esc} \approx \frac{n_{\rm rea}}{t}\,\overline{\alpha}\, T_{\rm esc}$

$$\mathcal{H}(\Theta) = \frac{1}{\overline{T_{\rm hit}}} - \frac{\Theta}{\overline{\alpha}\, T_{\rm esc}}\left(1 + \ln\left[\frac{\overline{\alpha}\, T_{\rm esc}}{\Theta\, \overline{T_{\rm hit}}}\right]\right) \quad \text{and} \quad \gamma = \frac{1}{\overline{T_{\rm hit}}}\left[1 - e^{-P_2^<(a)\,\overline{T_{\rm hit}}\,\mu}\right]$$

Kraichnan velocity ensemble

$\boldsymbol{v}$ Gaussian with zero mean and correlation $\overline{v_i(\mathbf{0},t)v_j(\boldsymbol{r},t')} = 2D_{ij}(\boldsymbol{r})\delta(t-t')$

$$D_{ij}(\boldsymbol{r}) = D_0\delta_{ij} - d_{ij}(\boldsymbol{r})/2, \quad d_{ij}(\boldsymbol{r}) = D_1[(d+1-2\wp)\delta_{ij}r^2 + 2(\wp d - 1)r_ir_j]$$

Lyapunov exponents $\lambda_k = D_1[d(d-2k+1) - 2\wp(d+(d-2)k)$ $\qquad 1 \le k \le d$

Separation $R(t)$ diffusive process with generator $M_2 = \dfrac{D_1(d-1)(1+2\wp)}{r^{\mathcal{D}_2-1}}\dfrac{\partial}{\partial r}\left(r^{\mathcal{D}_2+1}\dfrac{\partial}{\partial r}\right)$

Correlation dimension $P_2^<(r) \propto (r/L)^{\mathcal{D}_2}$ $\qquad \mathcal{D}_2 = \dfrac{d-4\wp}{1+2\wp} = d - \wp\dfrac{2(d+2)}{1+2\wp}$

Lognormal separations: $x(t) = \ln(R(t)/L)$ is a Brownian motion with drift (Gawedzki & Horvai 2004)

$$\mathrm{d}x(t) = \lambda_1\,\mathrm{d}t + \sqrt{2\Delta}\,\mathrm{d}W(t) \qquad \begin{cases}\lambda_1 = D_1(d-1)(d-4\wp)\\ \Delta = D_1(d-1)(1+2\wp)\end{cases}$$

Generator: $\tilde{M}_2 = \lambda_1\dfrac{\partial}{\partial x} + \dfrac{\Delta}{2}\dfrac{\partial^2}{\partial^2 x}$ $\qquad$ + reflective BC at $x = 0$

Feynman–Kac

$$n_2(t) = \overline{\mathrm{e}^{-\mu \int_0^t \theta(a-R(s))\,\mathrm{d}s}}$$

$$\psi(x,t) = \overline{\left[e^{-\mu \int_0^t \theta(\log(a/L)-x(s))\mathrm{d}s} \middle| x(0)=x \right]}$$

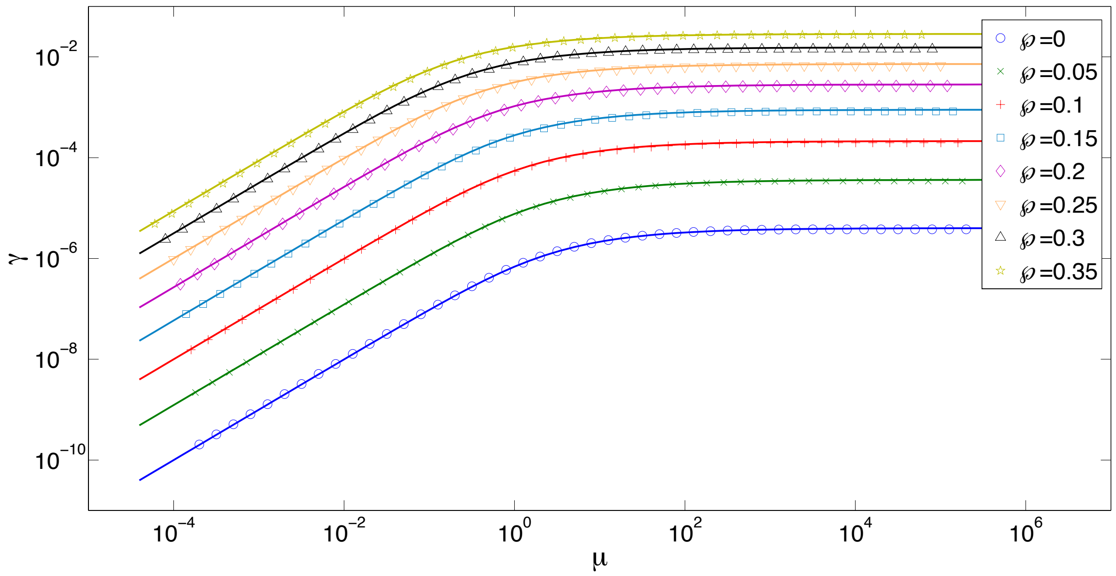
[Donsker–Varadhan 1975]

