2009 NCN@Purdue-Intel Summer School
Notes on Percolation and Reliability Theory

Lecture 6
3D nets in 3D world: Bulk Heterostructure Solar Cells

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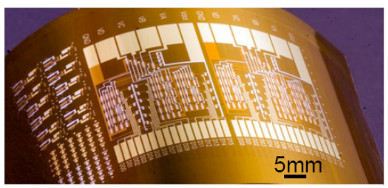
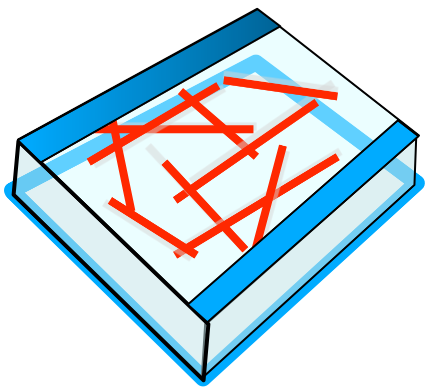
outline of lecture 6

1) **Introduction: definitions and review**
2) Reaction diffusion in fractal volumes
3) Carrier transport in BH solar cells
4) All phase transitions are not fractal
5) Conclusions

lectures 4, 5 and 6

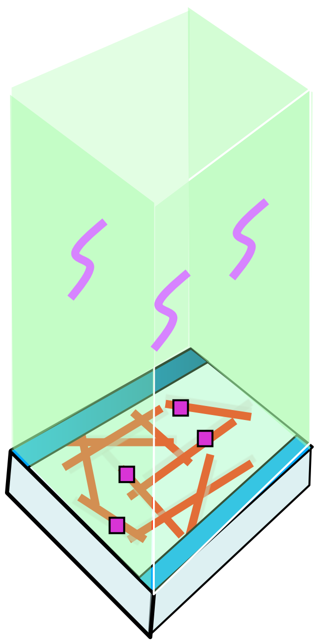
2D transport
in 2D Network



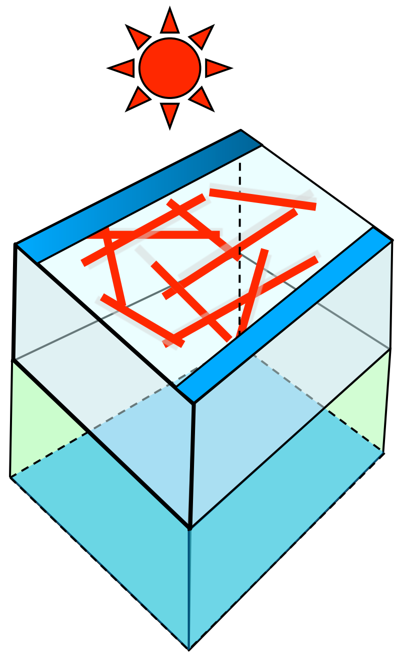


3D transport
towards 2D network

Nanobiosensors



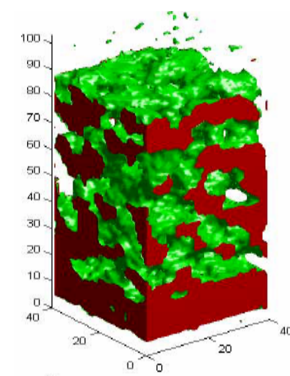
Fractal
electrodes



3D transport
in 3D network

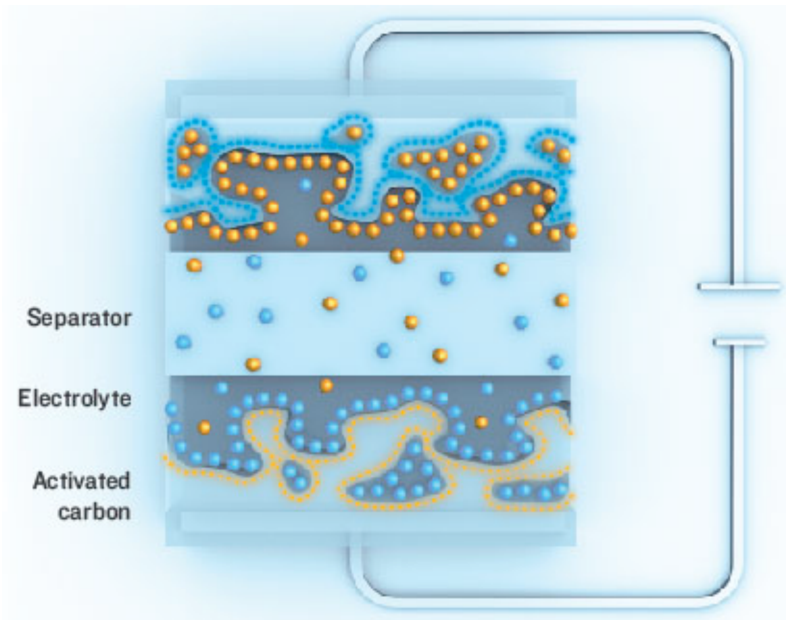
Supercapacitors

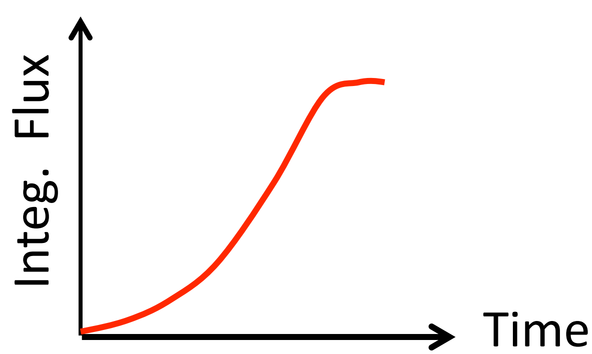
BH solar cell



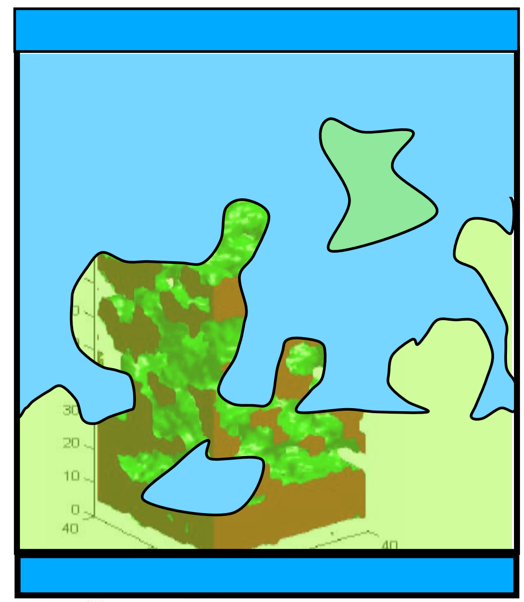
two types of 3D networks

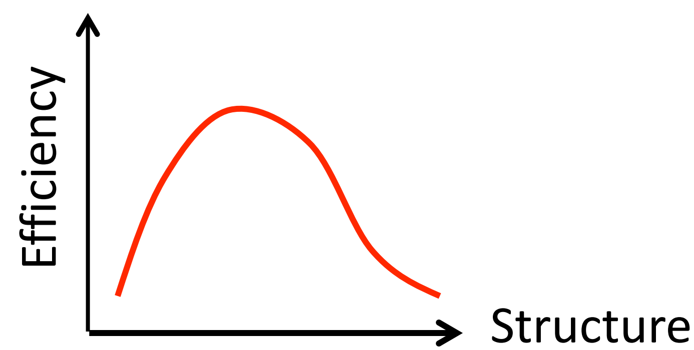
Fractal nets ....



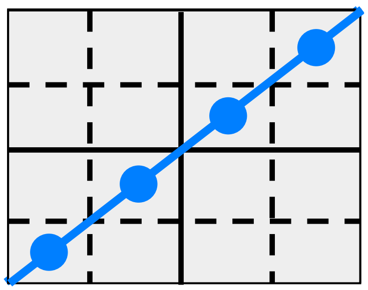


Spinodal nets ....

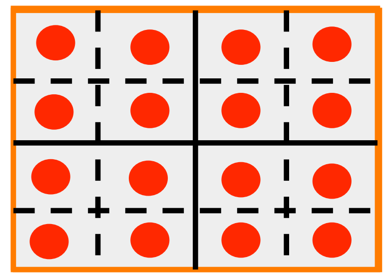




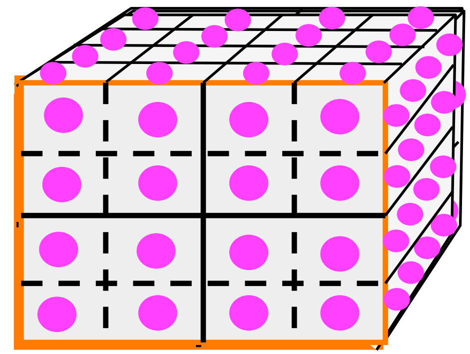
DF for a quasi-3D object…



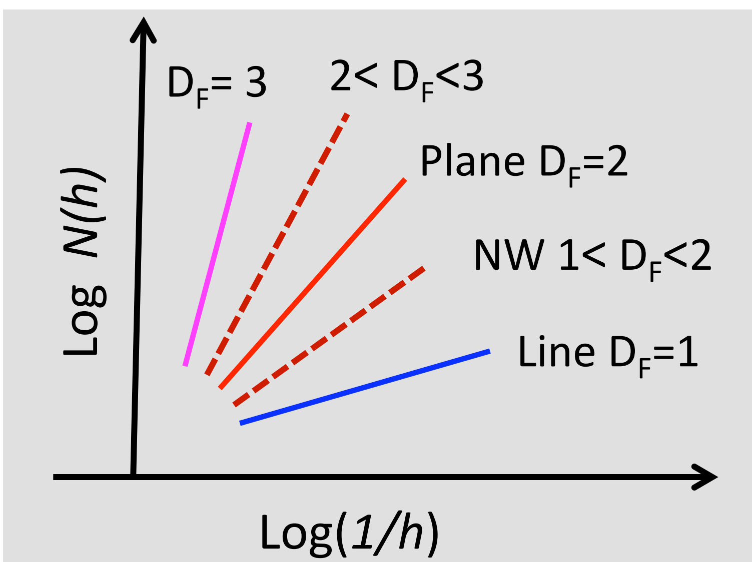
$N(h) \sim h^1$

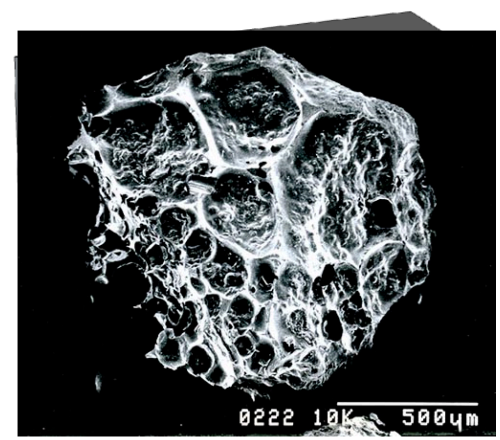


$N(h) \sim h^2$



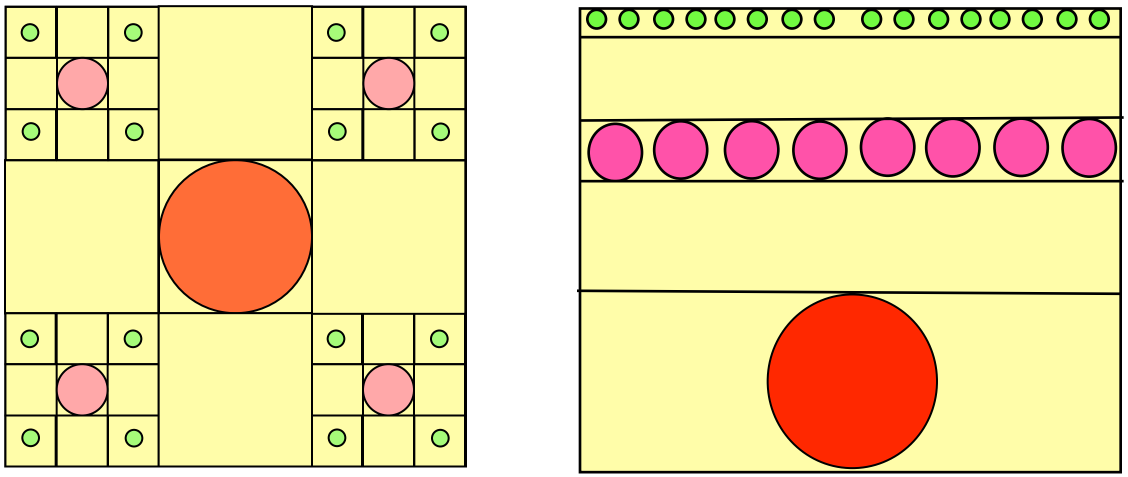
$N(h) \sim h^3$





DF for a ordered material ...

