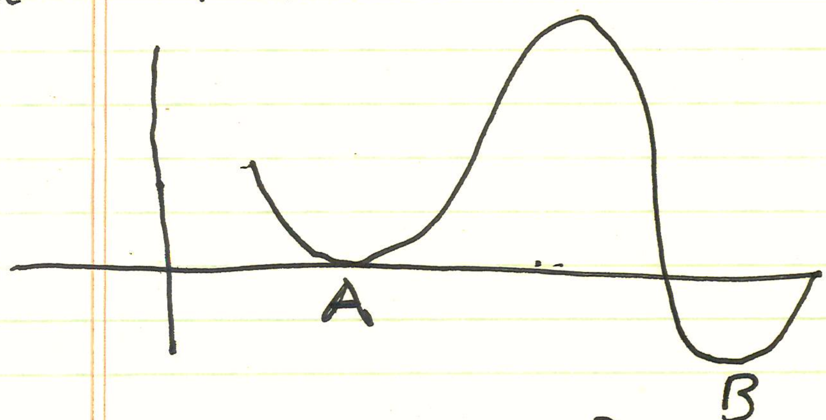
Kinetics IV : First Passage Times, Coagulation of Colloids, & Theory of Aggregation

i.) First Passage Time

Basic Question :

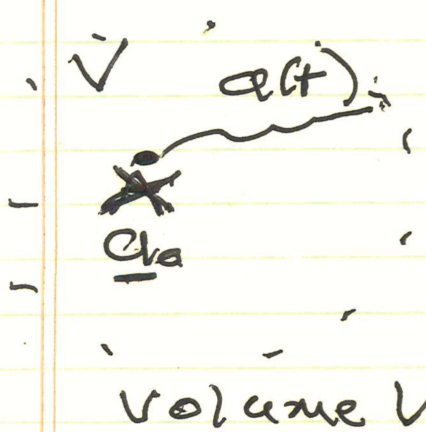
a la' Kramers



What is (average) time for A → B.
More generally, $P(T_{AB})$?

* [More precisely, what is time for first transit (passage) from A → B ?]

→ First Passage Time



$$\frac{dq}{dt} = \underline{V}(q) + \underline{\tilde{F}}(t)$$

surface ∂V (absorbing)

passage time distributed ↓
T distributed due noise !

→ First passage time is time to leave V. Noise → variable trajectory.

* → so $P(\underline{q}, t)$ → distribution of points not left at t is

$$P(\underline{q}, 0) = \delta(\underline{q} - \underline{q}_0)$$

starting pt.

$$P(\underline{q}, t)\Big|_{\partial V} = 0$$

Where:

$$\frac{\partial P}{\partial t} = \mathcal{D} P$$

→ F-P operator

$$= -\underline{\nabla}_q (\underline{v}(q) P) + \underline{\nabla}_q \cdot \underline{\underline{D}} \cdot \underline{\nabla}_q P$$

Now, for mean first passage time:

- $P \xrightarrow[t \to \infty]{} 0$ as all points leave, eventually and so encounter absorbing boundary.

so

- # of particles still confined at t is:

$$S(t) = \int_V dq \; P(q, t)$$

obviously, $\lim_{t \to \infty} S(t) \to 0$

Then, # leaving at t (in dt):

$$\underbrace{S(t, q_0)}_{\#\text{ at } t} - \underbrace{S(t+dt, q_0)}_{\#\text{ at } t+dt \text{ (less)}} = \underbrace{\rho(t, q)}_{\text{density of first passages (exits)}} dt$$

or

$$-\frac{dS}{dt}(t, q_0) = \rho(t, q_0)$$

and average:

$$T(q_0) = \int_0^t dt \; T \rho(t, q_0)$$

$$= \int_0^t dt \; t \left(-\frac{dS}{dt}(t, q_0) \right)$$

$$= t\, S(t, q_0) \Big|_0^t + \int_0^t dt \; S(t, q_0).$$

Then: $\underset{t\to\infty}{S} \to 0$ (faster than $1/t$)

$S(0) = 0$ (cell in)

$t \to \infty$

$$\tau(\underline{q}_0) = \int_0^\infty dt\; S(t, \underline{q}_0) = \int_0^\infty dt\; S(t, \underline{q}_0)$$

$$\tau(\underline{q}_0) = \int_0^\infty dt \int_V d\underline{q}\; P(\underline{q}_0, t)$$

or

$$\boxed{\tau(q) = \int_0^\infty dt \int_V d\underline{q}\; P(\underline{q}, t)}$$

