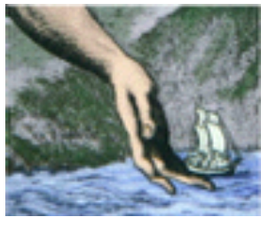
Non-equilibrium separation: from kidney on a chip to active sieving

Lydéric Bocquet
Laboratoire de Physique Statistique,
Ecole Normale Supérieure, CNRS

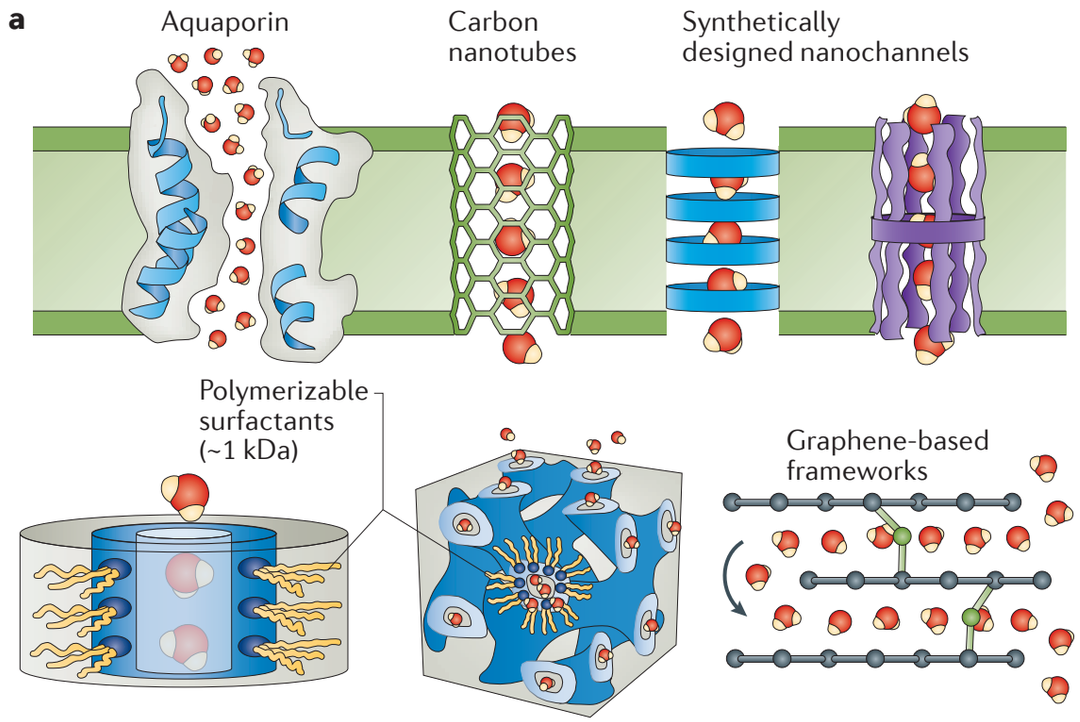
with **Sophie Marbach**



http://www.phys.ens.fr/~lbocquet

DESALINATION (AND ENERGY)

membrane process



Nature Materials Reviews (2016)

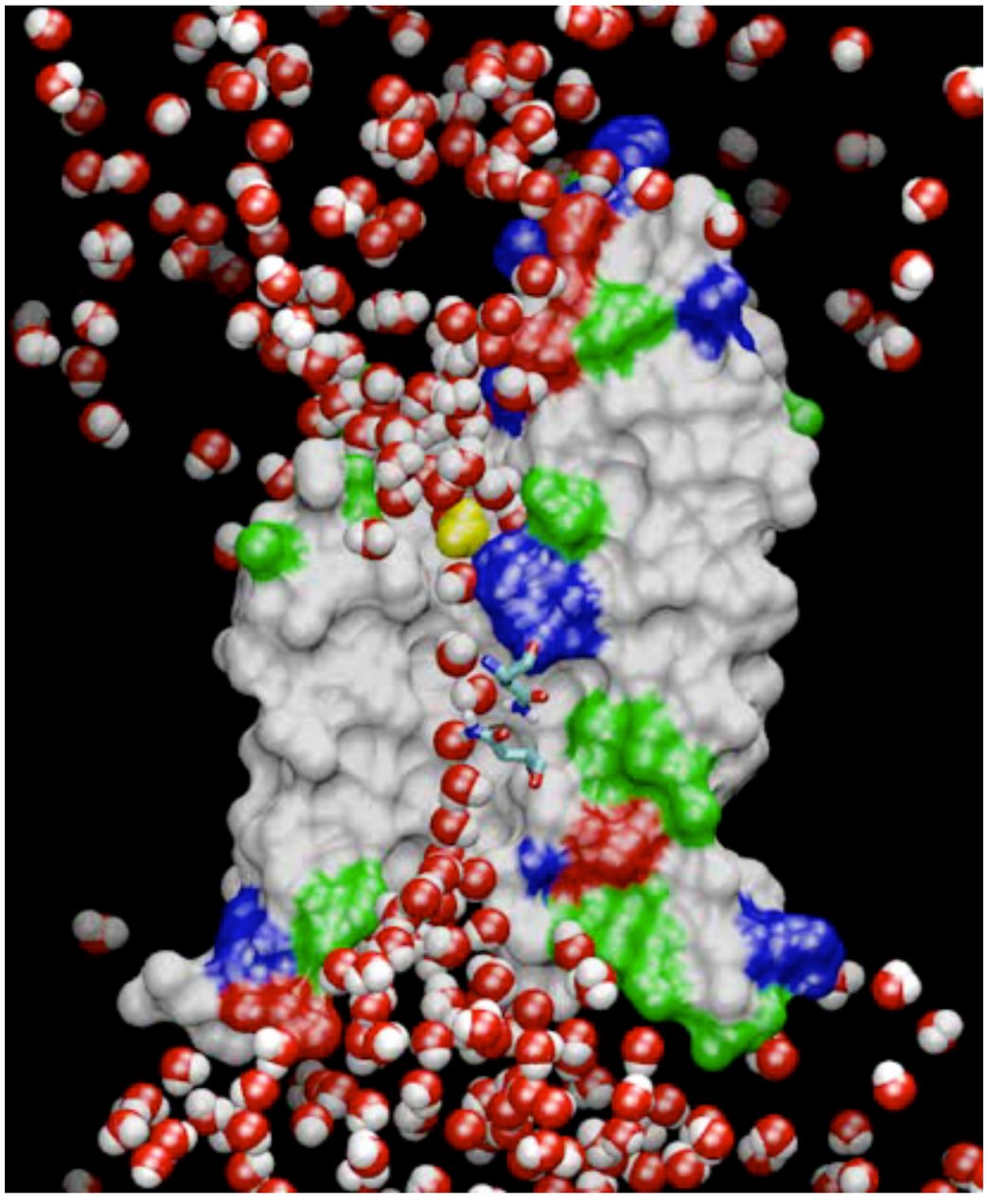
Science (2017)

sieving views: pass or reject

search for efficient pores, materials, structures to maximize separation efficiency

Park et al., Science (2017)

EFFICIENT BIOLOGICAL PORES



AQP-1

K. Schulten et al.

Bocquet-Charlaix, Chem Soc Rev (2010)
cf also Gravelle et al., PNAS (2013)

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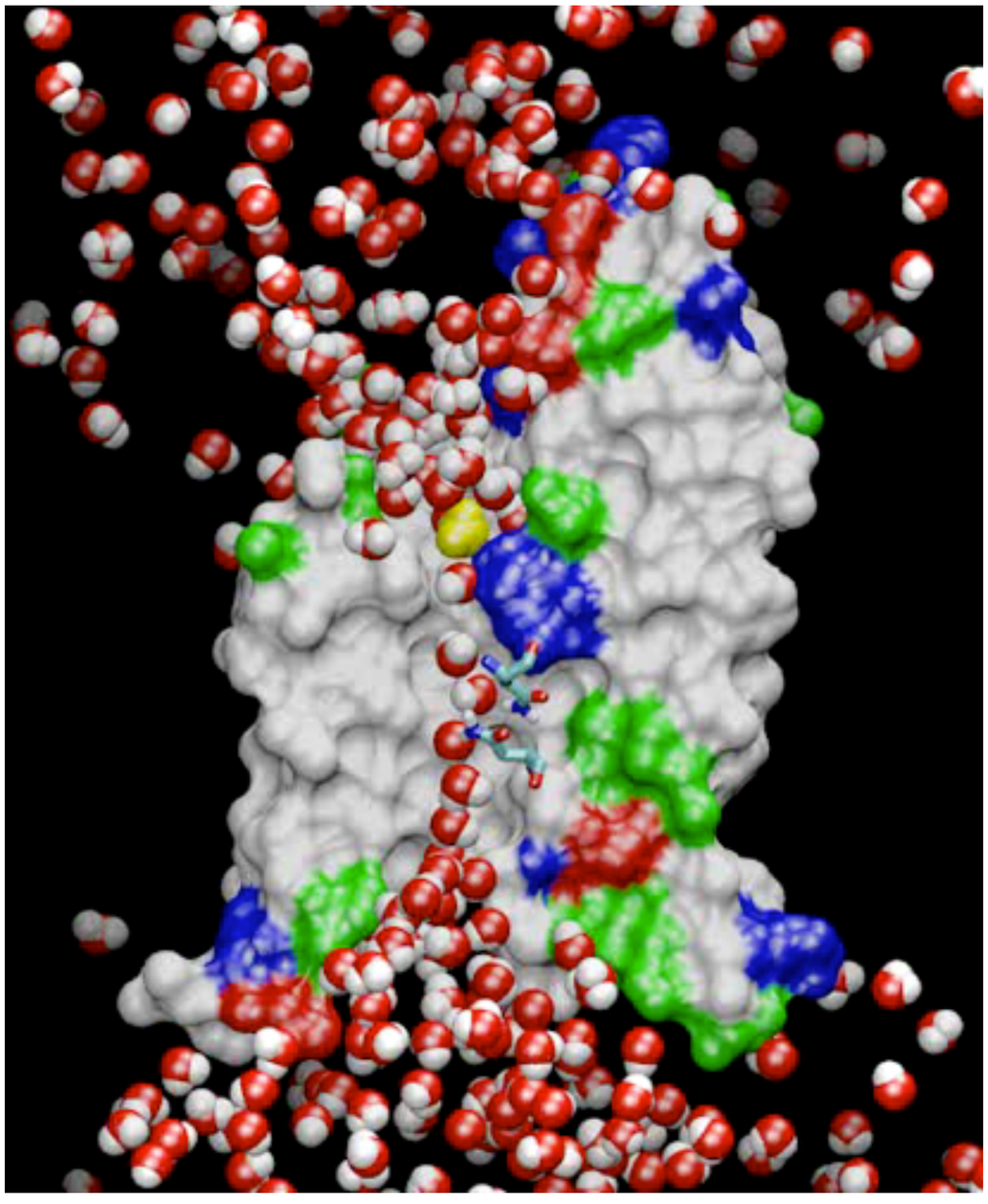

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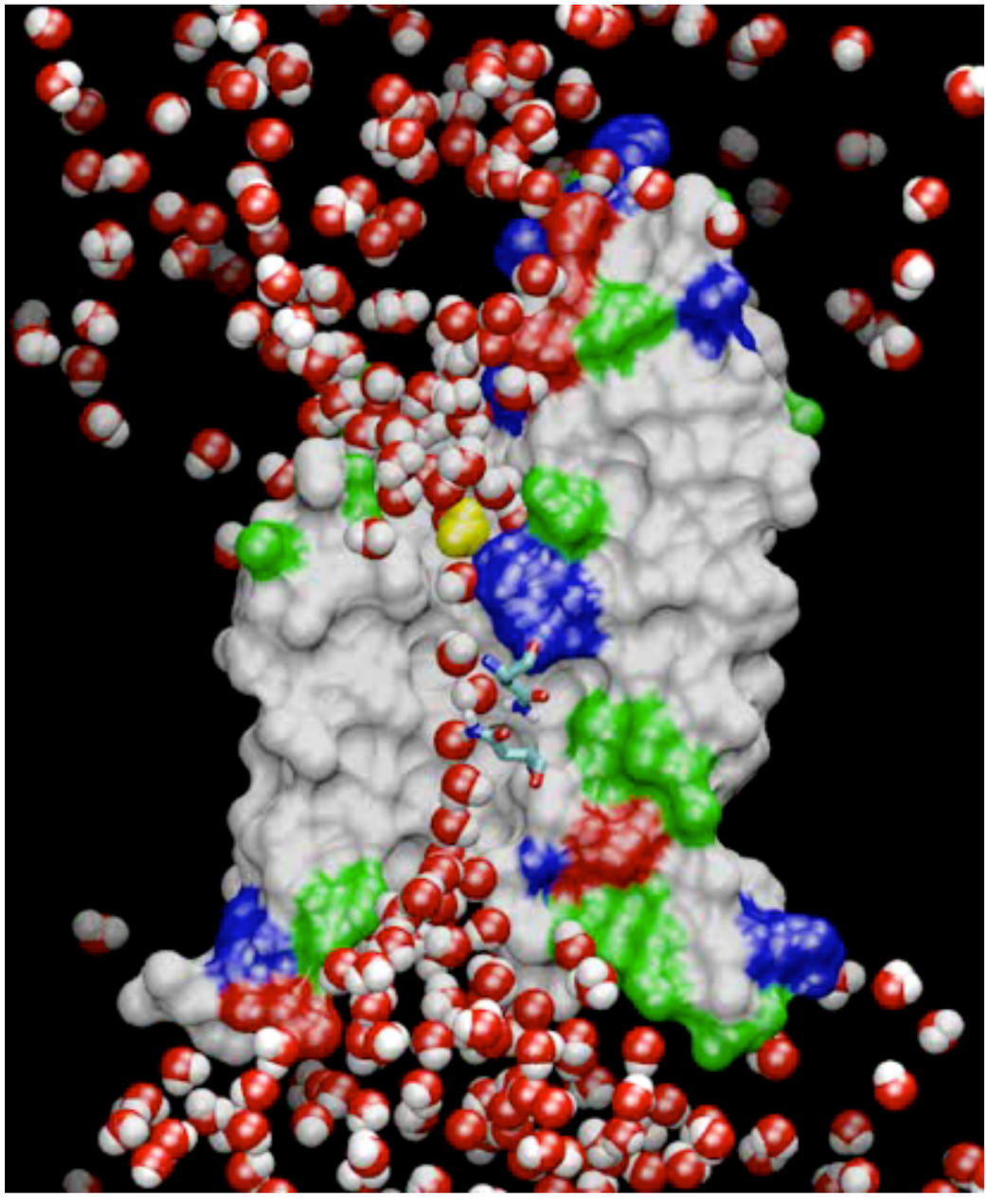

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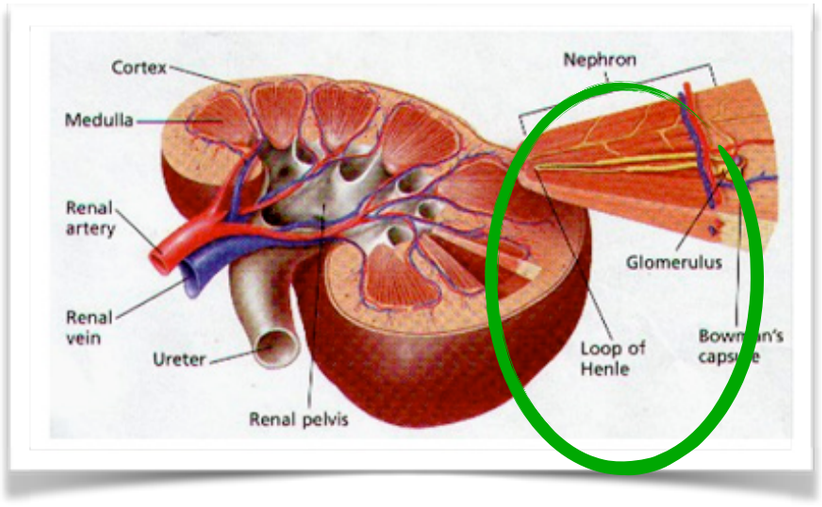

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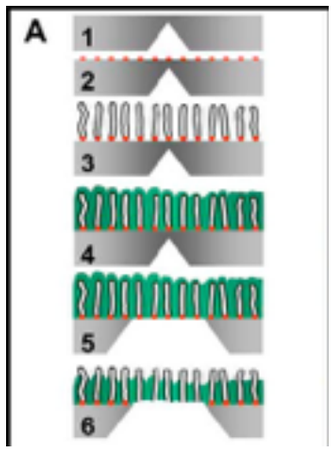
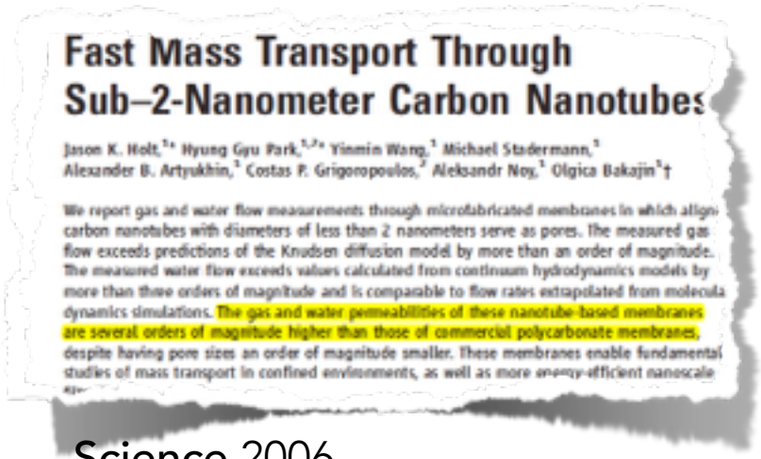
MIRACULOUS CARBON

Intringuing results … fluidic transport in carbon materials





Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes

Jason K. Holt,[1]* Hyung Gyu Park,[1,2]* Yinmin Wang,[1] Michael Stadermann,[1] Alexander B. Artyukhin,[1] Costas P. Grigoropoulos,[2] Aleksandr Noy,[1] Olgica Bakajin[1]†

We report gas and water flow measurements through microfabricated membranes in which align carbon nanotubes with diameters of less than 2 nanometers serve as pores. The measured gas flow exceeds predictions of the Knudsen diffusion model by more than an order of magnitude. The measured water flow exceeds values calculated from continuum hydrodynamics models by more than three orders of magnitude and is comparable to flow rates extrapolated from molecula dynamics simulations. The gas and water permeabilities of these nanotube-based membranes are several orders of magnitude higher than those of commercial polycarbonate membranes, despite having pore sizes an order of magnitude smaller. These membranes enable fundamental studies of mass transport in confined environments, as well as more energy-efficient nanoscale

Science 2006

also: Hinds et al., Whitby et al.

LETTER

doi:10.1038/nature193

Massive radius-dependent flow slippage in carbon nanotubes

Eleonora Secchi[1], Sophie Marbach[1], Antoine Niguès[1], Derek Stein[1,2], Alessandro Siria[1] & Lydéric Bocquet[1]

Nature 2016

also **MRS Bull.** (2017)

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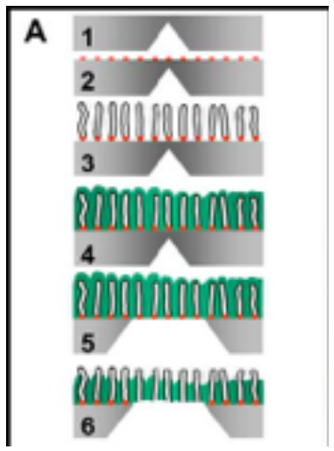

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Membranes of graphene-like materials

Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes

R. R. Nair,[1,2] H. A. Wu,[1,3] P. N. Jayaram,[2] I. V. Grigorieva,[1] A. K. Geim[1,2]*

Science 2012

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RESEARCH ARTICLE

NANOTECHNOLOGY

Ion transport in complex layered graphene-based membranes with tuneable interlayer spacing

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NonCommerci
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Chi Cheng,[1]* Gengping Jiang,[1]* Christopher J. Garvey,[2] Yuanyuan Wang,[1] George P. Simon,[1,3] Jefferson Z. Liu,[3,4]† Dan Li[1,3]†

Science Adv. 2016

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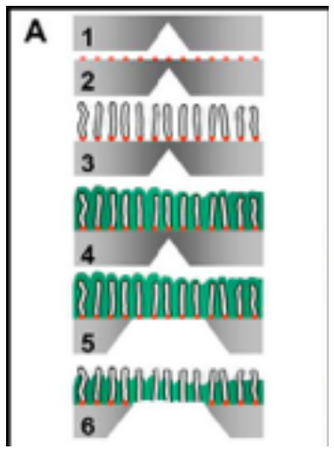

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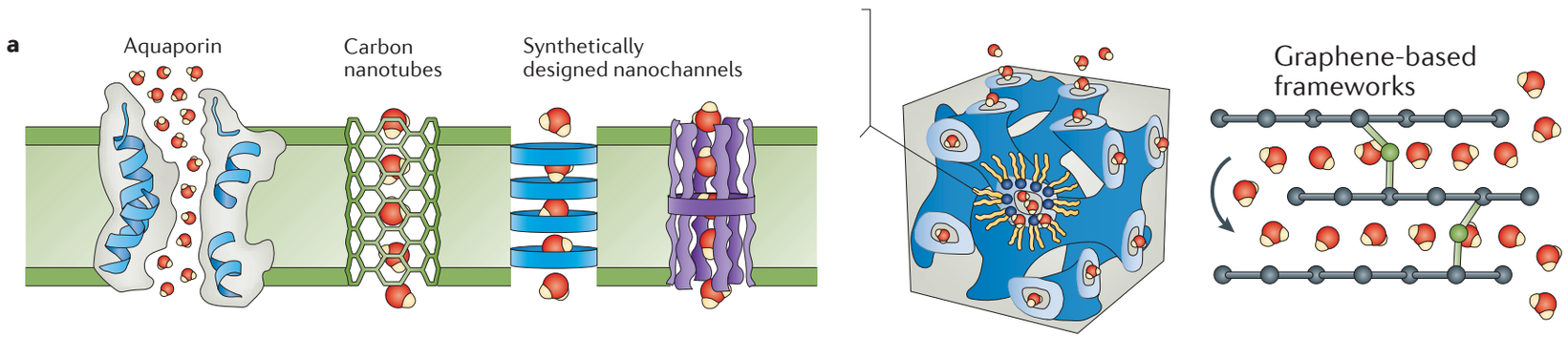
Science Adv. 2016

MIRACULOUS CARBON ?
NEW CARBON MEMBRANES !

SIEVING: A TRADE-OFF

reject or flow: being selective requires a bit of queuing



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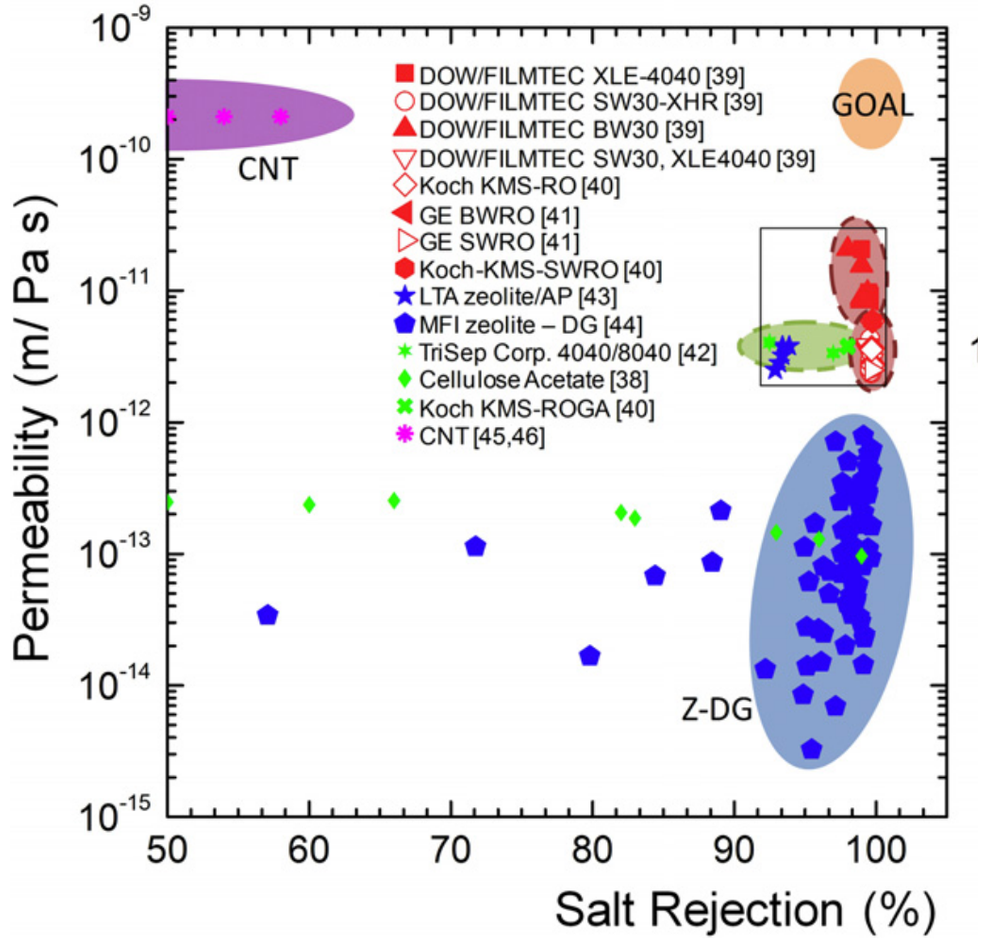

Humplik et al. (2011)

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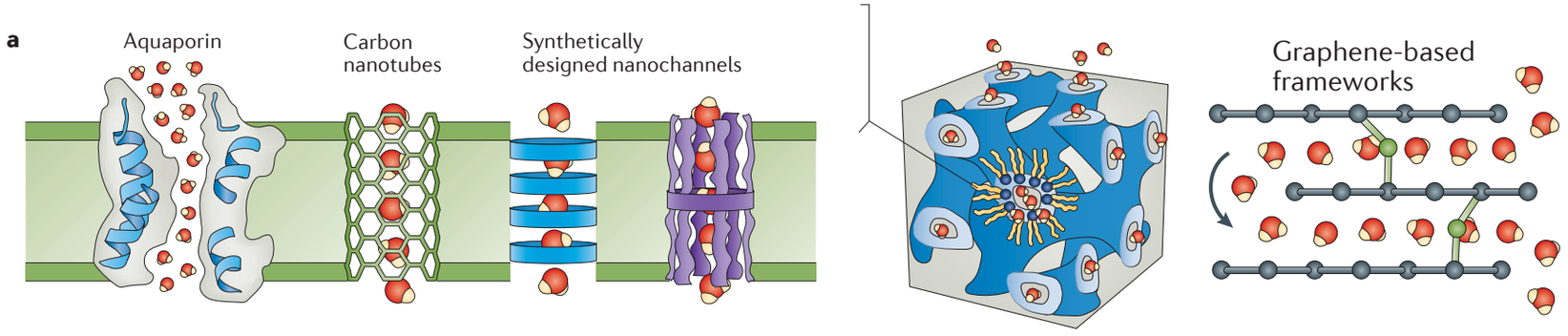

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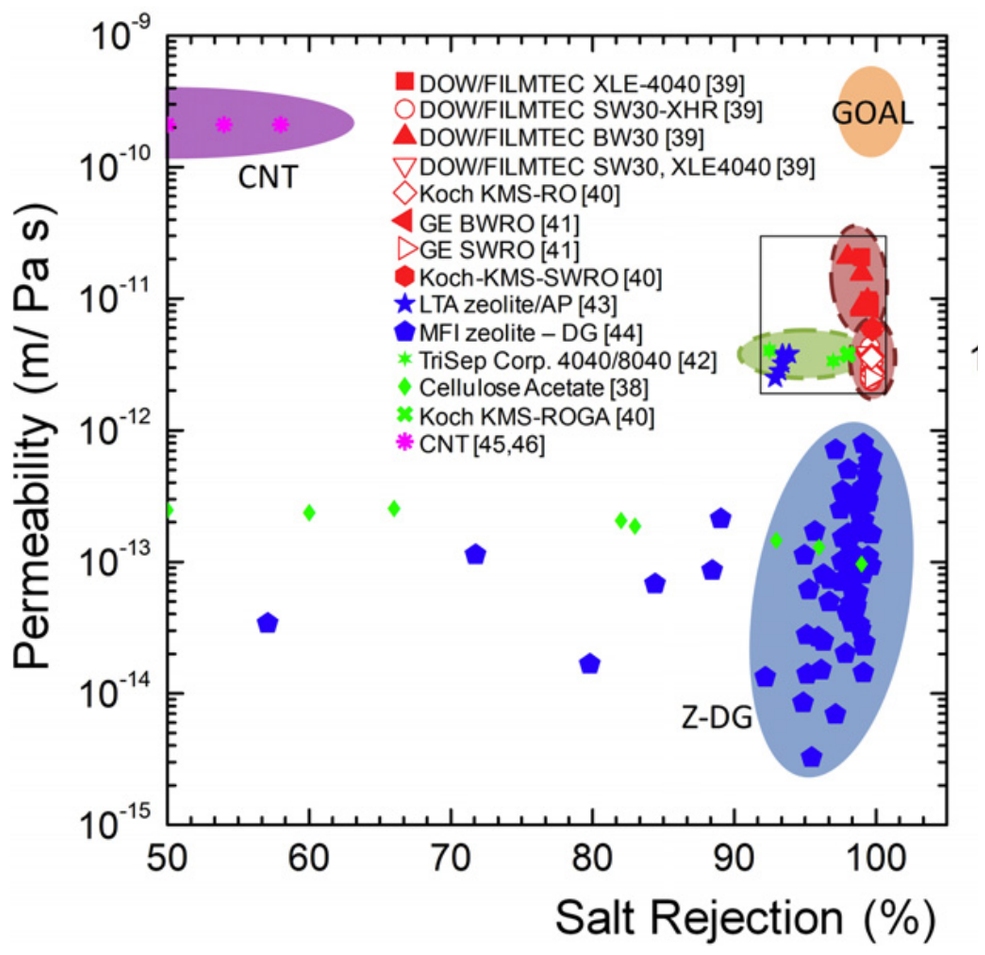
« *Line for a concert shows just how brilliant British people are at queuing* »



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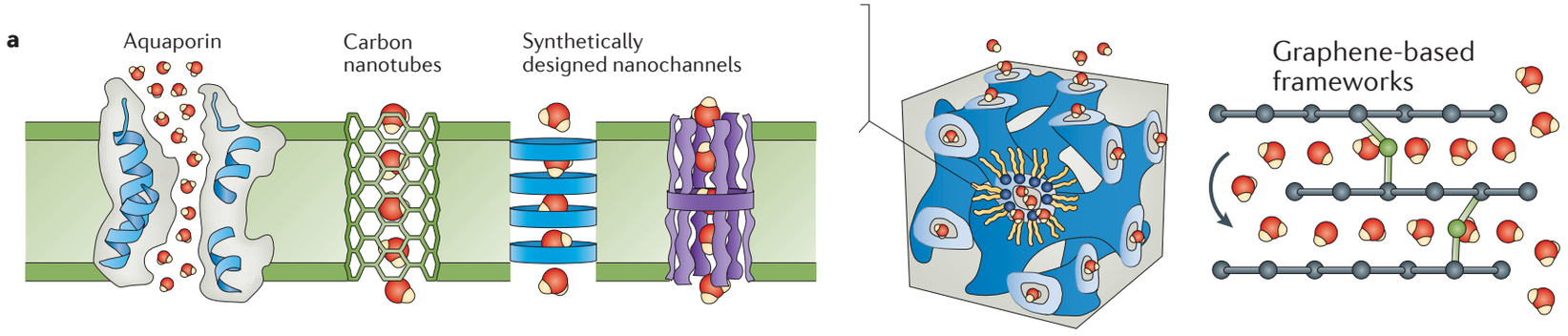

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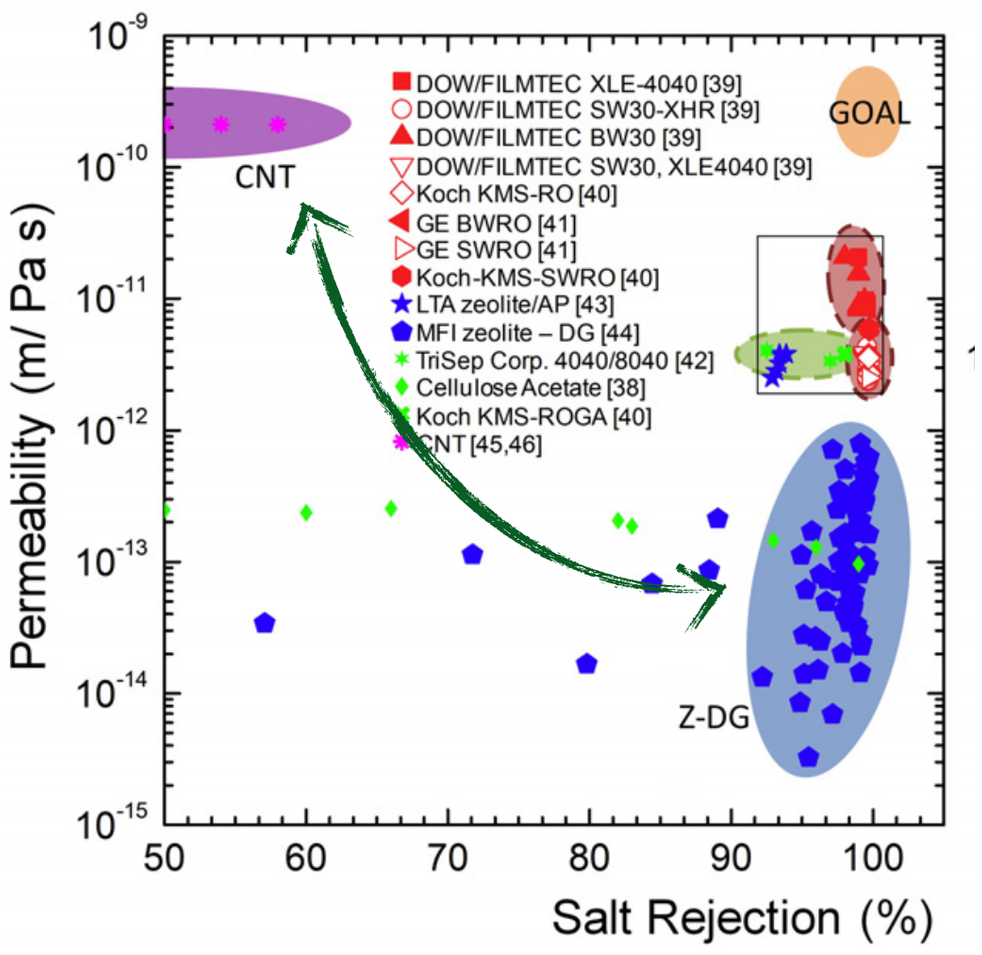


ain’t no such thing as
a free lunch

Humplik et al. (2011)

BEYOND ?