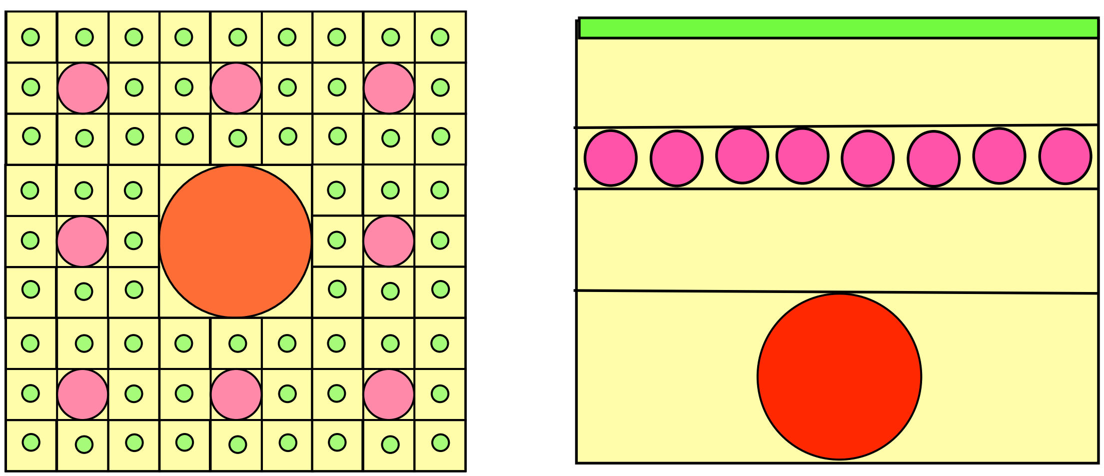
$$N_R = \left(R_R\right)^{-(D_F - 1)}$$



$N_R = 4$

$R_R = 3$

$D_F = 2.26$



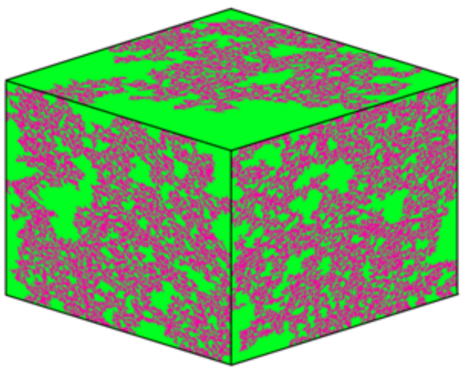
$N_R = 8$

$R_R = 3$

$D_F = 2.89$

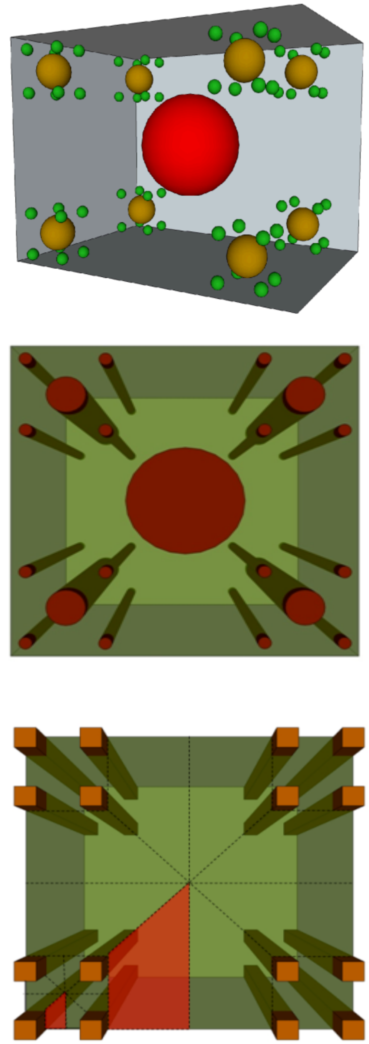
Cantor transform for quasi-3D Ojects

Determine D_F



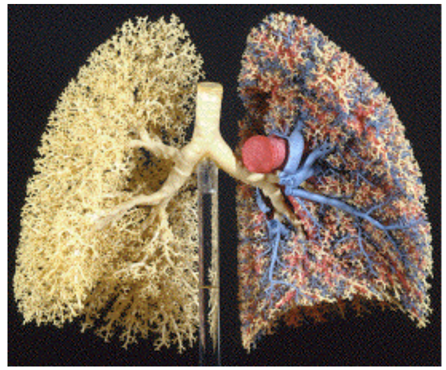
Cantor Transform

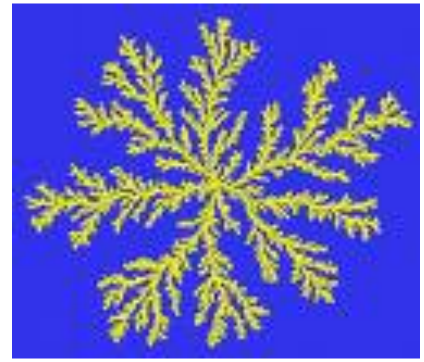
same D_F

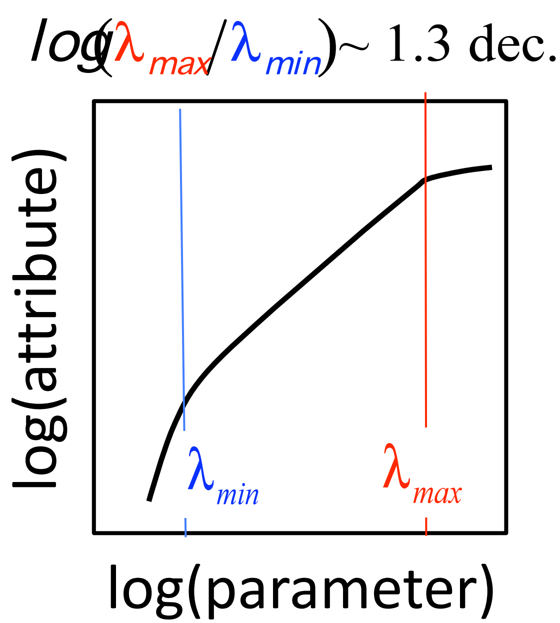


Solve the transport problem in equivalent regularized structures …

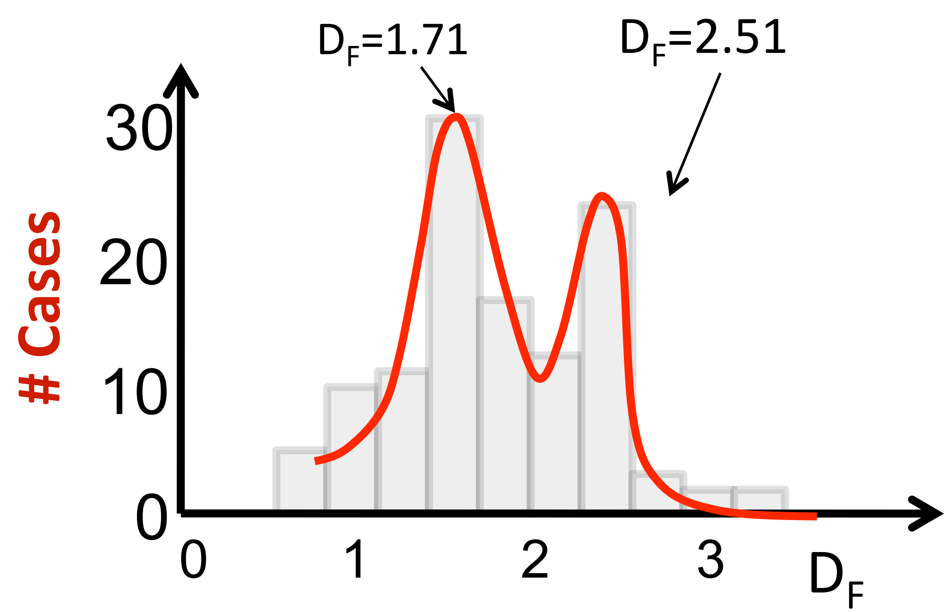
all fractals are finite …







Avnir et al., Science,1997



[Malcai, PRE, 1996]

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1) Introduction: definitions and review
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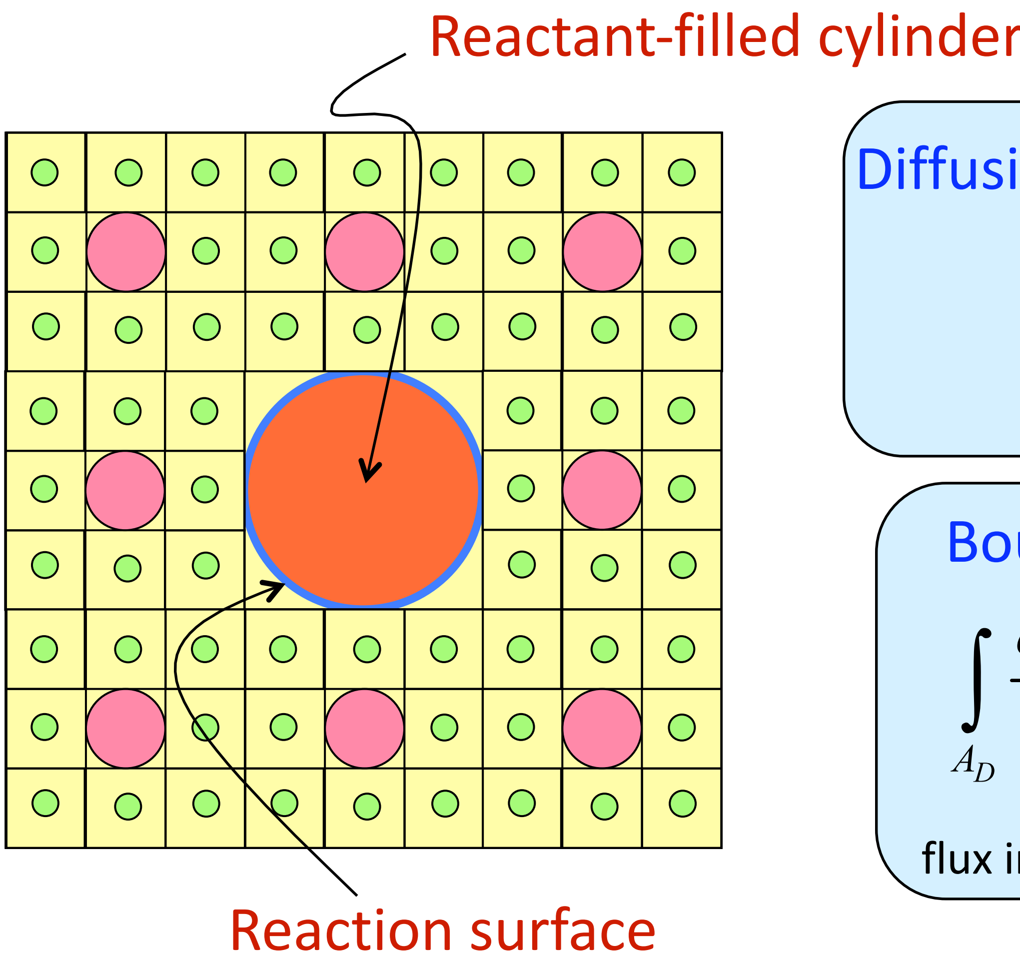
model of diffusion/capture …



Diffusion within the volume

$$\frac{de}{dt} = D\nabla^2 e$$

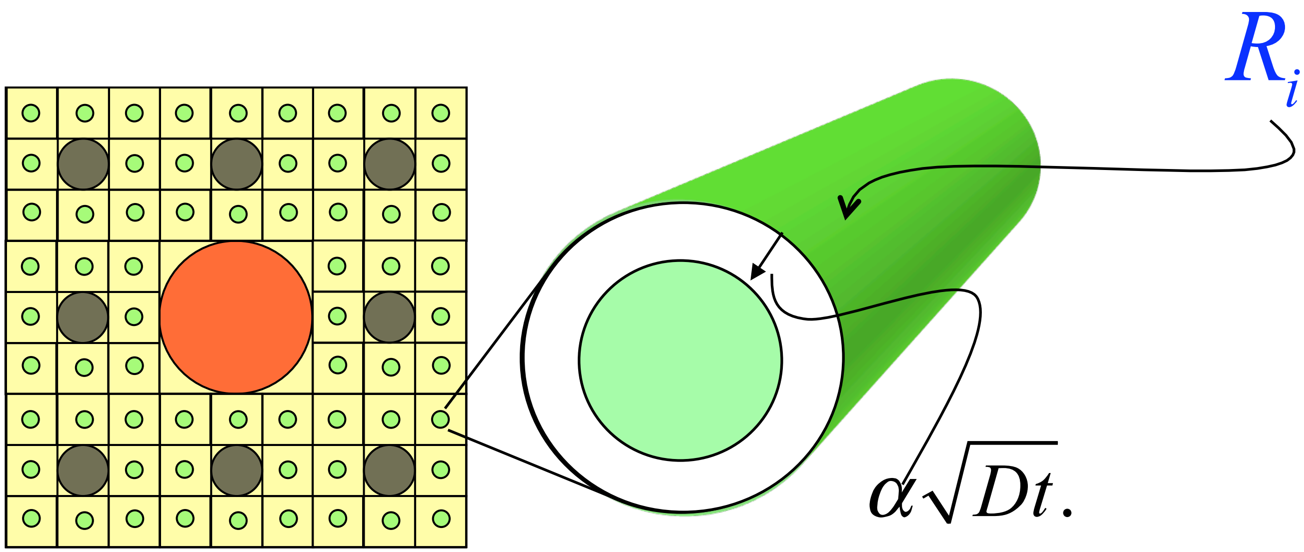
Boundary condition

$$\int_{A_D} \frac{dn}{dt} ds = D \int_{A_D} \nabla e \, ds$$

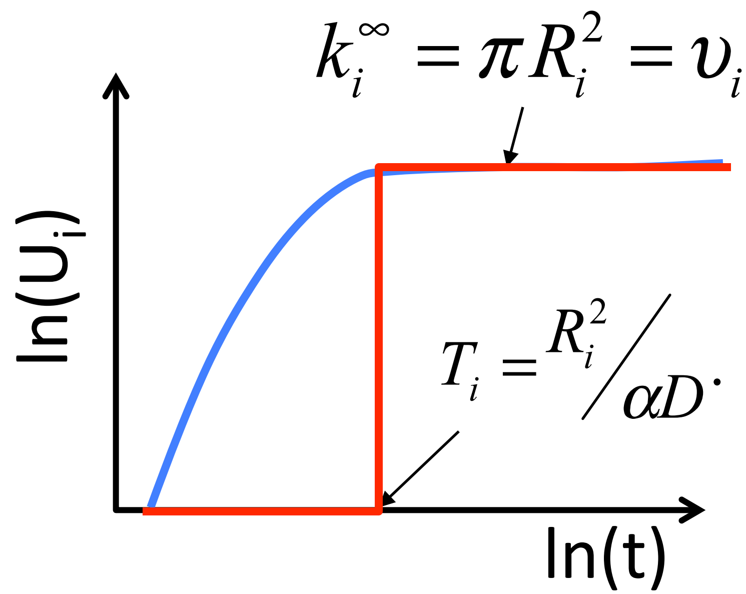
flux in material — surface flux

How long does it take for particles to diffuse to and react at the surface ?

depletion of a single void…



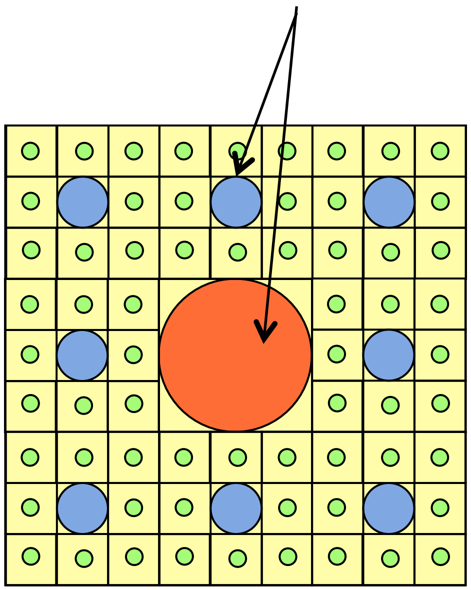
$$
\begin{aligned}
U_i(t) &= \pi R_i^2 - \pi\left(R_i - \alpha\sqrt{Dt}\right)^2 \\
&= 2\pi\alpha R_i\sqrt{Dt} - \pi\alpha^2 Dt \\
&= \pi R_i^2 \qquad (t > T_i)
\end{aligned}
$$

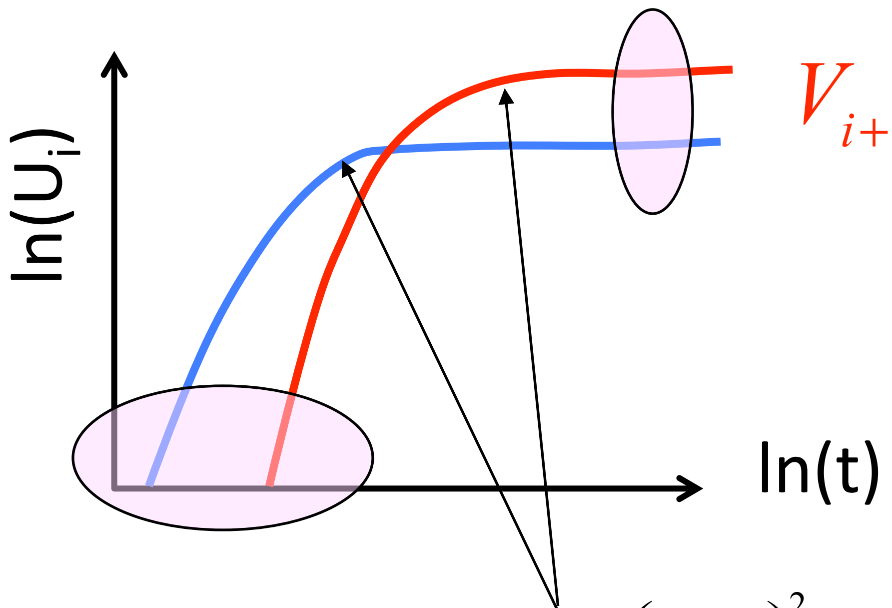


iteration levels and reaction rates…

$$V_i = \pi R_i^2 \times N_i \qquad V_{i+1} = \pi R_{i+1}^2 \times N_{i+1}$$

$$\frac{V_i}{V_{i+1}} = \left(\frac{R_i}{R_{i+1}}\right)^2 \times \frac{N_i}{N_{i+1}} \equiv \frac{N_R}{R_R^2} < 1$$





$$V_{i+1} > V_i$$

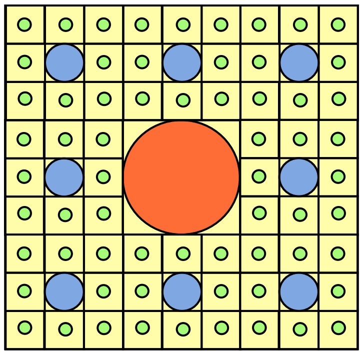
$$T_i = T_{i+1}\left(\frac{R_i}{R_{i+1}}\right)^2 = \frac{T_{i+1}}{R_R^2}$$

$$A_i = 2\pi R_i \times N_i \qquad A_{i+1} = 2\pi R_{i+1} \times N_{i+1}$$

$$\frac{A_i}{A_{i+1}} = \frac{R_i}{R_{i+1}} \times \frac{N_i}{N_{i+1}} \equiv \frac{N_R}{R_R} > 1$$

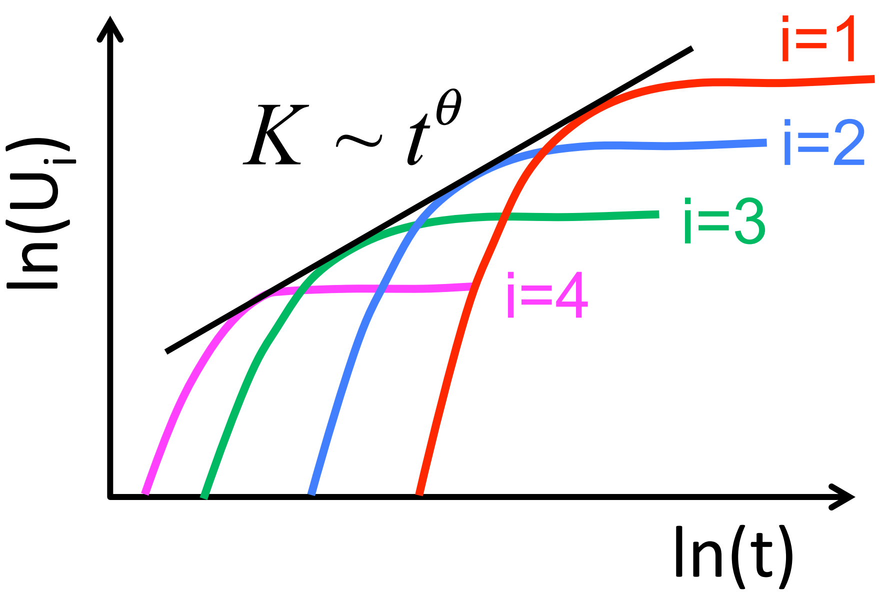
sequential depletion ...