Now,

$$P(q, 0) = \delta(\underline{q} - \underline{q}_0)$$

$$P(q, t) = e^{tD}\, \delta(\underline{q} - \underline{q}_0)$$

$$\frac{\partial P}{\partial t} = D P \qquad P(q, t) = e^{tD}\, \delta(\underline{q} - \underline{q}_0)$$

so

$$\boxed{\tau(\underline{q}_0) = \int_0^\infty dt \int d\underline{q}\; e^{tD}\, \delta(\underline{q} - \underline{q}_0)}$$

labeling by $\underline{q}$

$$T(\underline{q}) = \int_0^\infty dt \int d\underline{q}_0 \, e^{tD} \delta(\underline{q}-\underline{q}_0)$$

$$= \int_0^\infty dt \, \overbrace{\int dq_0 \, \delta(q-q_0)}^{\text{trivial}} \, \underbrace{e^{tD^\dagger} 1}$$

$D^\dagger$ = adjoint of D

$$\langle a | D | b \rangle = \langle b | D^\dagger | a \rangle$$

so

$$T(\underline{q}) = \int_0^\infty dt \, e^{tD^\dagger} 1$$

$$D^\dagger T(q) = \int_0^\infty dt \, D^\dagger e^{tD^\dagger} 1$$

$$= \int_0^\infty dt \, \frac{d}{dt} e^{tD^\dagger} 1$$

$$= -1$$

(upper limit $\to 0$, absorption on ∂U)

so

$$\boxed{D^\dagger T(q) = -1}$$

with $\tau(\underline{q}) = 0$ on ∂V.

(particle on bndy $\rightarrow$ out).

$$\boxed{\mathcal{D}^{+}\tau(\underline{q}) = -1}$$

$\hookrightarrow$ determines avg. first passage time.

For Kramers:

$$\frac{\partial n}{\partial t} = D\frac{\partial}{\partial x} e^{-U(x)/T} \frac{\partial}{\partial x}\left(e^{U(x)/T} n\right)$$

$$= \mathcal{D} n$$

$\Rightarrow$

$$\mathcal{D}^{+} n = D e^{U(x)/T} \frac{\partial}{\partial x}\left(e^{-U(x)/T} \frac{\partial n}{\partial x}\right)$$

$\Rightarrow$

$$\boxed{D e^{U(x)/T} \frac{\partial}{\partial x} e^{-U(x)/T} \frac{\partial}{\partial x} \tau(x) = -1}$$

gives τ.

Then

$$\frac{\partial}{\partial x}\left(e^{-u(x)/T}\frac{\partial}{\partial x}\tilde{T}\right) = \frac{e^{-u(x)/T}}{D}$$

$$e^{-u(x)/T}\frac{\partial}{\partial x}\tilde{T} = \int_a^x dx' \, \frac{e^{-u(x')/T}}{D}$$

$$\frac{\partial \tilde{T}}{\partial x} = e^{u(x)/T}\int_a^x dx' \, \frac{e^{-u(x')/T}}{D}$$

$\Rightarrow$

first passage time

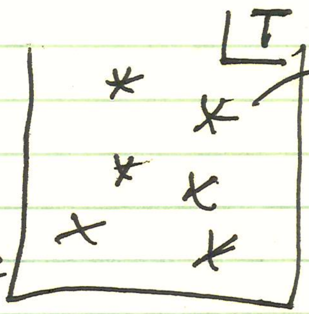
$$\boxed{T(x) = \frac{1}{D}\int_x^b dy \, e^{u(y)/T}\int_a^y dz \, e^{-u/T}}$$

Higher dimensions:

- path integral
- computation

b.) Coagulation

- charged, in electrolyte

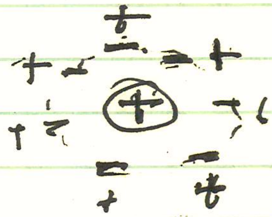


→ Diffusing, $D \sim T/L$

→ system of colloidal particles walking randomly

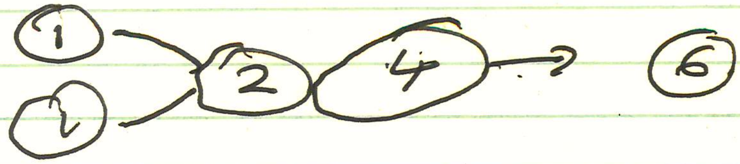
→ Each particle has "sphere of influence"
- i.e. λ_D (Debye Length)