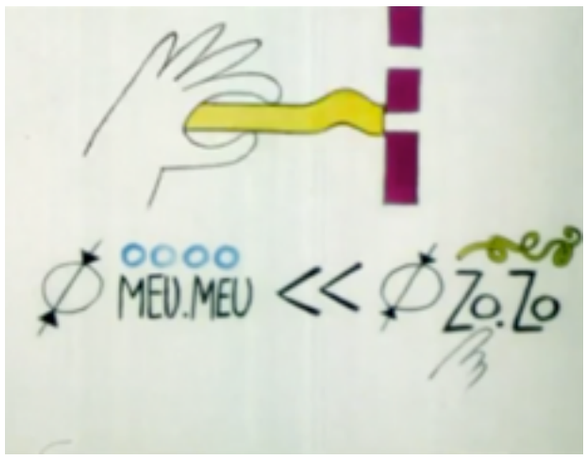
- passive sieving is very frustrating: one can improve materials (carbon), pores structure (AQP), optimize process (R&D), etc.

  … but a real breakthrough in membrane science ?

- need for alternative avenues for separation

SEPARATION, A CARTOON

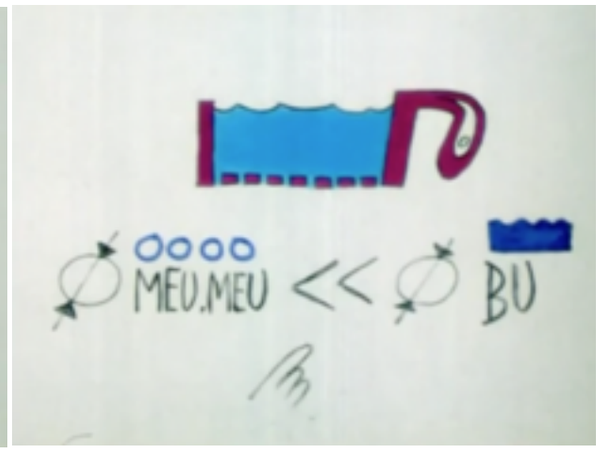
Les Shadocks, « la logique des passoires »



SEPARATION, A CARTOON

Les Shadocks, « la logique des passoires »

THE GRAAL !



CREDO:

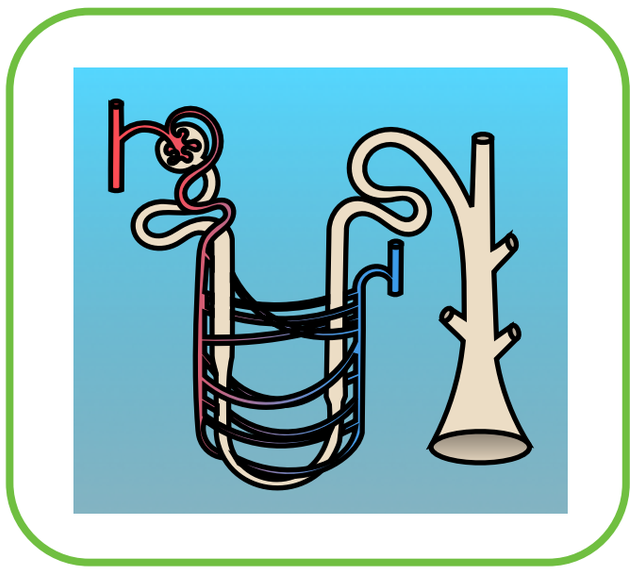
- IMPOSSIBLE SOLUTIONS EXIST AT NANO SCALES
- NEED TO GO BEYOND SIEVING VIEWS

ALTERNATIVE STRATEGIES

From traditional Passive sieving…

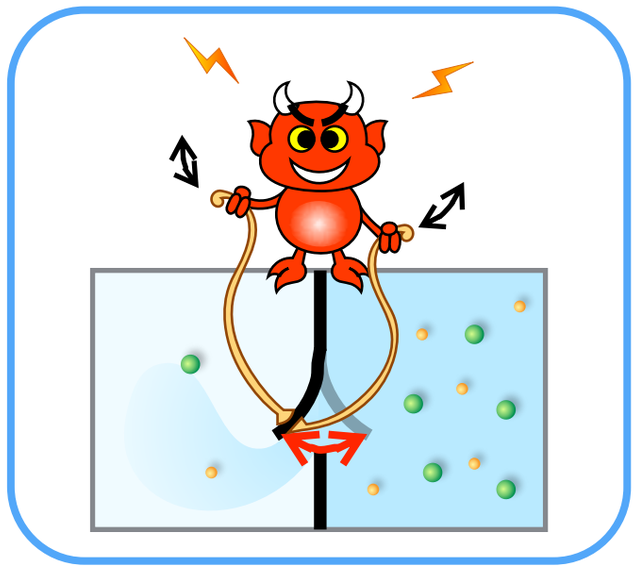
…to ***active*** sieving

bio-inspired



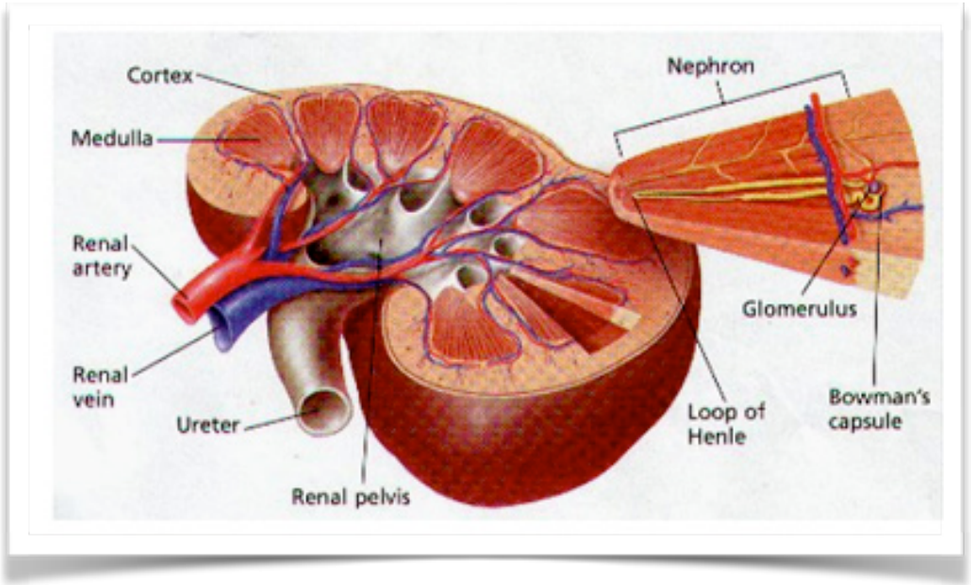
kidney filtration

dynamic separation and osmosis

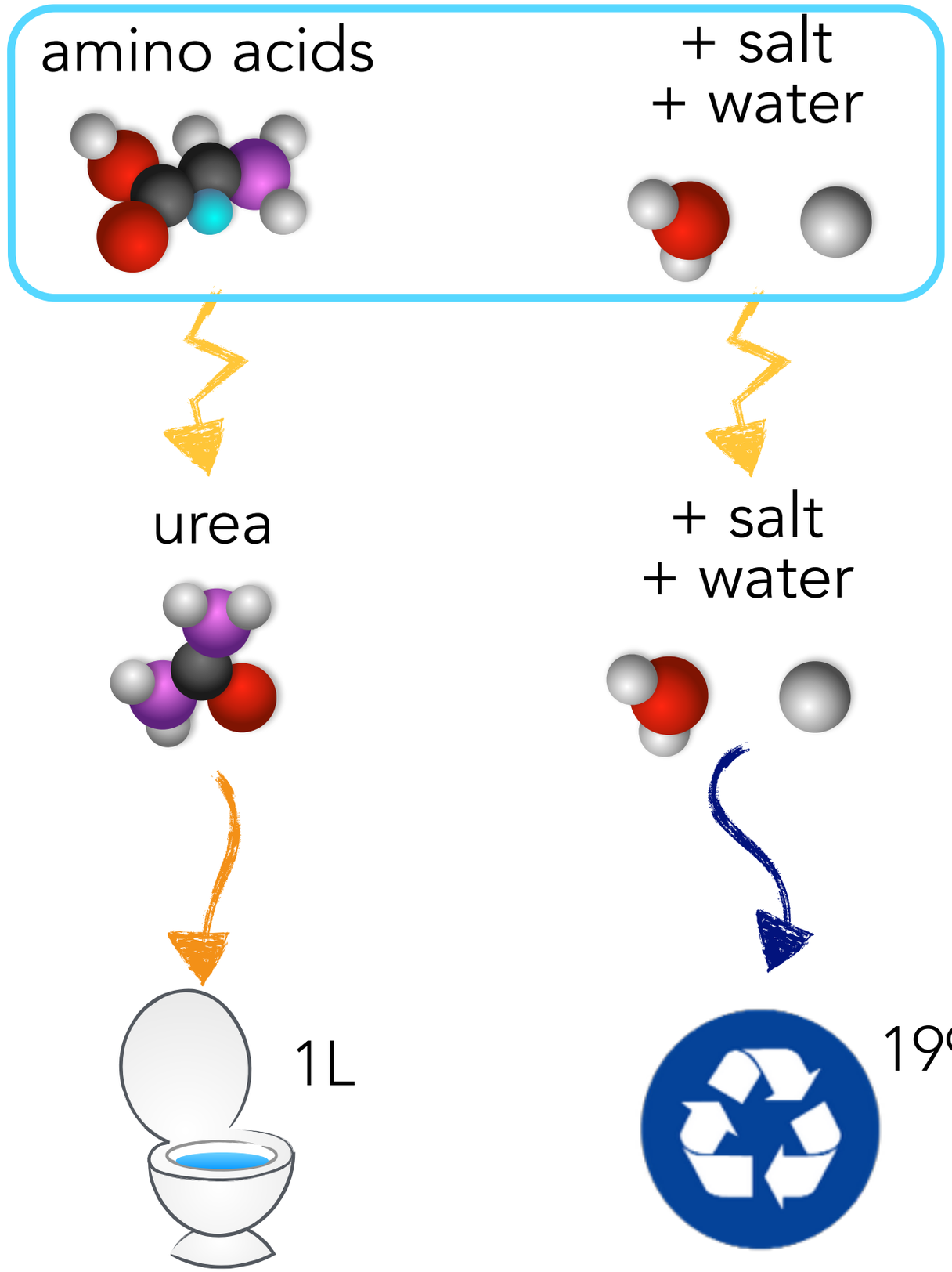


1. Kidney filtration: a non-conventional separation strategy

KIDNEY FILTRATION

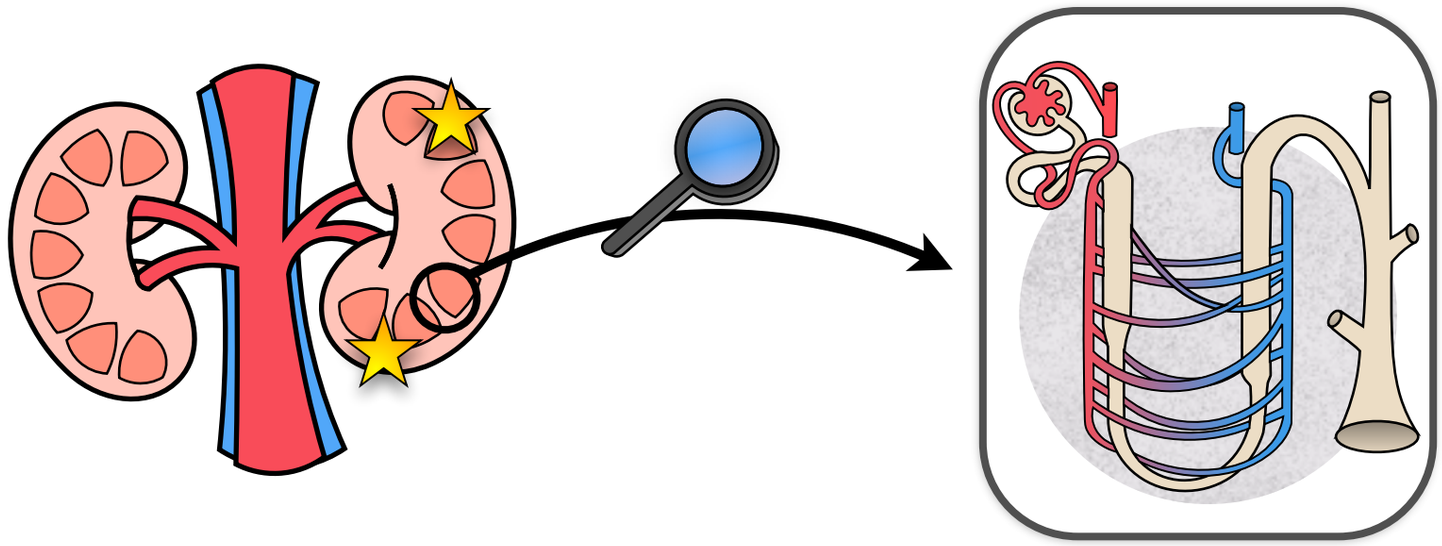


- 200 liter of water readsorbed/day
- 1.5kg NaCl



INTRIGUING KIDNEYS

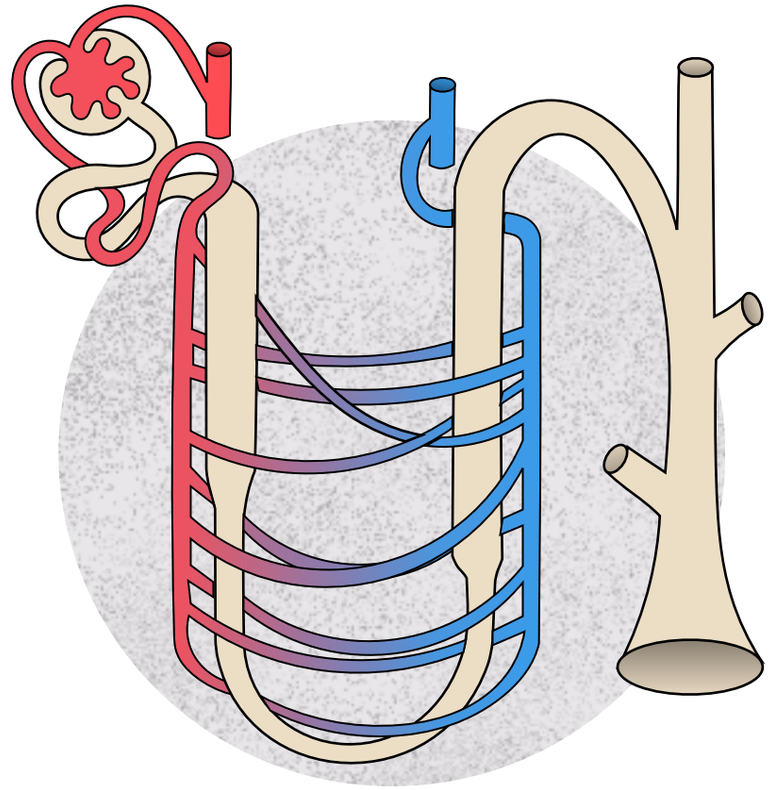
- **Invariant** : the U-shaped filtration tube



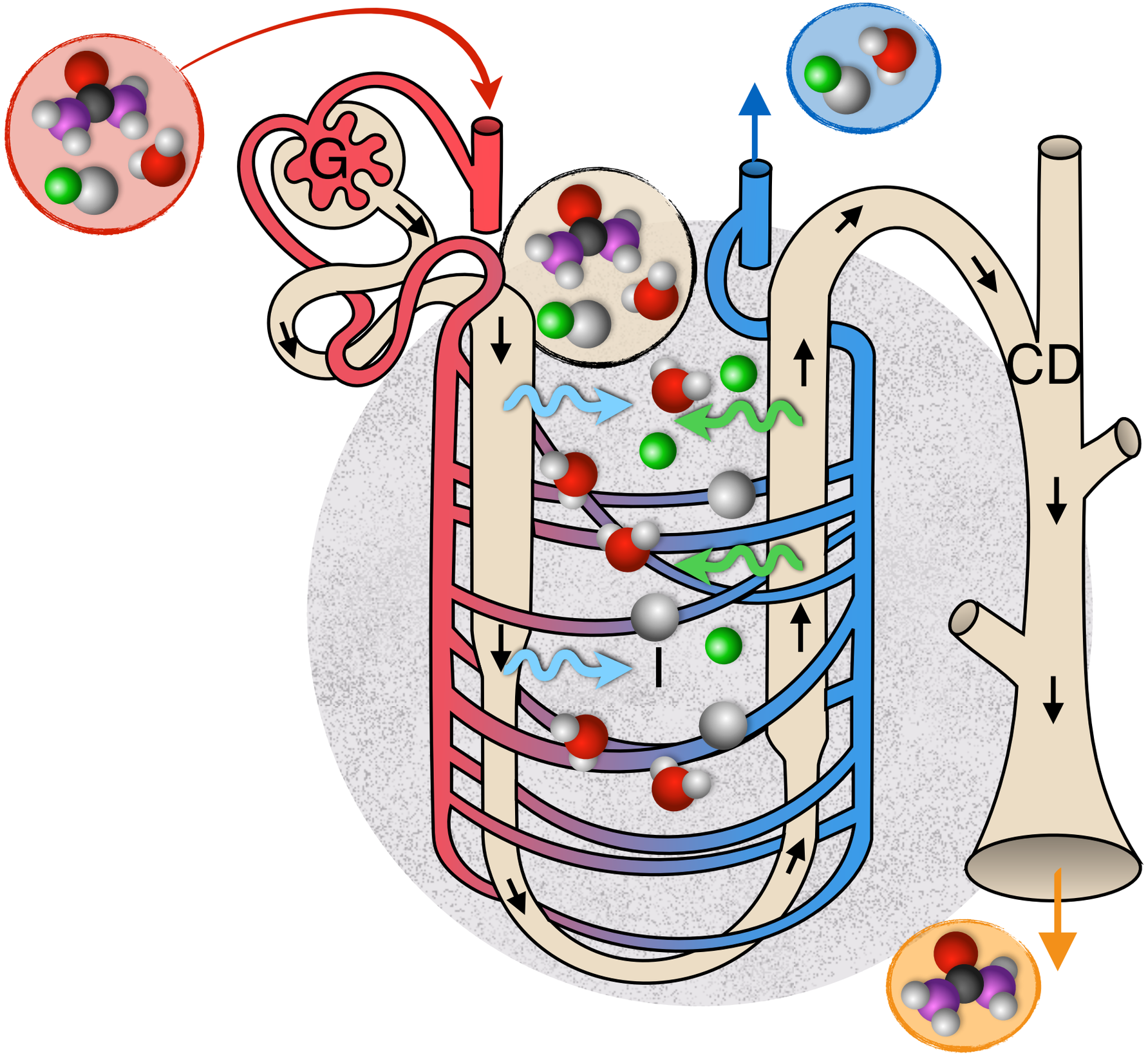
- **Efficient** : 1/1000 power for dialysis

- **Low pressure** : 1/100 pressure for reversed osmosis

basic feature of the kidney filtration ?



A SUBTLE MACHINERY



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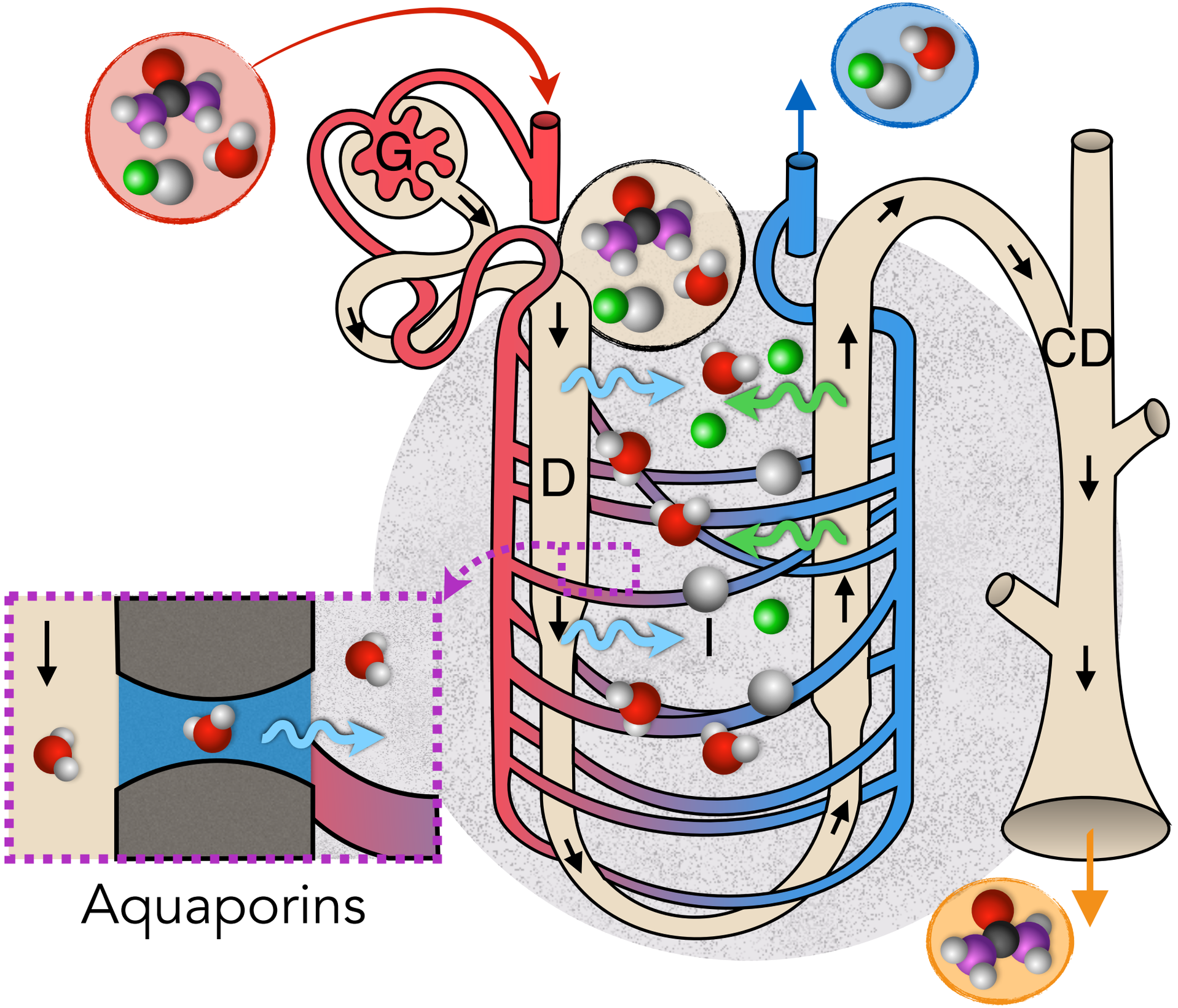

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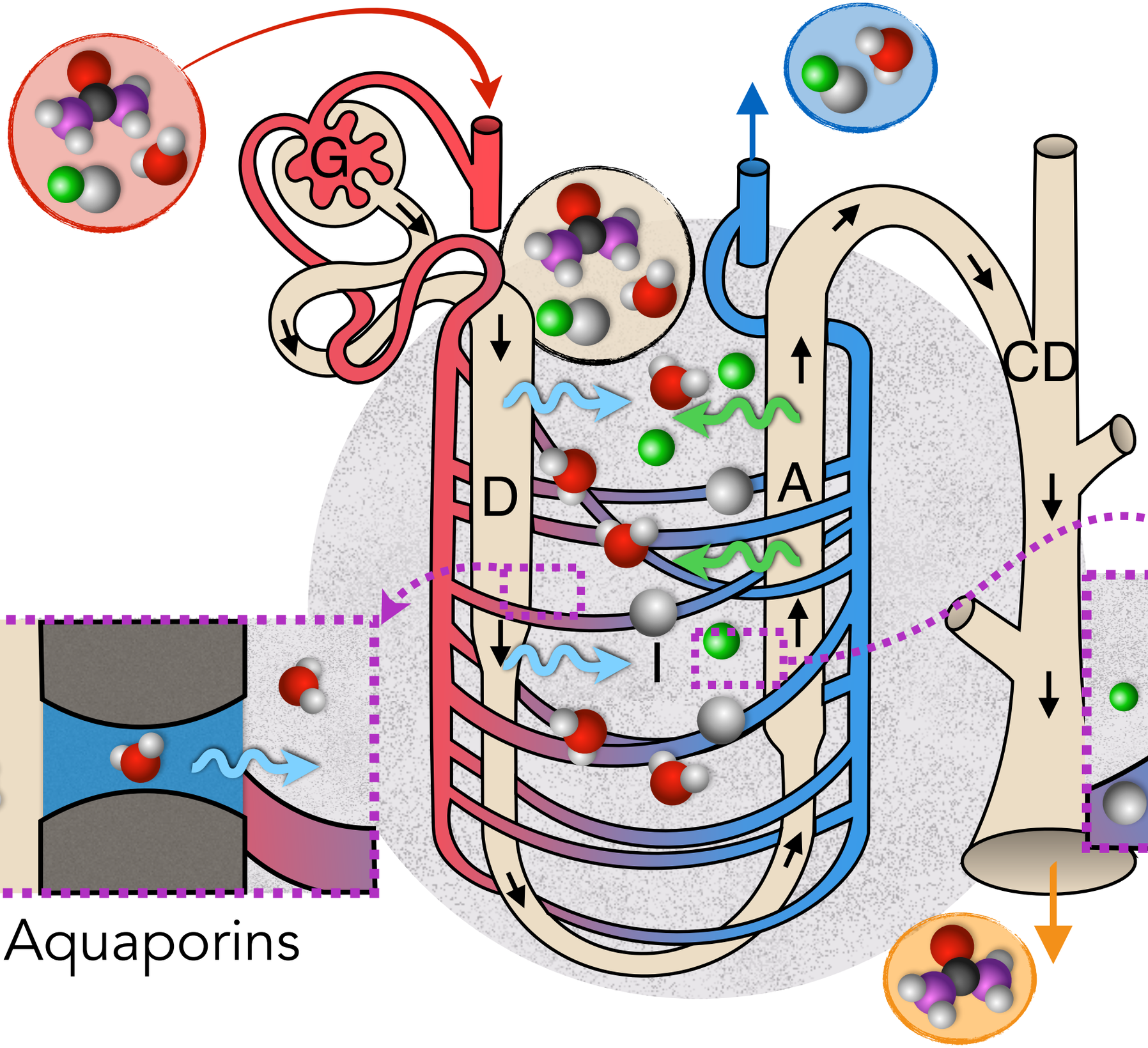
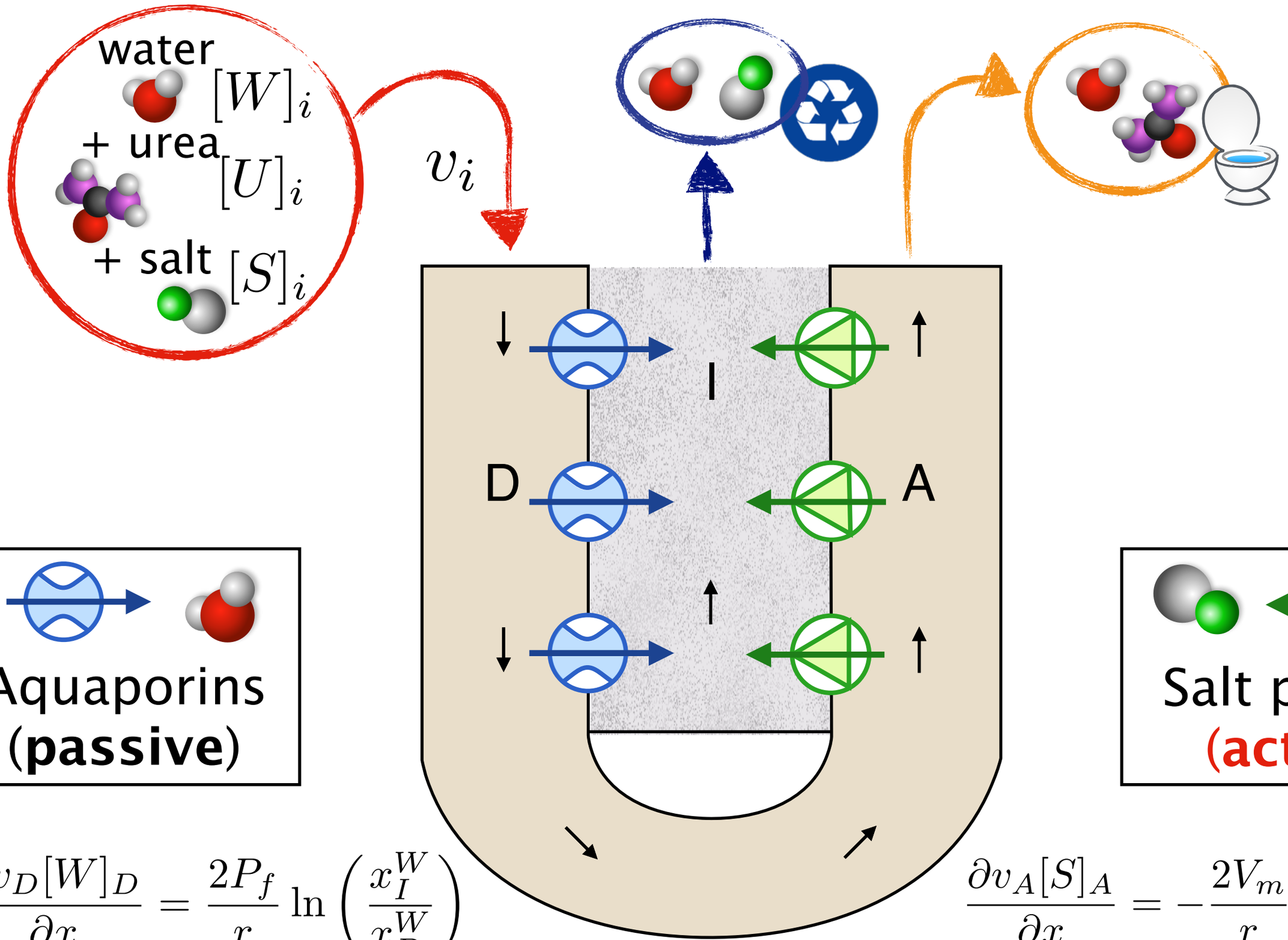