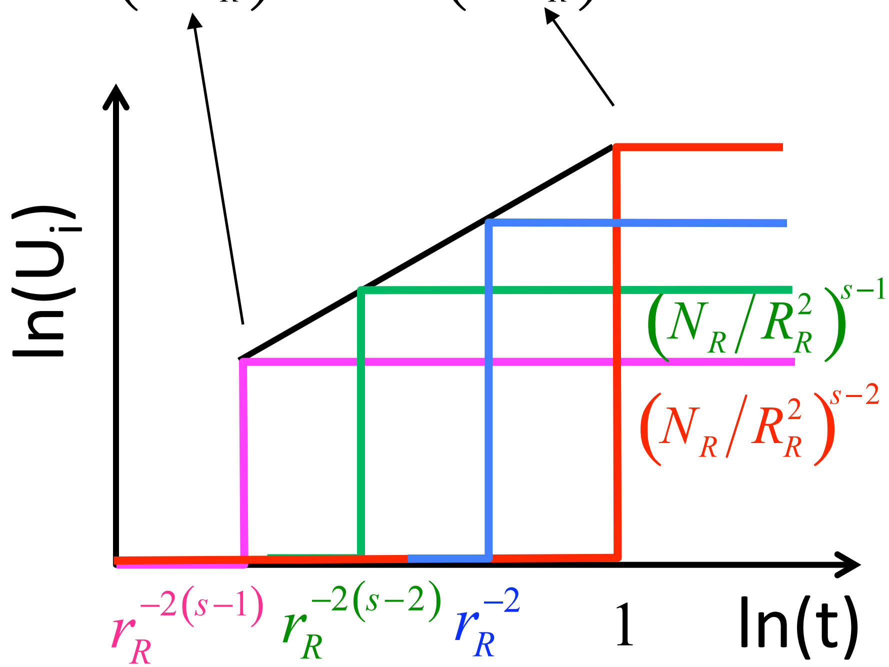
De Gennes Limit ...



$$\theta \sim \left[log \frac{1 - R_R^{\,D_F - 3}}{R^{s(3-D_F)} - 1} \Big/ -2s\, log\, R_R \right] \sim \frac{3 - D_F}{2}$$

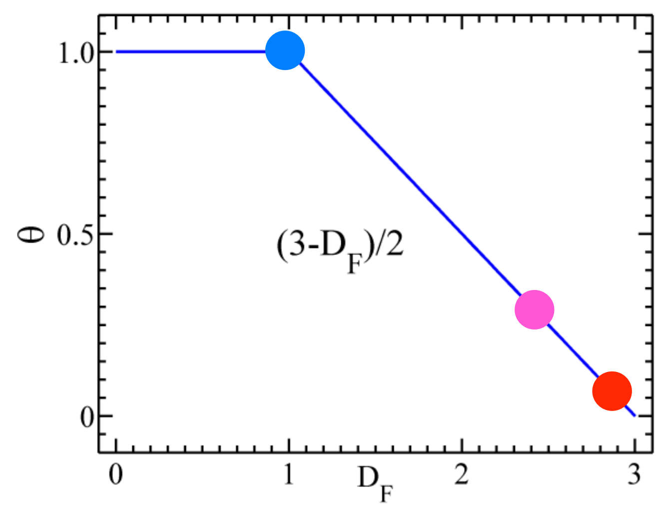
$$\theta = \frac{log\left(N_R / R_R^2\right)^{s-1} - log \sum_{k=p}^{s} \left(N_R / R_R^2\right)^{k-1}}{log\left(1/R_R^2\right)^{s-1} - log\left(1/R_R^2\right)^{p-1}}$$

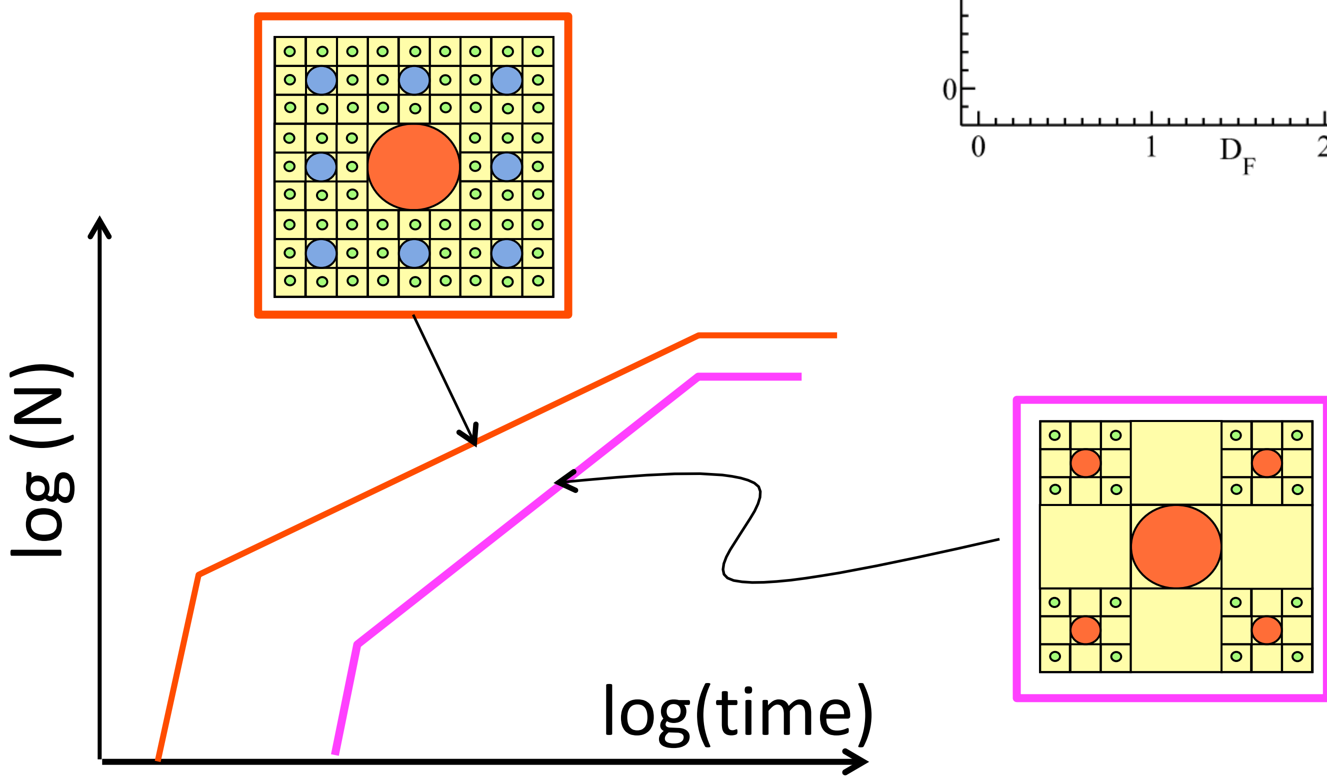




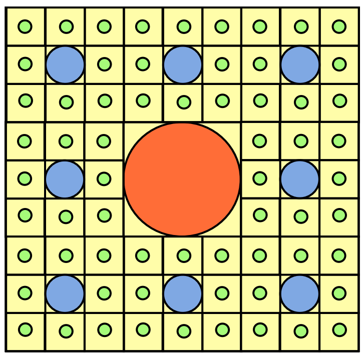
what does this all mean …

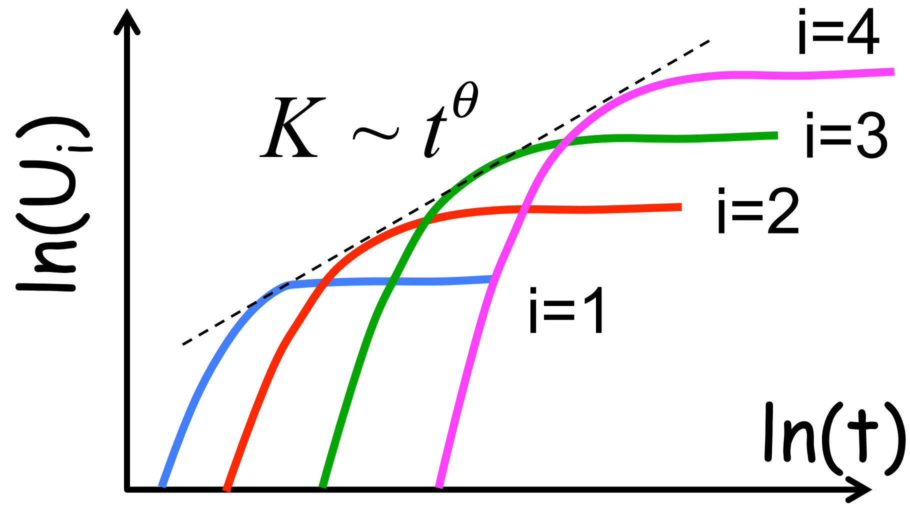
$$N(t) \propto \rho_0 t_s^{\left(\frac{3-D_F}{2}\right)}$$

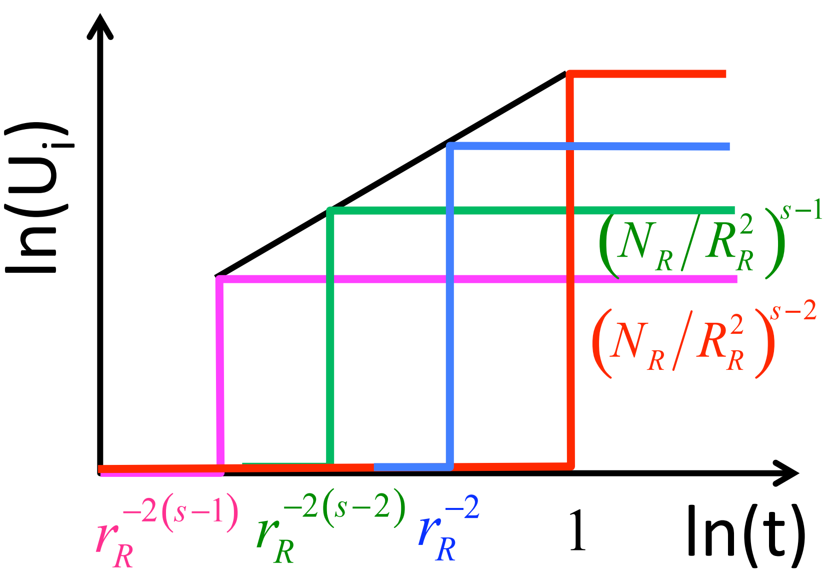


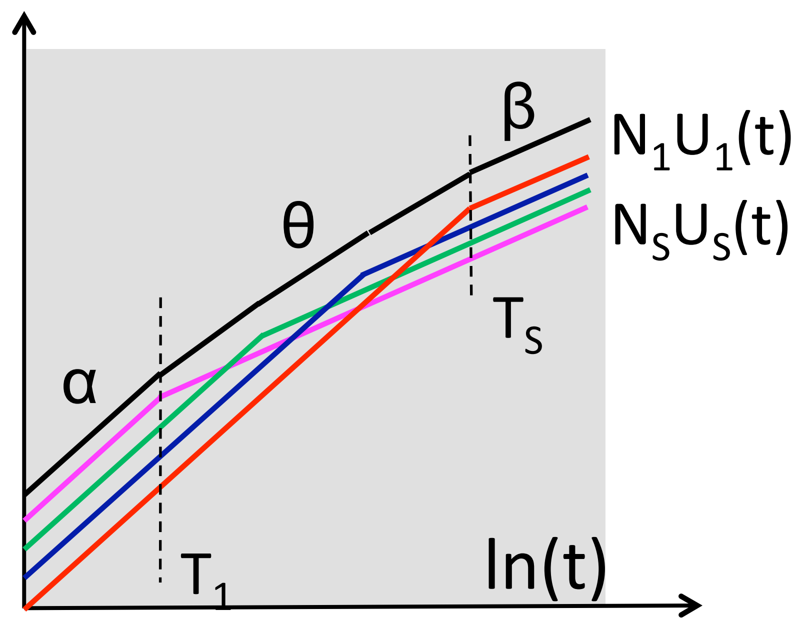


better basis functions for finite systems…









sequential depletion with better basis

$$U_i(t) = A_i\left({}^{t}\!/\!_{T_i}\right)^{\alpha} \qquad 0 < t < T_i$$

$$= A_i\left({}^{t}\!/\!_{T_i}\right)^{\beta} \qquad t > T_i,$$

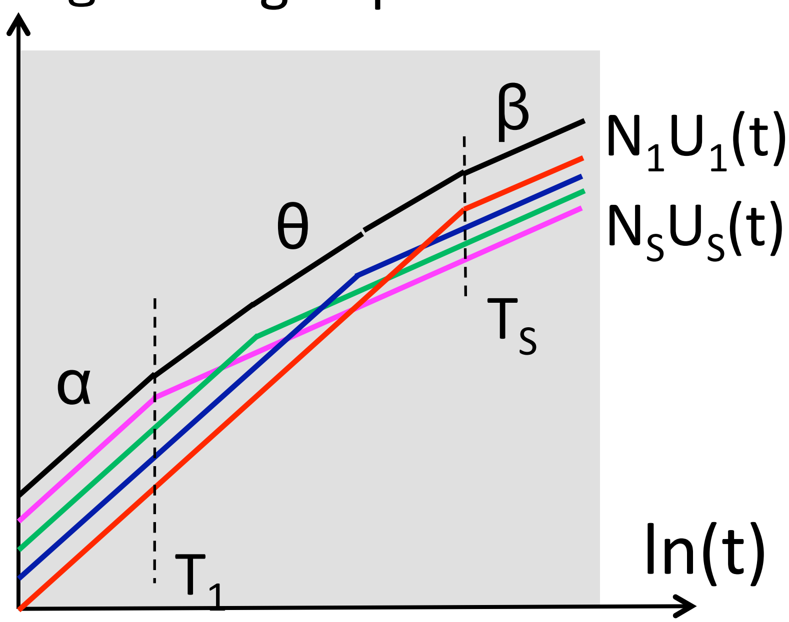
$$d = 1 + \delta - \gamma\alpha - D_F \qquad b = 1 + \delta - \gamma\beta - D_F,$$

d = diffusivity parameter

g = integral parameter

$$A_i \propto (R_R)^{(i-1)\delta} \qquad T_i \propto (R_R)^{(i-1)\gamma}$$

$$N_R = N_{i-1}/N_i \rightarrow N_i \propto N_R^{s-i}.$$

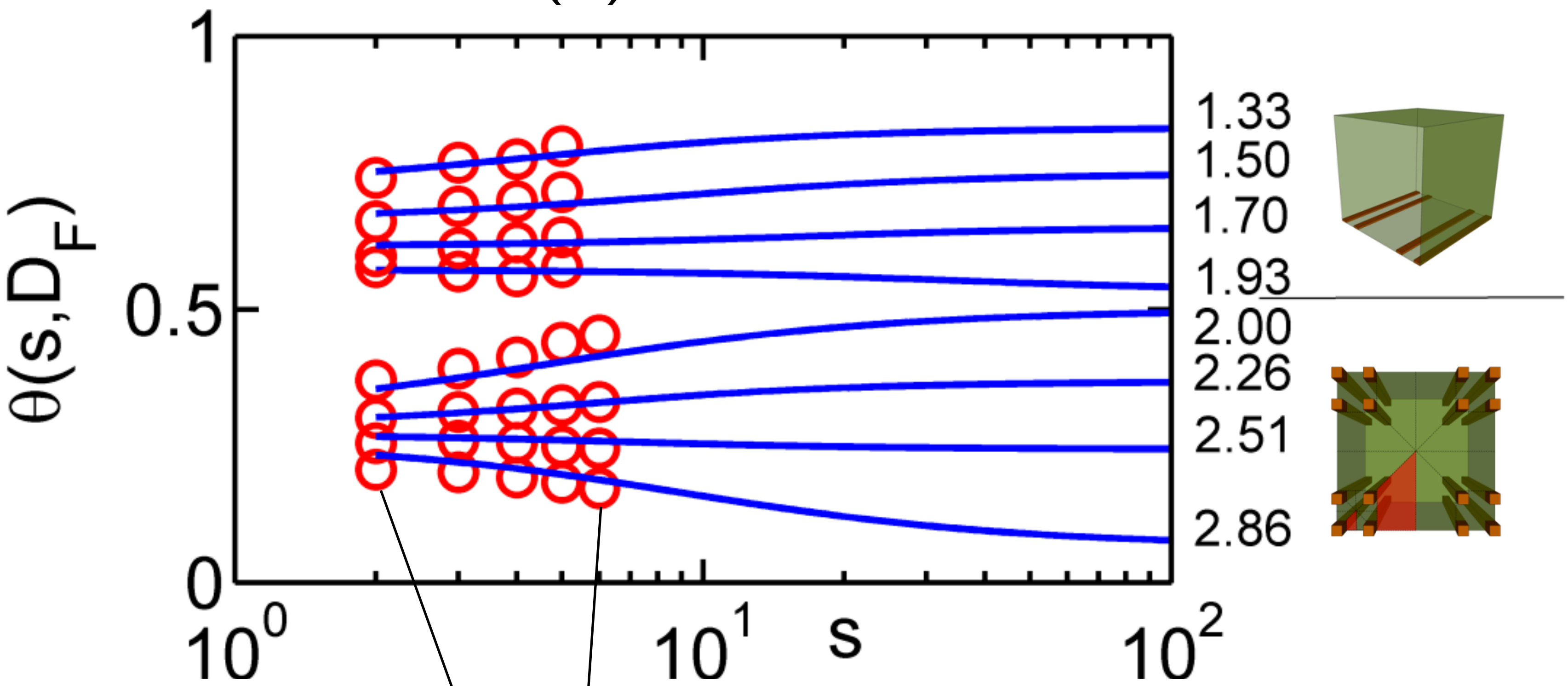


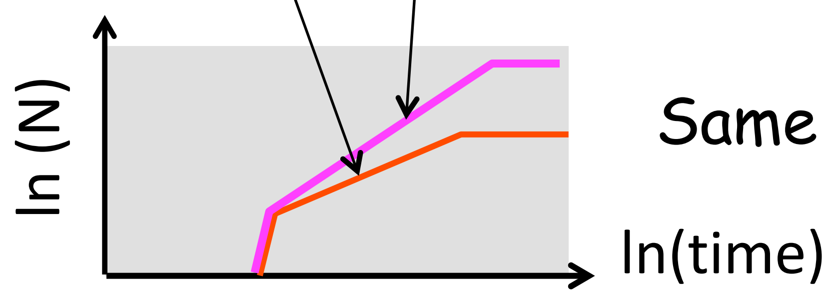
$$\theta(s, D_F) = \frac{\log\left(V(T_s)/V(T_1)\right)}{\log\left(T_s/T_1\right)}$$