→



particles colliding
- merge to larger particle
i.e. "sticky" collisions

- Evolution:
  - 1 + 1 → 2
  - 2 + 1 → 3
  - 3 + 2 → 5



so, have population #'s density:

$$\frac{d}{dt} \nu_2 = \underset{1+1}{(\text{production})} - \underset{1+2,3,4\ldots}{(\text{"destruction"})}$$

Δ

$$\frac{d}{dt} \nu_3 = \underset{2+1}{(\text{production})} - \underset{3+1,2,\ldots}{(\text{"destruction"})}$$

etc.

production (n-particle) $\sim \# \nu_p \nu_q$

$p+q=n$

destruction (n-particle) $\sim \# \nu_n \sum_{i=1}^{N} \# \nu_i$

so, have classic $\left\{\begin{matrix}\text{input}\\\text{out}\end{matrix}\right\}$

birth-and-death model for populations:

birth → from smaller

$$\frac{d}{dt}\nu_n = C_{ij}\sum_{\substack{i,j\\ i+j=n}} \nu_i \nu_j$$

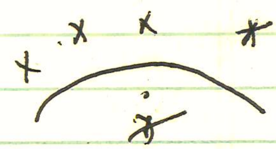
$$- \sum_i C_{in}\, \nu_i \nu_n$$

→ death, absorption into larger.

Now, need rate constants!

What sets rates? → Particles interact by walking randomly together. – Diffusion!

– density diffuses



$$\frac{\partial n}{\partial t} = D\nabla^2 n, \qquad D = T/\beta$$

influence

$$n = \text{const}, \qquad t=0 \quad |r| > R$$

$$n = 0, \quad |r| = R \qquad t > 0$$

absorption

symmetry $\Rightarrow$

$$\partial_t(rn) = D\frac{\partial^2}{\partial r^2}(rn)$$

$X \equiv rn$ $\qquad X\Big|_{t\to\infty} = a + br$

$\Rightarrow$

$$n = \nu\left[1 - \frac{R}{r} + \frac{2R}{r\sqrt{\pi}}\int_0^{(r-R)/(2Dt)^{1/2}} e^{-x^2}\,dx\right]$$

$t \to \infty$.

Since particles "diffuse" together

$$\frac{\partial}{\partial t}\,\bullet^{\nu} \sim \overset{A}{4\pi R^2}\,\overset{\Gamma}{\left(D\frac{\partial n}{\partial r}\Big|_R\right)}$$

$$\sim 4\pi R D \nu.$$

$\nu \equiv$ density factor.

1-6. rate $= 4\pi D\, r^2 \frac{\partial n}{\partial r}\Big|_R$

$$= 4\pi D R \nu\left(1 + R/(\pi D t)^{1/2}\right)$$

So, For mergers:

$$J_{i,k}\, dt = 4\pi D_{ik}\, r_i r_k \, dt$$

$$D_{i,k} = D_i + D_k \qquad \rightarrow \text{indep motion}$$

So $\Rightarrow$

$$\boxed{\frac{dr_k}{dt} = 4\pi \left(\frac{1}{2} \sum_{i+j=k} r_i r_j D_{ij} R_{ij} - r_k \sum_{j=1}^{\infty} r_j D_{kj} R_{kj} \right)}$$

