$k(0)=0$
initially
empty system)
$\to\infty$ 1
t
$\to 0$
z^k

Sid Redner, Lecture 13

f=3

Consider another example: $K_{ij} = ij$

Consider monomers with f functional reactive subgroups
Dimer: $2f-2$  (4) Trimer: $3f-4$  (5)

In general, $kf - 2(k-1) = (f-2)k+2$. Then $K_{ij} = [(f-2)i+2][(f-2)j+2]$
$= (f-2)^2 ij + 2(f-2)(i+j) + 4$. $f=2 \Rightarrow K_{ij} = c$
f large $\Rightarrow K_{ij} \sim ij$ (linear polymers)

So, $$\dot{c}_k = \frac{1}{2}\sum_{\substack{i,j\\ i+j=k}}' ij\, c_i c_j - \sum_i i c_i\, k c_k$$

Set $\sum_i i c_i = 1$, then
↑ total mass (M_1) stays const $=1$

Then $$\dot{c}_k = \frac{1}{2}\sum_{i,j}' ij\, c_i c_j - k c_k$$

Define $$M_n \equiv \sum_{k=1}^{\infty} k^n c_k \quad (M_1 = 1)$$

Then $$\dot{M}_0 = \frac{1}{2} M_1^2 - M_1 = -\frac{1}{2} \Rightarrow M_0 = 1 - \frac{t}{2} \quad (*)$$

Recall that $k=i+j$
$$\sum_k \sum_{i,j} \delta_{i+j,k}\, ij\, c_i c_j = \sum_{i,j} ij\, c_i c_j = M_1^2$$

$M_0 = 0$ @ $t=2$??
$M_0 < 0$ @ $t > 2$? Pathological behavior

$$\dot{M}_1 = \frac{1}{2}\sum_{i,j}(i+j)\, ij\, c_i c_j - \sum_k k^2 c_k = M_2 \underbrace{M_1}_{1} - M_2 = 0 \Rightarrow \dot{M}_1 = 0$$

$$\dot{M}_2 = \frac{1}{2}\sum (i+j)^2\, ij\, c_i c_j - \sum k^3 c_k = \underbrace{M_1}_{=1} M_3 + M_2^2 - M_3 = M_2^2$$

$$M_2(0) = \sum_{k=1}^{\infty} k^2 \delta_{k,1} = \underline{\underline{1}}$$

So, $M_2 = \frac{1}{1-t} \to \infty$ as $t \to 1$. ??
gelation at $t_g = 1$?

$\dot{M}_3 = 3 M_3 M_2 = \frac{3}{1-t} M_3$, all higher moments diverge @ t=1

A sign of phase transition in the system.
↑ these divergences in moments

Need to redefine moments:

$$M_n = \underbrace{\sum_{sol} k^n c_k}_{\text{solution}} + \underbrace{k_{max}^n\, c_{k_{max}}}_{\text{gel}} \Leftarrow \text{2 phases}$$

the largest cluster
$k_{max} = gm$
("always start w/ monomers)

$c_{k_{max}} = \frac{1}{m}$ ← gel cluster concentr'n

gm ← gel cluster mass

Suppose we start with m monomer clusters
define gel size gm, $g \equiv$ gel fraction

$$M_0 = \sum_{sol} c_k + \frac{1}{m}$$ as $m \uparrow$ the $\frac{1}{m}$ term becomes negligible

$$M_1: \; 1 = \overbrace{\sum_{sol} k c_k}^{M_1} + \frac{1}{m} g m \Rightarrow \boxed{M_1 = 1 - g}$$

$\sum_{sol} k c_k = 1 - g$

$$M_2: \; \sum_{sol} k^2 c_k + \underbrace{\frac{1}{m}(gm)^2}_{\sim m}$$

2nd & higher moments diverge in the m→

①

Reconsider

$$\dot{M}_0 = \frac{1}{2}(1-\overset{M_1=1-g}{g})^2 - (1-g) = \frac{g^2_{(t)}-1}{2} =$$

@ $t > t_g = 1$

$$= \begin{cases} 1 - t/2 & t<1 \text{ by gelation} \\ \text{exponentially} \to 0 \text{ as } t\to\infty \end{cases}$$