Aquaporins

Salt pumps

U-SHAPE OSMOTIC EXCHANGER



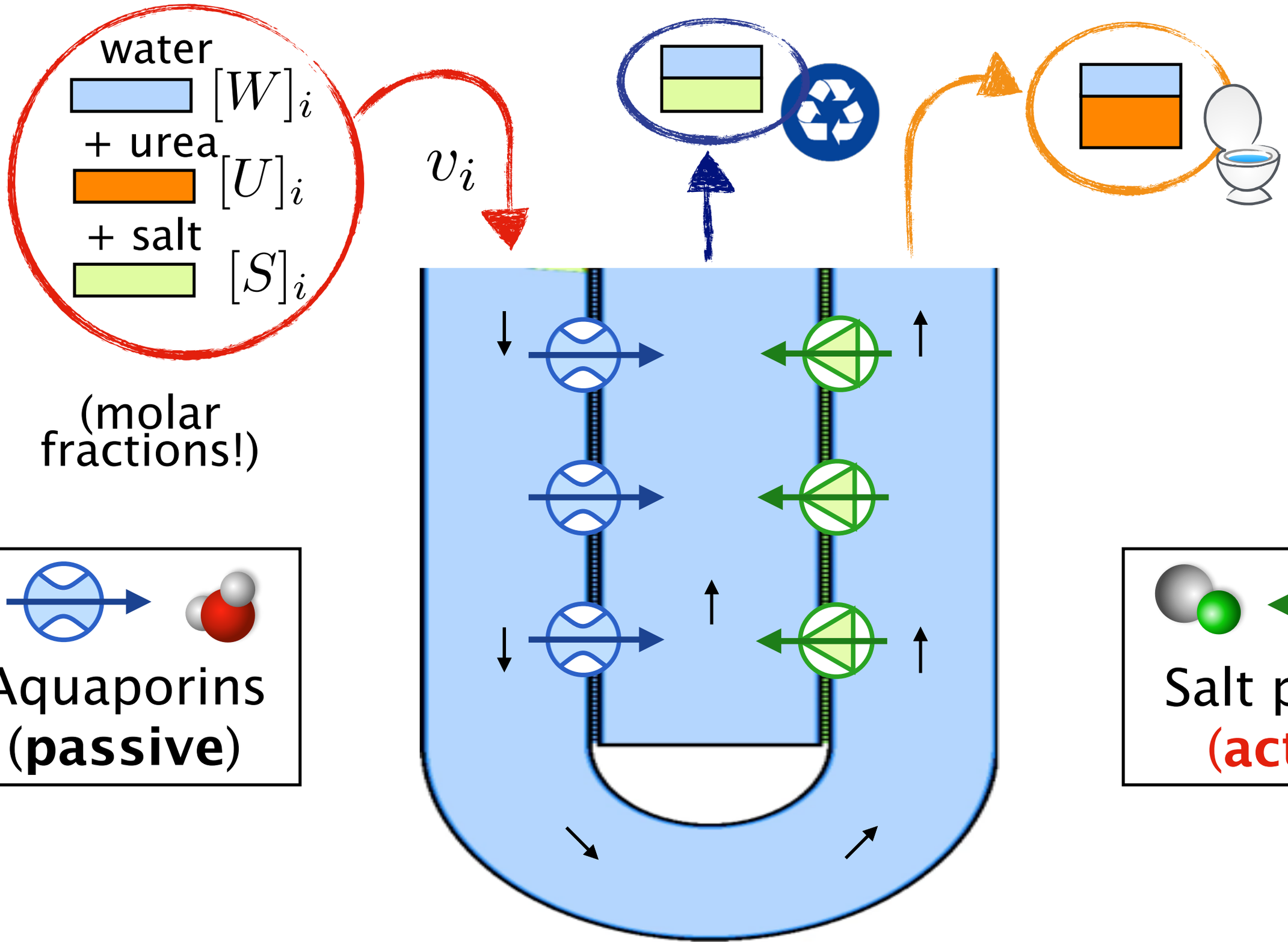
Aquaporins (**passive**)

Salt pumps **(active)**

$$\frac{\partial v_D [W]_D}{\partial x} = \frac{2P_f}{r} \ln\left(\frac{x_I^W}{x_D^W}\right)$$

$$\frac{\partial v_A [S]_A}{\partial x} = -\frac{2V_m}{r} \frac{[S]_A}{K + [S]_A}$$

U-SHAPE OSMOTIC EXCHANGER



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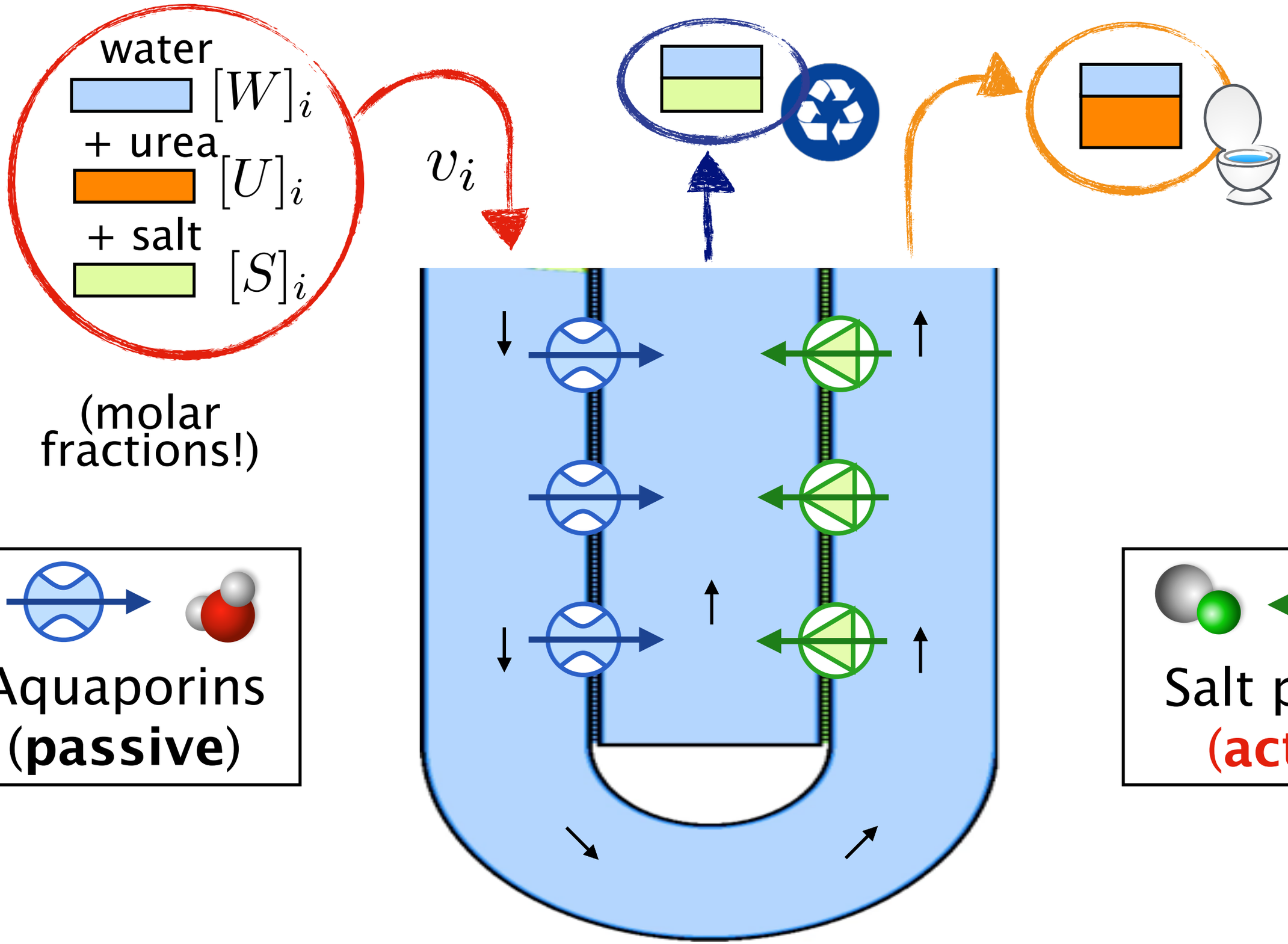
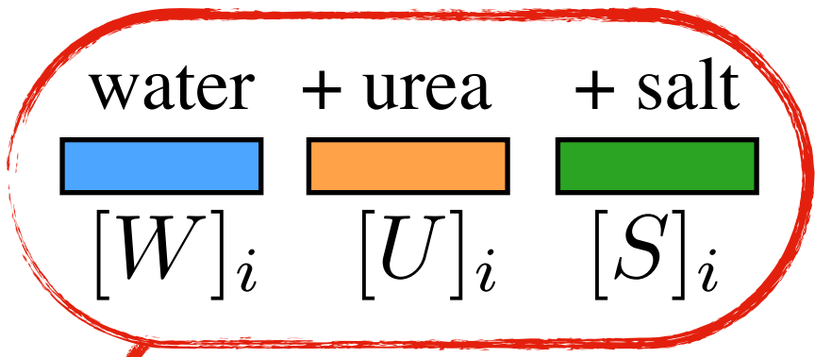
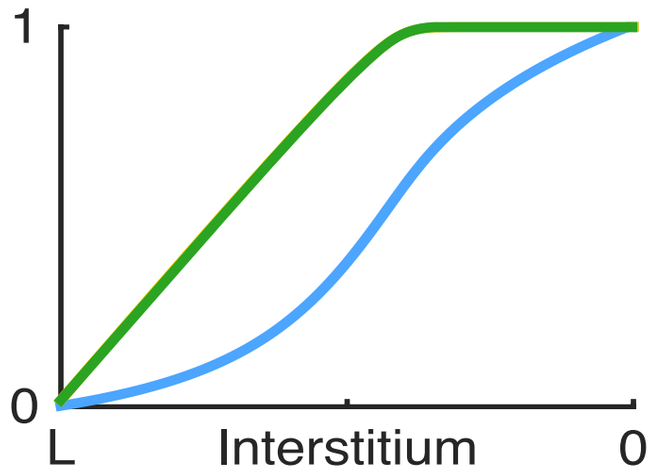
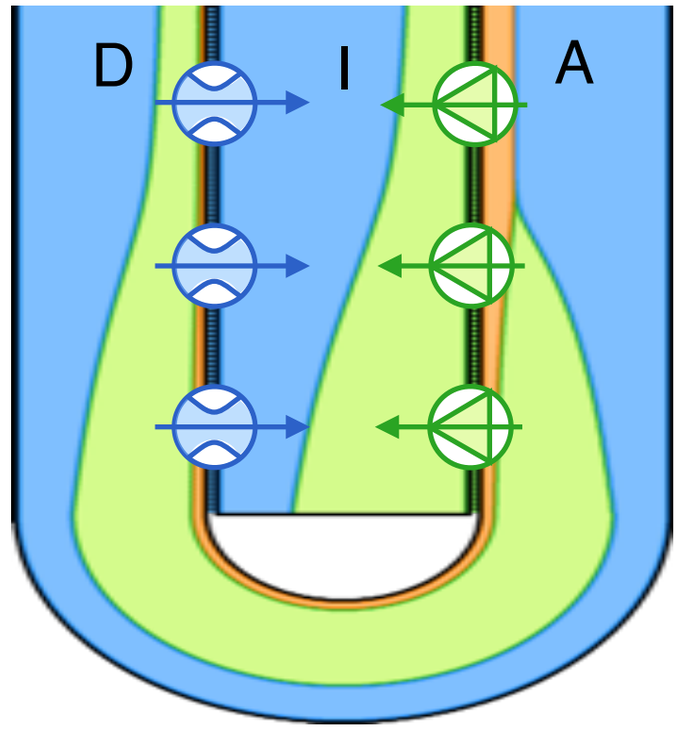


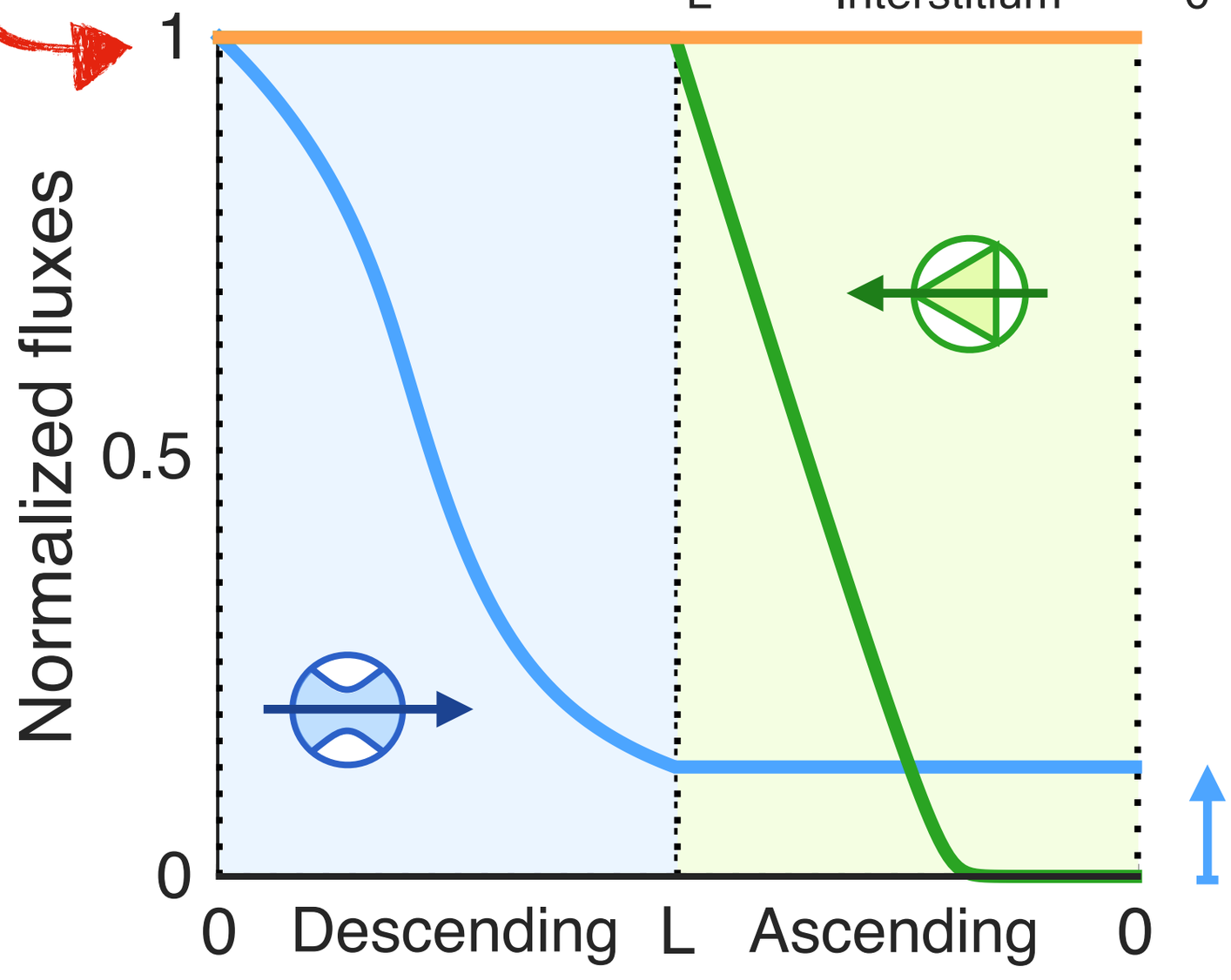
SIMPLE LOOP MODEL







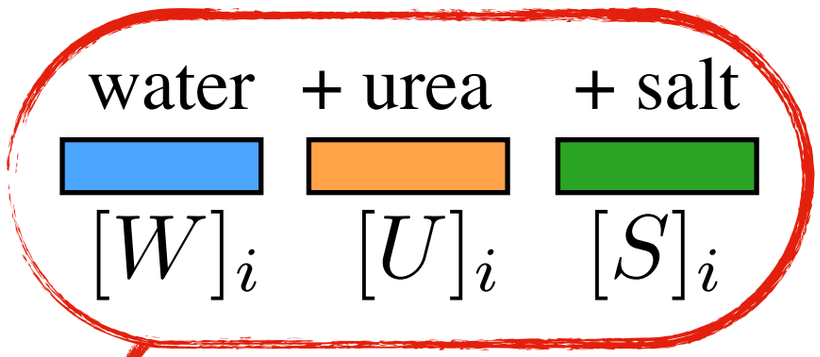
v_i

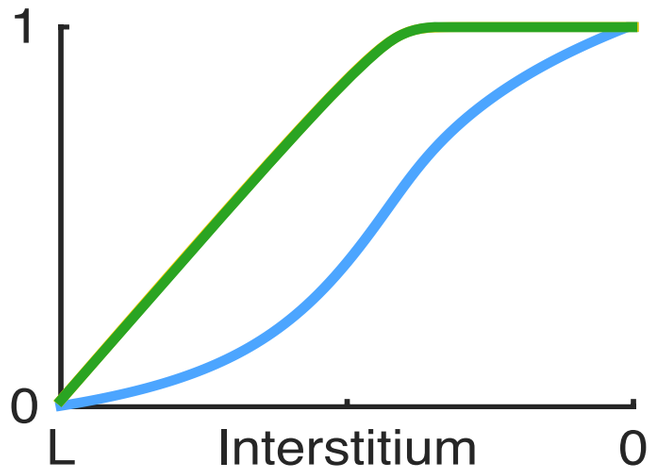


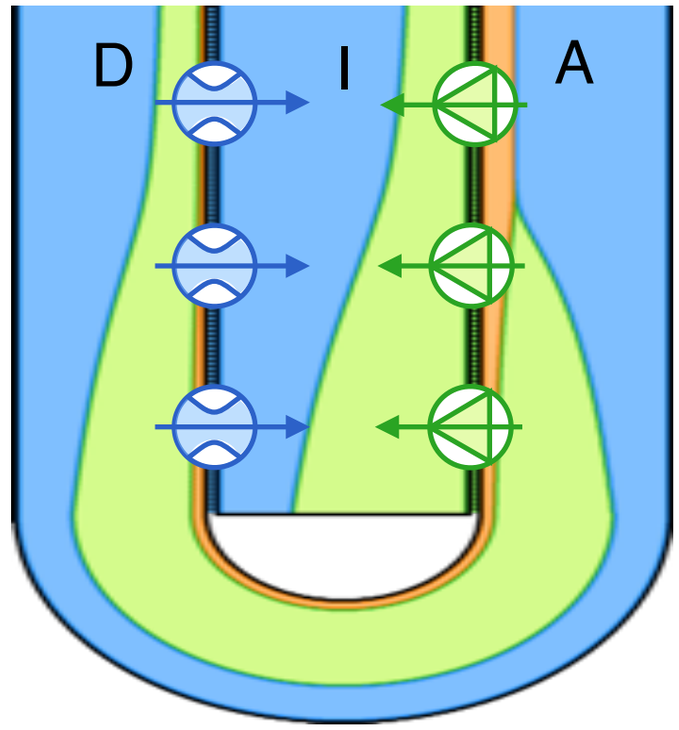
$$\eta \geq \frac{[U]_i}{[U]_i + [S]_i}$$

η=out/in water flux

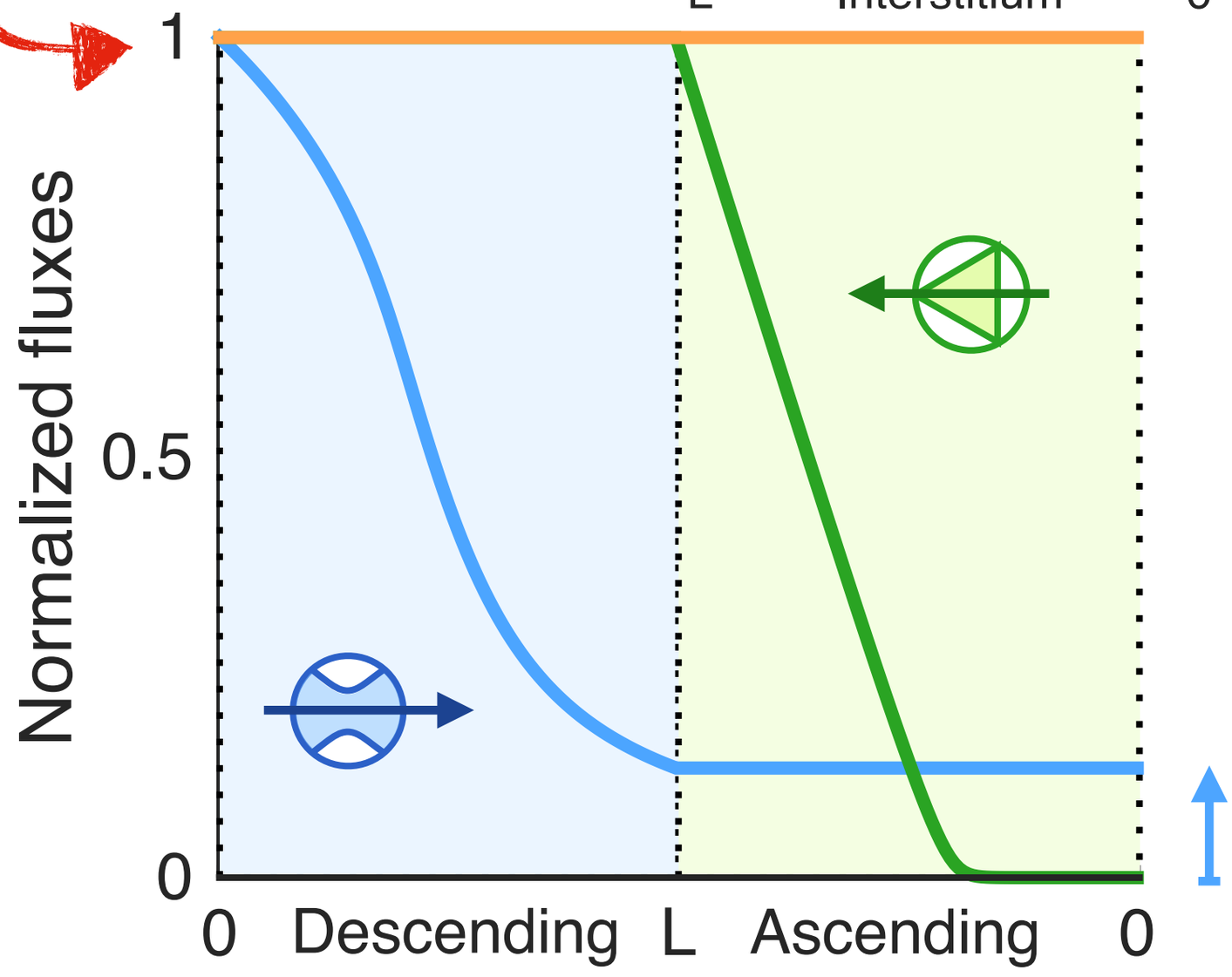
SIMPLE LOOP MODEL







v_i

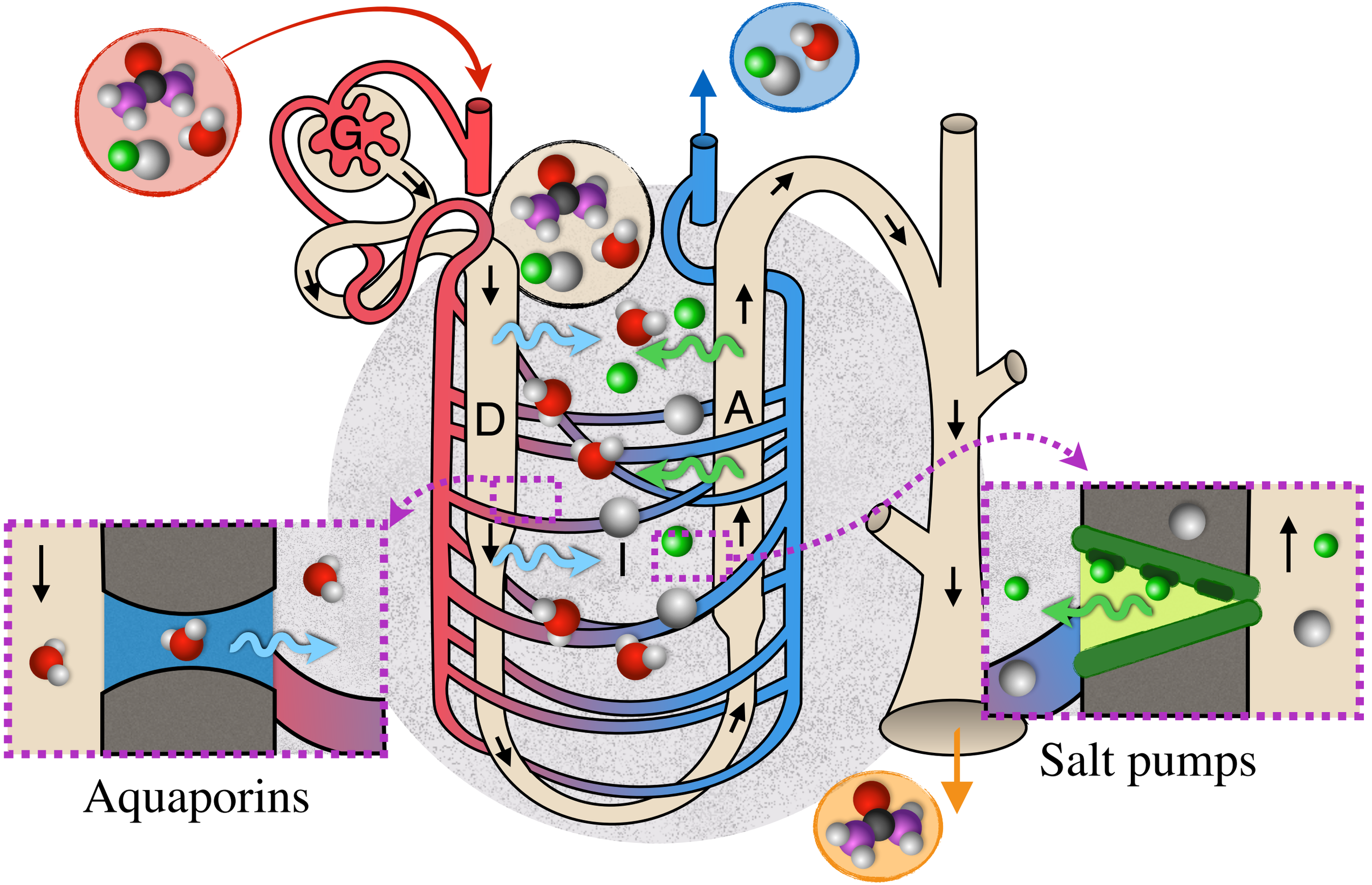


10% water loss = death

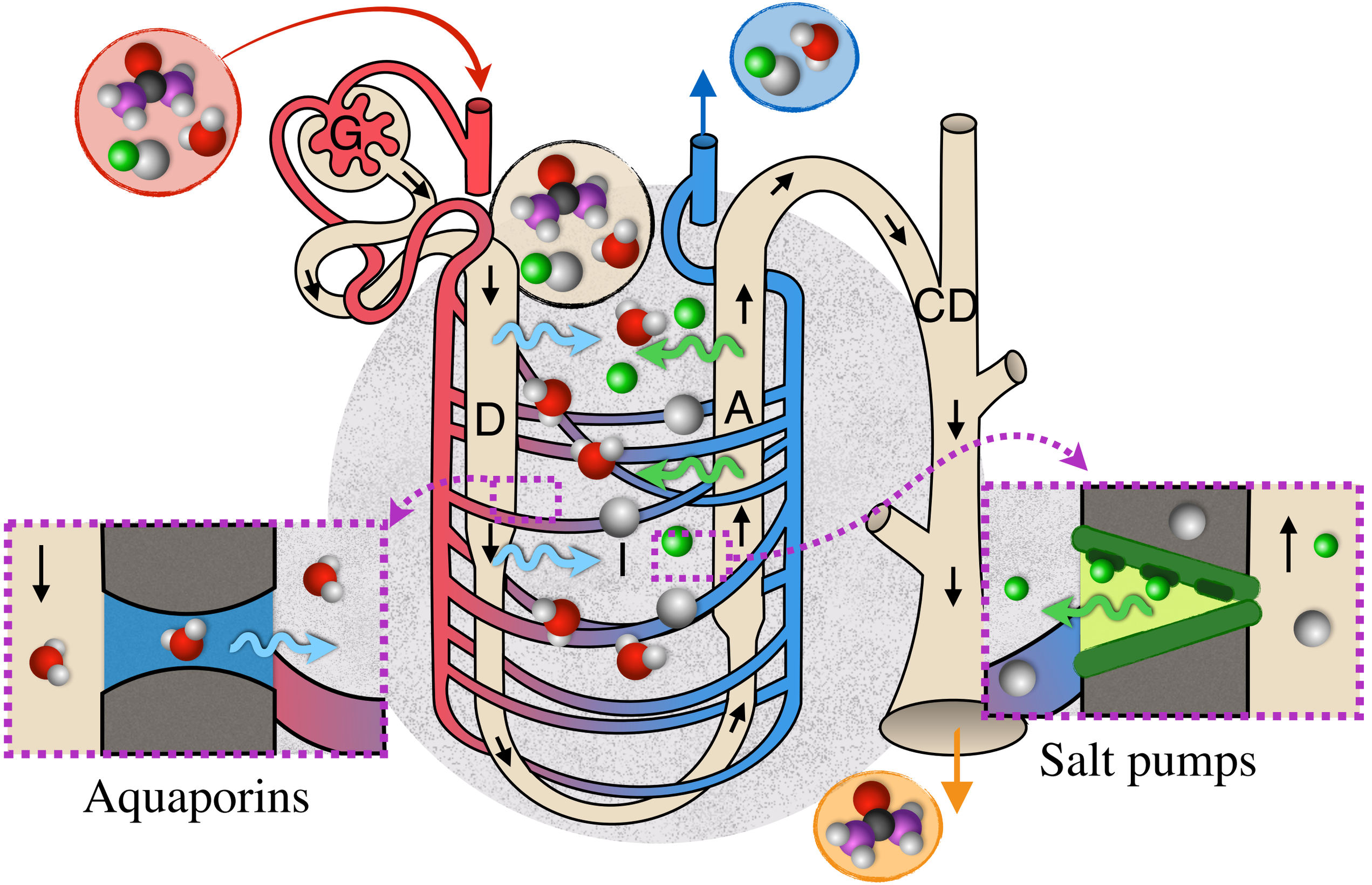
$$\eta \geq \frac{[U]_i}{[U]_i + [S]_i}$$