Population Equation,

Further simplify:

$$R_i = R_k = R$$

$$D_j = D$$

$$D_i R_i = DR$$

$$D_{ik} R_{ik} = 2DR$$

$\underline{\underline{\infty}}$

$$\frac{d\nu_k}{dt} = 8\pi DR\left(\frac{1}{2}\sum_{i+j=k}\nu_i\nu_j - \nu_k\sum_{j=1}^{\infty}\nu_j\right)$$

$$\tilde{T} := 4\pi DRt$$

$\underline{\infty}$

$$\boxed{\frac{d\nu_k}{d\tilde{t}} = \sum_{i+j}\nu_i\nu_j - 2\nu_k\sum_{j=1}^{\infty}\nu_j \qquad k = 1, \ldots}$$

then $\sum_{k}$

$$\frac{d}{d\tilde{t}}\left(\sum_{k=1}^{\infty}\nu_k\right) = \underbrace{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\nu_i\nu_j}_{\text{(rel. constr. sum)}} - 2\sum_{k=1}^{\infty}\sum_{j=1}^{\infty}\nu_k\nu_j$$

$$= -\left(\sum_{k=1}^{\infty}\nu_k\right)^2$$

$\underline{\infty}$

$$\boxed{\sum_{k=1}^{\infty}\nu_k = \nu_0 \big/ 1+\nu_0\tilde{T}}$$

Now, can solve for populations:

$$\frac{d}{dt}\nu_1 = -2\nu_1 \sum_{k=1}^{\infty} \nu_k$$

$$= \frac{-2\nu_1\nu_0}{1+\tau\nu_0}$$

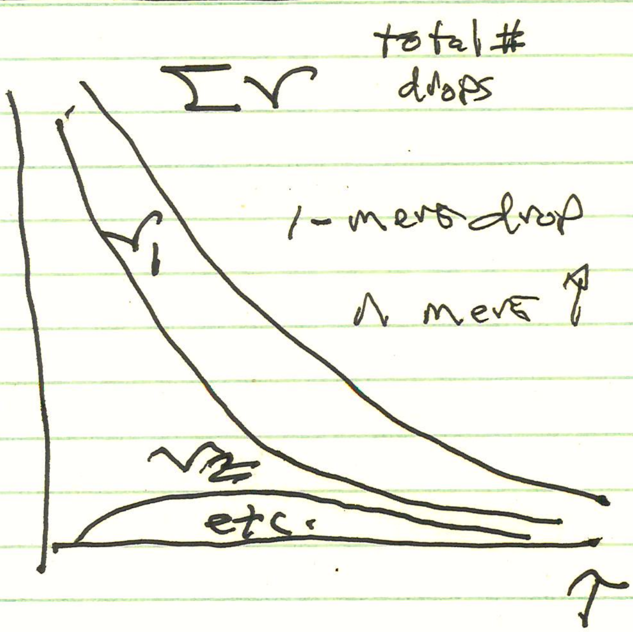
so

$$\nu_1 = \nu_0 \Big/ (1+\nu_0\tau)^2$$

and similarly,

$$\boxed{\nu_k = \nu_0\left[(\nu_0\tau)^{k-1} \Big/ (1+\nu_0\tau)^{k+1}\right]}$$

$k = 1, 2, \ldots$



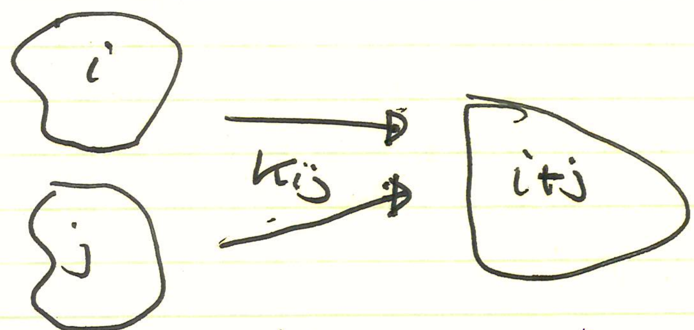
1-mer drop

n mer ↑ then ↓ to n+1

Now,

- discussion is typical of aggregation

i.e. process by which clusters join irreversibly when two meet



$$A_i + A_j \xrightarrow{k_{i,j}} A_{i+j}$$

examples: milk curdling
blood coagulation
planet/grain formation

- basic description is system of Master eqns:

$$\frac{d}{dt} c_k = \frac{1}{2} \sum_{i+j=k} k_{ij} c_i c_j - c_k \sum_{i \geq 1} k_{ik} c_i$$

birth (emission into) — death (emission from)

paradigm

N.B: Master equation

- $$\frac{d}{dt}P_k(t) = \sum \alpha_{i,k}\, P_i(t) - \sum \alpha_{k,j,l}\, P_k(t)$$

- general rate / birth-death model

- α's $= \alpha(P)$ possible

- best thought of à la Q.M.