$$= \beta + \frac{1}{\gamma(s-1)\log(R_R)}\left[\log\left(\frac{R_R^{b\times s}-1}{R_R^{b}-1}\right) - \log\left(\frac{R_R^{d\times s}-1}{R_R^{d}-1}\right)\right]$$

finite size exponents

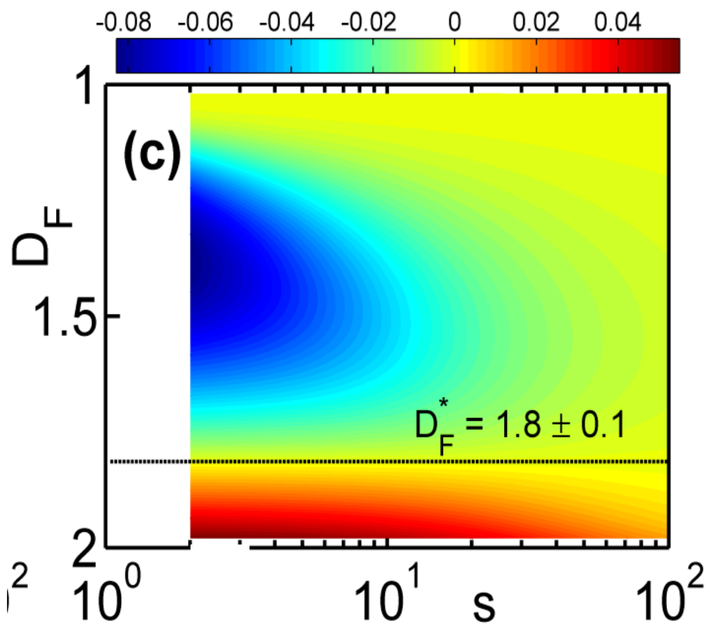
$$V(t) \propto t^{\theta(s,D_F)}$$

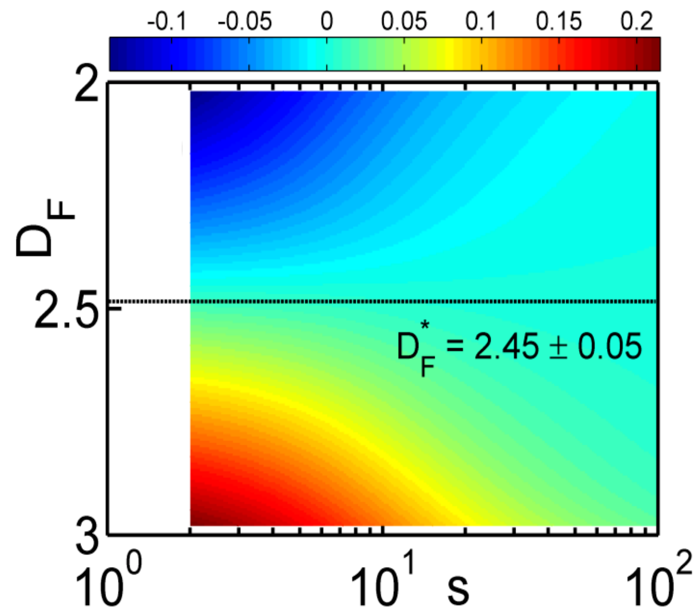


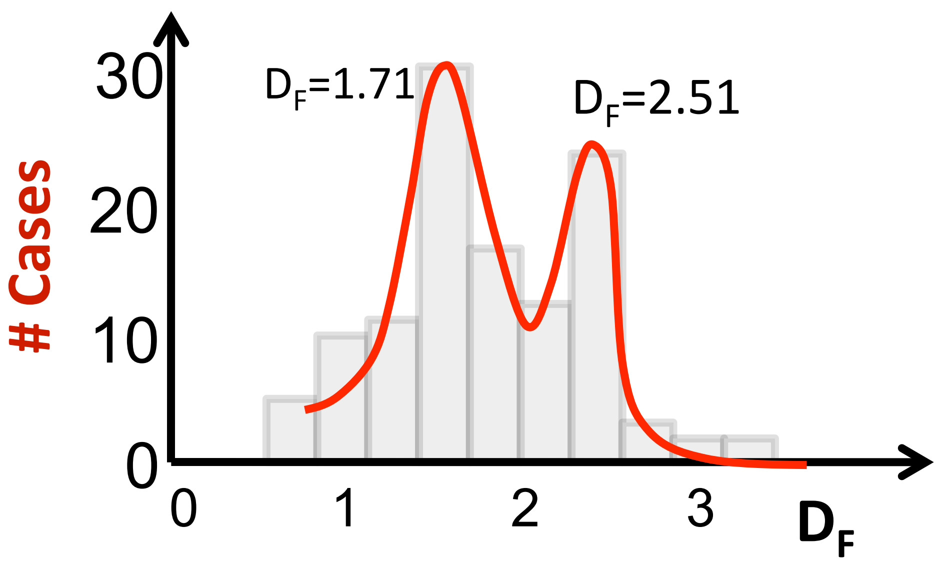


Same DF, but different size …

critical dimension: an enduring puzzle







At critical dimension, the time response of the device does not change with size!

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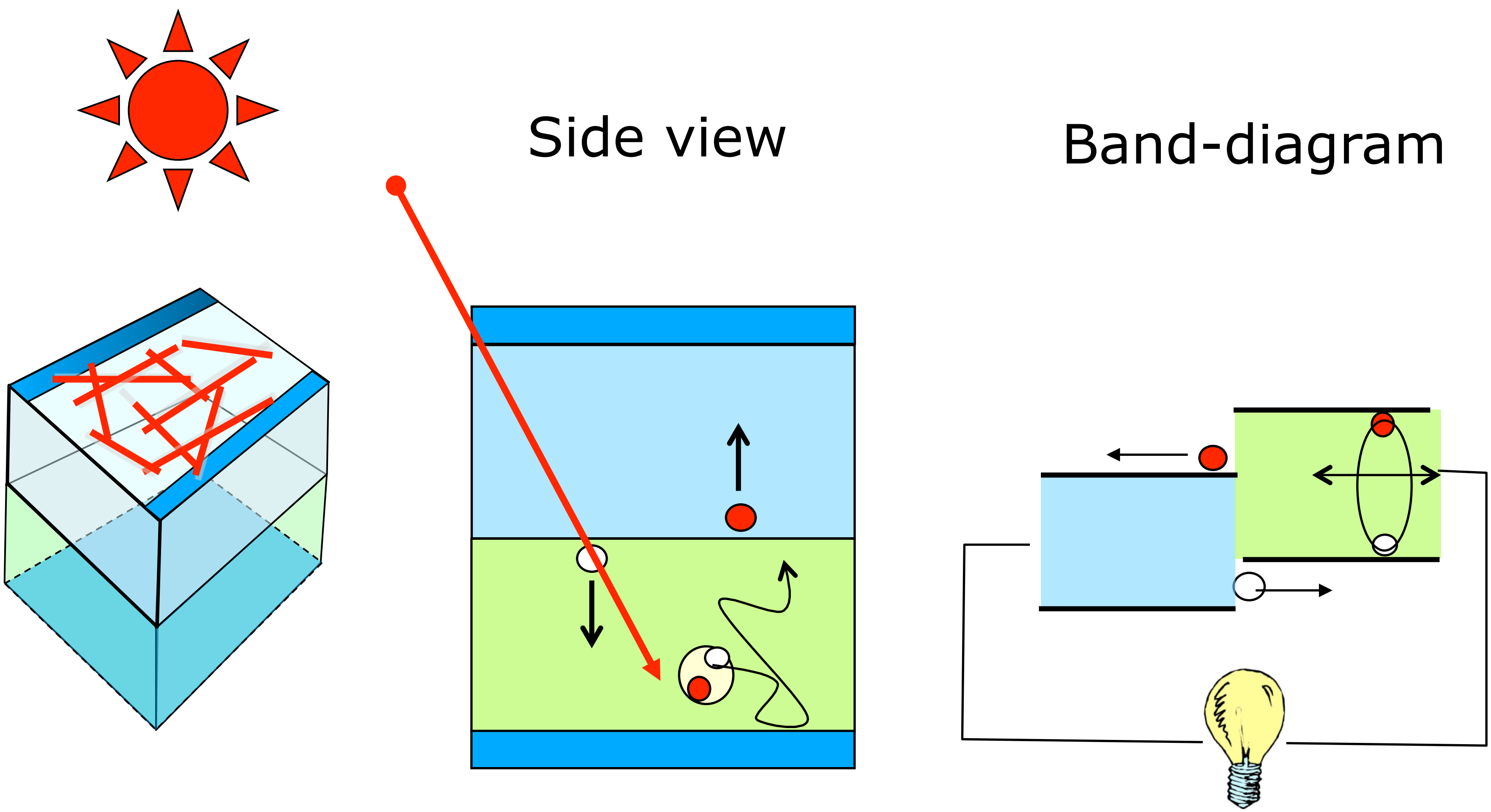
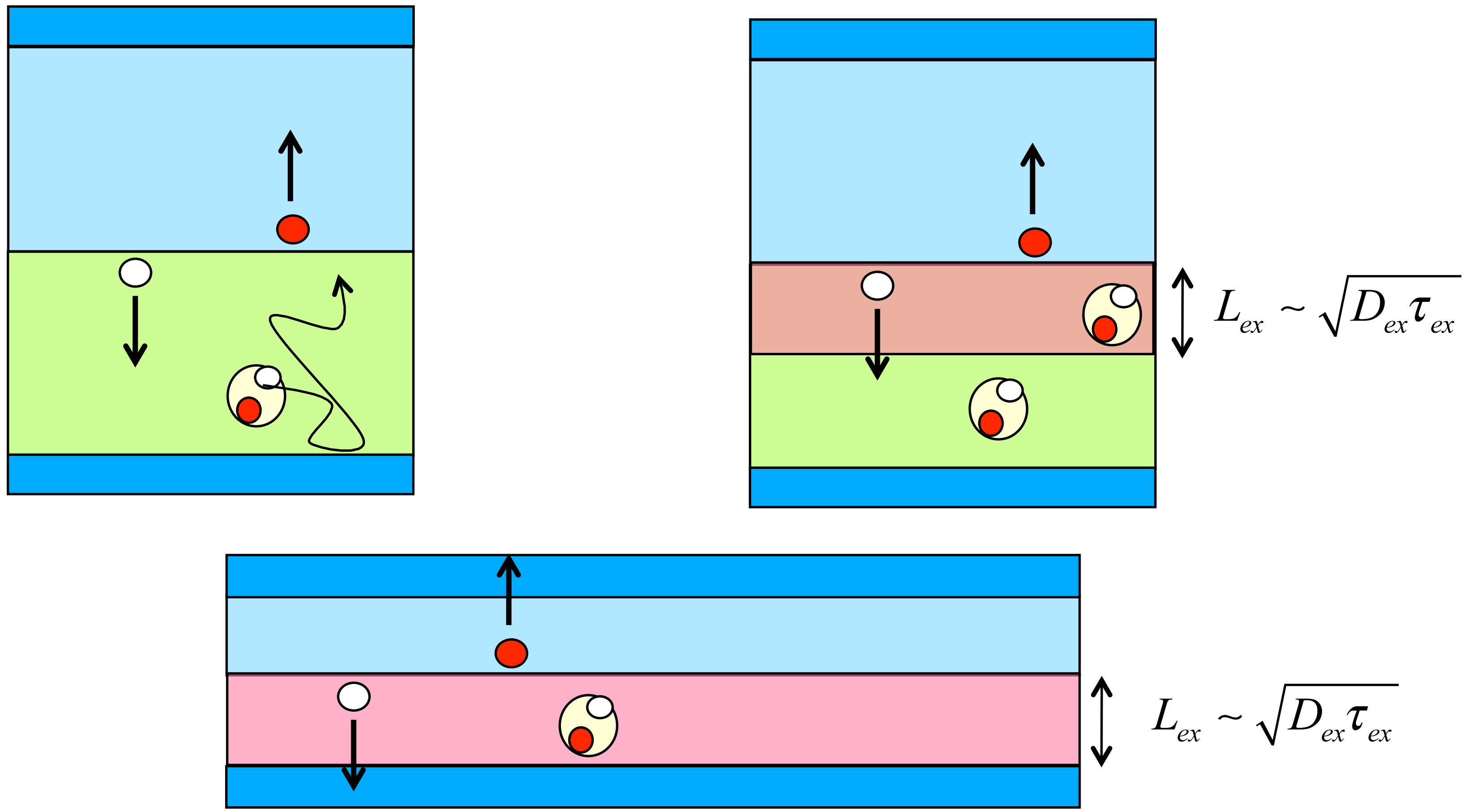
transport in solar cells ...



Exciton recombination before dissociation at the junction makes it a poor cell ...

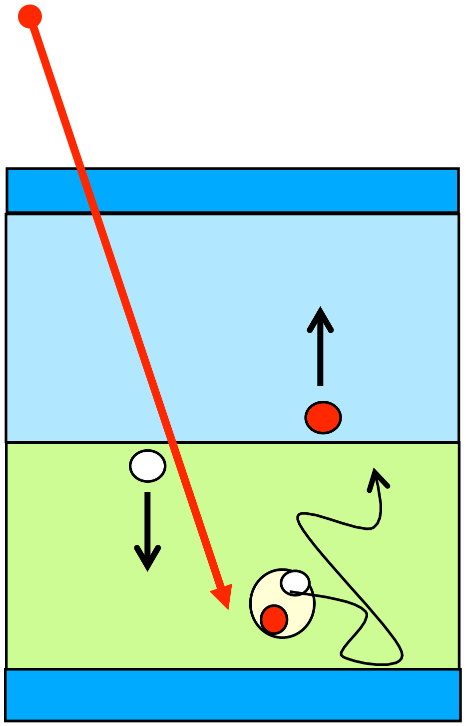
problem of exciton recombination …



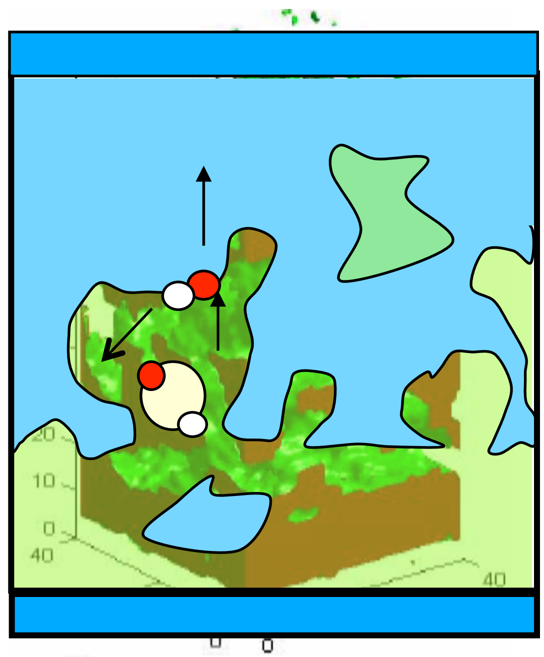
Making such thin film is essentially difficult,
the layers will short out …