η=out/in water flux

BACK INTO THE STRUCTURE



BACK INTO THE STRUCTURE



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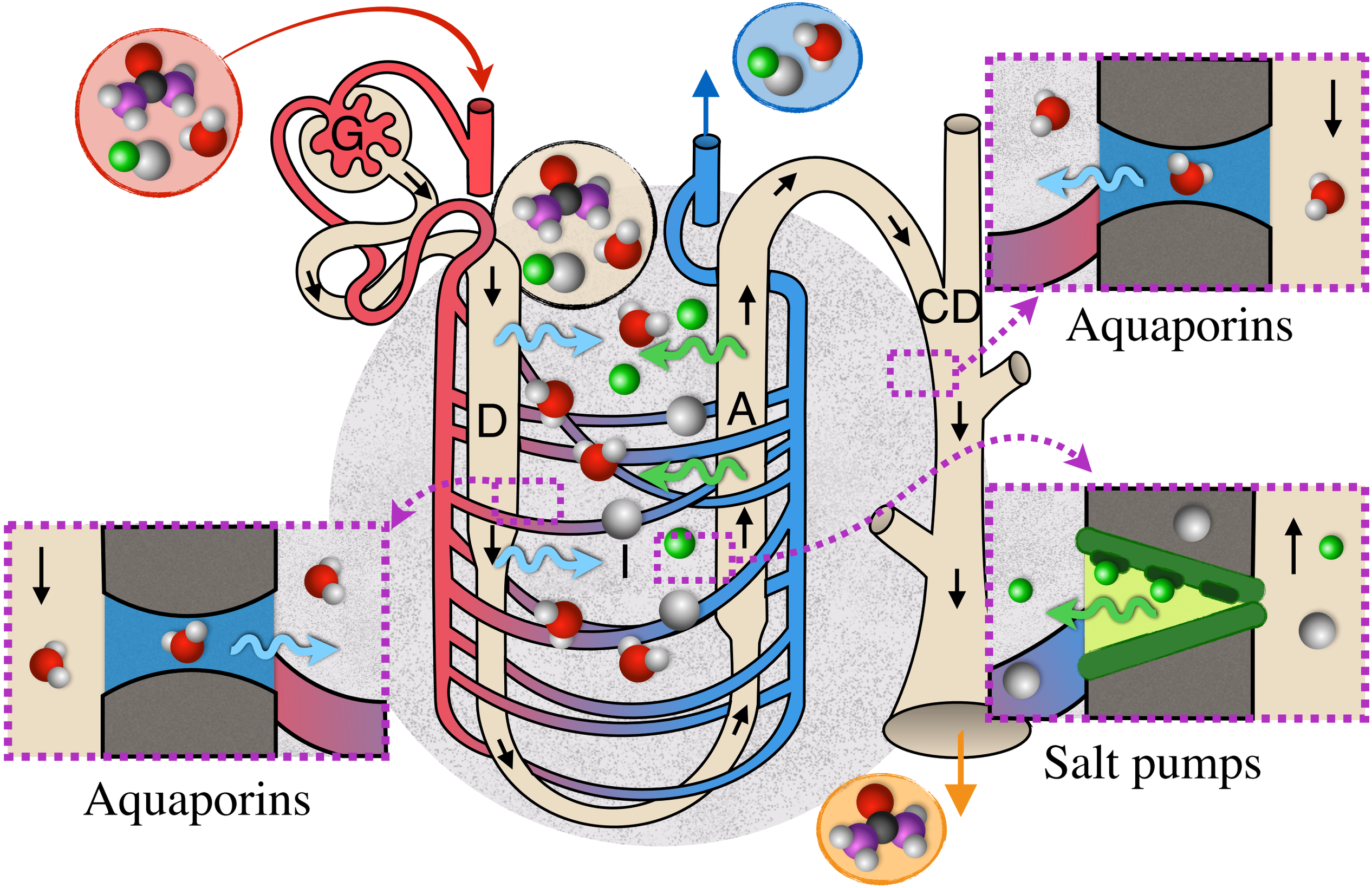
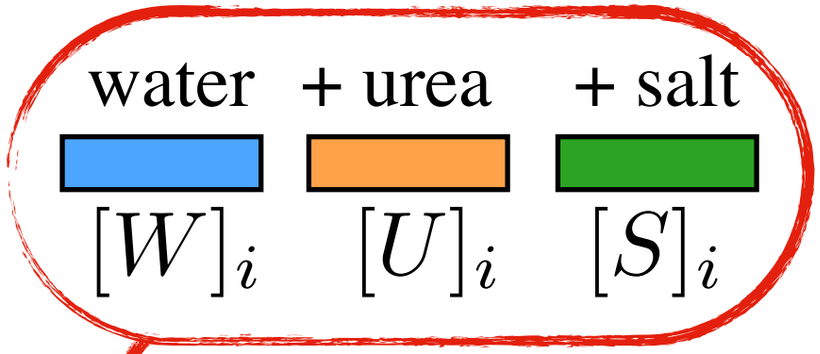
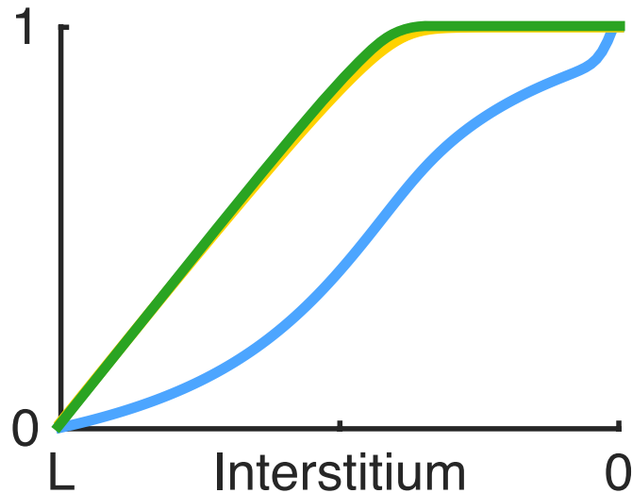
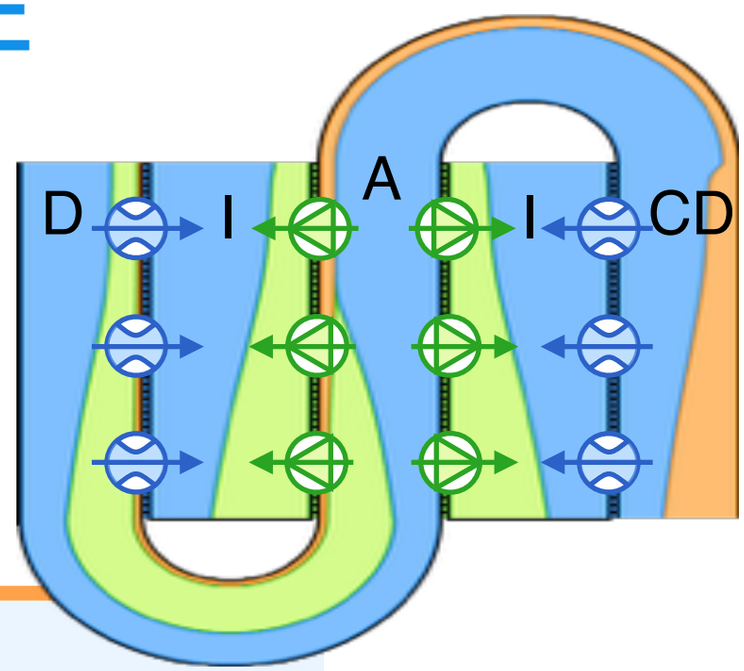
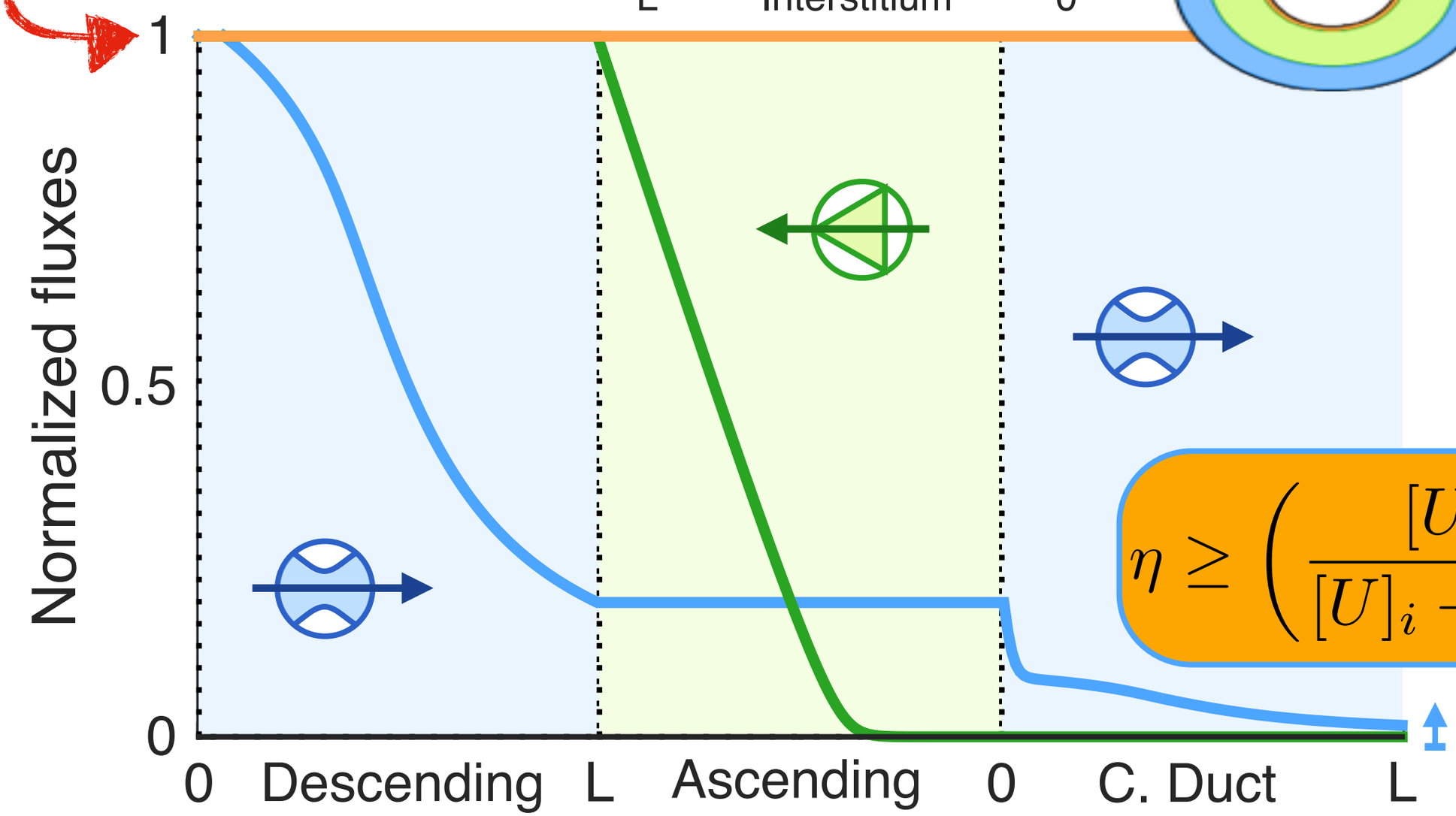


SERPENTINE STRUCTURE



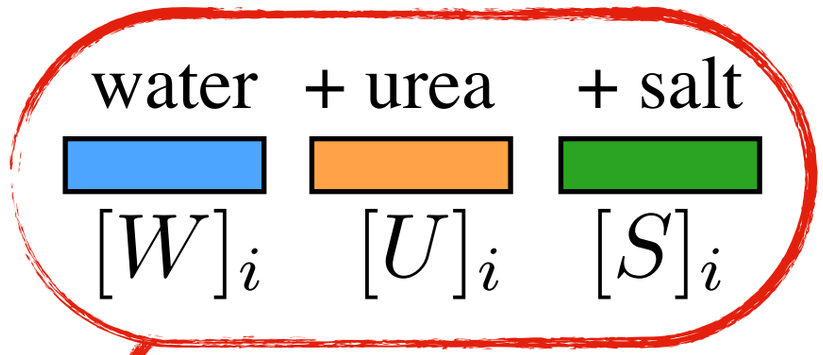


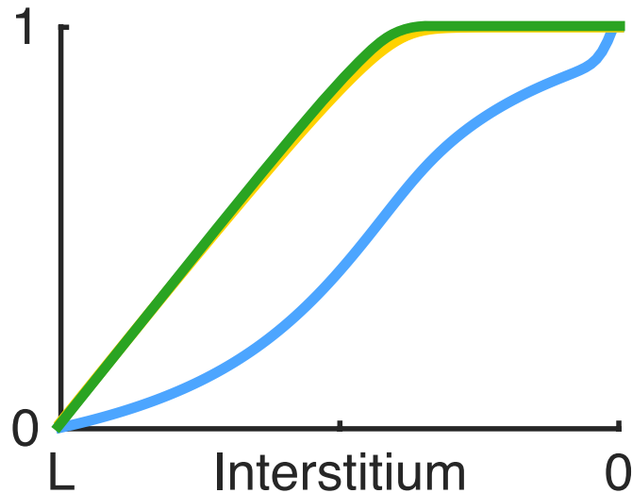


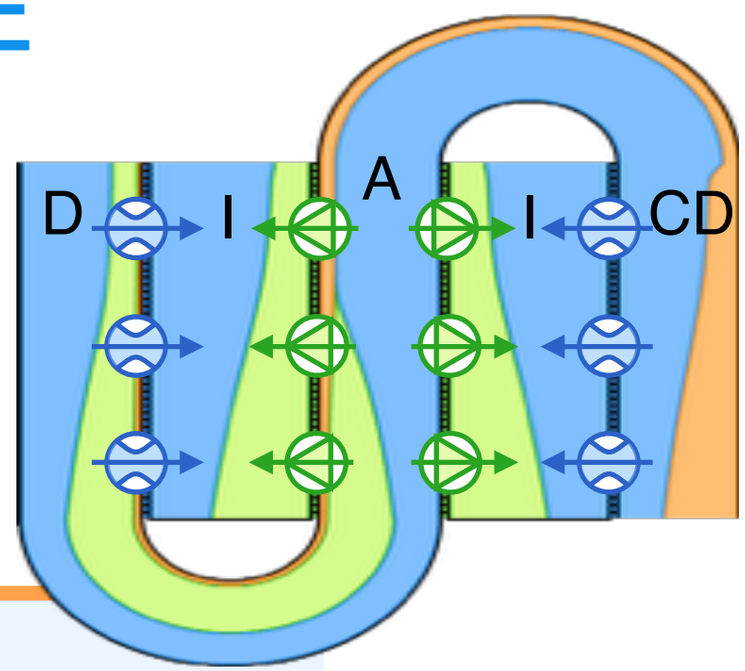


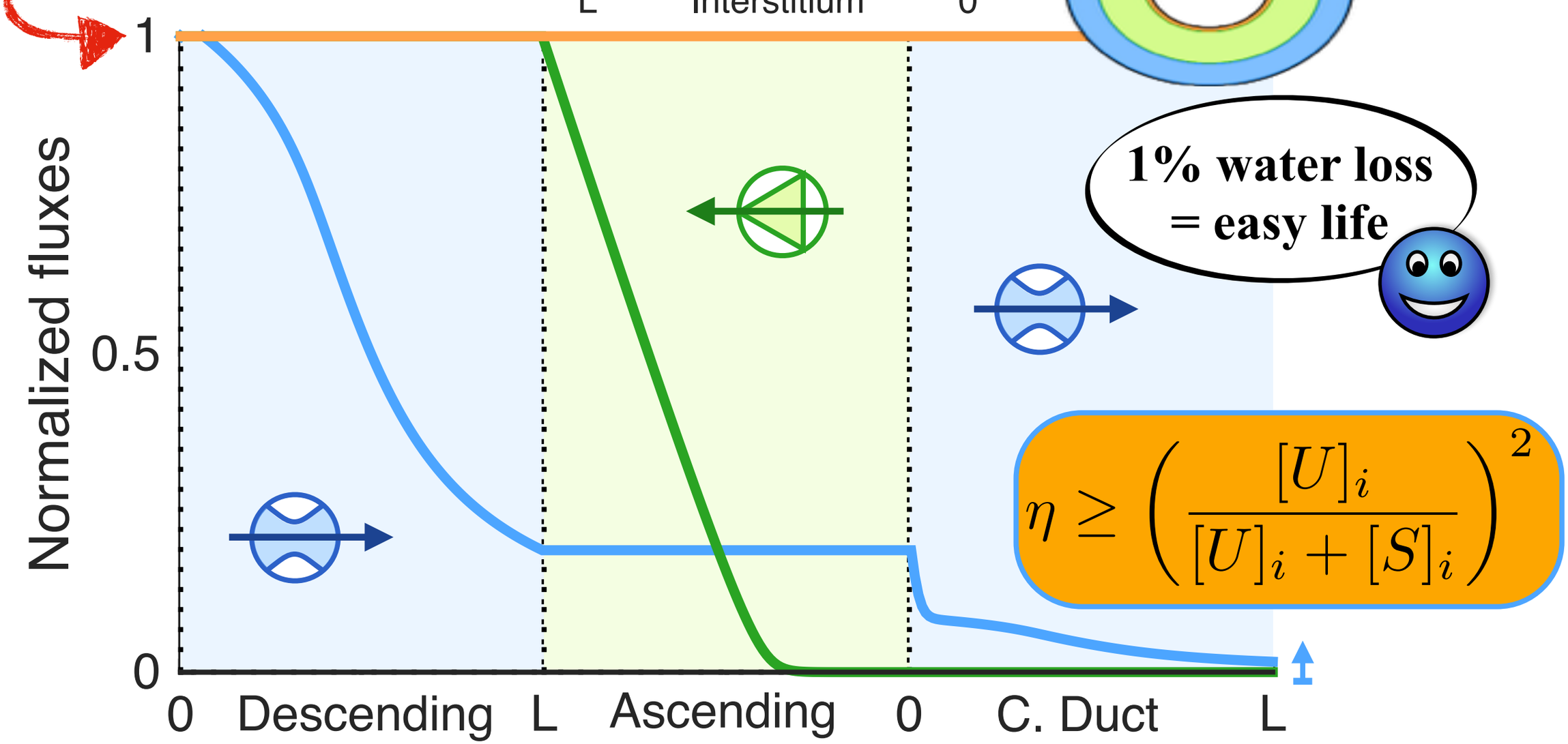
$$\eta \geq \left(\frac{[U]_i}{[U]_i + [S]_i} \right)^2$$

SERPENTINE STRUCTURE

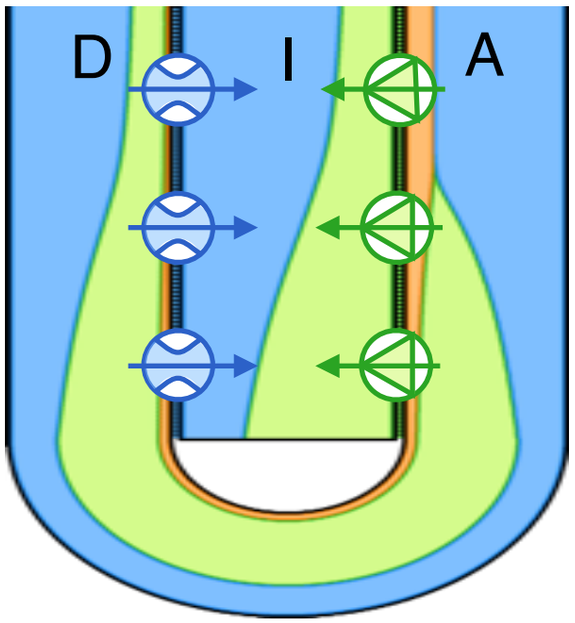






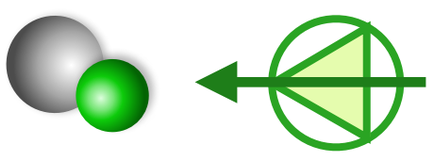


ENERGY CONSUMPTION ?



$$\mathcal{P} \propto v_i [S]_i e_{\mathrm{ATP}}$$

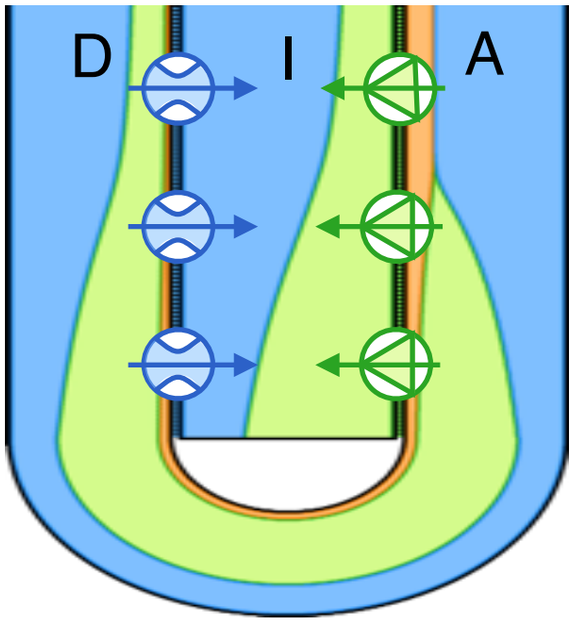
Energy consumption via ATP



Salt pumps

(active)

ENERGY CONSUMPTION ?



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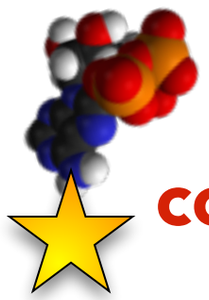
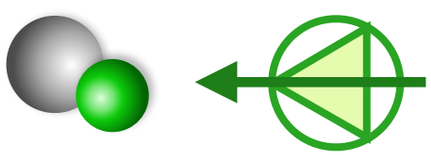


Energy consumption via ATP



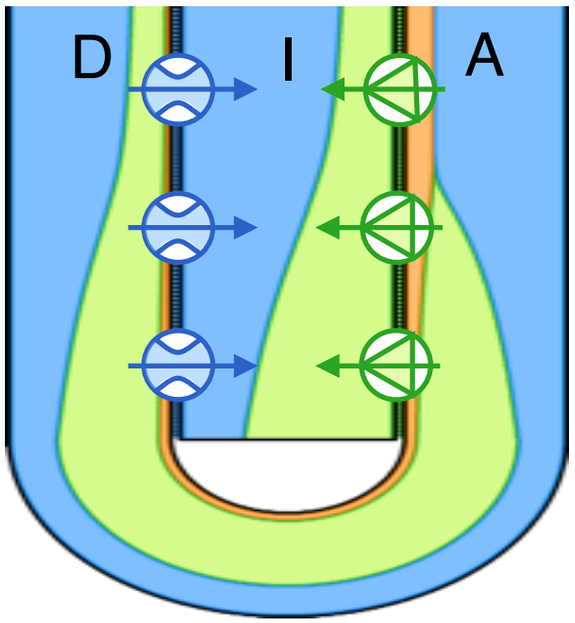
Salt pumps

(active)

$$\eta \sim \frac{[U]_i}{[U]_i + [S]_i}$$

water loss ratio

ENERGY CONSUMPTION ?



Salt pumps
(active)

$\mathcal{P} \propto v_i [S]_i e_{\mathrm{ATP}}$

Energy consumption via ATP

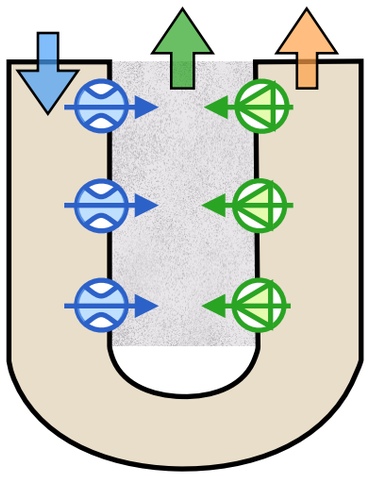
+ →

$\mathcal{P} \propto v_i [U]_i \dfrac{e_{\mathrm{ATP}}}{\eta}$

$\eta \sim \dfrac{[U]_i}{[U]_i + [S]_i}$

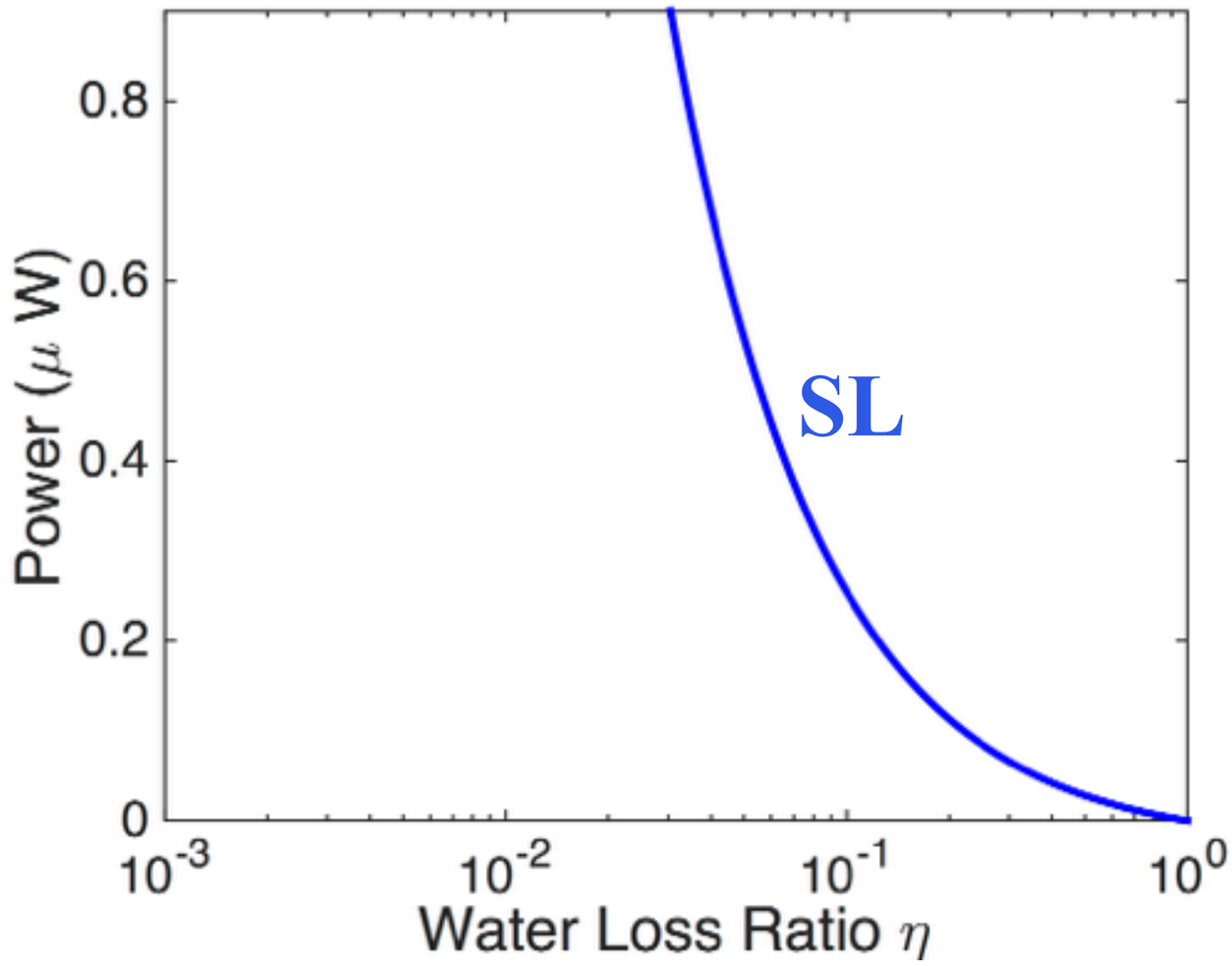
water loss ratio

ENERGY CONSUMPTION ?



Simple Loop = SL

$$\mathcal{P} \propto v_i [U]_i \frac{e_{\mathrm{ATP}}}{\eta}$$



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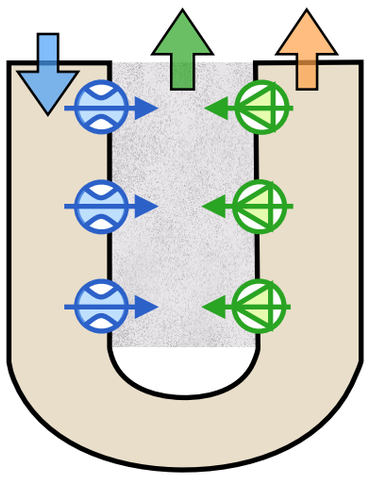

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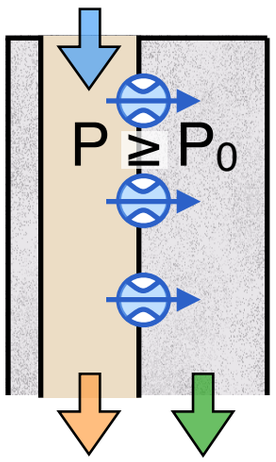
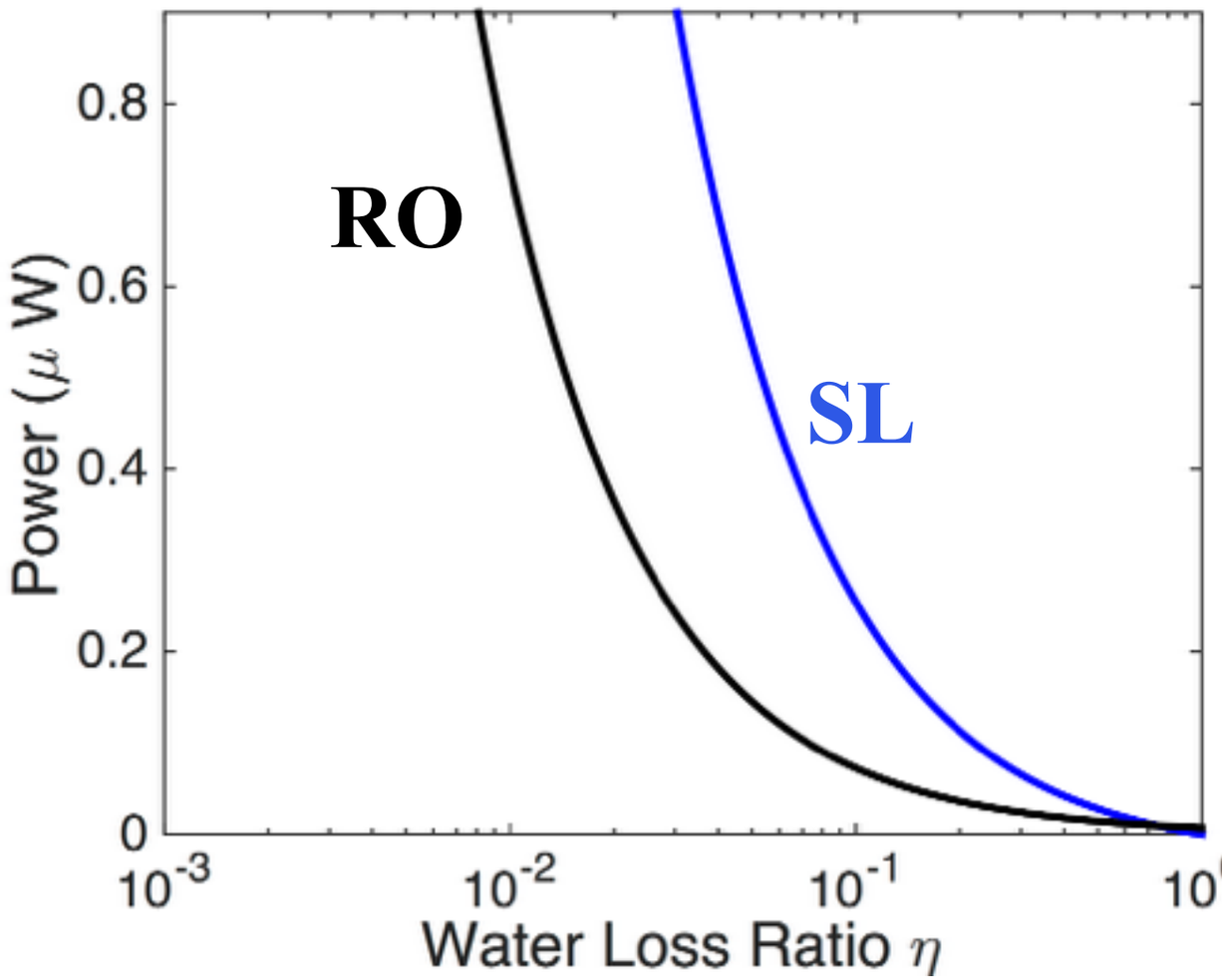
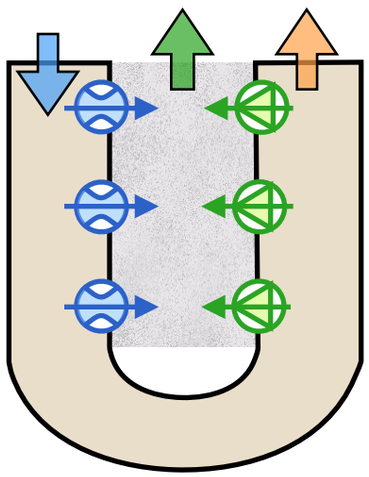


Reverse Osmosis = RO

$$\mathcal{P} \propto v_i [U]_i \frac{RT}{\eta}$$



ENERGY CONSUMPTION ?



