Chapter 14

Fundamentals of mass transfer

（传质学基础）

Diffusion: From heat to mass transfer

"三传一反"

Type	Heat transfer	Momentum transfer	Mass transfer
Potential	T	$\mathbf{u}$	x_A
Flow rate	$\mathbf{q}$	$\boldsymbol{\tau}$	$\mathbf{J}^*_\mathrm{A}$
Requiring gradient of	temperature	velocity	concentration fraction
Constitutive equation	$\mathbf{q} = -k\nabla T$	$\boldsymbol{\tau} = \mu(\nabla\mathbf{u} + \mathbf{u}\nabla)$	$\mathbf{J}^*_\mathrm{A} = -CD_\mathrm{AB}\nabla x_\mathrm{A}$
	Fourier's law	Newton's law	Fick's law
Transport coefficient	thermal conductivity k [W/(m·K)]	dynamic viscosity μ [N·s/m^2]	binary diffusivity D_AB [m^2/s]
Note	room-temperature and ordinary scales	Newtonian fluid	binary dilute mixture

关注基础图像、基本理论

注重类比对比、求同存异！

[1] V. G. Levich. *Physico-chemical Hydrodynamics*. Wiley, Russia, 1959

[2] R. B. Bird, *et al*, *Transport Phenomena*, 2nd ed. Wiley, New York, 2002

[3] J. A. Wesselingh, R. Krishna. *Mass Transfer in Multicomponent Mixtures*. Delft University Press, Delft, 2006

[4] 王涛. *高等化工传递原理*. 北京, 科学出版社, 2020

如有兴趣余力，可钻研参考书

Outline

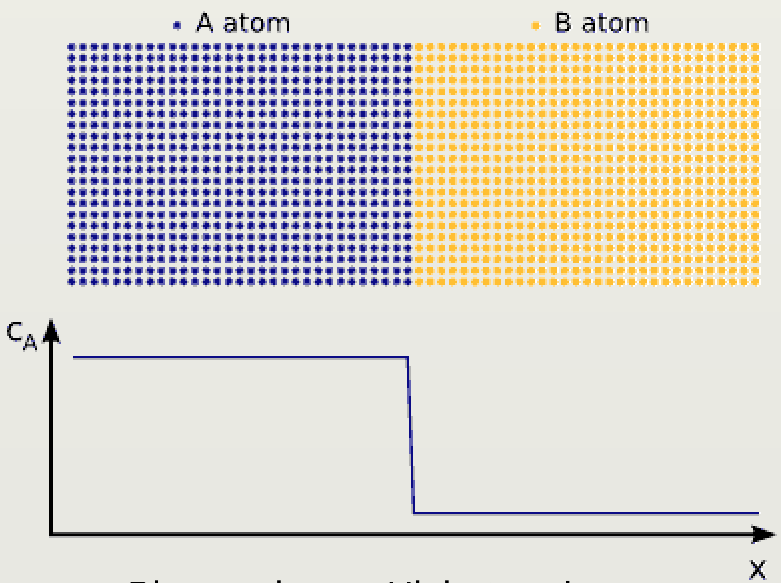
- Fundamentals
  - ☺ Mass diffusion: historical review and physical origin
  - ☺ Fick's law, diffusivity, and mass balance equation
  - ☺ Examples of mass advection-diffusion
- Beyond Fick's law
  - ◆ Mass transfer: advanced applications and retrospect of Fick's law
  - ◆ Ions in electrolytes: multi-component, non-ideal and multi-physical effect
  - ◆ Micro-/nano-pores: geometry, history and confinement effect

Basic concepts: mass diffusion

Mass in transit:

- mass diffusion ← species concentration fraction difference in a mixture
- advection ← average motion of the mixture
- … ← …

Driven forces



Binary mixture: High $C_i \rightarrow$ Low C_i

Mass diffusion:

- Driven by ∇x_i in the inhomogeneous mixture
- Resulting in the relative transfer $u_i - u \propto \nabla x_i$