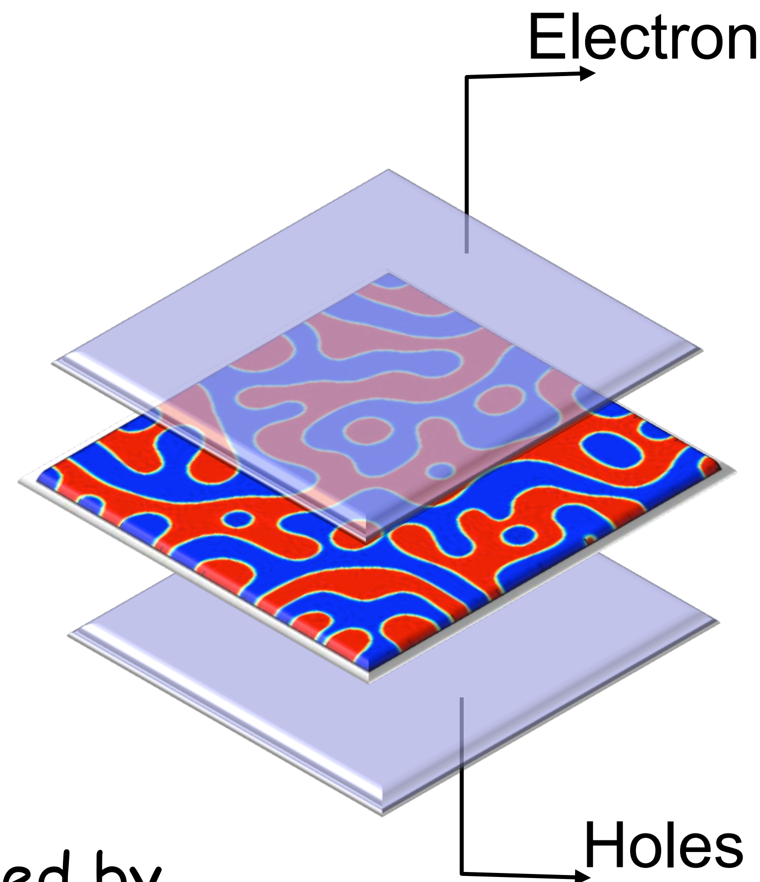
meso-structured organic solar cells

Side view



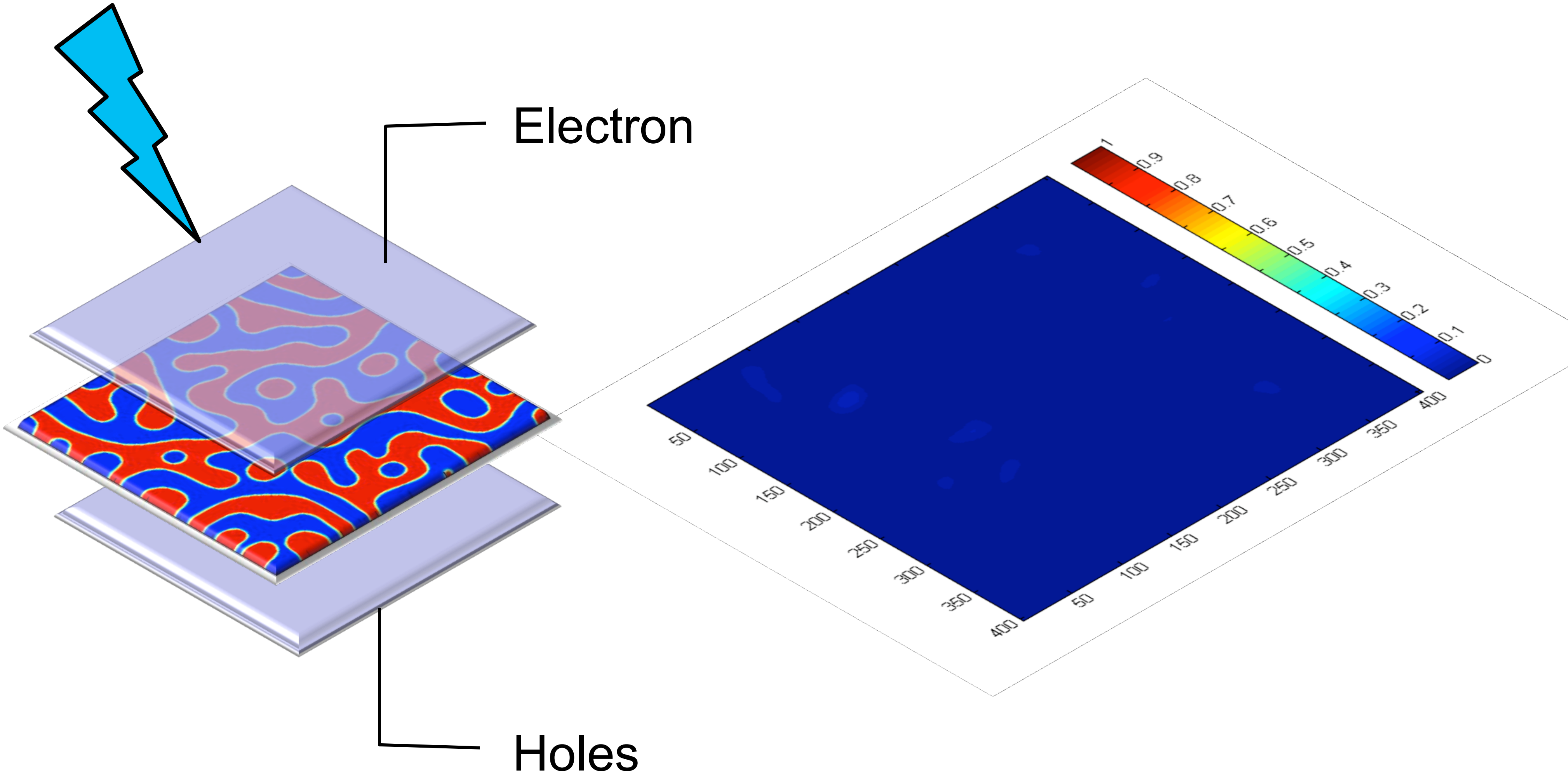
Mixed Layers



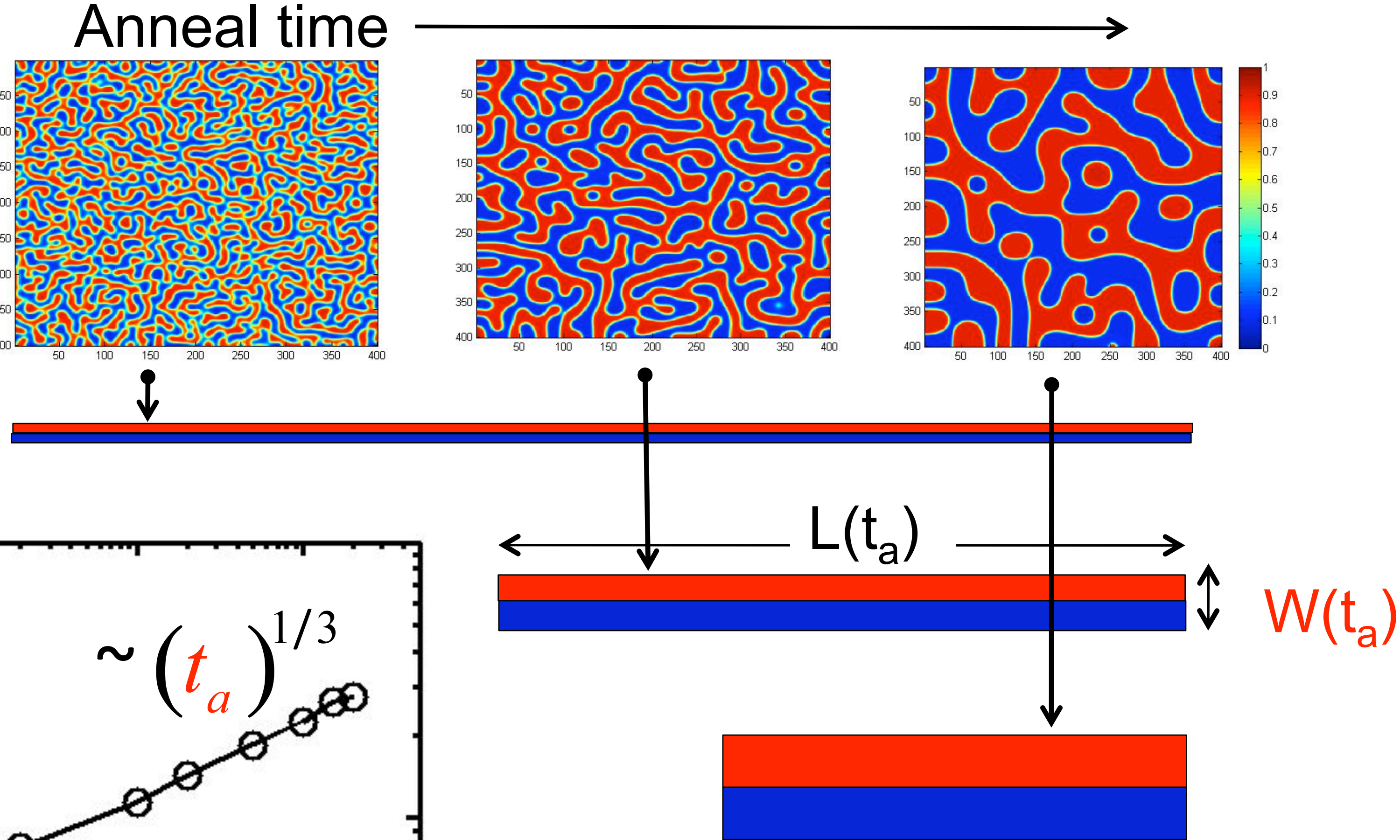


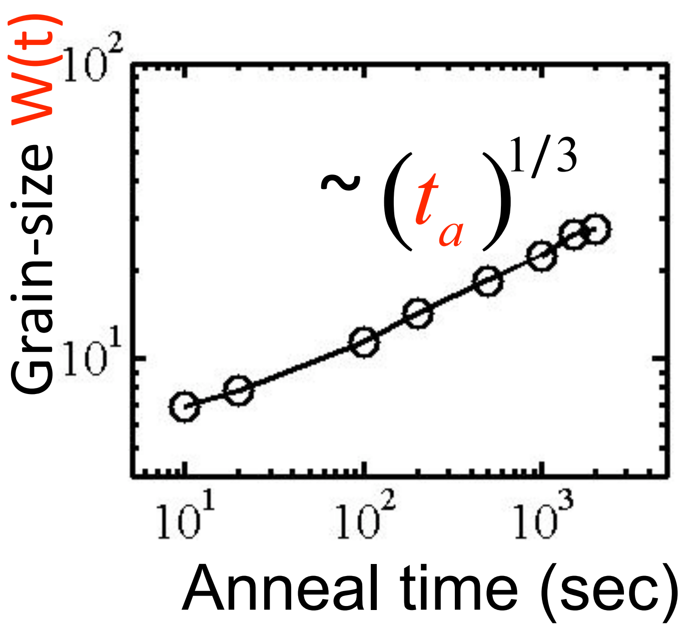
Phase segregation dominated by Spinodal decomposition

response of BH cells to light pulses



demixing/self-organization into thin films

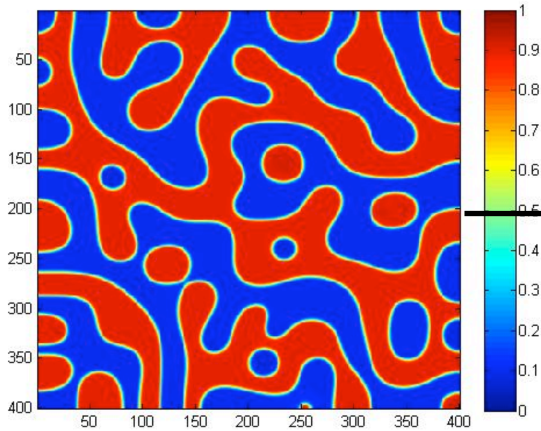


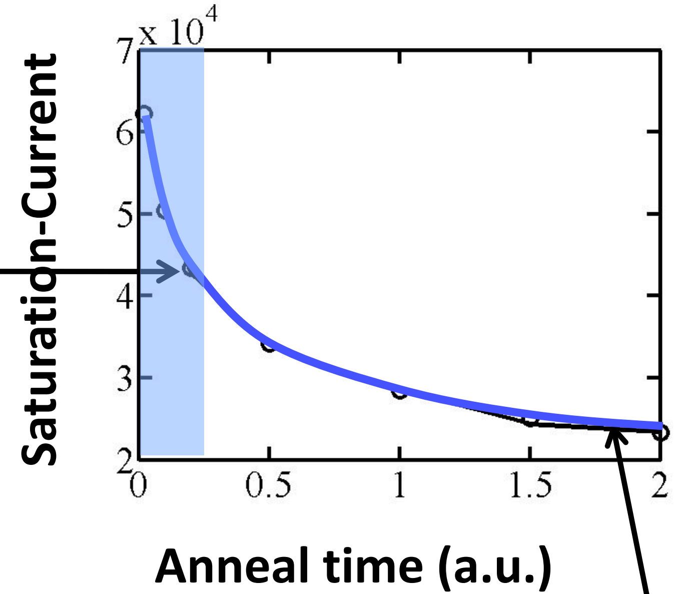


$$L(t)\times W(t)=\frac{Area}{2}$$

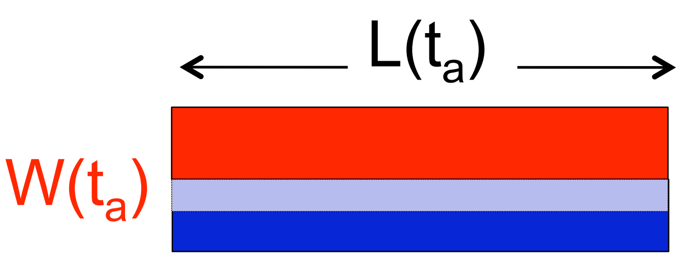
$$L(t)\sim\frac{Area}{2t_a^{1/3}}$$

exciton recombination current …





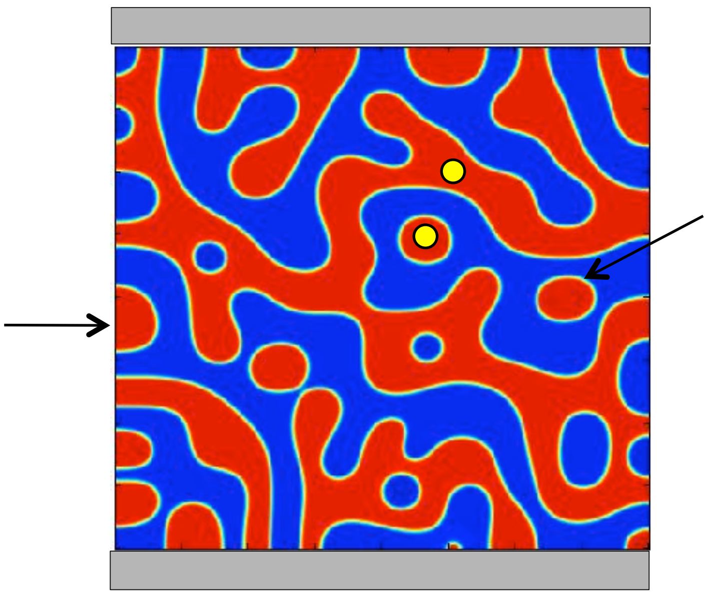
$$I = \frac{Q}{\tau_{ex}} \sim \sqrt{\frac{D_{ex}}{\tau_{ex}}} \frac{1}{t_a^{1/3}}$$



$$Q = q\sqrt{D_{ex}\tau_{ex}} \times L(t_a)$$

Form defines function ….