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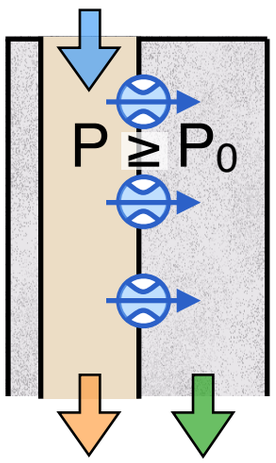

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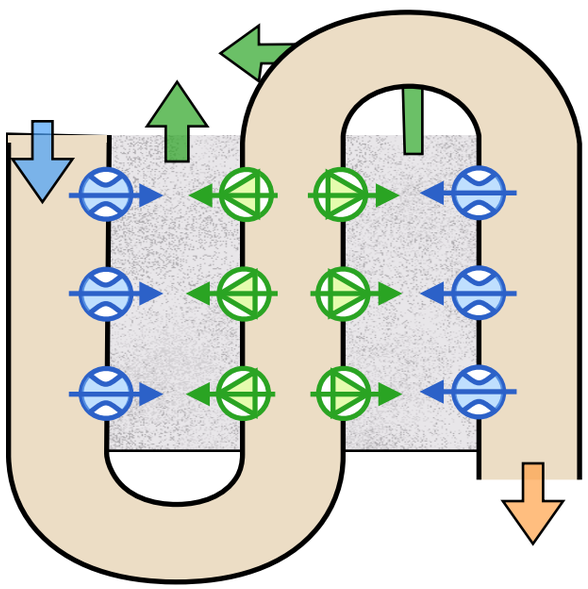
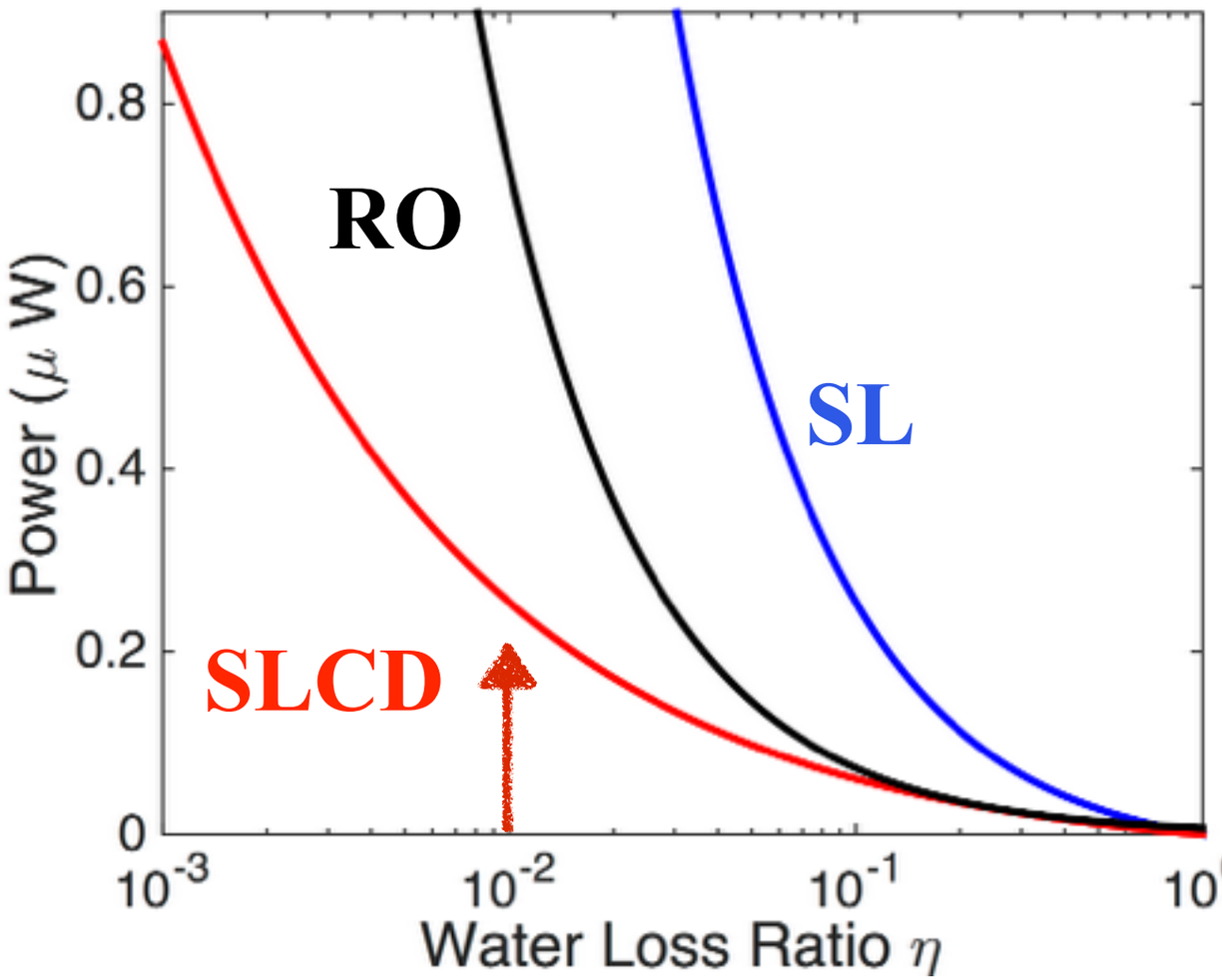


Simple Loop + Collecting Duct = SLCD

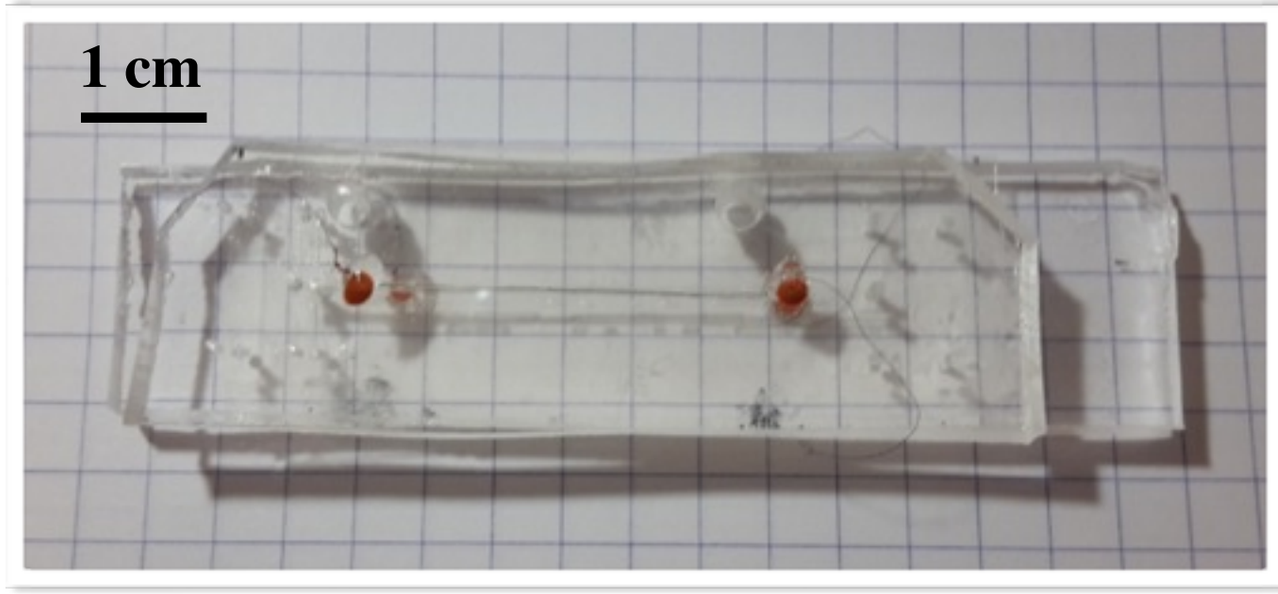
$$\mathcal{P} \propto v_i [U]_i \frac{e_{\mathrm{ATP}}}{\sqrt{\eta}}$$



serpentine far more efficient

S. Marbach, L. Bocquet, ***Phys. Rev. X*** (2016)

KIDNEY ON A CHIP



INSTITUT
PIERRE-GILLES
DE GENNES
Pour la microfluidique

Benoit Laborie

Work in progress…

SOME CONCLUSIONS

- kidney-inspired separation is very efficient, both in terms of separation and energy

- amenable to microfluidic artificial devices (hard but feasible)

- many potential applications:

  - water pretreatment in desalination (costly !)

  - detailed ions separation

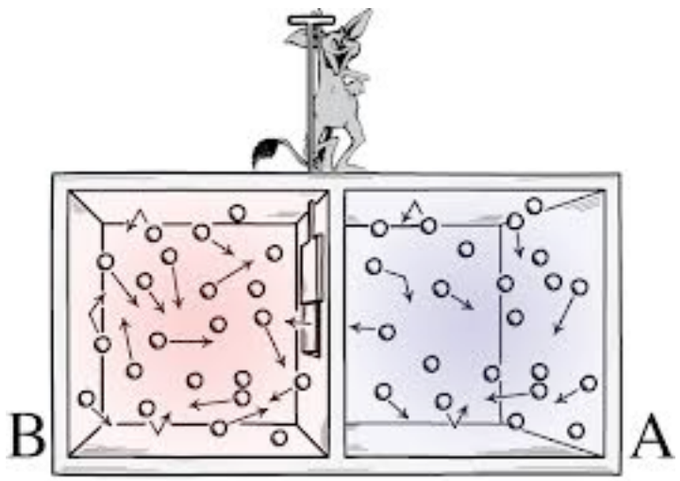
  - the dream: new (portable) dialysis solutions ???

S. Marbach, L. Bocquet, ***Phys. Rev. X*** (2016)

2. Active strategies for sieving

TOWARDS ACTIVE SIEVING

- Maxwell demons would be the « ultimate » separation device…

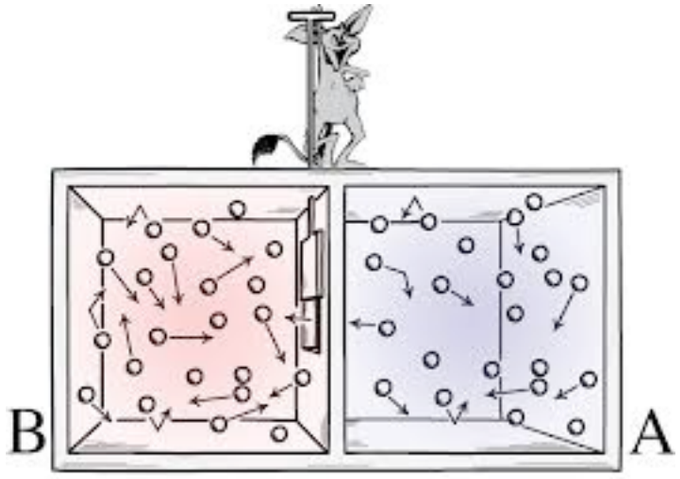


- … but impractical to develop artificially (read/convert info)

- develop more primitive functions, but amenable to (large-scale) membrane separation

TOWARDS ACTIVE SIEVING

- Maxwell demons would be the « ultimate



« *A Maxwell demon operating at the entrance of a nightclub* »

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TOWARDS ACTIVE SIEVING

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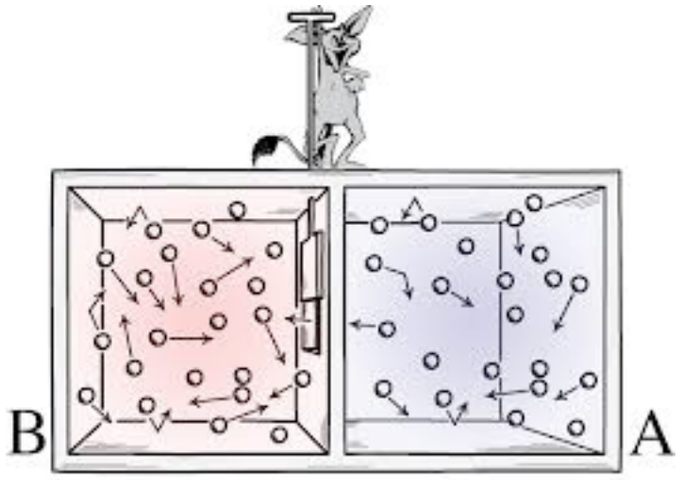

« *A Maxwell demon operating at the entrance of a nightclub* »

- … but impractical to develop artificially (read/convert info)

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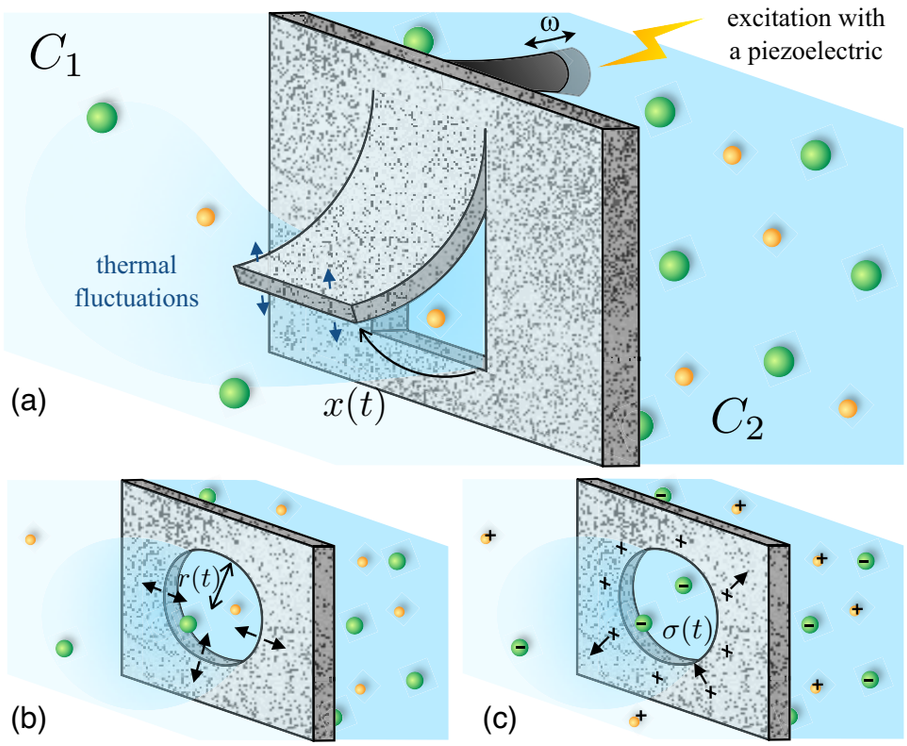
Q: ACTIVE SEPARATION ?
INJECT ENERGY AT PORE SCALE ?

ACTIVE SIEVING

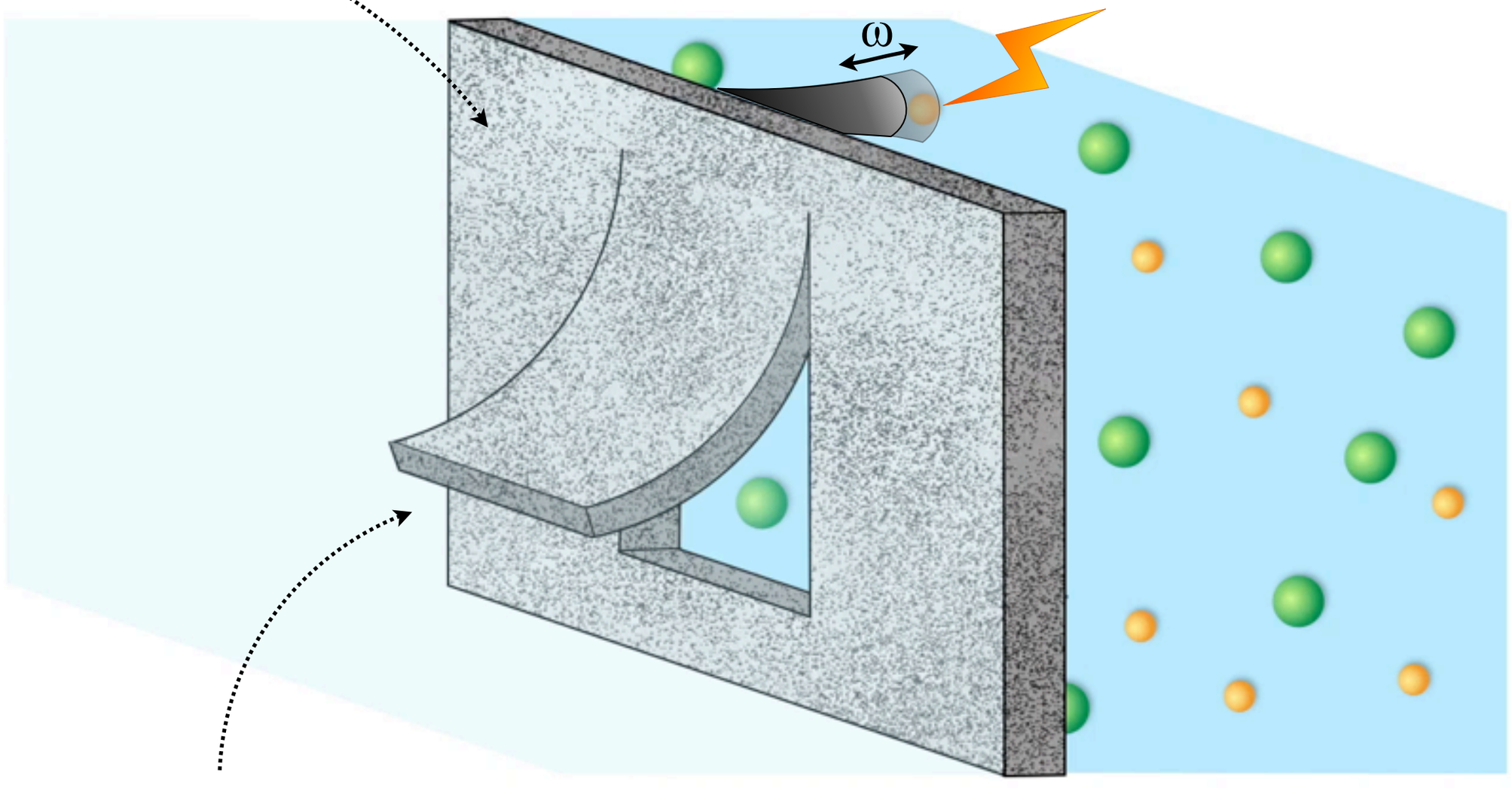
Q: inject energy at pore scale and explore how this modifies separation *(bypass some second principle limitations ??)*

- start by exploring simplest systems, toy models
- here, active pores: driven gates and doors



nano door in a membrane

external excitation at frequency ω with a piezo



thermal fluctuations of door opening

nano door in a membrane

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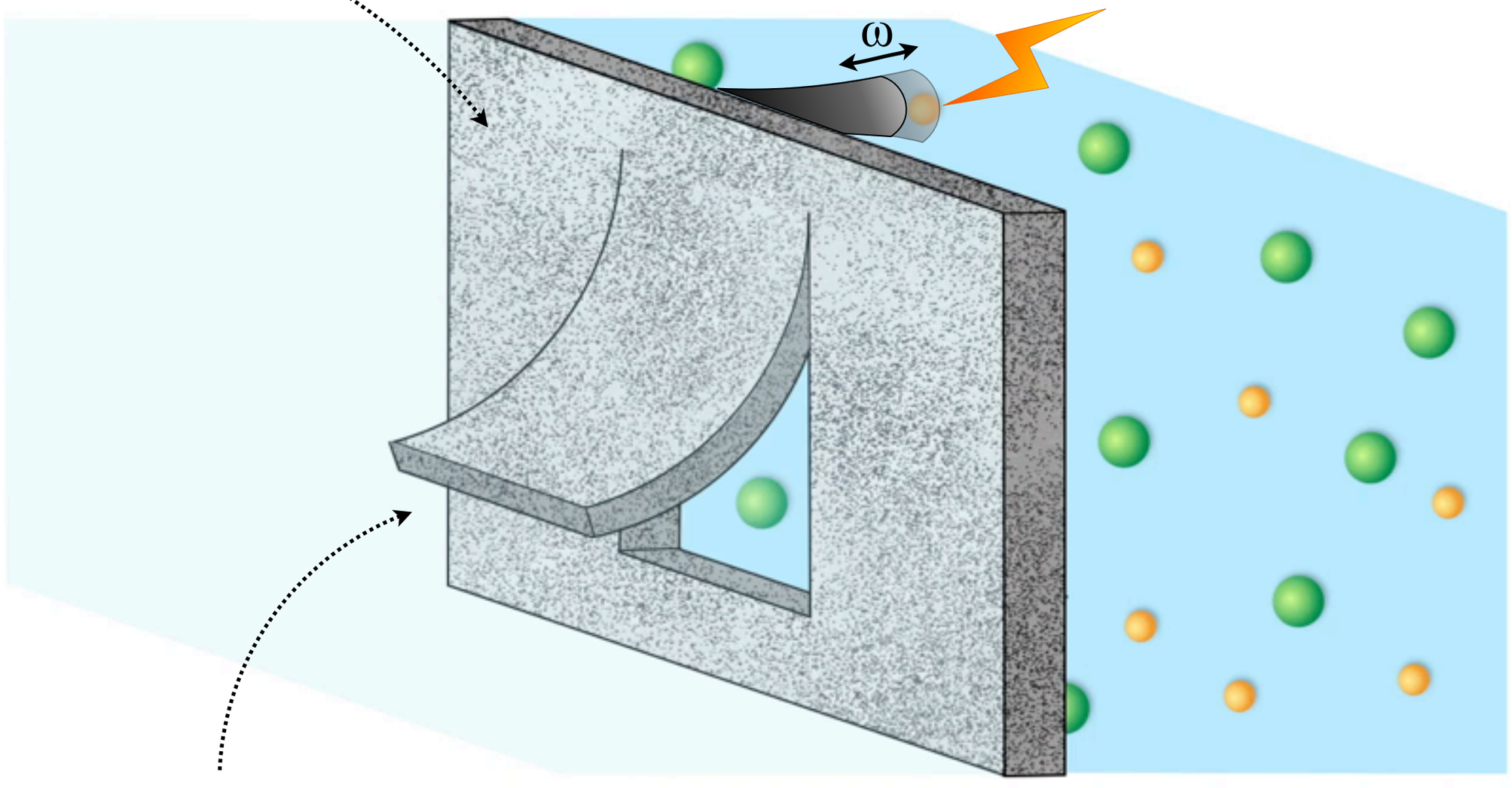
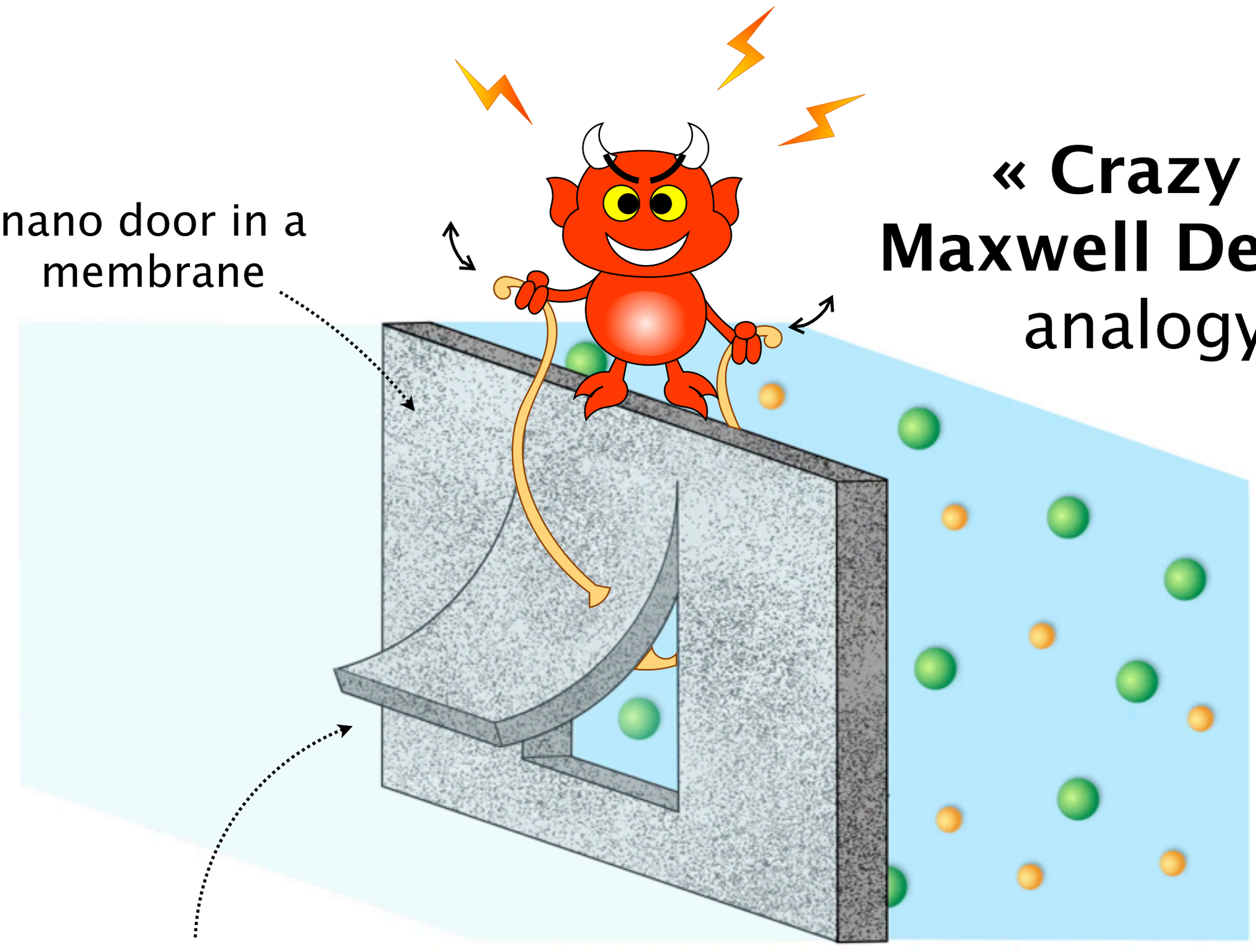
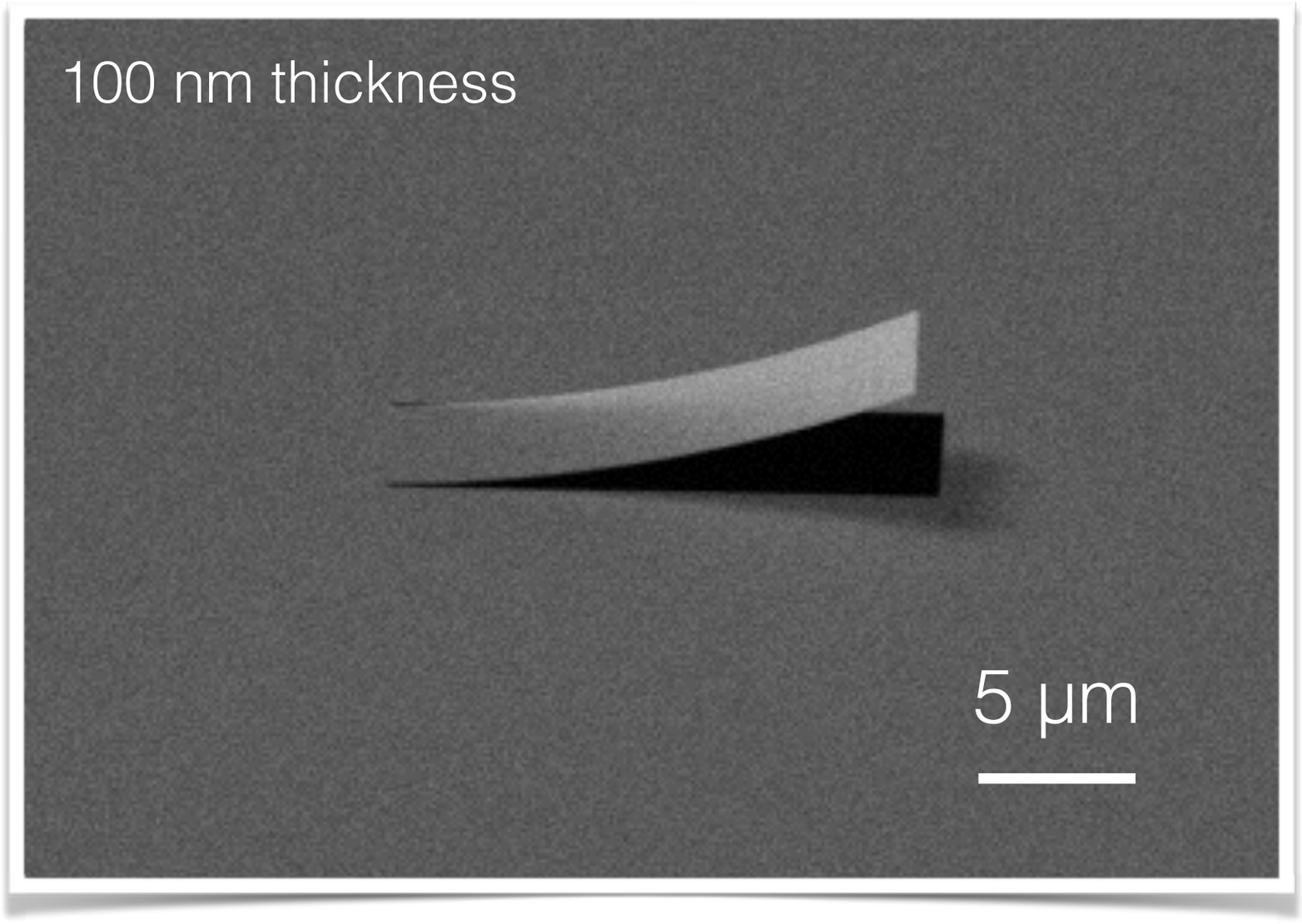


thermal fluctuations of door opening

« Crazy »
Maxwell Demon
analogy



DESIGN NANODOORS



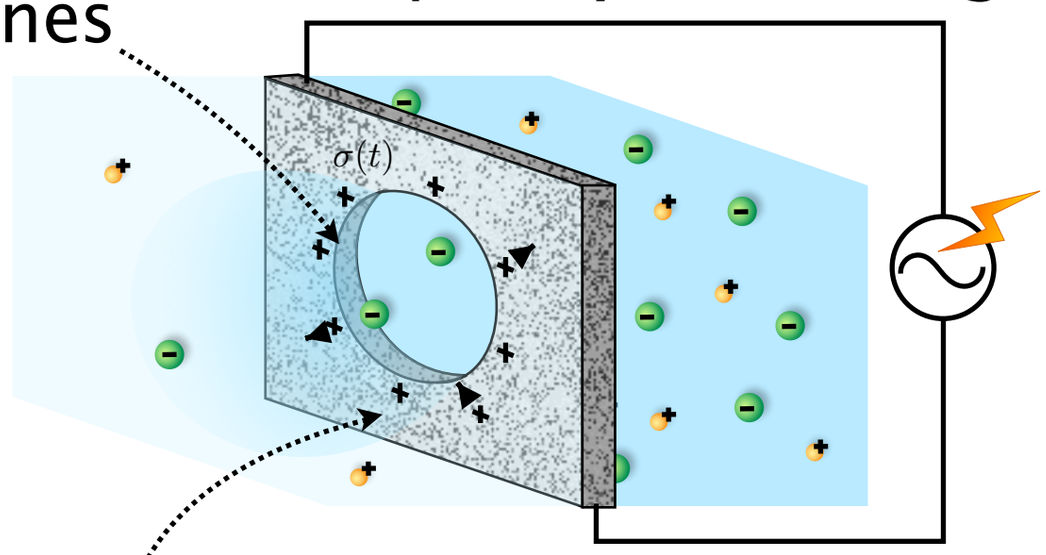
Carved with FIB in SEM

SEM image of Si-N membrane with « nano » door

ALSO, DRIVEN CHARGE GATING

Conductive membranes

external forcing at frequency ω with a generator



thermal fluctuations of surface charge

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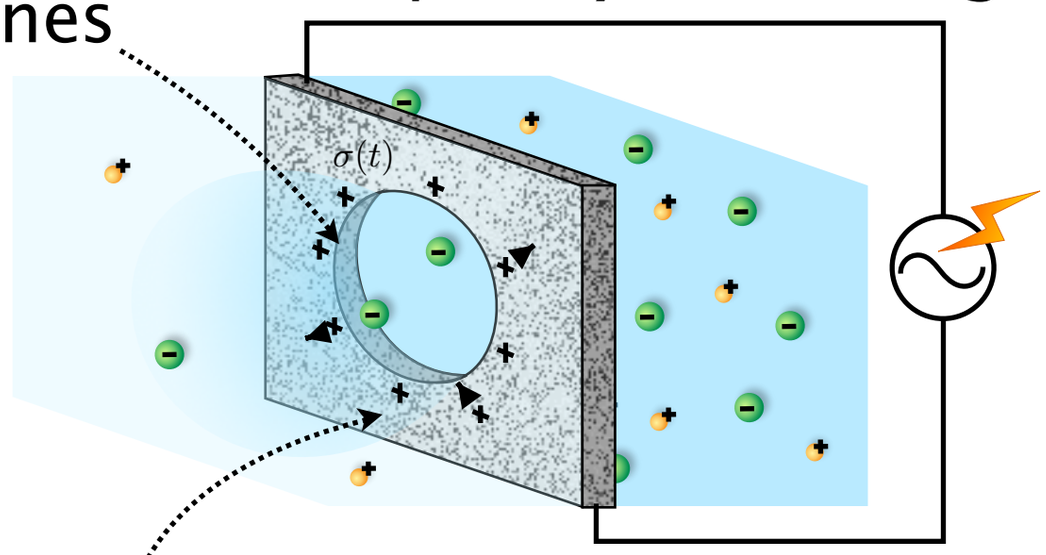