F-P. is subset of Master:

$$P(x, t+\Delta t) = \int d(\Delta x)\, \underbrace{T(\Delta x, \Delta t)}_{\text{small step probability}}\, P(x-\Delta x, t)$$

- model is 'bare bones', assumes:
  - → spatial homogeneity (formulate with sedimentation!)
  - → dilute → higher order interactions negl.
  - → shape independence → (point particle)
  - → thermodynamic limit

Basic equation conserves <u>Mass Density</u>

$c\ (\to\ p)$

$M \to \sum k c$

$$\boxed{M(t) = \sum_{k \geq 1} k\, c_k(t)}$$

$$\frac{dM}{dt} = 0$$

$\Leftrightarrow$

$$\frac{dM}{dt} = \sum_k k \frac{dc_k}{dt}$$

$$= \sum_k \sum_{i+j=k} \tfrac{1}{2} K_{ij} \overset{k}{(i+j)} c_i c_k$$

$$- \sum_k \sum_i K_{ik}\, k\, c_i c_k$$

relabeling $\to$

$$= 0$$

→ Many approaches to solution:

- exact, some cases
- moments
- recursion

etc.

see Krapivsky, et al.

One Example: Gelation

Gelation: Aggregation rate increasing with cluster mass

$$\frac{dc_k}{dt} = \sum_{\substack{i,j \\ =k}} K_{i,j}(c)\, c_i c_j - \ldots$$

$\Rightarrow$ condensation to single cluster
– or Jello – in finite time
$\rightarrow$ gelation time.

Similar $\Rightarrow$ finite time singularity
turbulence $\rightarrow$ $V(\ell)$ cascade
rate $\uparrow$ as $\ell \downarrow$.

After gelation time:

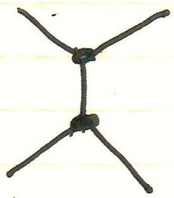
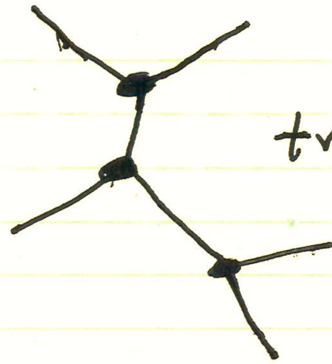
2 phases
gel $\rightarrow$ infinite cluster
sol $\rightarrow$ finite clusters (mass $\downarrow$)

Consider:

monomers: f-functional reactive groups

i.e. $f = 3$

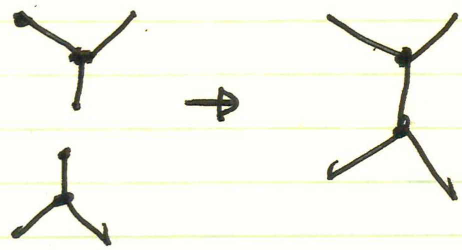
monomer

 dimer ;  trimer

f → # functional reactive endgroups.

2 merge ⇒ (2 monomer → dimer)

dimer:



[2f − 2 reactive endgroups

trimer : 3f − 4

⋮

k-mer : $kf - 2(k-1)$ ← # endgroups for k-mer.

$= (f-2)k + 2.$

[i.e. branching increase reactivity with size!] ← key.

↓

so

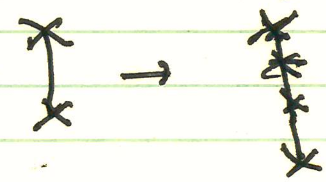
$k_{ij} \sim$ [# endgroup i] [# endgroup j]

$$k_{ij} = \left[(f-2)i + 2\right]\left[(f-2)j + 2\right]$$

$$= (f-2)^2 ij + 2(f-2)(i+j) + 4$$

$f = 2 \rightarrow$ linear polymers

$k_{ij} = 4$



$k = \text{const.}$

$f > 2 \rightarrow$ kernel is linear combo. of const, sum, product

$\sim af^2 + bf + c.$

So, natural model is <u>product</u> <u>kernel</u> — (equivalent to Erdos-Renyi rndm graph)

$k_{ij} = ij$

so master equation:

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} ij\, c_i c_j - k c_k \sum_{i \geq 1} i c_i$$

normalizing $\sum i c_i = M.$

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} ij\, c_i c_j - k c_k.$$

→ will condense to giant 'gel cluster', of entire system.