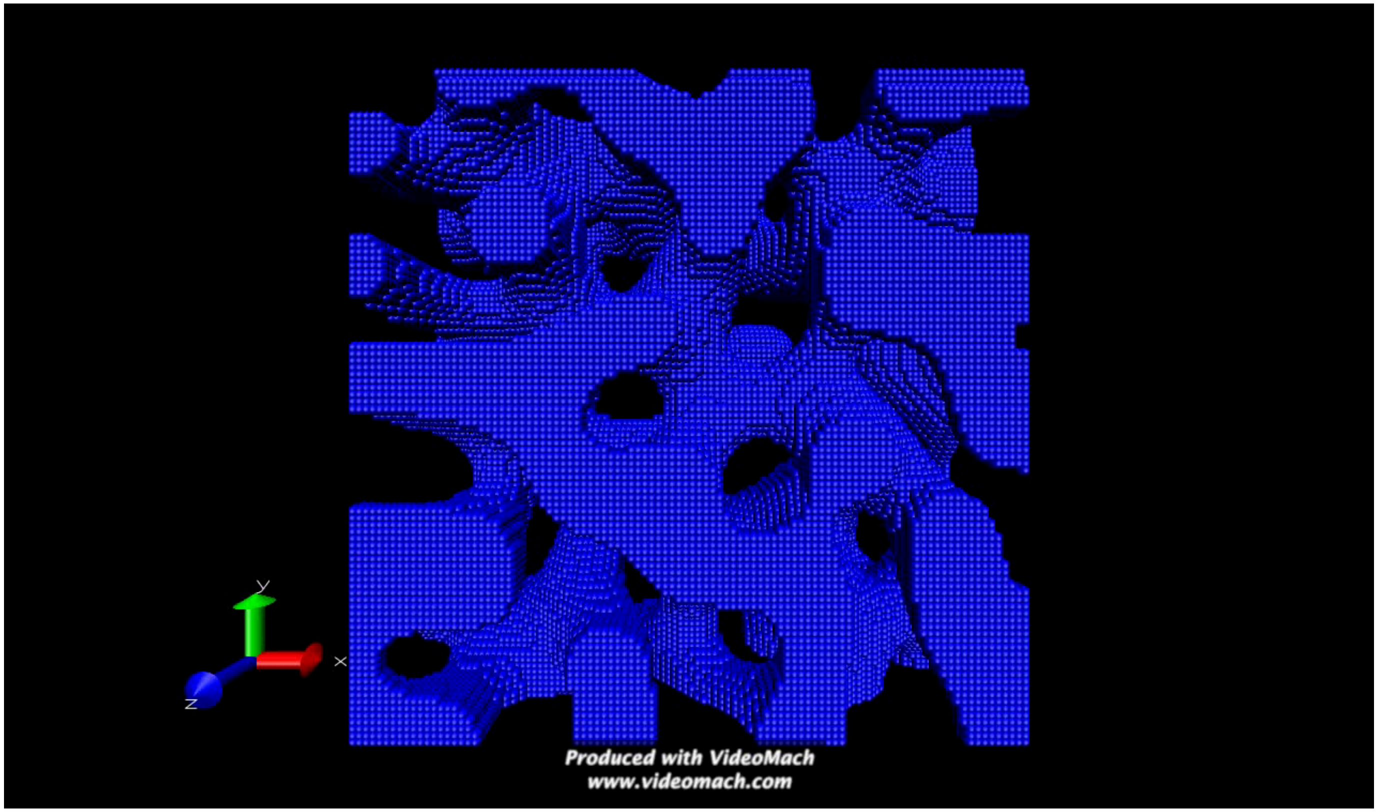
not really equivalent
(escaping to the contact)



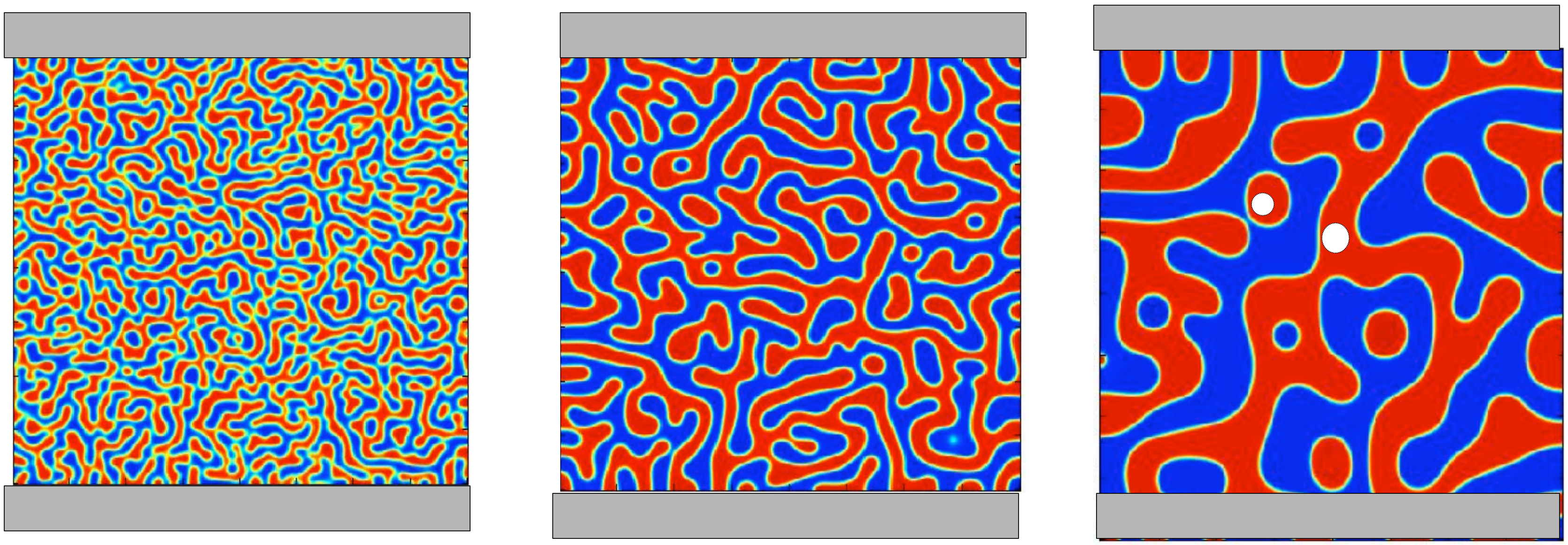
At short anneal time, a large fraction of excitons can dissociate, but cannot escape to contacts

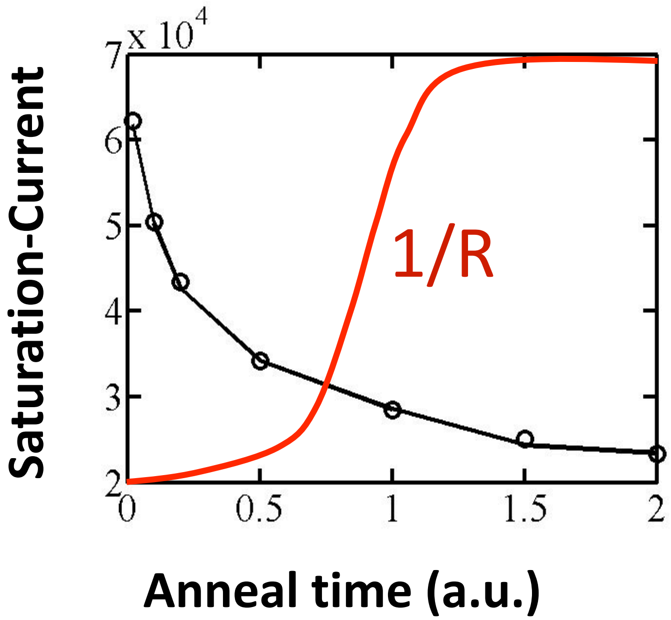
morphology in 3D view

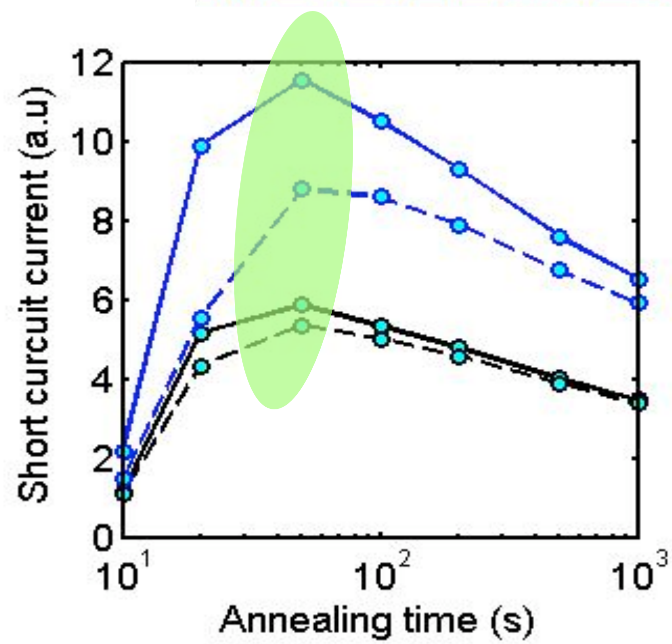
Phase segregated material after a certain anneal time t …..



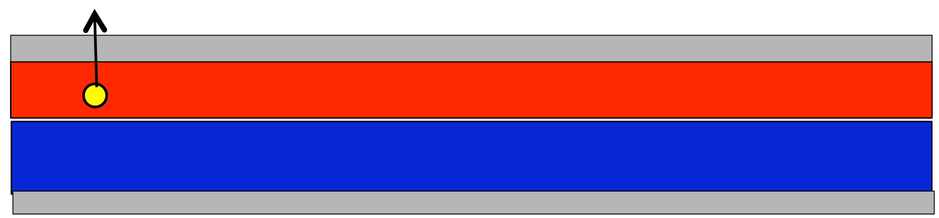
highly efficient optimal structure



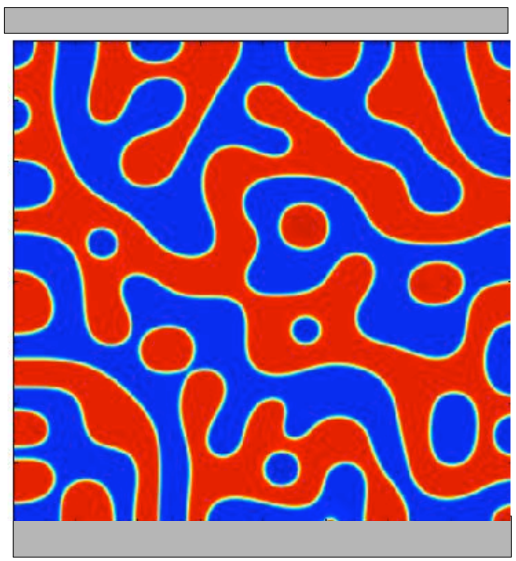




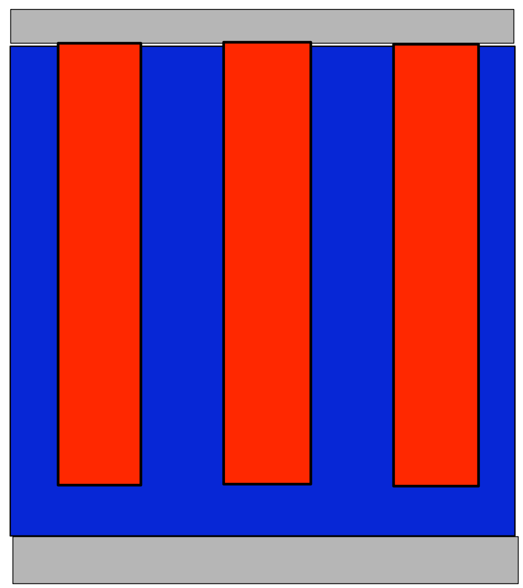
ordered vs. spinodal films



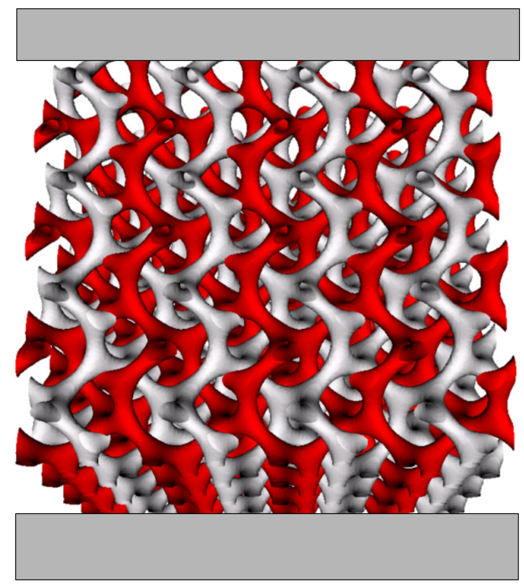
Spinodal



Ordered



Double Gyroid

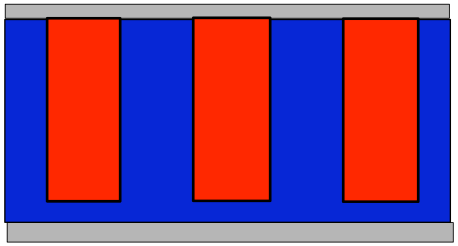


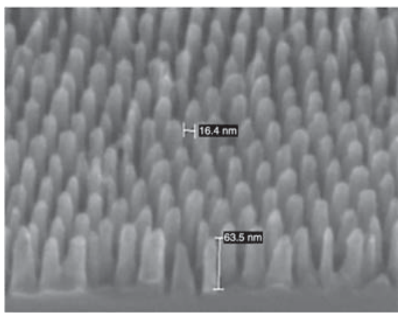
DF easily controlled by annealing

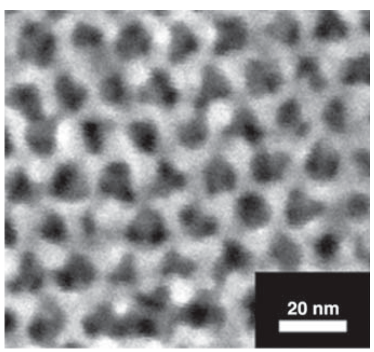
DF controlled by lithography ...

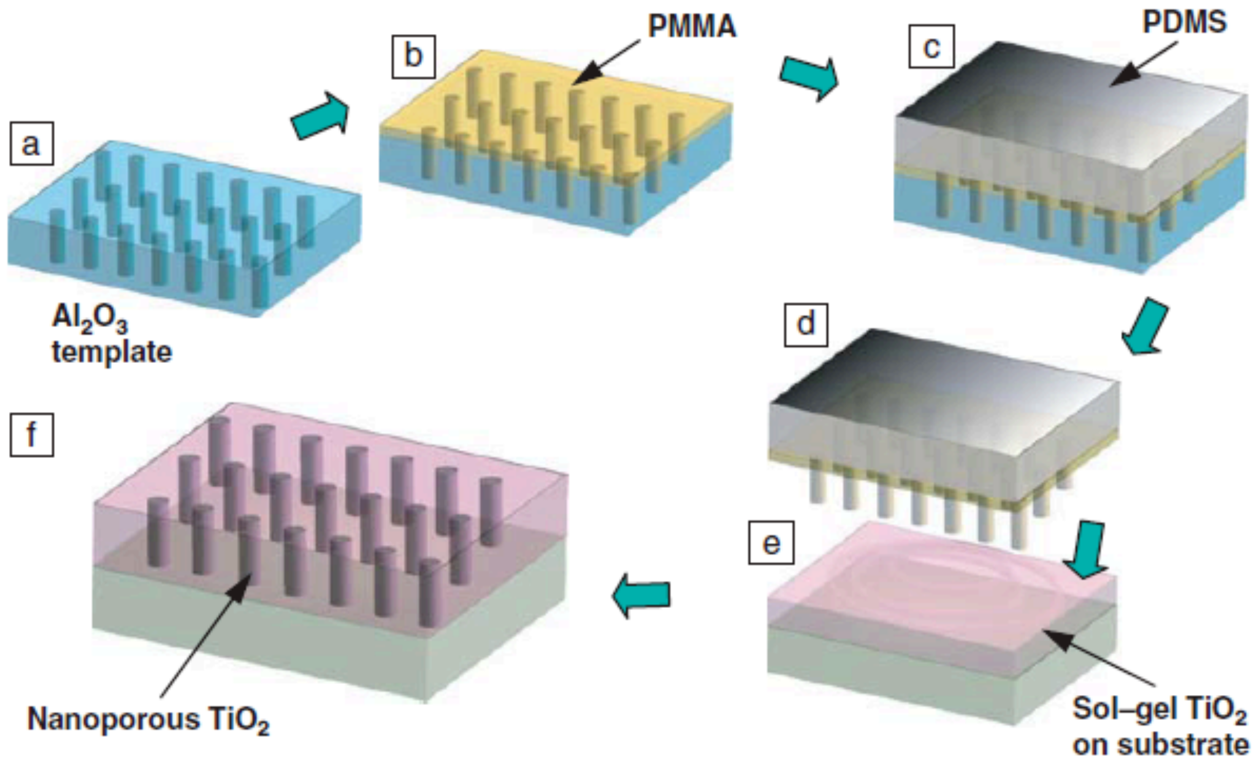
Inexpensive, but DF in limited range

ordered bulk heterostructure solar cells



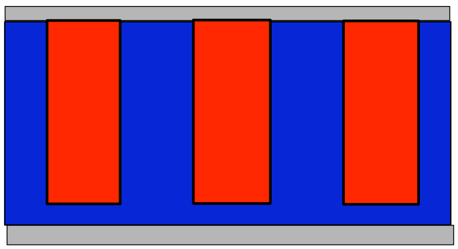


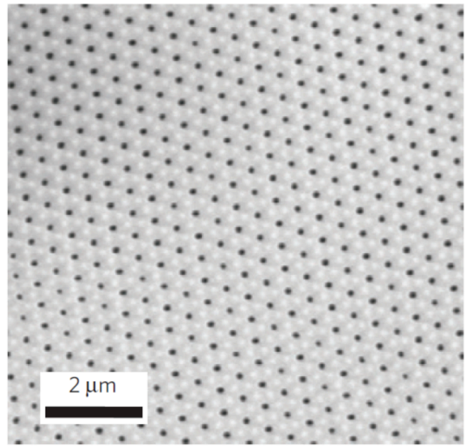


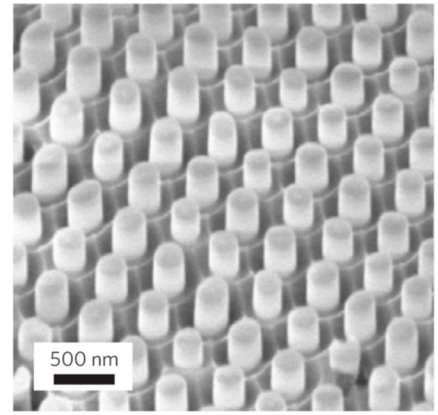


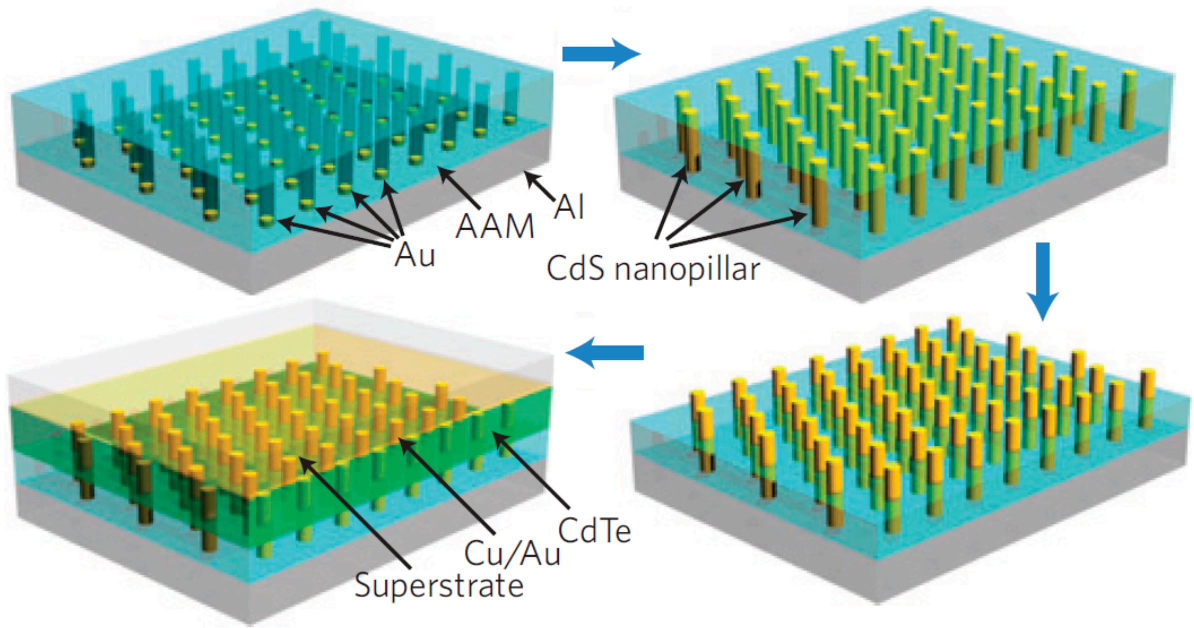
McGehee, MRS Bulletin, Feb. 2009
A. Javey, Nature Materials, July 2009