Feynman–Kac formula: $\dfrac{\partial \psi}{\partial t} = \tilde{M}_2 \psi - \mu\theta(\log(a/L) - x)\psi$

with the boundary conditions $\psi(x,0) = 1$, $\psi|_{x=-\infty} = 0$ and $\left.\dfrac{\partial \psi}{\partial x}\right|_{x=0} = 0$

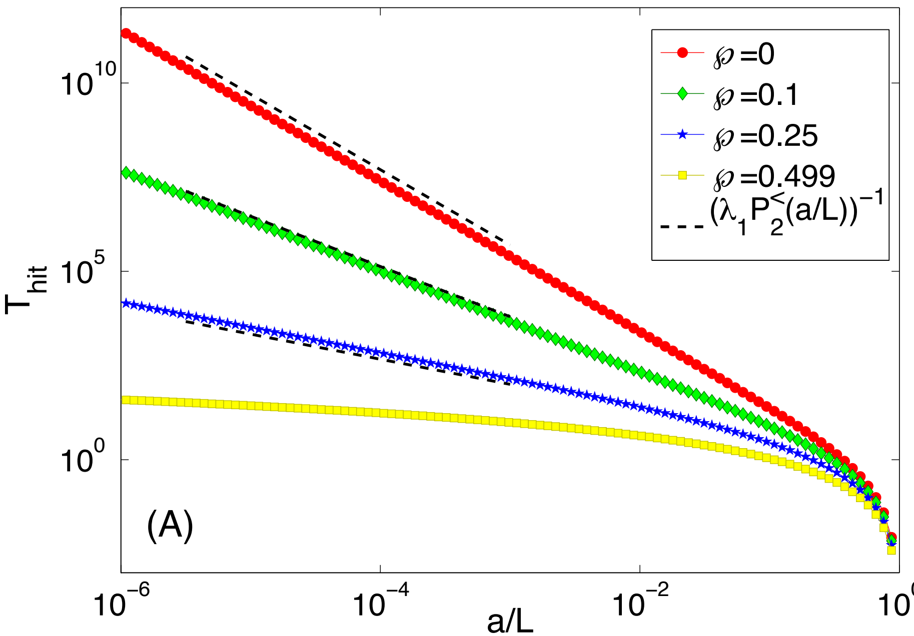
Effective rate γ = largest eigenvalue of $\mathcal{L} = \tilde{M}_2 - \mu\theta(\log(a/L) - x)$

Transcendental equation: $\gamma = \inf\{\sigma : F(\sigma; \lambda_1, \Delta) = 0\}$



Dependence on parameters

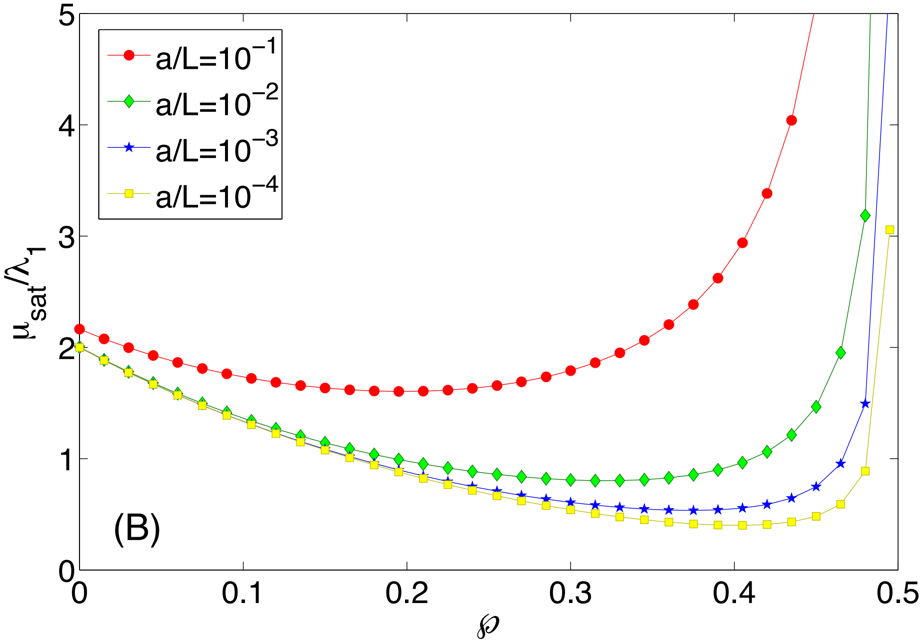
Dependence on the reaction scale a



$\overline{T_{\mathrm{hit}}} \sim (1/\lambda_1) P_2^<(a)$ when $a \ll L$

Kac recurrence lemma

Dependence on compressibility $\wp$



Non-monotonic behavior

Conclusions

- Effective reaction rates relate to two-particle dynamics and to the large deviations of the local time spent at a distance smaller than the interaction radius

- The effective rate can be computed for particles transported by velocities given by the compressible smooth Kraichnan model

- Extension to the non-smooth case: in Kraichnan, the distance is then a Bessel process. Local time statistics?

- The proposed formalism extends to more complicated dynamics
  Ex: inertial particles with a position/velocity phase-space dynamics and reaction rates that depend on both distances and velocity differences