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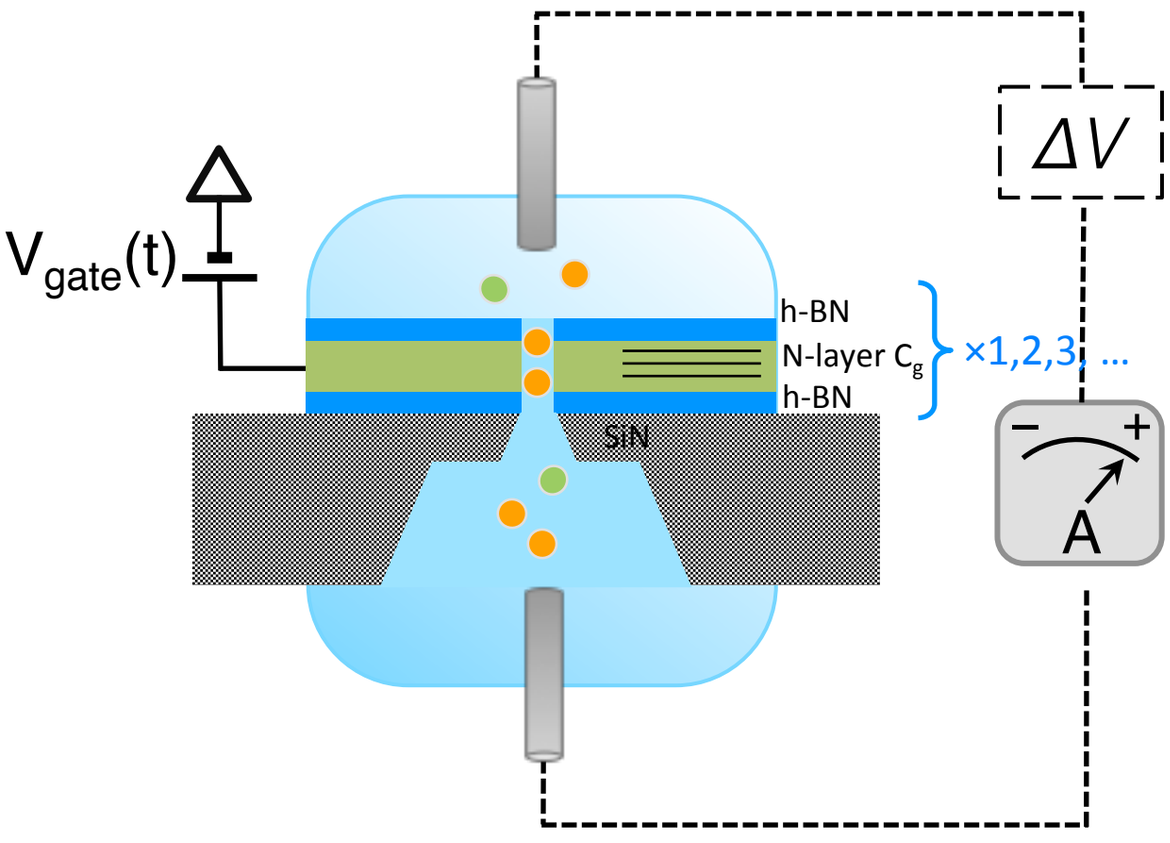
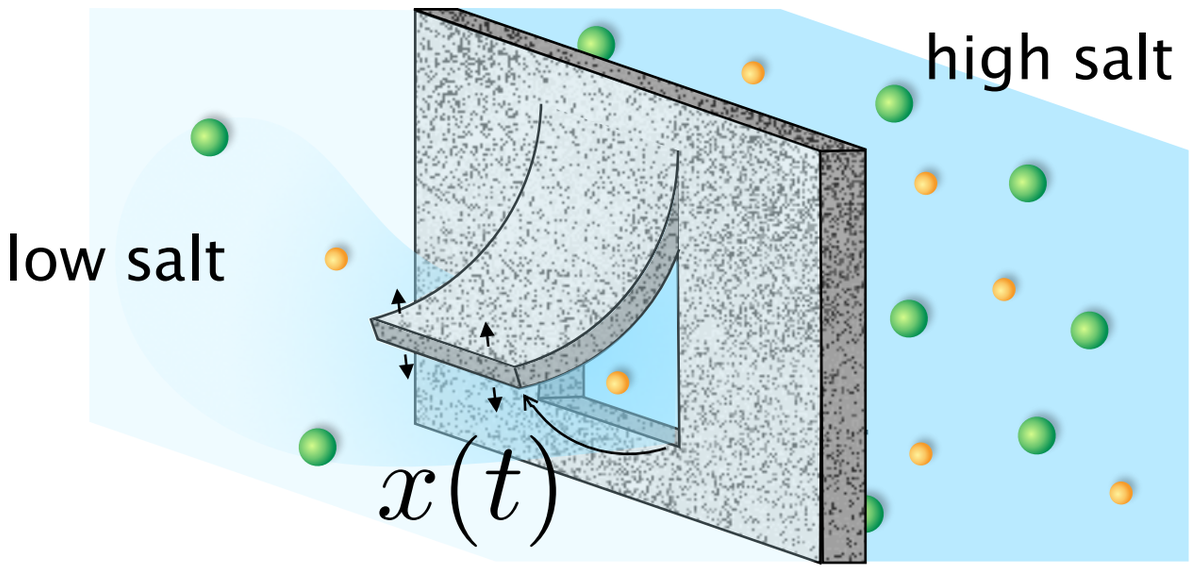


TOY MODEL FOR ACTIVE PORES



concentration difference

$$C = C_{high\ salt} - C_{low\ salt}$$

… door with opening x(t)

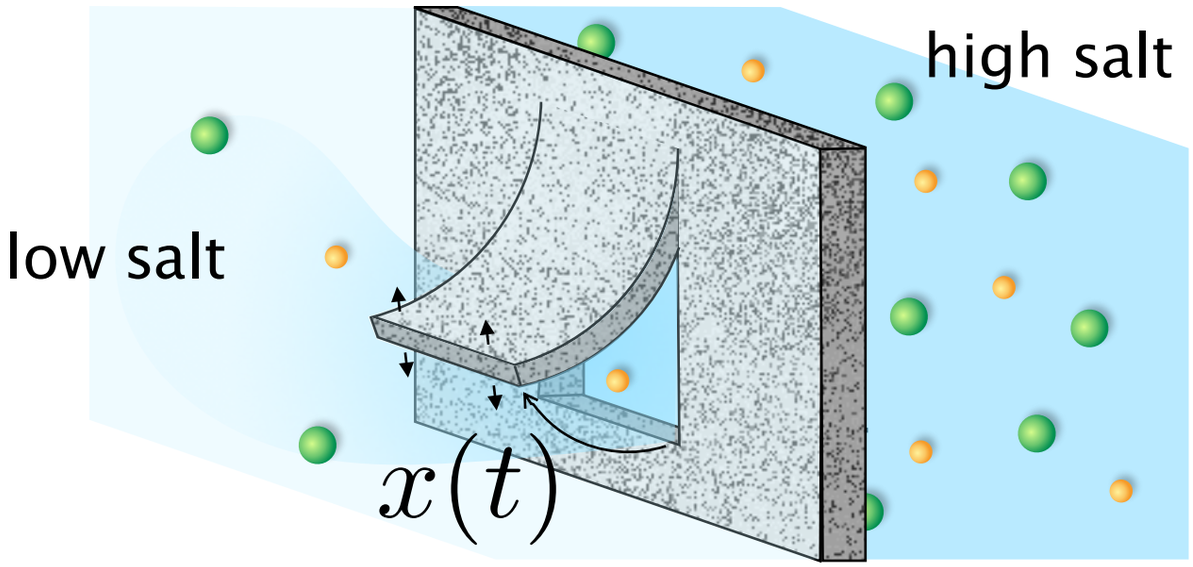
$$\frac{dC}{dt} = -k|x|C$$

[Leakage Equation]

solute mobility k

introduced by
R. Zwanzig ***J. Chem. Phys.***
(1990-92)

TOY MODEL FOR ACTIVE PORES



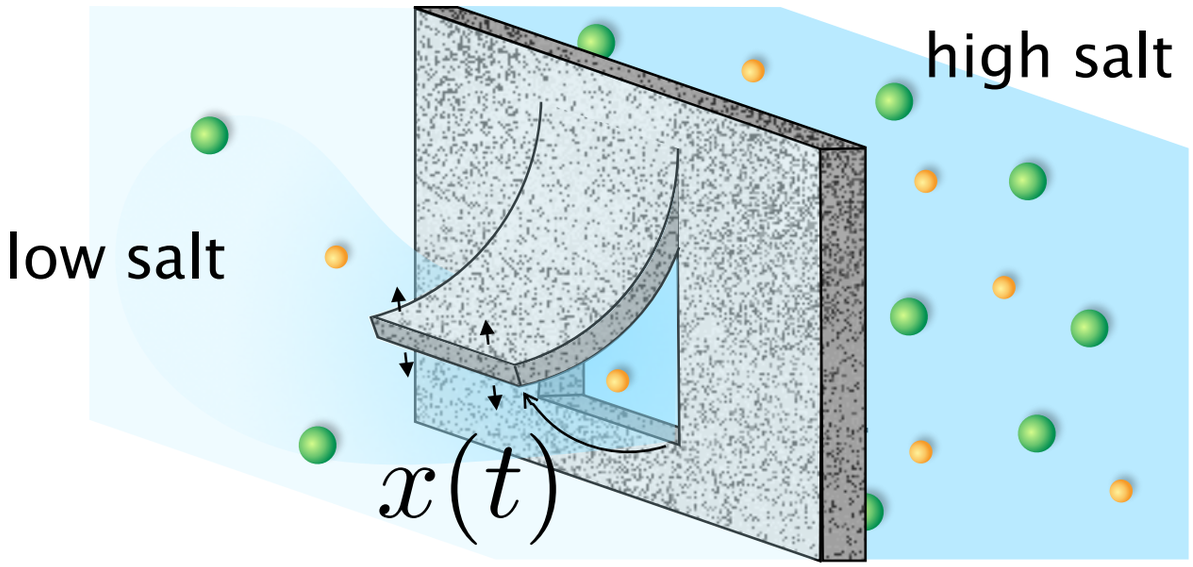
Dynamics of the nano-door

$$< x >= x_0 \sin(\omega t)$$

forcing frequency

[Gate Forcing]

TOY MODEL FOR ACTIVE PORES



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very small pore, beware of fluctuations!

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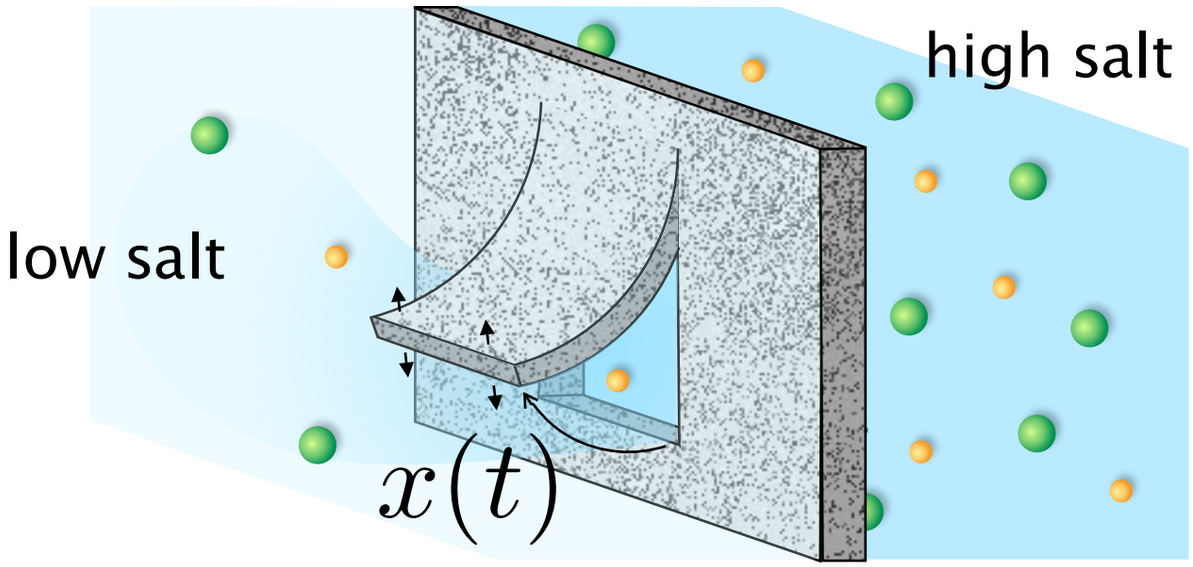


Dynamics of the nano-door

$$< x >= x_0 \sin(\omega t)$$

forcing frequency

[Gate Forcing]

very small pore, beware of fluctuations!

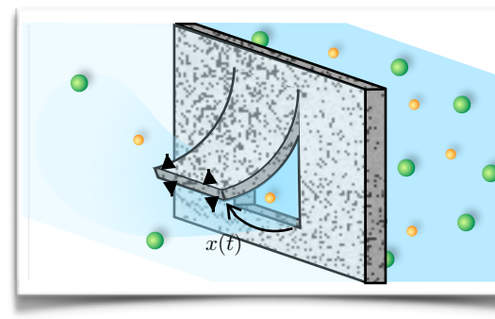
$$\delta x = x - < x > \qquad < \delta x^2 >= \theta$$

$$\frac{d}{dt}(\delta x) = -\lambda \delta x + f(t)$$

noise damping

[Gate Fluctuations]

AVERAGING OVER NOISE



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[Gate Dynamics]

(Fokker-Planck equation analytically solvable in some cases)

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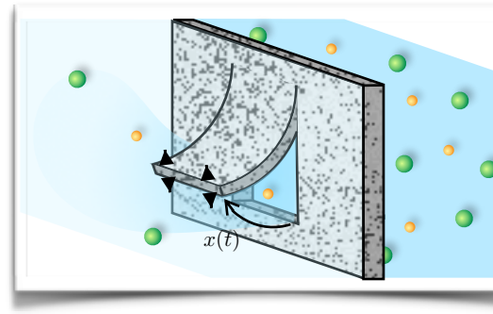

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[Gate Dynamics]

$$\frac{\partial \bar{C}}{\partial t} = -K(x)\bar{C} + \lambda\theta \frac{\partial^2 \bar{C}}{\partial x^2} + \frac{\partial \left(\lambda(x - x_0) - \frac{dx_0}{dt}\right)\bar{C}}{\partial x}$$

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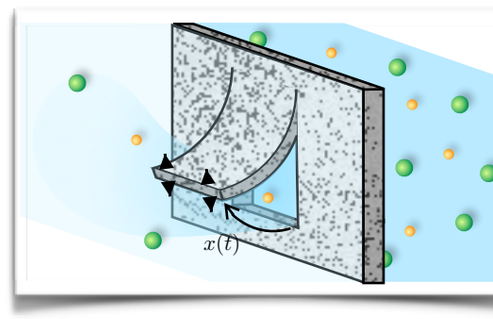
AVERAGING OVER NOISE



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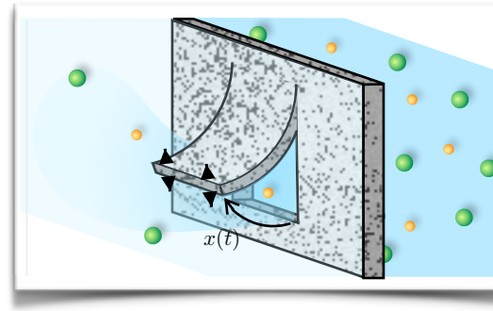
$$\frac{\partial \bar{C}}{\partial t} = -K(x)\bar{C} + \lambda\theta \frac{\partial^2 \bar{C}}{\partial x^2} + \frac{\partial \left(\lambda(x - x_0) - \frac{dx_0}{dt}\right)\bar{C}}{\partial x}$$

$$\langle C(t) \rangle$$

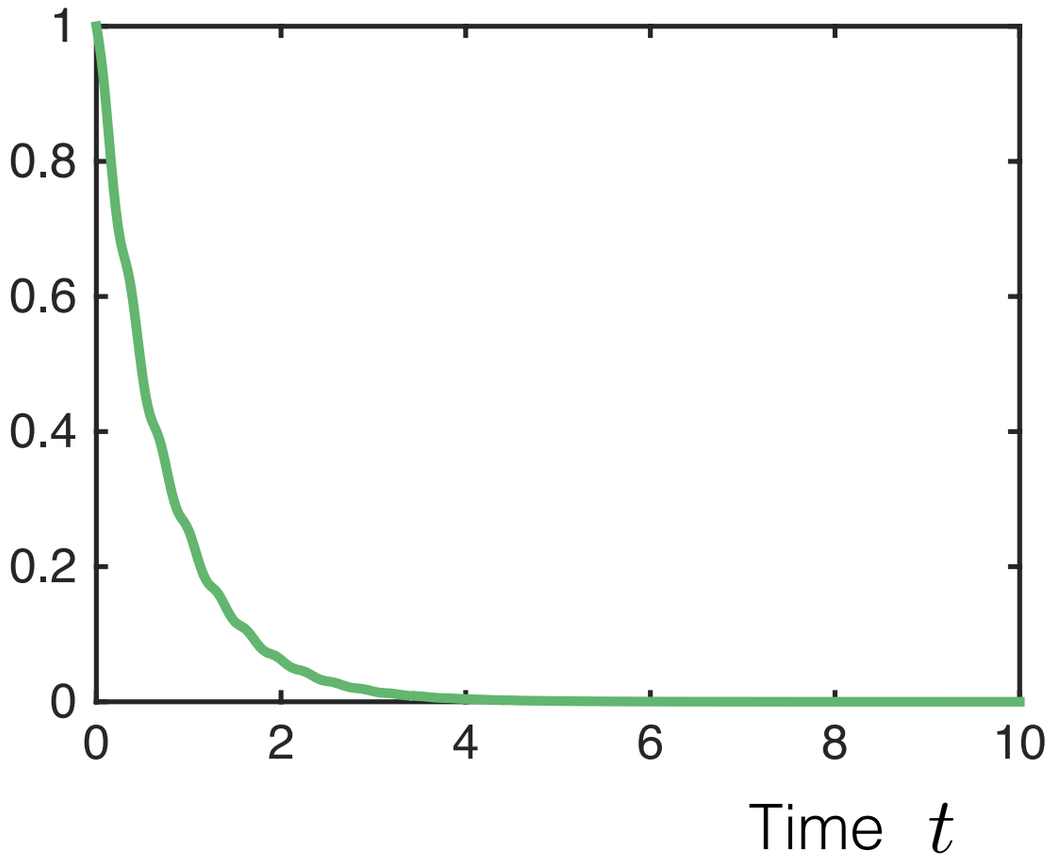
Evolution of the noise-averaged concentration

(Fokker-Planck equation analytically solvable in some cases)

AVERAGING OVER NOISE



$$\langle C \rangle = \langle C_2 - C_1 \rangle$$



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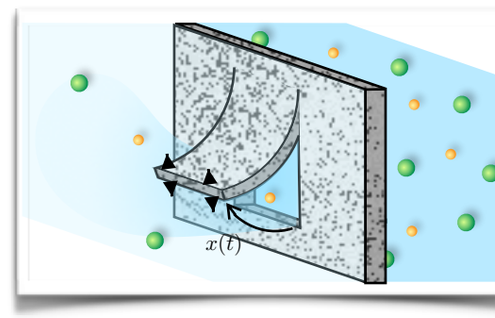

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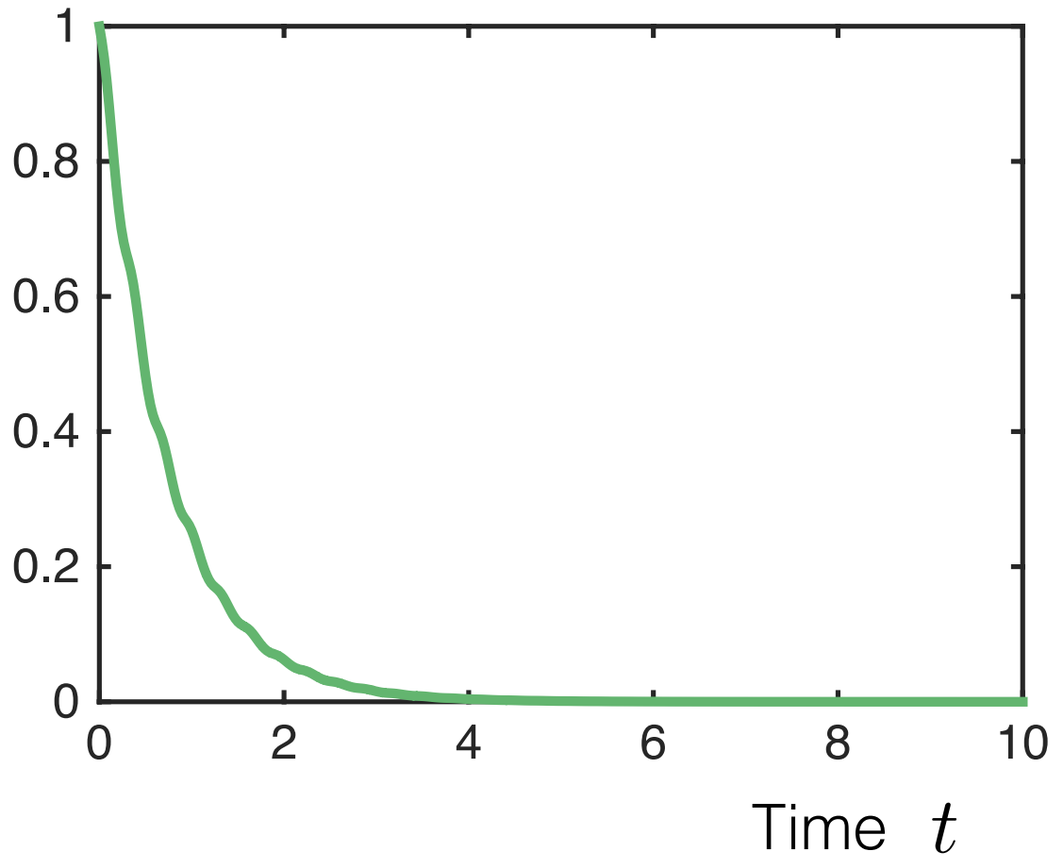
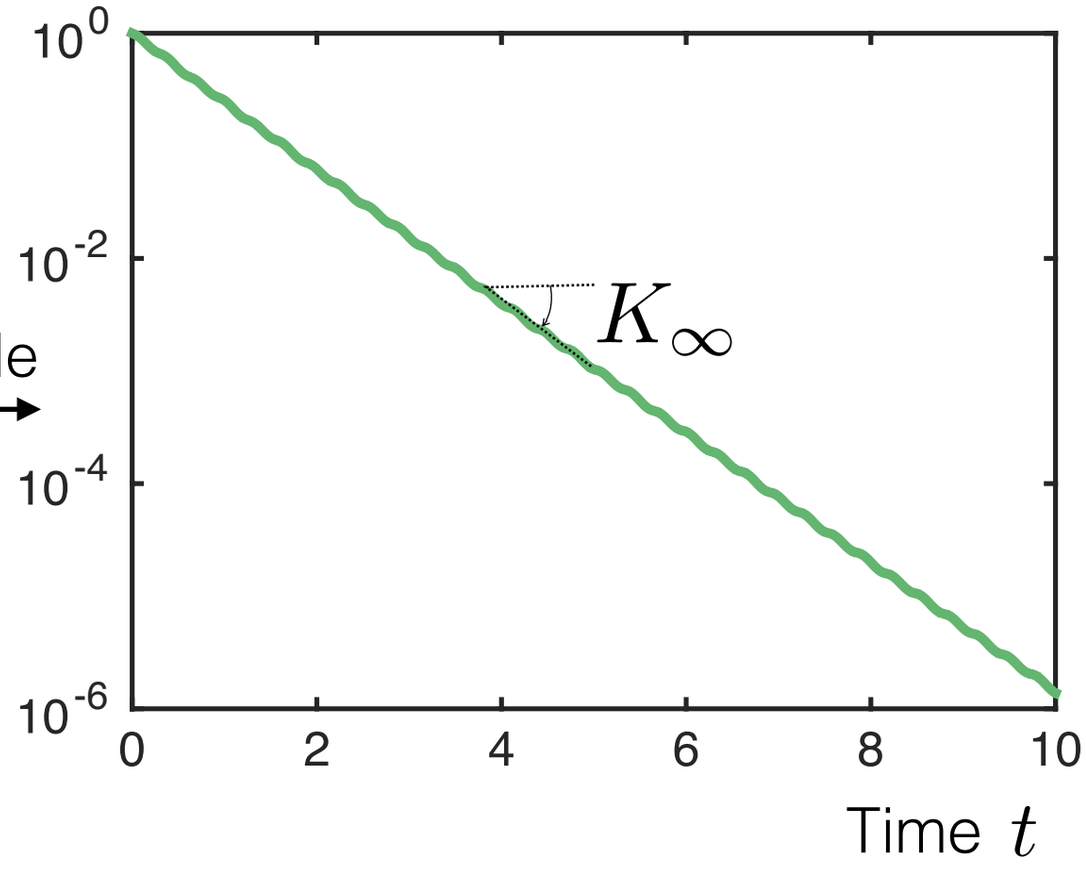


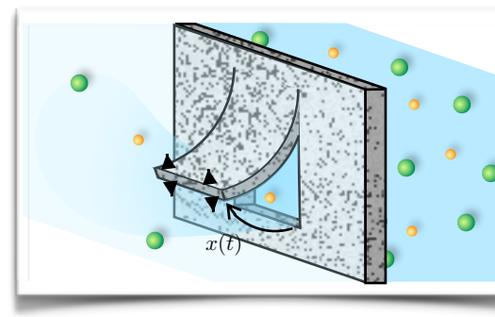
log scale

$$\langle C \rangle = \langle C_2 - C_1 \rangle$$



$$\langle C(t) \rangle \sim \exp(-K_\infty t)$$

AVERAGING OVER NOISE



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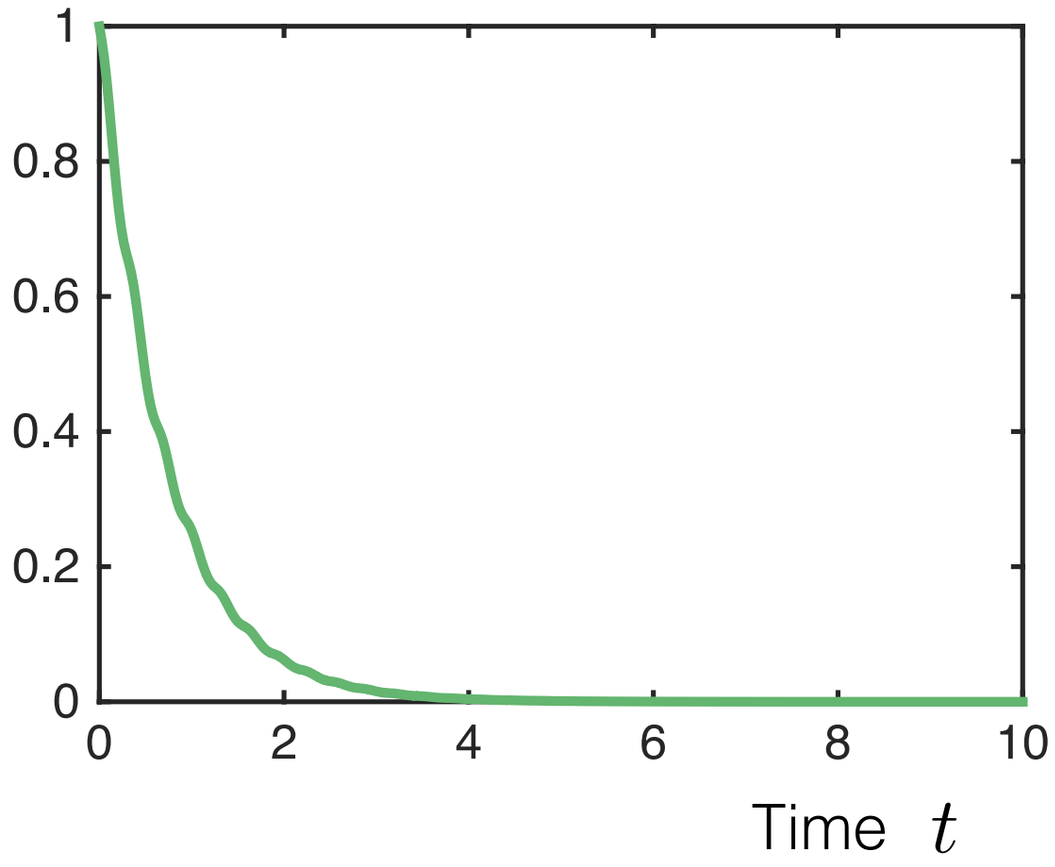

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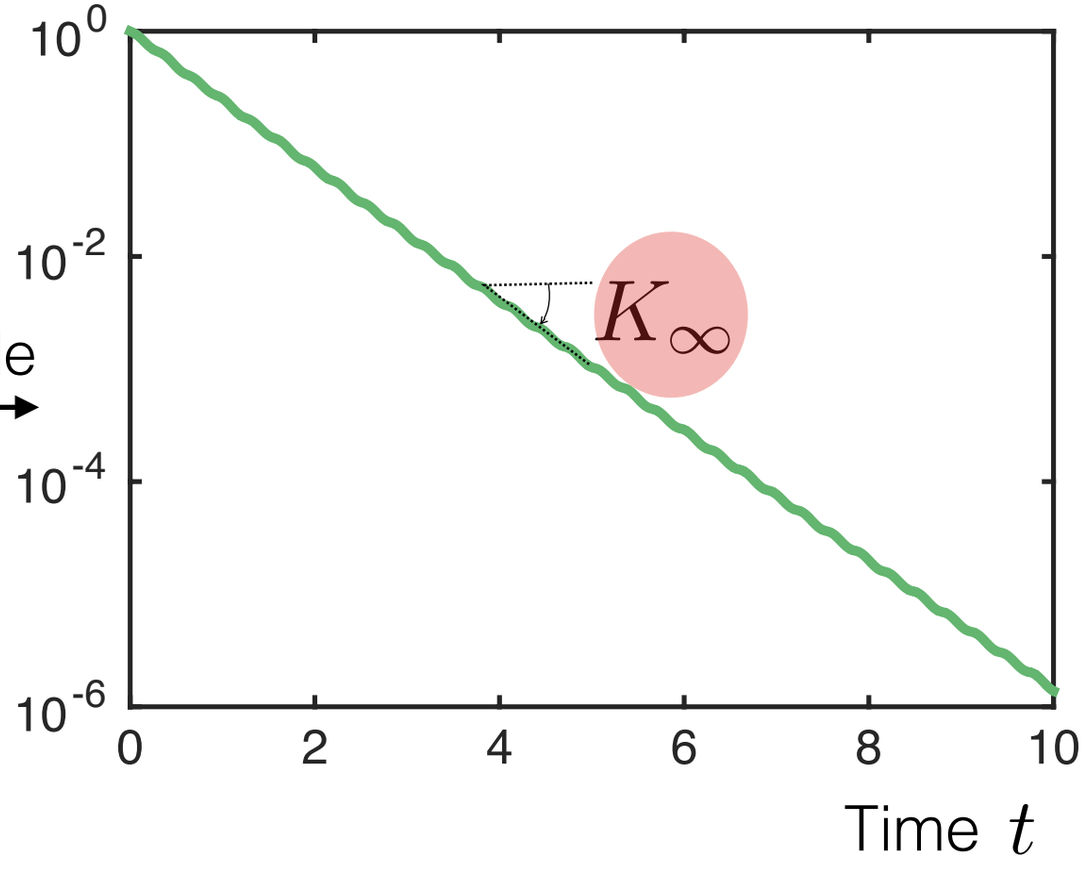