ordered bulk heterostructure solar cells



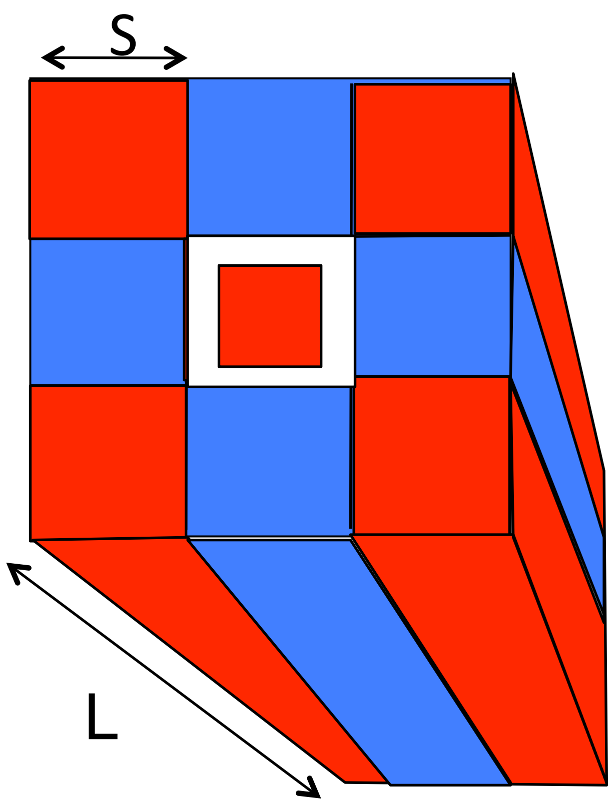






A. Javey,
Nature Materials,
July 2009

the balancing act ...



Finger density ...

$$N_F \sim 1/2S^2 \quad V_F = LS^2$$

Fraction of the charge collected/finger ...

$$F(S) \sim 4S \times \sqrt{D_{ex}\tau_{ex}} / 2S^2$$

$$\sim 2\sqrt{D_{ex}\tau_{ex}} / S$$

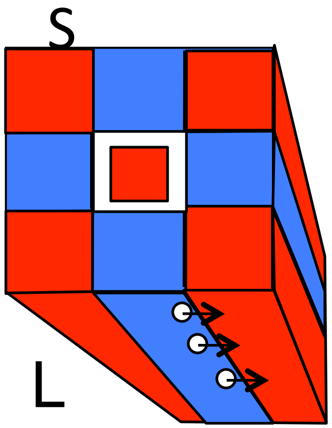
Two blocks

Total charge collected ...

$$Q_{ex} = P \times V_F \times F(S) \times N_F$$

$$\sim PL\sqrt{D_{ex}\tau_{ex}} / S$$

the balancing act ...

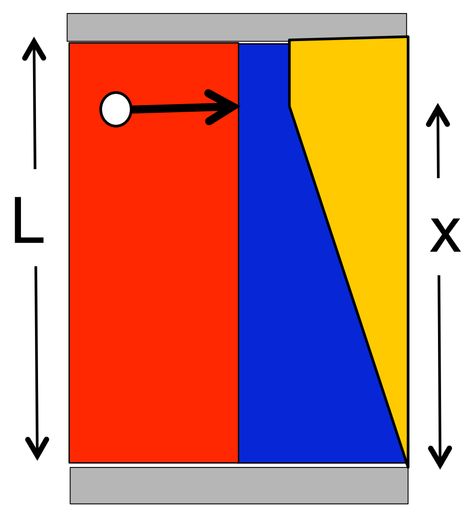


Transit time for charge injected at x ...

$$Q_e(x) = q\left[(L-x)n_1 + (x/2)n_1\right]$$

$$J_e = qDn_1/x \Rightarrow \; t(x) = (L-x) + x^2/2$$

Average transit time ...



$$T = \int_0^L dx\, t(x) = L^2/3D$$

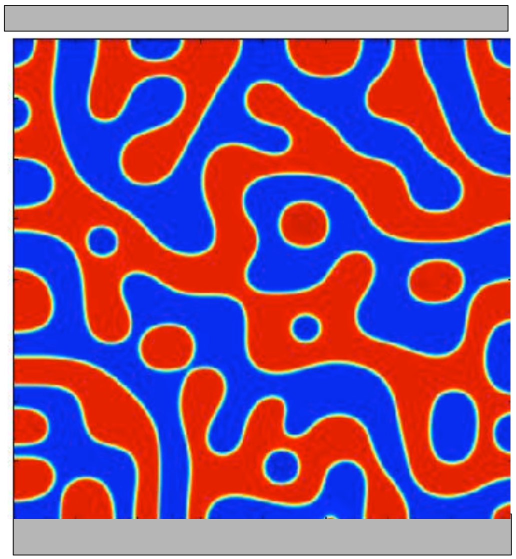
Output current...

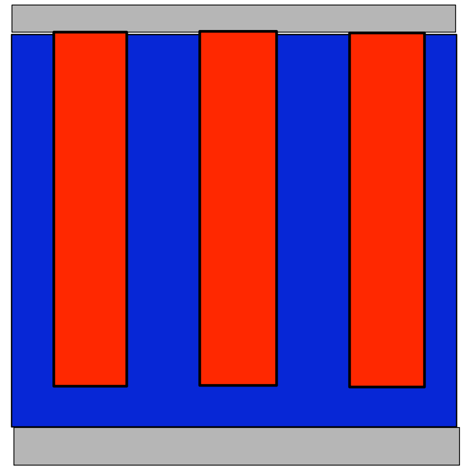
$$I \;= Q/T = qPL\sqrt{D_{ex}\tau_{ex}}/S/\left(L^2/3D_e\right)$$

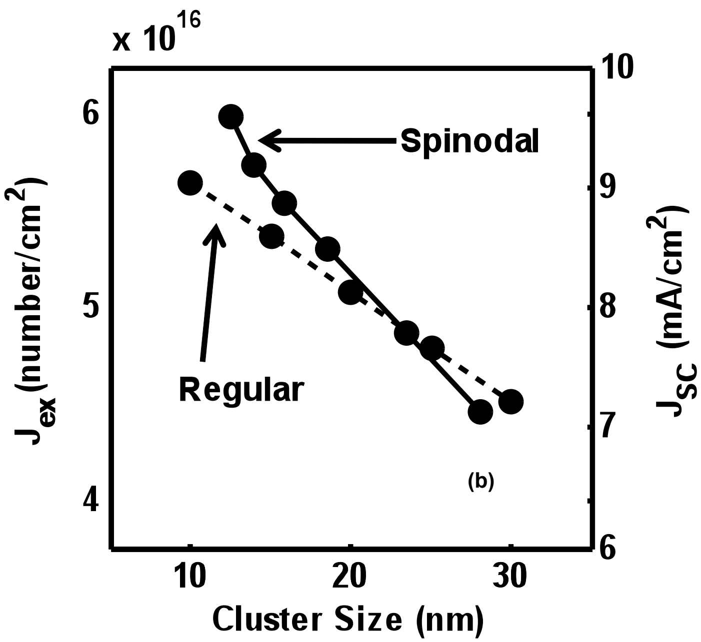
$$= \left(3D_e\sqrt{D_{ex}\tau_{ex}}P/SL\right)$$

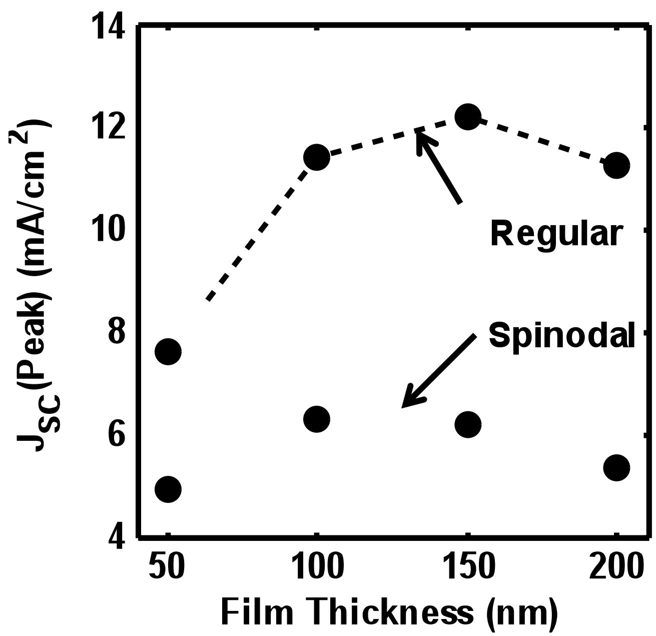
Optimal length (~ absorption length) and S ~ diffusion length

ordered bulk hetero structure solar cells





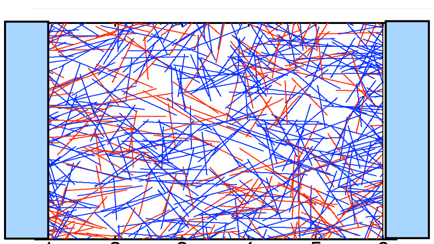


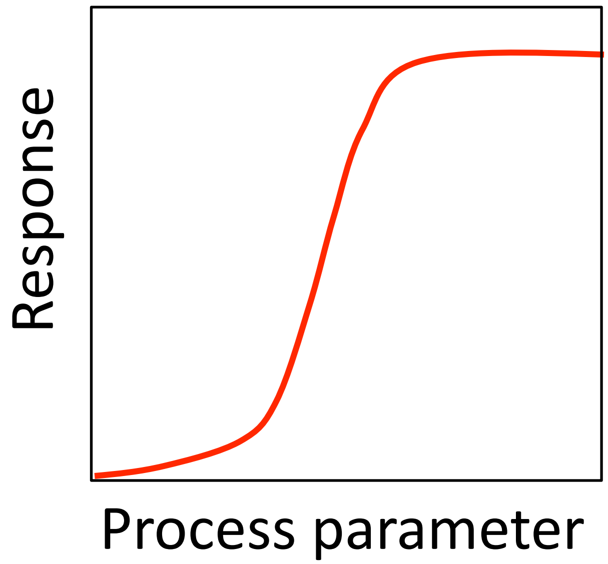


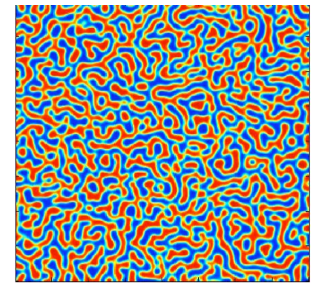
outline of lecture 6

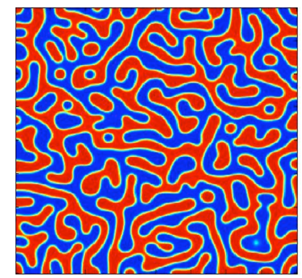
1) Introduction: Definitions and Review
2) Reaction diffusion in fractal volumes
3) Carrier transport in BH solar cells.
4) All phase transitions are not fractal
5) Conclusions

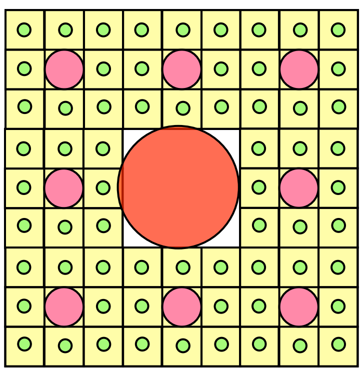
percolative vs. non-percolative transitions



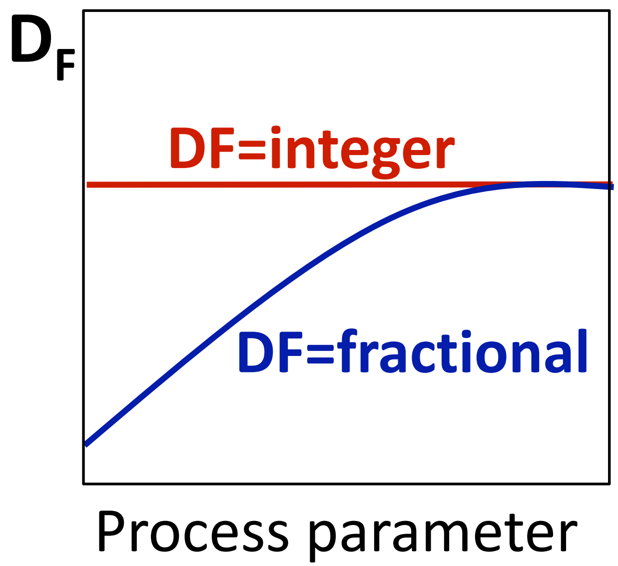


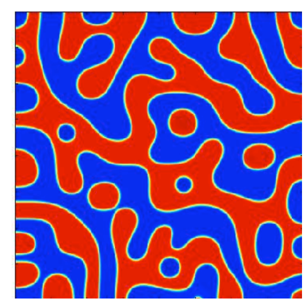






Scale invariance

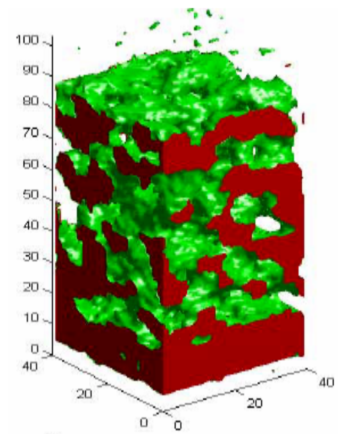


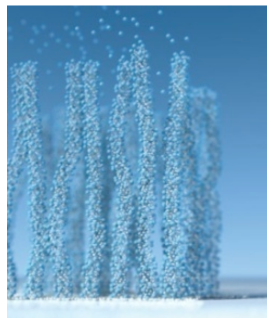


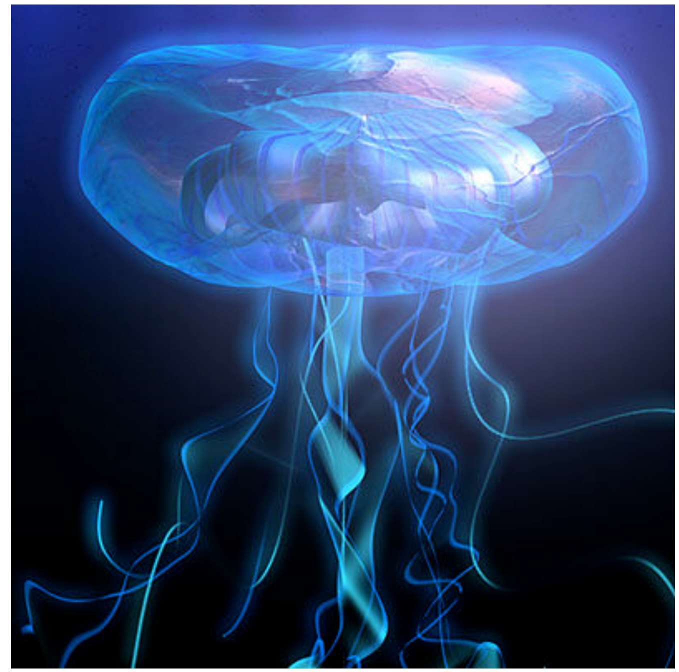
conclusions

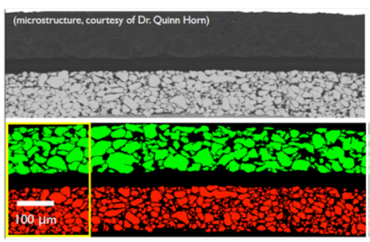
- Discussed two important problems relevant to electronic devices that can easily be addressed via theory of random systems.
- The time-exponent of a reaction-diffusion problem on fractal network is defined by its dimension and size. If the design can use critical dimension, then scaling up is simplified.
- There is an optimal annealing time for spinodal BH solar cell. Regularized cell improves performance significantly at the expense of increased process cost.