] to be shown later

$\dot{M}_0 = 0$ if $g=1$, which takes ∞ time

So the (*) is regulated. The system has many finite clusters + one "gel" one of size gM, $g<1$

(expect $O(1)$)

Now, solve MEs

$K_{ij} = ij$

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

generating f'n, defined differently from 64

$$\text{So, } \sum_k k\left[\dot{c}_k = \frac{1}{2}\sum_{ij}{}' ij\, c_i c_j - k c_k\right] e^{yk}$$

$$\underset{\text{deriv. wrt } t}{E_t} = \frac{1}{2}\overset{\text{unrestricted sum}}{\sum_{ij}} (ij)\overbrace{(i+j)}^{k} c_i c_j e^{yi} e^{yj} - \sum_k k^2 c_k e^{yk} =$$

$$= \frac{1}{2}\sum_{ij}\left[(i^2 c_i) e^{yi} (j c_j) e^{yj} + (j^2 c_j) e^{yj} (i c_i) e^{yi}\right] - \sum_k k^2 c_k e^{yk}$$

$$E_t = \underset{\text{deriv. wrt } y}{E_y} E - E_y \Rightarrow \boxed{E_t = E_y(E-1)}$$

Burgers eq'n

$$(**) \quad \boxed{E_t + (1-E)E_y = 0}$$

Solve (**) by the method of characteristics:

$$\text{Consider } \frac{dE(y,t)}{dt} = \underbrace{\frac{\partial E}{\partial t}}_{E_t} + \underbrace{\frac{\partial E}{\partial y}}_{E_y}\frac{\partial y}{\partial t} = 0$$

$y = y(E,t)$

2)

n^{n-1}

$n!$

n^n

k

$> tg = 1$

e
n
ter
, which takes ∞ time
+
$\ll 1$
ect $O(1)$
y
yk
)
urgers eq'n
$y(E,t)$

Along $\frac{\partial y}{\partial t} = (1-E)$, $\frac{dE}{dt} = 0$ ⟹ E is const along characteristic curves

So, $y(t) = (1-E)t + f(E)$ [E = const !]

Init. cond.: $\underline{t=0}$ $y(0) = f(E) = E(0)$ $e^{y} = \log E$
(monomers only)

$y(t=0) = f(E(t=0))$

Then $E(y, t=0) = e^{y}$ (from def'n of $E(y,t)$) → $y = \log$

So, $y(t=0) = \log E$

$E(y, t=0) = \sum_k k C_k^{(t)} e^{yk}\Big|_{t=0} = e^{y}$.

$$y(t) = (1-E)t + \log E$$

$$e^{y} = E e^{t} e^{-Et}$$

$$\underbrace{Et}_{Y}\, e^{-Et} = \underbrace{t e^{y-t}}_{X}$$

So, $\boxed{Y e^{-Y} = X}$

Lagrange inversion formula:

Consider $Y = \sum A_n X^n$ power series for the inverse f'n

Note that $X \simeq Y$ for small Y

Cauchy integral $A_n = \frac{1}{2\pi i} \oint \frac{Y}{X^{n+1}} dX$ ⊜

contour ∫ around the origin

$$⊜ \frac{1}{2\pi i} \oint \frac{Y}{(Ye^{-Y})^{n+1}} (1-Y) e^{-Y} dY$$

expand with Taylor series

$$\frac{1}{2\pi i} \oint \frac{Y}{f(Y)^{n+1}} f'(Y) dY$$

small circle around the origin in Y space since $X \simeq Y$ at the origin

$$A_n = \frac{n^{n-1}}{n!} \Leftarrow A_n = \frac{1}{2\pi i} \oint \sum_{k \geq 0} \frac{n^k}{k!} (Y^{k-n} - Y^{k+1-n})$$

expand the exp

$1/Y$ coeff.