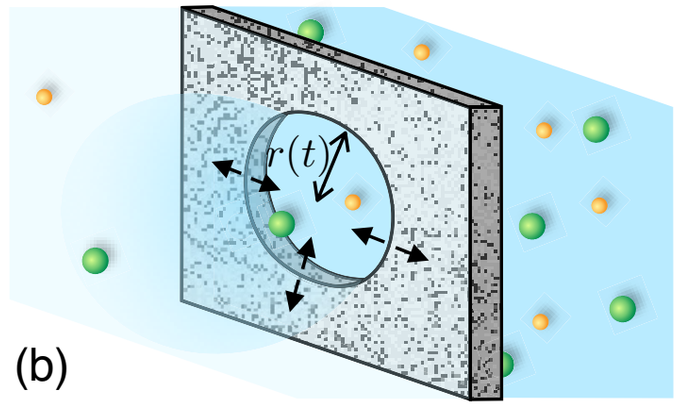
$$\langle C(t) \rangle \sim \exp(-K_\infty t)$$

Solute Permeance

SOME ANALYTICAL CASES

…in some cases: *eg* circular pore

$$\langle r(t) \rangle = r_0(1 + \epsilon \cos(\omega t))$$



$$\langle C(t) \rangle \sim \exp(-K_\infty t)$$

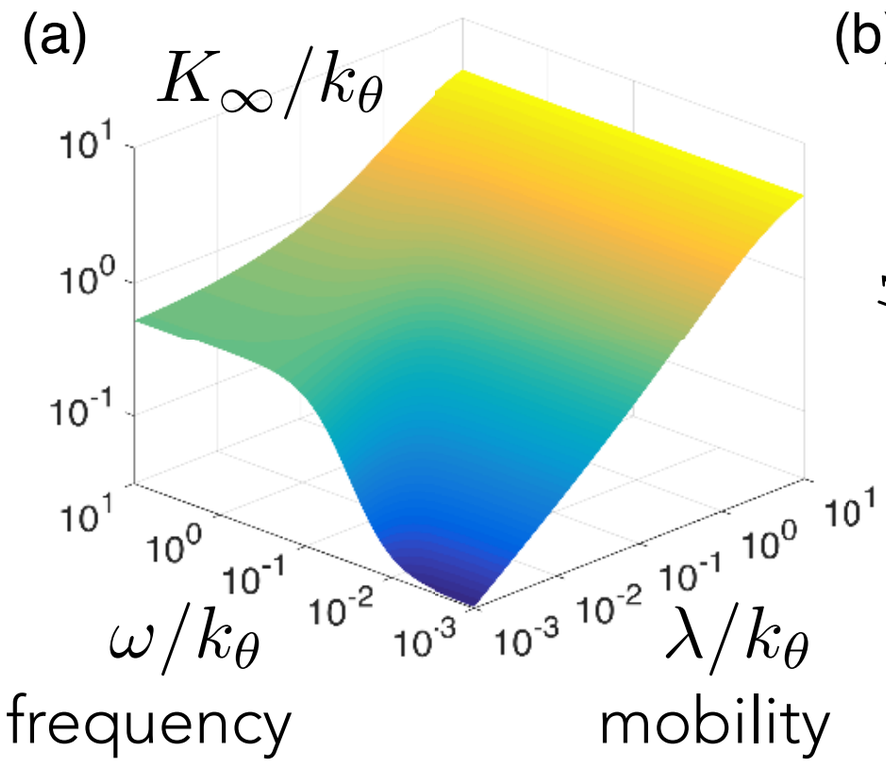
$$K_\infty(\omega) = \lambda/2 \left(\left(1 + \frac{4k'\theta}{\lambda} \right)^{1/2} - 1 \right) + k' r_0^2 \left(1 + \frac{4k'\theta}{\lambda} \right)^{-1}$$
$$+ k' \frac{r_0^2 \epsilon^2}{2} \left(\frac{\left(1 + \frac{4k'\theta}{\lambda} \right)^{-1}}{1 + (\frac{\omega}{\omega_c(\lambda)})^2} + \frac{(\frac{\omega}{\omega_c(\lambda)})^2}{1 + (\frac{\omega}{\omega_c(\lambda)})^2} \right)$$

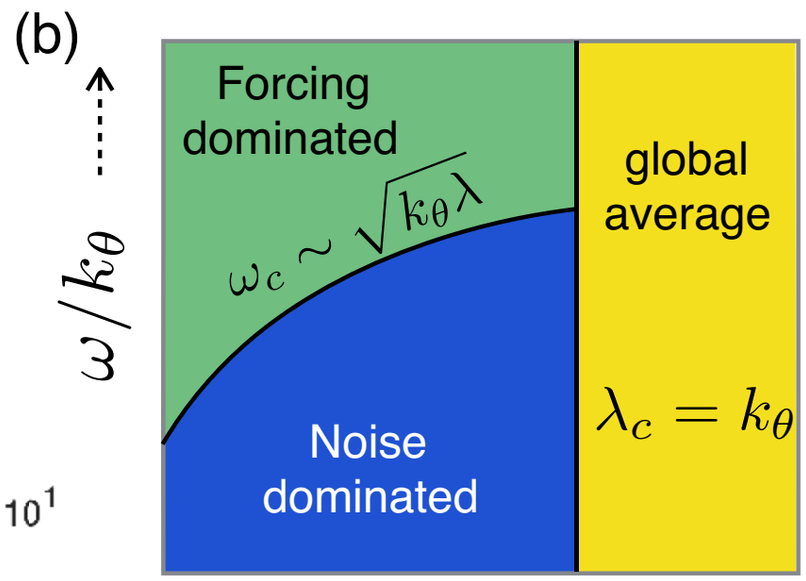
cutoff $\omega_c \sim \sqrt{k\lambda\theta}$ (mobility/damping/noise)

= various regimes for separation

COMPLEX SIEVING DIAGRAM

sieving depend on frequency (and door prop)





various (non-trivial) limiting behaviors, retrieved by scaling

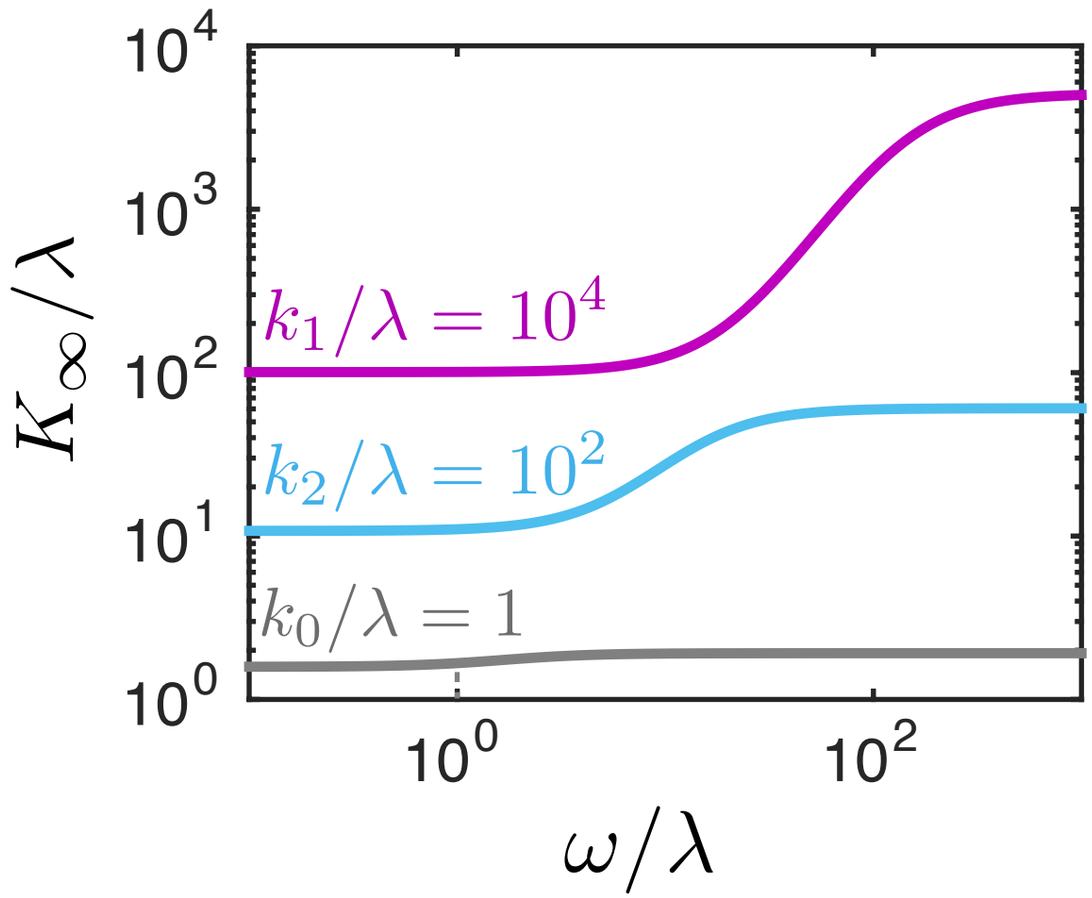
$$K_\infty \underset{\omega \ll \omega_c}{\sim} \lambda^{1/2}$$

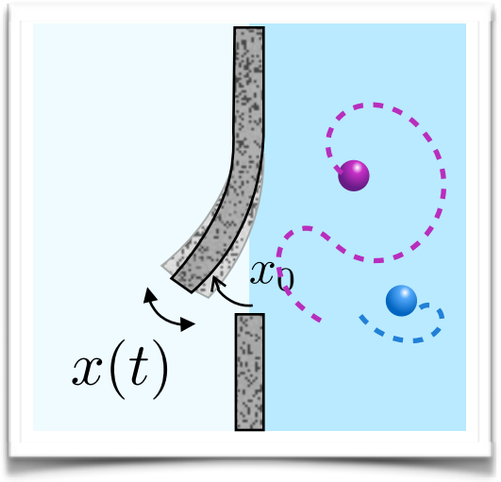
scaling in viscosity
$\sim 1/\eta^{1/2}$

$$K_\infty(\omega) \underset{\omega \gg \omega_c}{\sim} k' r_0^2 \epsilon^2/2$$

GATING ON MOBILITY

Permeance for various solute mobilities





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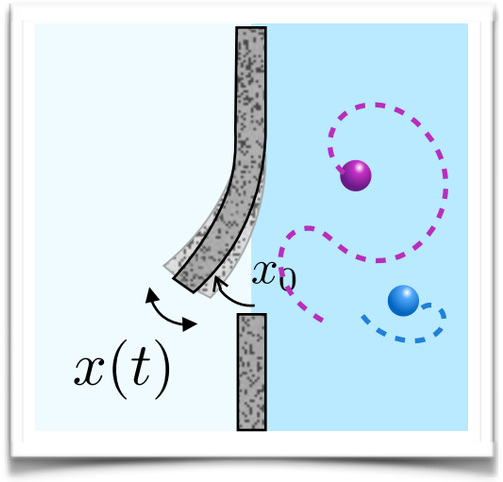
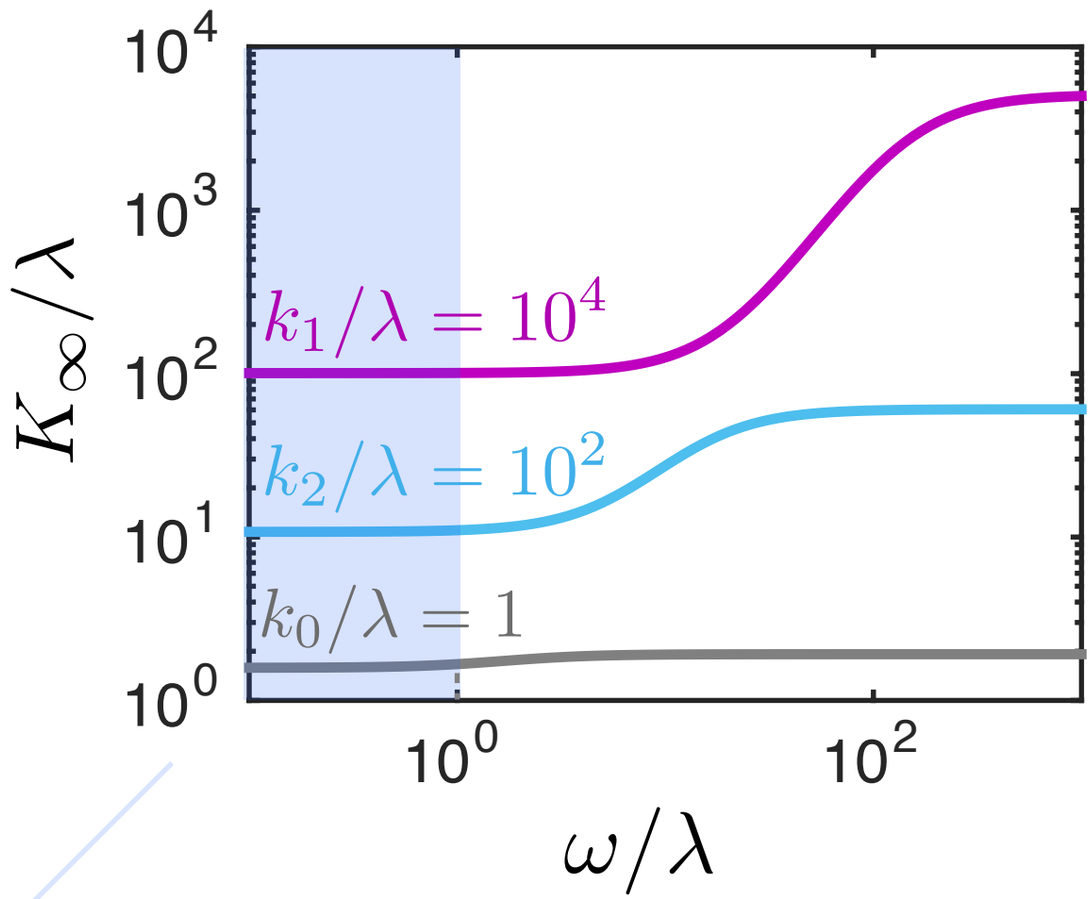
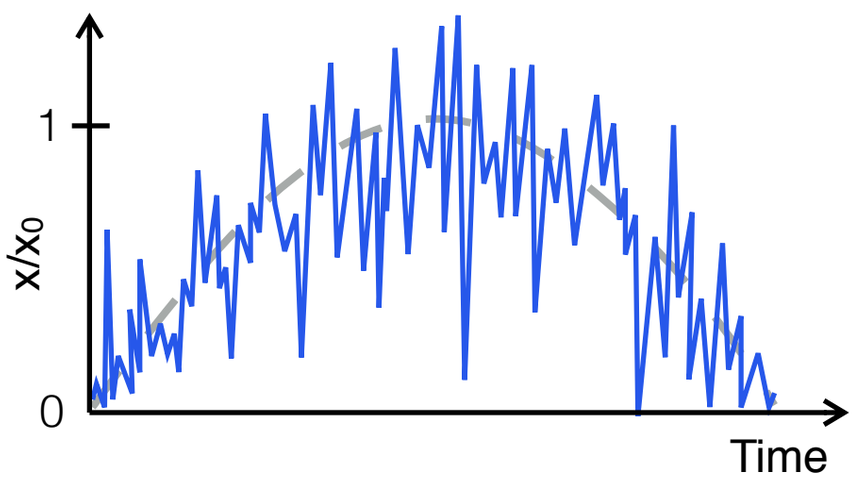




Noise dominated



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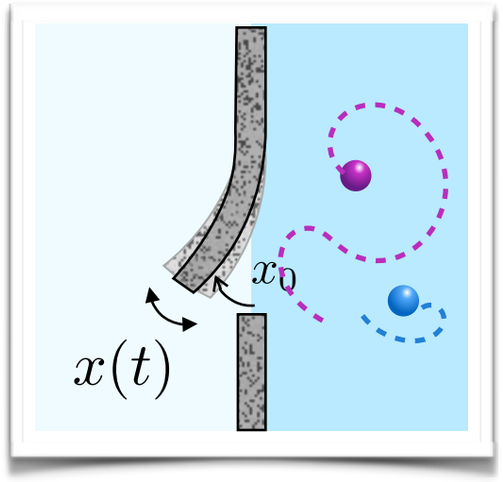

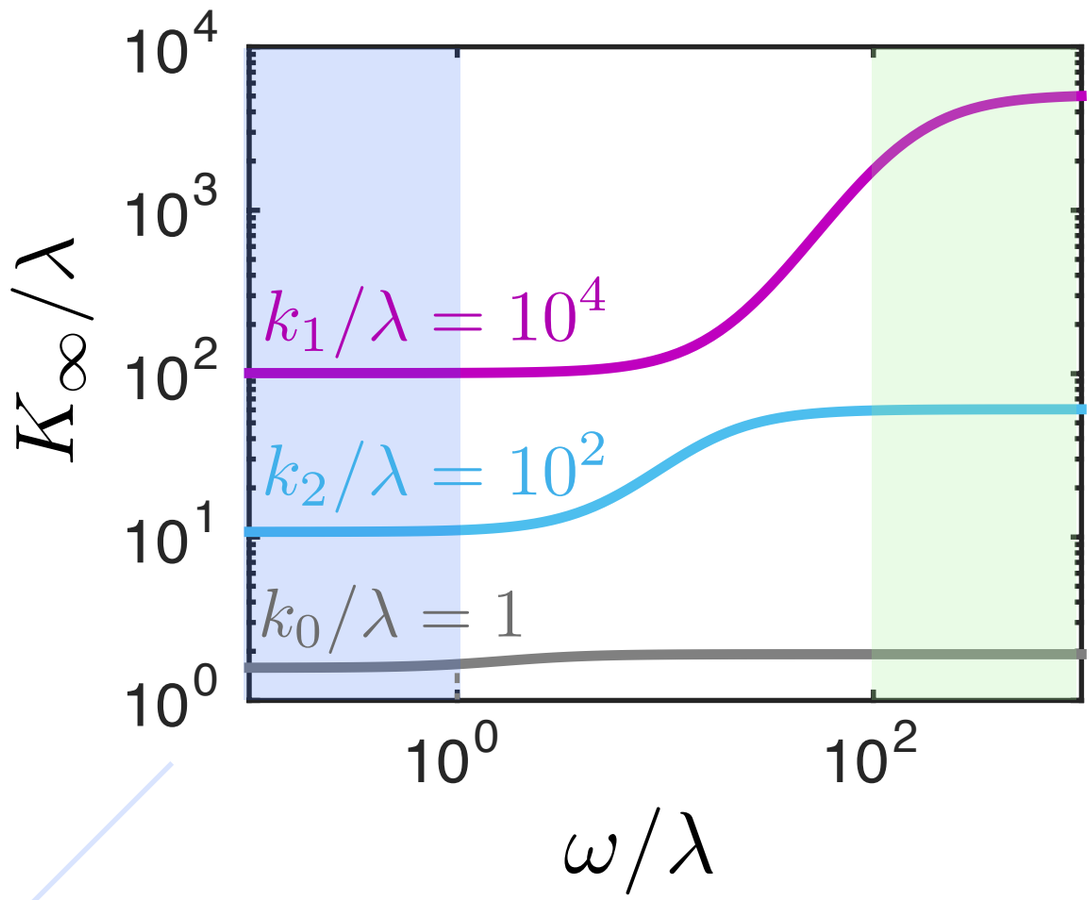

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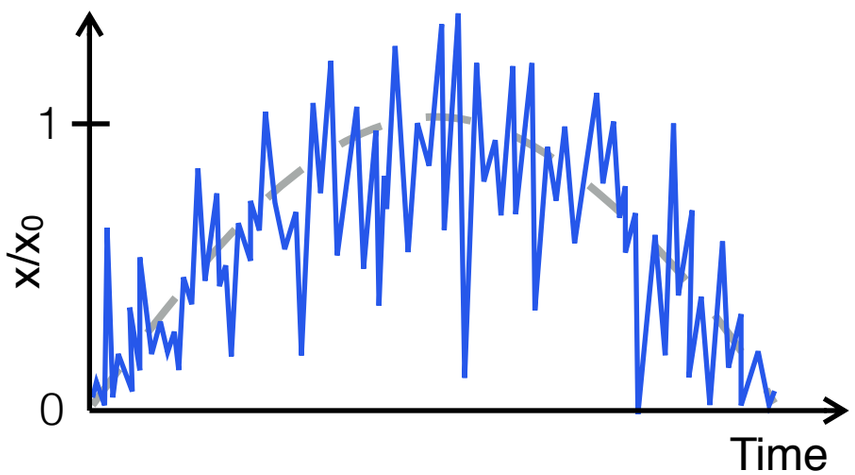
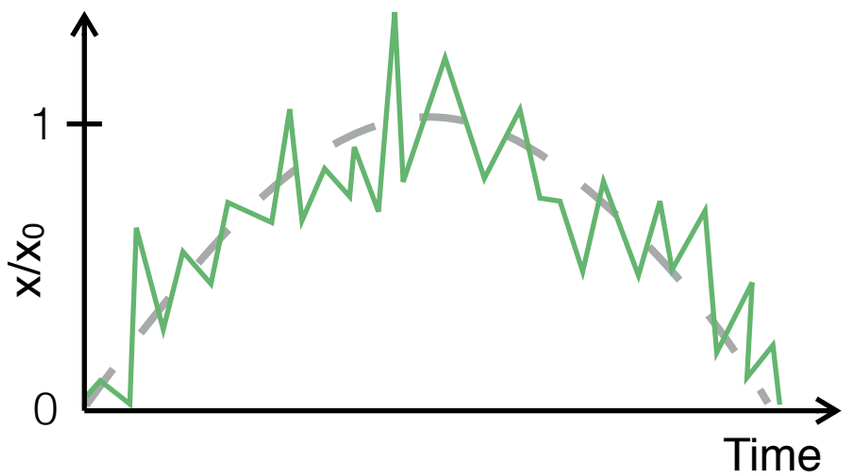


Forcing dominated



GATING ON MOBILITY

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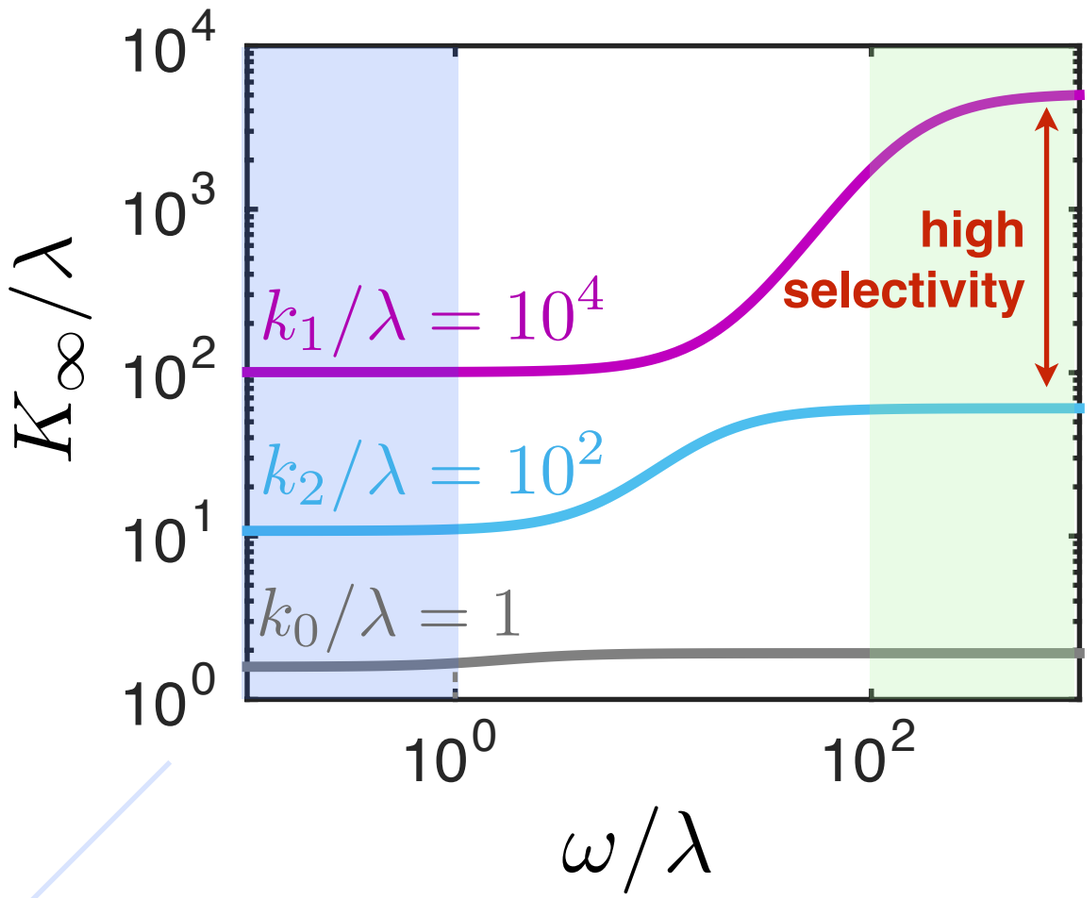

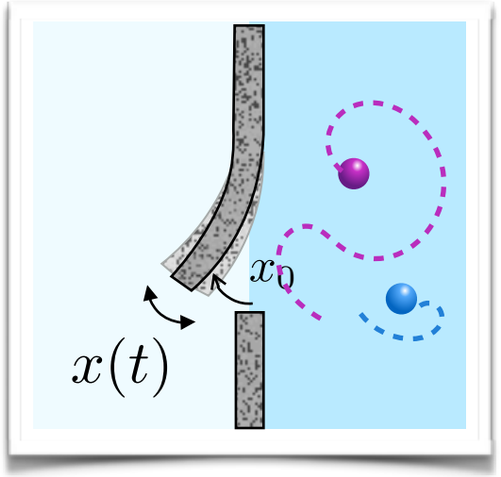

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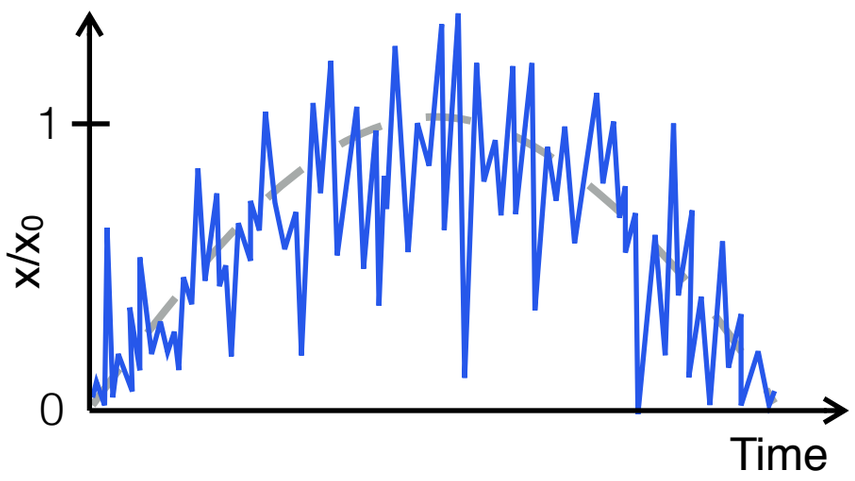

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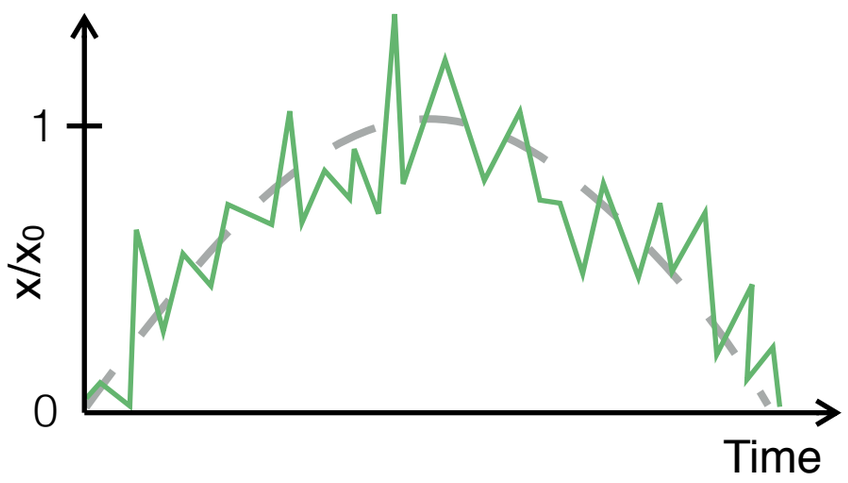

GATING ON MOBILITY

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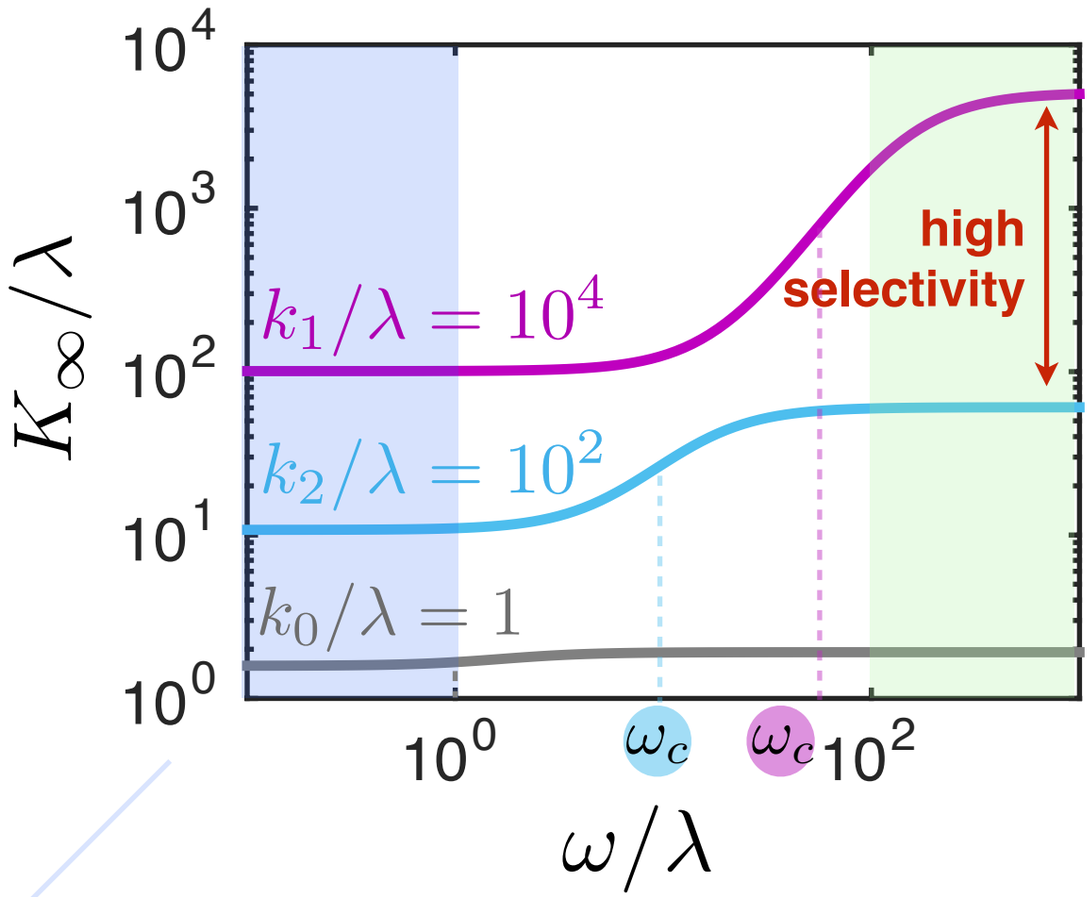
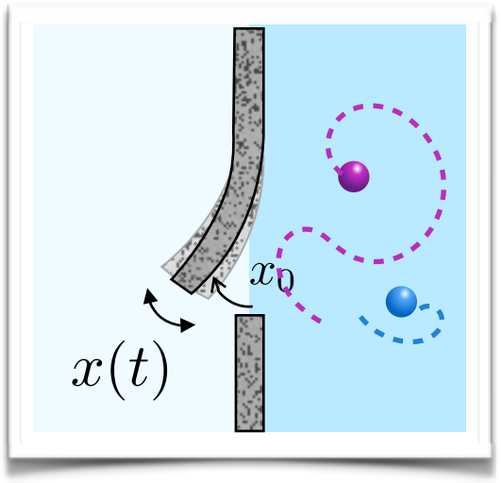
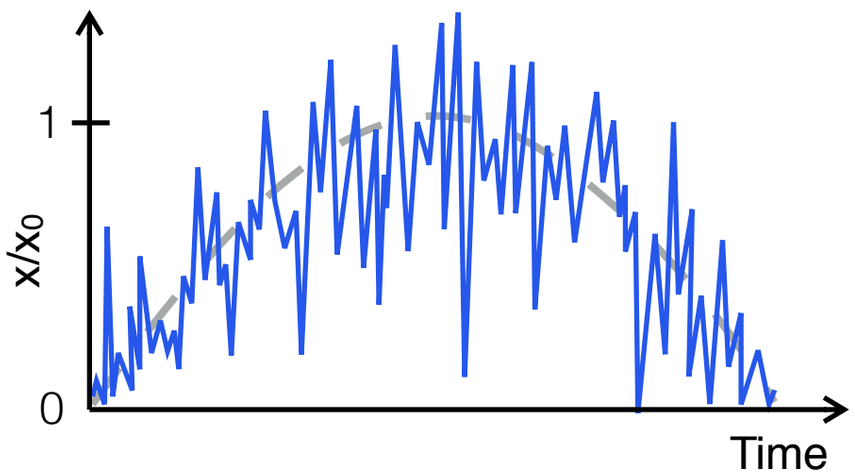




$$\omega_c \sim \sqrt{k\lambda\theta}$$

solute mobility

Noise dominated



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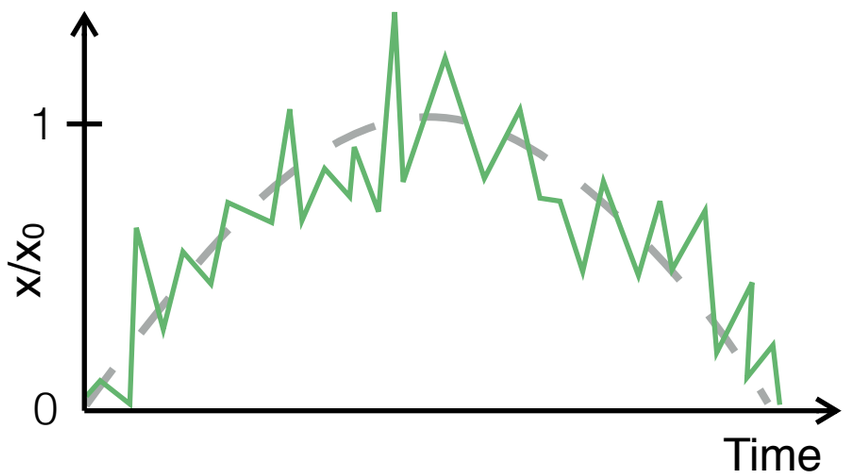