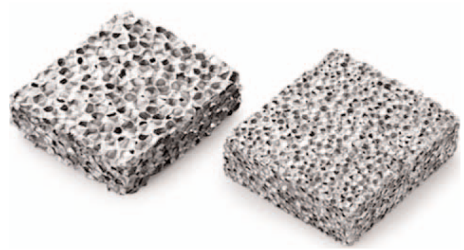
Random material and biomimetic design











Life at the edge of equilibrium thermodynamics uses geometry in remarkable ways … description of that geometry is essential in understanding the function of biomimetic materials and devices

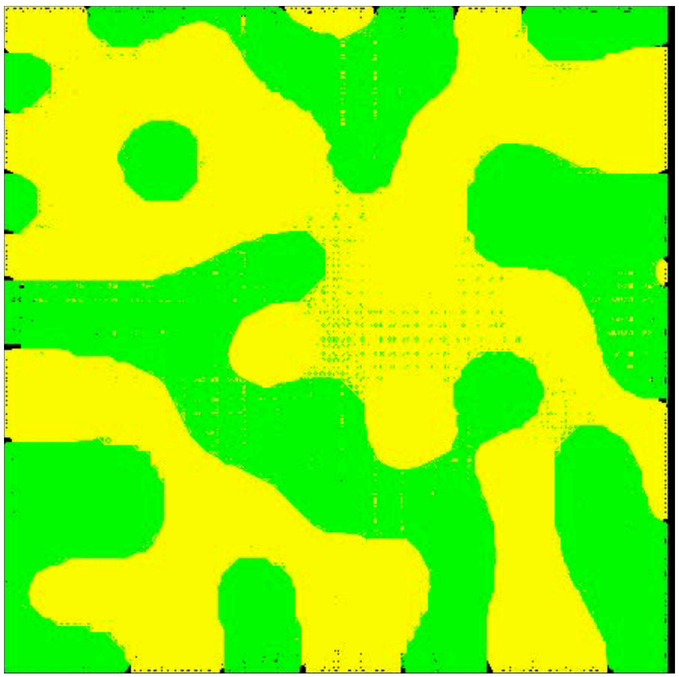
figure credits and backup slides

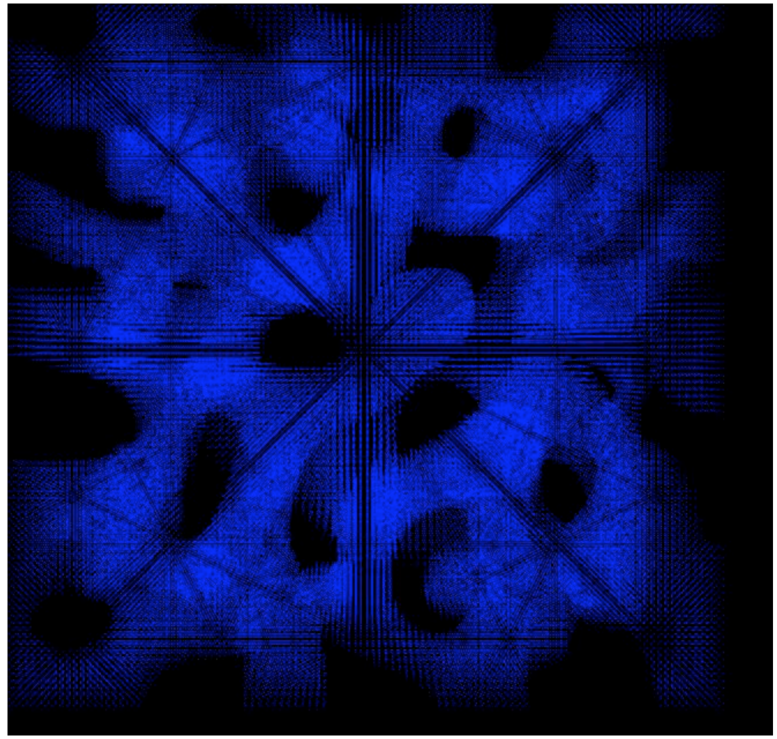
Activated charcoal:
http://www.chemistryland.com/CHM107Lab/Exp01_AirFilter/Lab/micrographActivatedCharcoal2.jpg
Porous electrode: http://www.centronast.com/archives/146
Battery: http://www.pemdesign.de/getimg.php?id=45

Ref. Mixed solar cell: Peter Peumans, Ph.D. Thesis, 2003.

Appendix

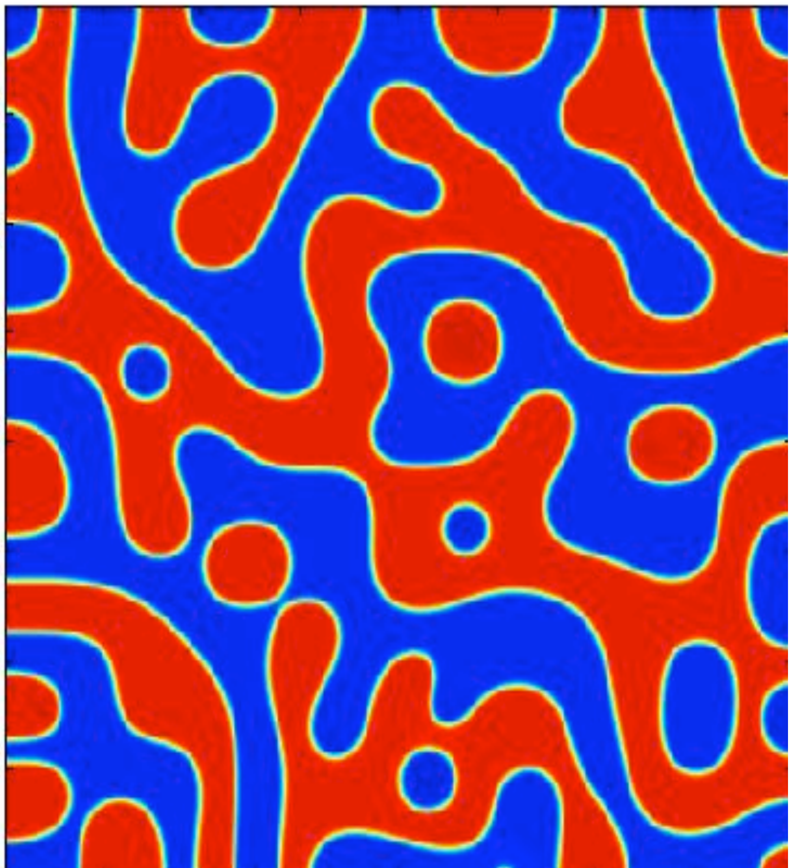
morphology in 3D view





double gyroids for solar cells

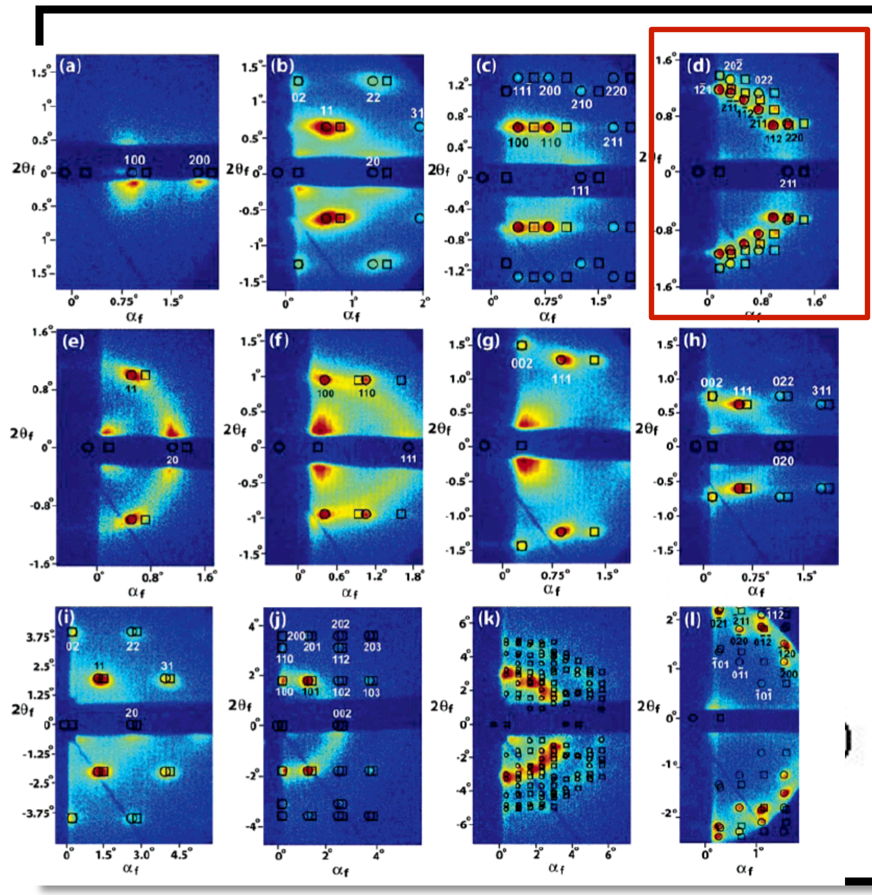
Top Electrode



Bottom Electrode

http://www.psc.edu/science/teragyroid.html

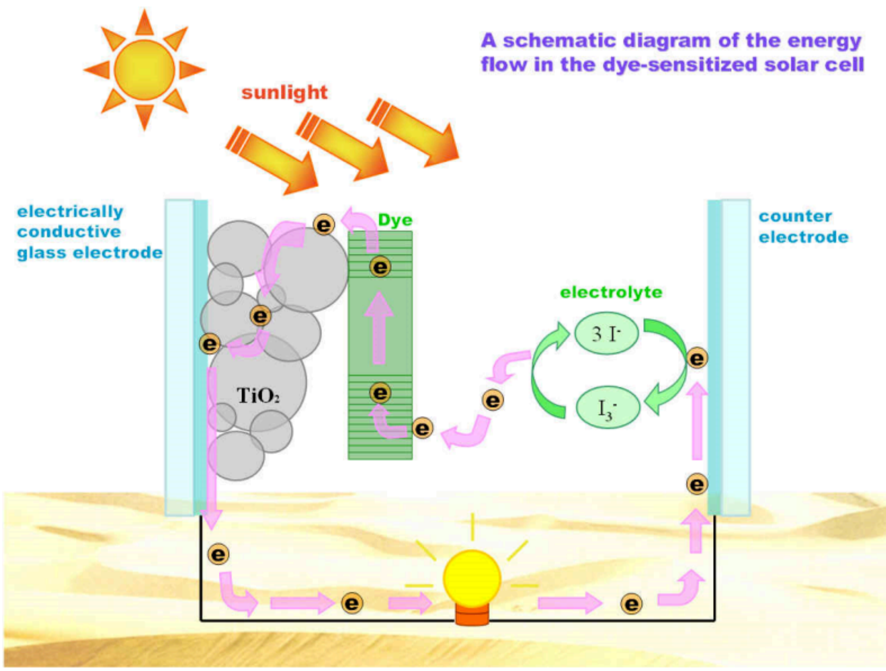
GISAXS Plots



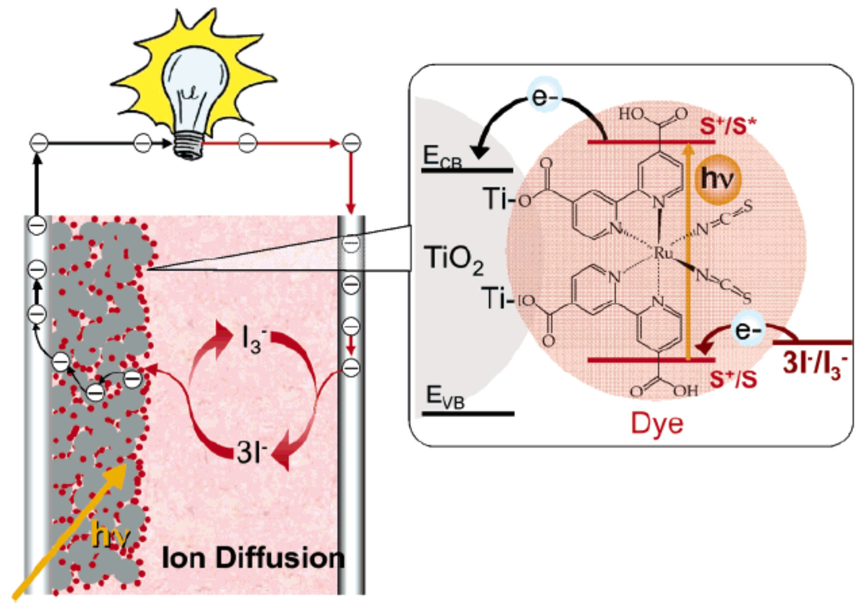
Hillhouse, Langmuir, 23, 10, 2007. p 5689

2.2. Grazing Incidence Small-Angle X-ray Scattering (GISAXS)

Dye-sensitized Solar Cells



www.postech.ac.kr/chem/mras/eunju.jpg

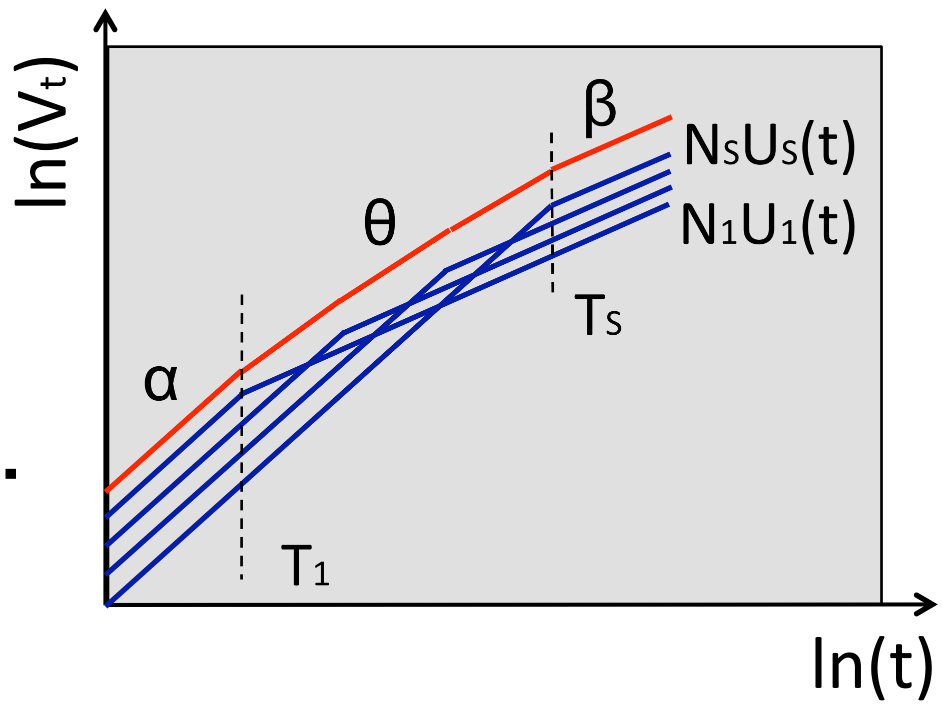


DSSC, Grätzel , Inorganic chemistry, 2005

sequential depletion with better basis …

$$V(T_s)=\sum_{i=1}^{s} N_i U_i(T_s)$$

$$=N_R^{s-1} R_R^{\gamma\beta(s-1)} \frac{1-\left(R_R^{(\delta-\gamma\beta)}/N_R\right)^s}{1-\left(R_R^{(\delta-\gamma\beta)}/N_R\right)}.$$



$$V(T_1)=N_R^{s-1} \frac{1-\left(R_R^{(\delta-\gamma\alpha)}/N_R\right)^s}{1-\left(R_R^{(\delta-\gamma\alpha)}/N_R\right)}.$$

$$\theta(s\to\infty, D_F)=\frac{1+\delta-D_F}{\gamma}.$$

$$\theta(s, D_F)=\beta+\frac{1}{\gamma(s-1)\log(R_R)}\left[\log\left(\frac{R_R^{bs}-1}{R_R^{b}-1}\right)-\log\left(\frac{R_R^{ds}-1}{R_R^{d}-1}\right)\right],$$

phase space for response of finite fractals