$$⊜ \frac{n^{n-1}}{(n-1)!} - \frac{n^{n-2}}{(n-2)!}$$

$k'-n = -1$, $k' = n-1$

$k''+1-n = -1$, $k'' = n-2$

So, $Y = \sum_{n \geq 1} \frac{n^{n-1}}{n!} X^n$

So, $Et = \sum_{n \geq 1} \frac{n^{n-1}}{n!} t^n \left(e^{y-t}\right)^n$

$$\frac{n^{n-1}n}{n!} - \frac{n^{n-2}(n-1)n}{n!} ⊜ \frac{\cancel{n^n} - \cancel{n^n} + n^{n-1}}{n!}$$

$$E = \sum_{n \geq 1} \frac{n^{n-1}}{n!} e^{ny} e^{-nt} t^{n-1}$$

Recall that $E = \sum_{k \geq 1} k C_k^{(t)} e^{yk}$

$$\longrightarrow \boxed{C_k^{(t)} = \frac{k^{k-2}}{k!} t^{k-1} e^{-kt}}$$

Stirling appr'n:

$$C_k \sim \frac{k^{k-2}}{(k/e)^k \sqrt{2\pi k}} t^{k-1} e^{-kt} \sim$$

$$k^{k-2} k^{-k} k^{-1/2} = k^{-5/2}$$

$$\sim \frac{1}{\sqrt{2\pi}\, k^{5/2}} \exp\left[-kt - k + (k-1)\log t\right] \sim$$

neglect @ large k

$$\sim \frac{1}{\sqrt{2\pi}\, k^{5/2}} \exp\left[-k(t-1) + k\log t\right] \sim$$

$$k(1-\xi_0-\frac{\xi_0^2}{2}\dots)$$

$$\sim \frac{1}{\sqrt{2\pi}\, k^{5/2}} \exp\left[k\xi_0 + k\log(1-\xi_0)\right] \sim$$

$t = 1-\xi_0$

$t-1 = -\xi_0$

$$\sim \frac{1}{\sqrt{2\pi}} \frac{1}{k^{5/2}} \underbrace{e^{-k\xi_0^2/2}}_{e^{-k(1-t)^2/2} = e^{-k/k^*}}$$

$t<1 \rightarrow$ exponential cutoff

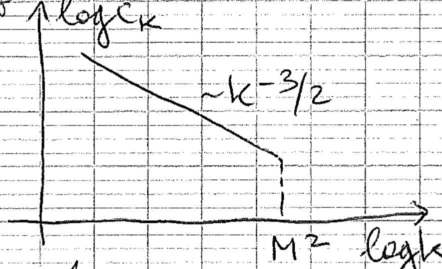
Cutoff for

$$k^* = \frac{2}{(1-t)^2}$$

$t \to 1$: $\boxed{C_k \sim k^{-5/2}}$

signals gel appearance → power-law cutoff

Before:



$$C_k \sim \frac{1}{k^{3/2}} \Rightarrow M = \int_1^{k_{max}} k C_k \, dk =$$

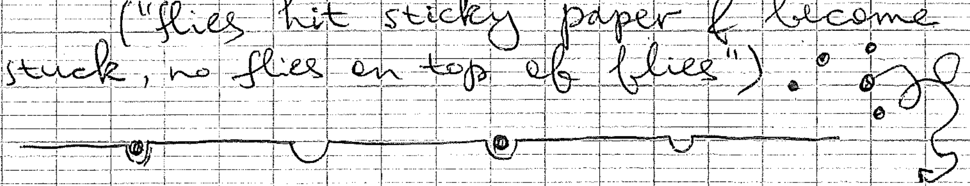
$$= \int_1^{k_{max}} \frac{dk}{k^{3/2}} \sim k_{max}^{1/2} \rightarrow k_m \sim M^2,$$

"hard cutoff" @ M^2, w/exponential decay @ around M^2

Adsorption

("flies hit sticky paper & become stuck, no flies on top of flies")

(1D)



Monomers diffuse & hit the traps

$$\dot{p} = 1-p \Rightarrow p(t) = 1-e^{-t}$$

p: fraction of covered sites

[trivial]

Ex

2/3

&

1

a

of

no

due

>n

1st term

m-1

loca

whe

dime

absor

2nd ter

one en

inciden

is ou

m-in

In

en