GATING ON MOBILITY

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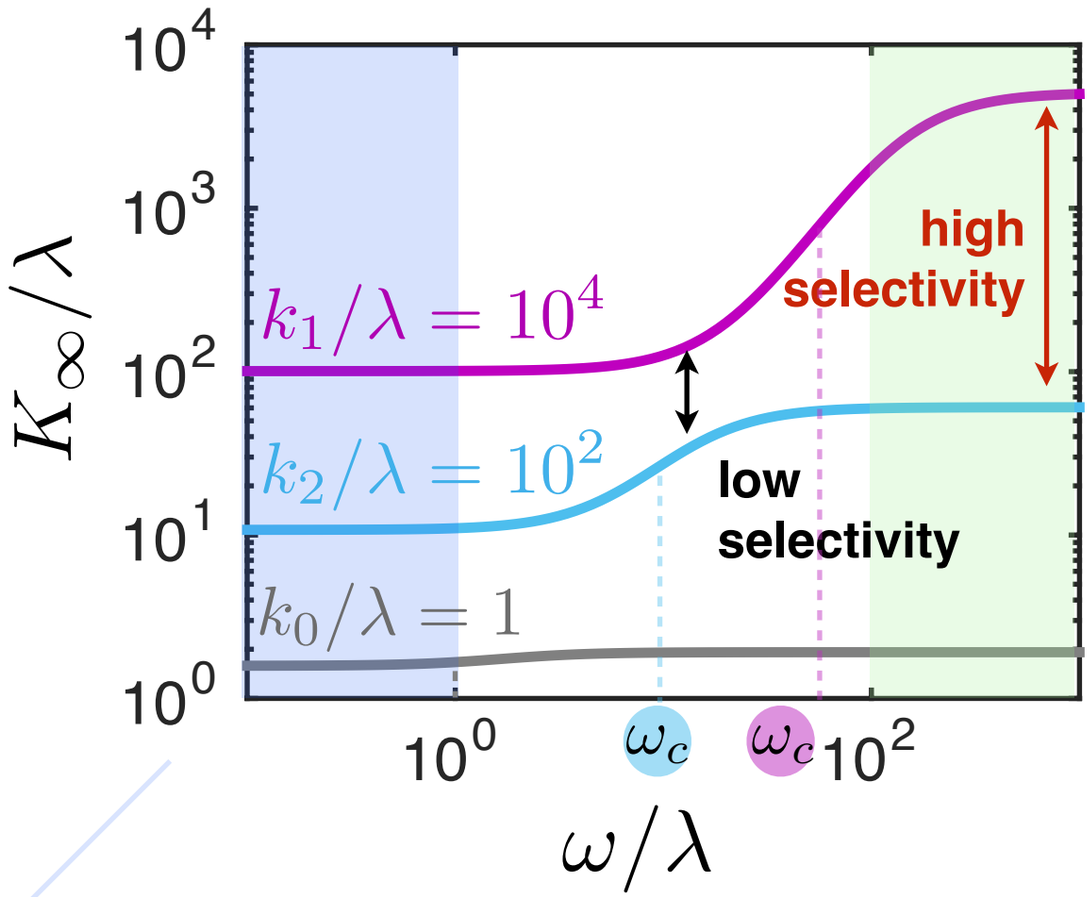

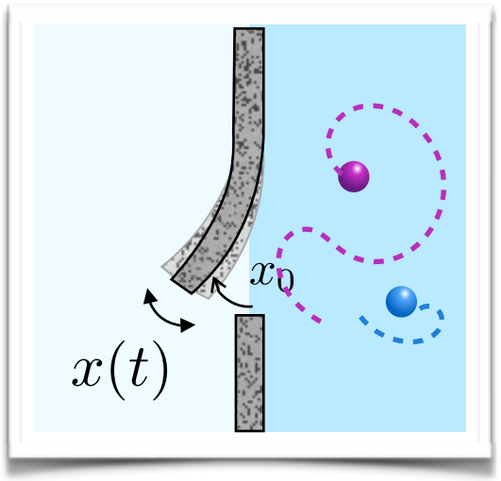

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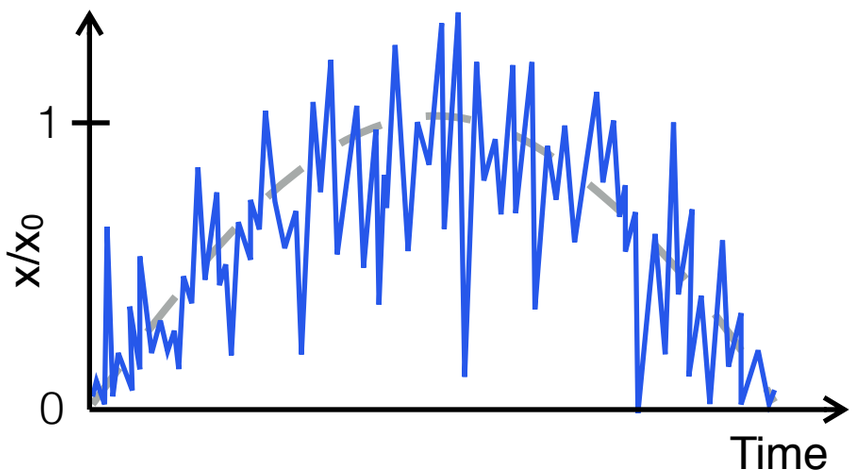

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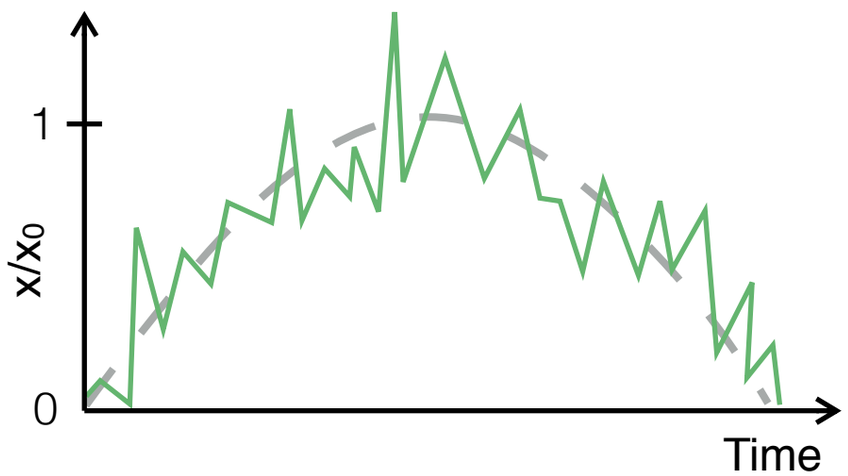
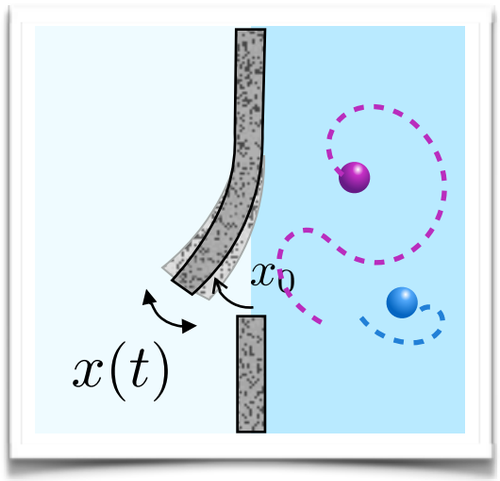
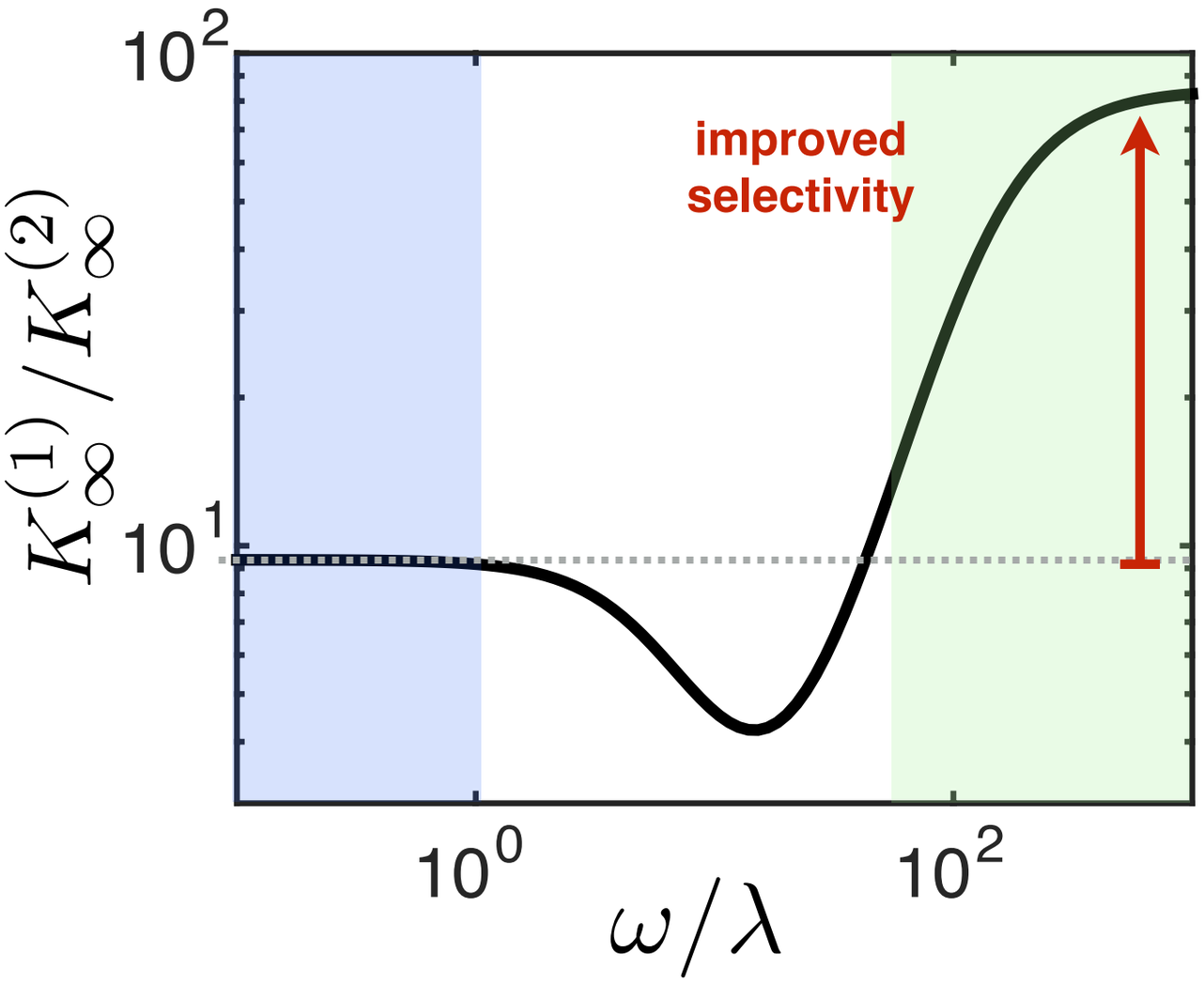


GATING ON MOBILITY

Define **selectivity** as :

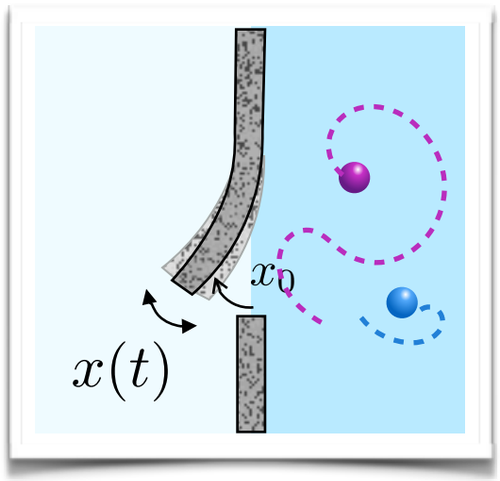
$$K_\infty^{(1)} / K_\infty^{(2)}$$





model can be extended with further ingredients (size gating, …)

GATING ON MOBILITY



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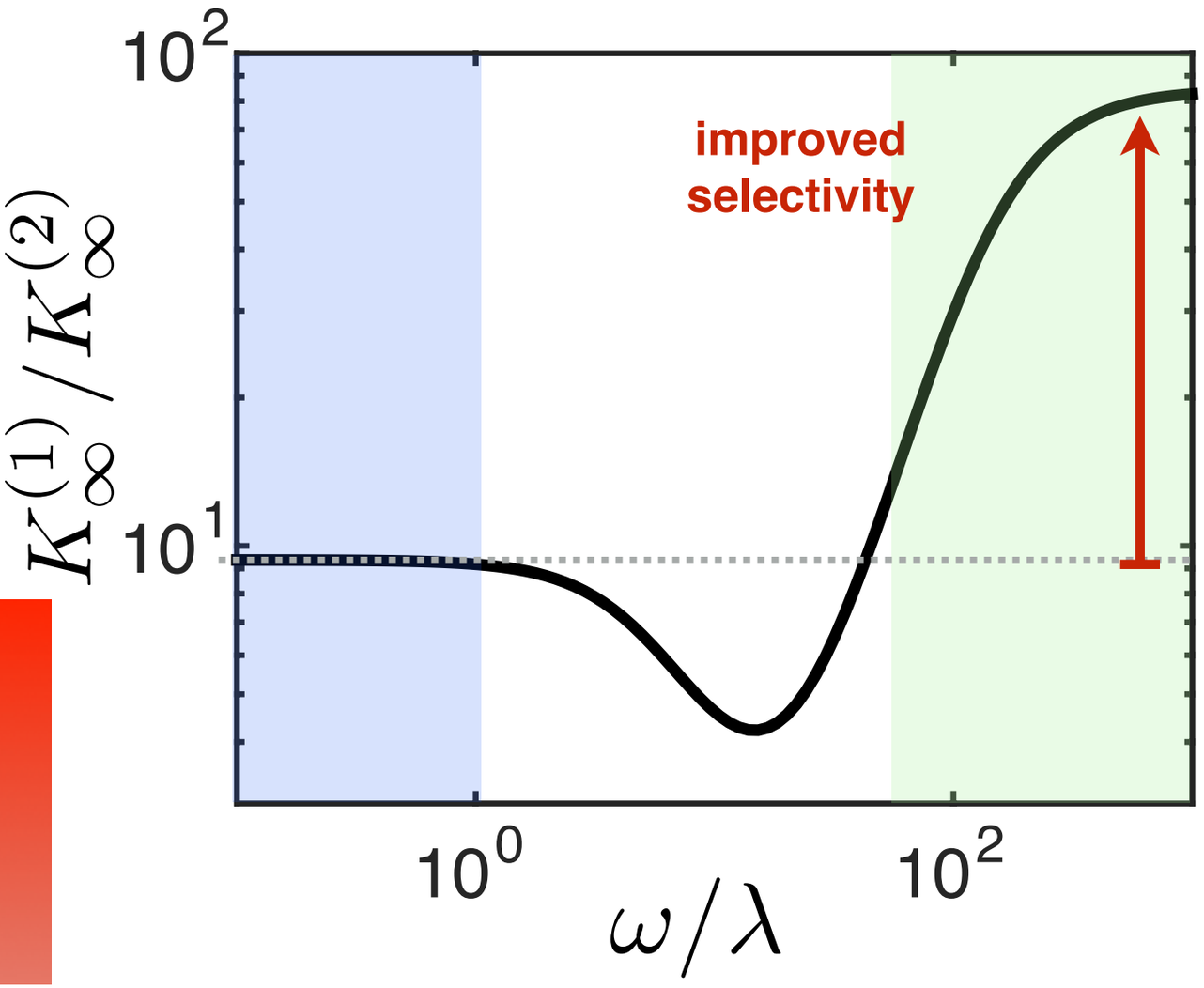
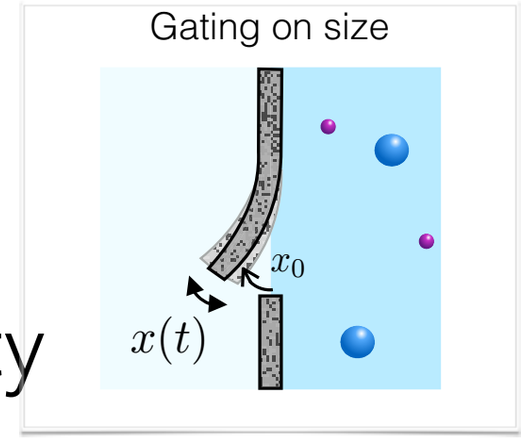


HUGE POTENTIAL TO TUNE MEMBRANE DYNAMICALLY PROPERTIES

model can be extended with further ingredients (size gating, …)

DYNAMICAL OSMOSIS



- pass… or not: intermittent semi-permeability = intermittent osmosis ? $\Delta\Pi(\omega)$

- estimate: use « *permeance* ⇔ *osmosis* » symmetry

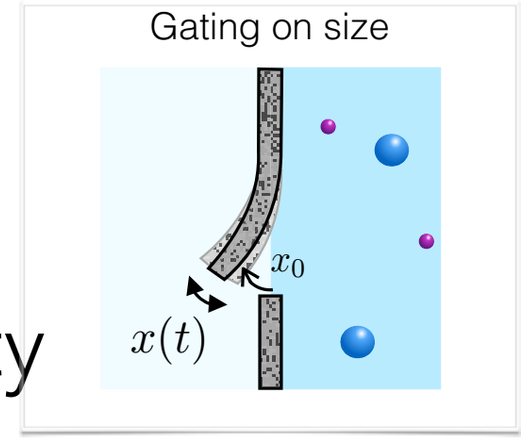
Kedem-Katchalsky, cf also Marbach, et al. J Chem Phys (2017)

osmosis $\Delta\Pi = \sigma \times k_B T C$

reflection coef.

solute permeance $K_\infty \propto (1 - \sigma)$

DYNAMICAL OSMOSIS



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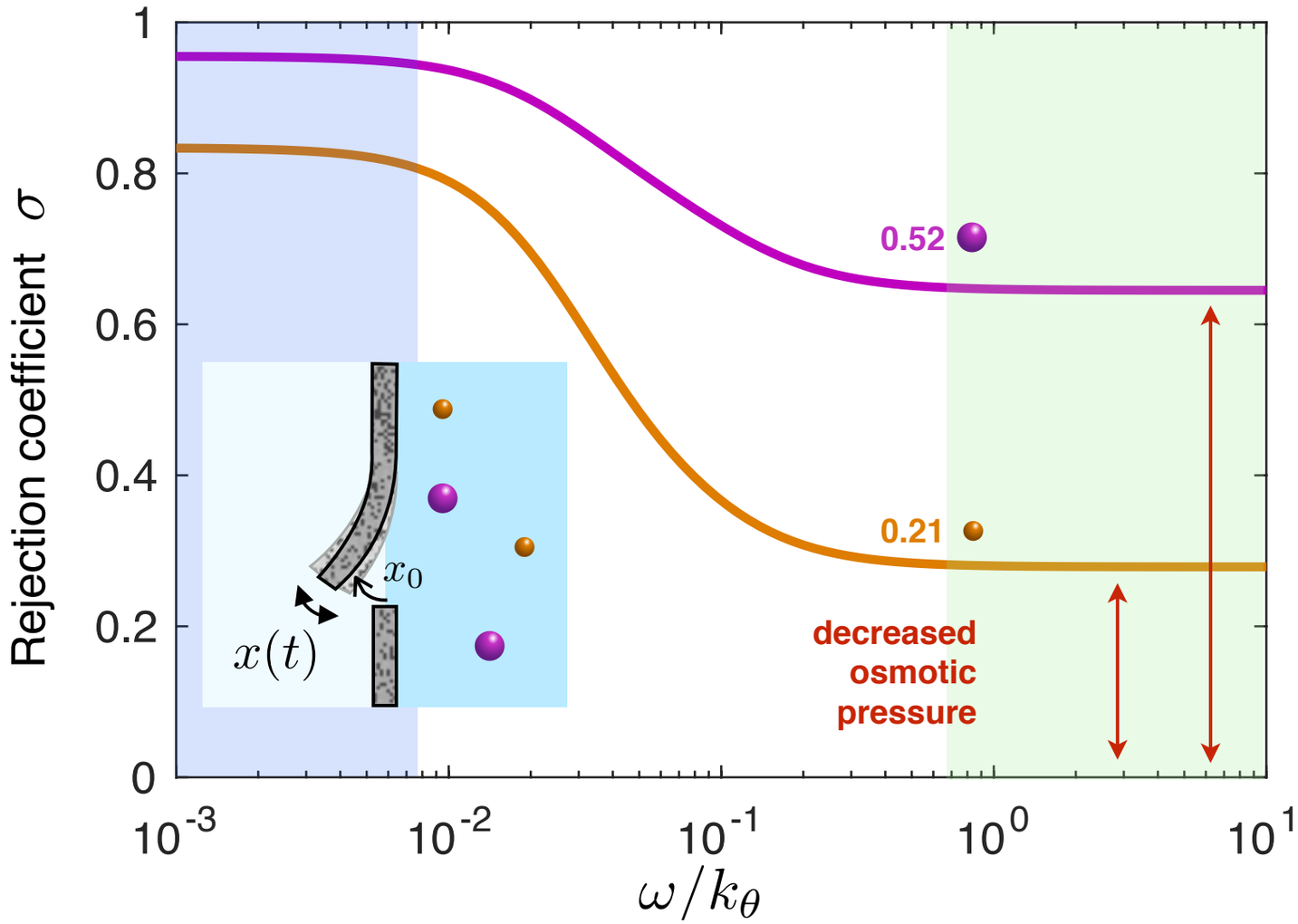
osmosis $\Delta\Pi = \sigma \times k_B T C$ reflection coef.

solute permeance $K_\infty \propto (1-\sigma)$

$$1-\sigma(\omega) \propto K_\infty(\omega)$$

DYNAMIC OSMOTIC PRESSURE

$$\Delta\Pi(\omega) = \sigma(\omega) \times k_B T C$$

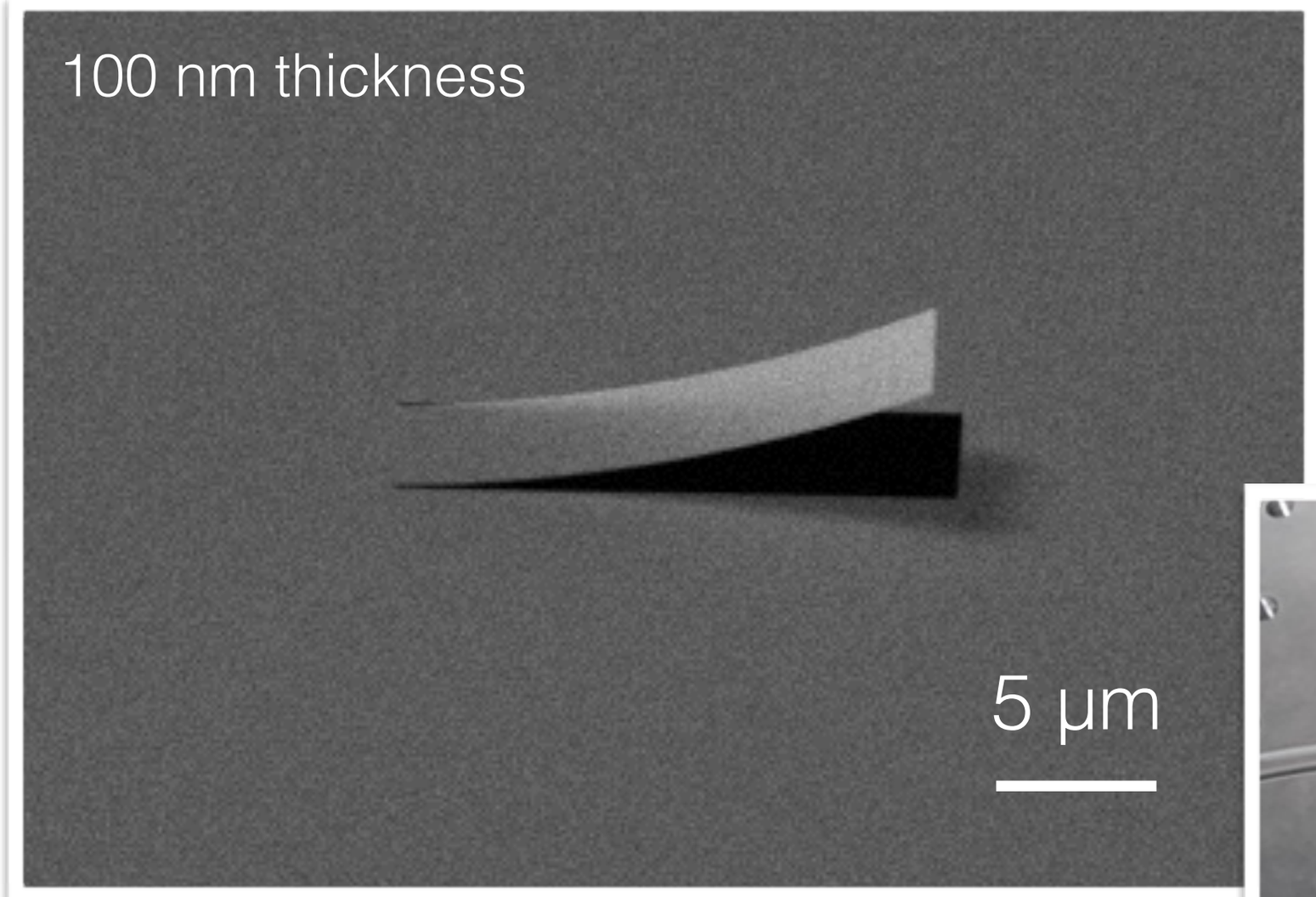


DYNAMICALLY TUNABLE OSMOTIC PRESSURE

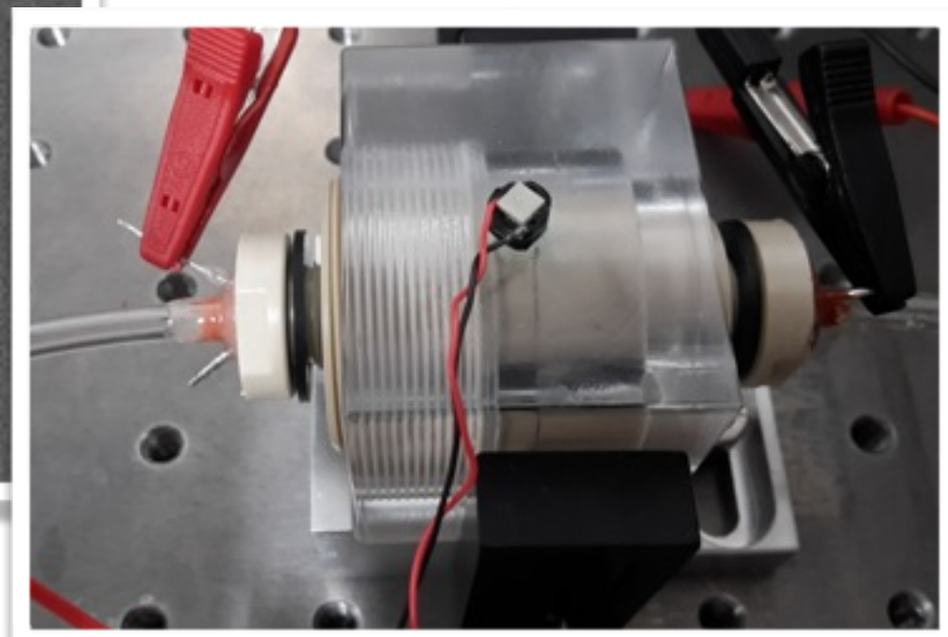
raise many questions (mixtures, molecular view, apps, …)

S. Marbach, L. Bocquet, *to appear in J. Chem. Phys. (2017)*

TORWARDS EXPERIMENTS



Sophie Marbach
with A. Niguès



SEM image of Si-N membrane with « nano » door
Q: (diffusio-) osmotic transport of salts, polymer separation, etc.

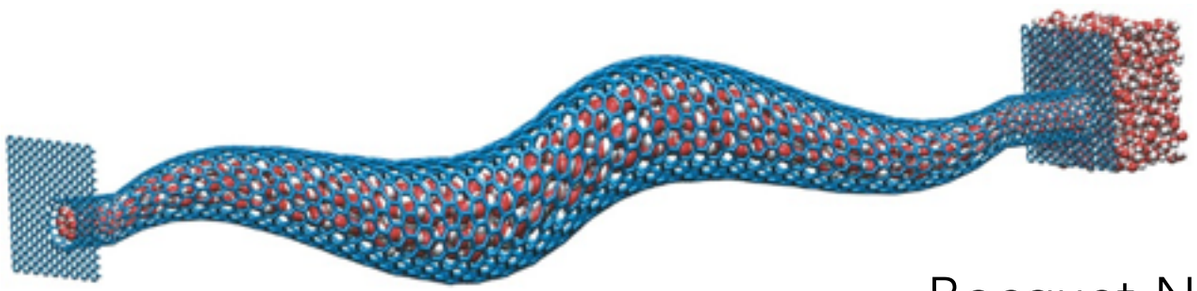
SOME CONCLUSIONS

- toy models, need to be extended to more realistic descriptions… but point to the many opportunities in developing active strategies for separation

- active sieving (in the tracks of active matter…)

- to bypass some limitations of standard membrane science: tunable sorting, trade-off …

- beyond: active nanofluidics



Bocquet-Netz, Nature Nano (2015)

COLLABORATORS

Micromégas team, Ecole Normale Supérieure, Paris

S. Marbach,

and Alessandro Siria, A. Niguès, E. Secchi, L. Jubin, J. Comtet, H. Yoshida, B. Laborie, L. Canale, A. Poggioli, V. Kaiser

Marbach & Bocquet, to appear in **J. Chem. Phys.** (2017)
Marbach & Bocquet, **Phys. Rev. X** (2016)
Marbach, Yoshida & Bocquet, **J. Chem. Phys.** (2017)
Yoshida, Marbach & Bocquet, **J. Chem. Phys.** (2017)
Secchi et al. **Nature** (2016); **Phys. Rev. Lett.** (2016)

ERC AG *Micromégas*
ERC SG *NanoSoft*

http://www.phys.ens.fr/~lbocquet