Solving:

– Gel → singularity!

– detect singularity by moments:

- finite system
- initial mass M

→ gel ⇒ cluster with gM
fraction

concen. $1/M$

Decompose moments:

$$M_n = \sum_{k \geq 1} k^n c_k$$

$$= \sum_{sol} k^n c_k + (k^n c_k)_{gel}$$

Σ finite   inf.

so
$$M_0 = \sum_{sol} c_k$$

$$M_1 = \sum_{sol} k c_k + g$$

$$M_2 = \sum_{sol} k^2 c_k + g^2 \mathcal{M}$$

$$M_3 = \sum_{sol} k^3 c_k + g^3 \mathcal{M}^2$$

$\rightarrow M_2, M_3 \ldots$ diverse in thermo limit

$\rightarrow$ prior to gelation, $t < t_g$
$g(t) = 0$, so all M_n finite

$\therefore$ suggests look at second moment.

now

$$\frac{dM_2}{dt} = \sum_{k \geq 1} k^2 \frac{dc_k}{dt}$$
$$= \frac{1}{2} \sum_{i \geq 1} \sum_{j \geq 1} (i+j)^2 (i c_i)(j c_j)$$
$$- \sum k^3 c_k \quad \text{(norm } M_0\text{)}$$

$$\left((i+j)^2 \to \underbrace{k^2}_{}\overset{1\text{ term}}{\to} ij \right)$$

$$\frac{dM_2}{dt} = \sum_{i\geq 1} \sum_{j \geq 1} (i^2 c_i)(j^2 c_j)$$

$$= M_2^2$$

or

$$\frac{dM_2}{dt} = M_2^2 \to M_2 \text{ diverges at } t_g = 1$$

gelation time

(see Krapivsky for details)

→ higher moments go slower.

→ Zeroth moment:

$$M_0 = N$$

$$\sum_k c_k = N$$

$$\frac{dN}{dt} = \frac{1}{2} \sum_{\substack{i\geq 1 \\ j \geq 1}} i c_i \, i c_j \quad - \sum_k c_k$$

normalization

$$= 1/2 - 1$$

$$N(t) = 1 - \frac{1}{2} t \quad ??$$

This is a consequence of using :

$$\sum_{k\geq 1} k\, c_k = 1$$

above gel point.

Valid only for finite clusters

⇒ should write:

$$\sum_{k\geq 1} k\, c_k = 1-g$$

sol, only.

then, repeating :

$$\frac{dN}{dt} = \frac{1}{2}(1-g)^2 - (1-g)$$

$$= (g^2-1)/2 \qquad t > t_g.$$

N stops only when $g \to 1$, at infinite time.

Another approach :

⇝ Generating function

$$\mathcal{E}(y,t) = \sum_{k\ge 1} k\, c_k(t)\, e^{yk}$$

$\downarrow$

Gen Fcty (exponential)

$k\, e^{yk} \ast \frac{dc_k}{dt}$ given; k

$$\frac{d\mathcal{E}}{dt} = \frac{1}{2}\sum_{i\ge 1}\sum_{j\ge 1}(i+j)\, ij\, c_i c_j\, e^{yk} - \sum_{k\ge 1} k^2 c_k\, e^{yk}$$

$$= \frac{1}{2}\sum_{i\ge 1} i^2 c_i\, e^{yi}\sum_{j\ge 1} j\, c_j\, e^{yj} + \frac{1}{2}\sum_{i\ge 1} i\, c_i\, e^{yi}\sum_{j\ge 1} j^2 c_j\, e^{yj} - \sum_{k\ge 1} k^2 c_k\, e^{yk}$$

$$= (\mathcal{E}-1)\frac{\partial \mathcal{E}}{\partial y}$$

$\Rightarrow$

$$\frac{\partial \mathcal{E}}{\partial t} + \mathcal{E}\frac{\partial \mathcal{E}}{\partial y} + \frac{\partial \mathcal{E}}{\partial y} = 0$$

and note similarity to Burgers Eqn.

$$\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial x} - \nu \partial_x^2 v = 0$$

$\Rightarrow$ shock! – finite time singularity.

See Krapivsky for more!

Key Point:

$\Rightarrow$ get as finite time divergence or singularity.

$\Rightarrow$ get via k increasing with ω.