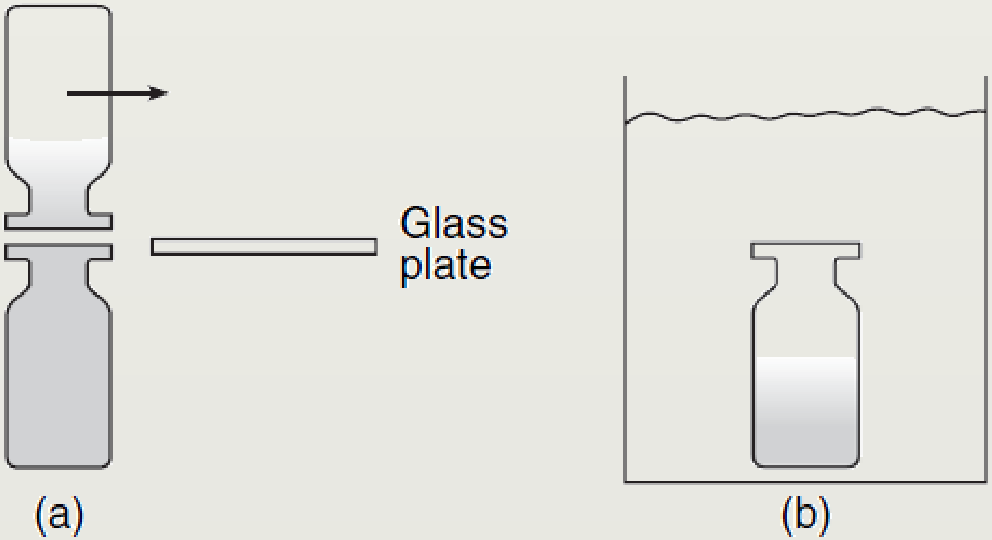
Brief history: gas and liquid

Thomas Graham (1856)

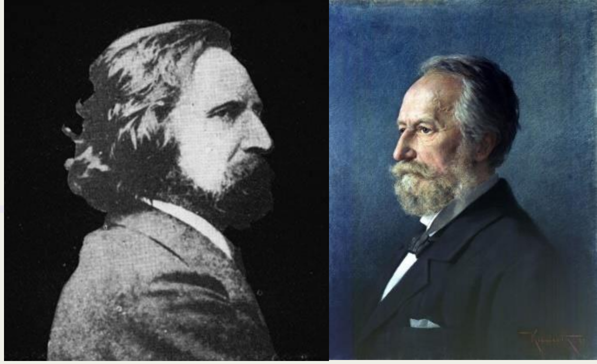
- Gas and Liquid diffusion

Graham's experimental results (1828-1833)

- Liquid diffusion much slower than gas diffusion **Why? Viscosity?**
- Flux caused by diffusion ∝ Concentration fraction difference



Milestone I: Fick's law



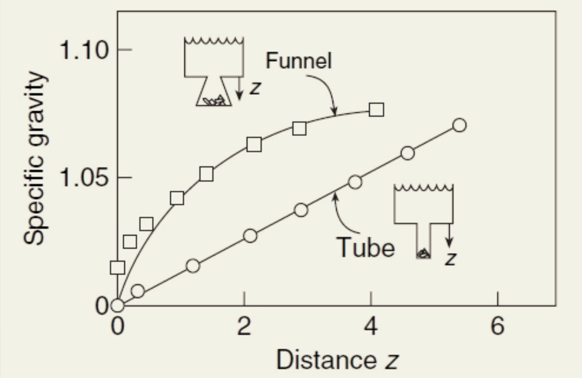
Adolf Fick

- Fick's law for diffusion (1855)

*"It was **quite natural to suppose**, that this law for the diffusion of a salt in its solvent **must be identical with** that, according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success, to the diffusion of electricity in a conductor."*

Analogy!

*"If, in a cylindrical vessel, dynamic equilibrium shall be produced, the differences of concentration of any two pairs of strata must be proportional to the distances of the strata in the two pairs, ... **Experiment fully confirms this proposition**."*



- Extension to multi-component case: Maxwell-Stefan's law (1866-1871)

[1] A. Fick, V. On Liquid Diffusion. *Philosophical Magazine*, **10**(63): 30–39, 1855 (Translated from "Fick, A. Ueber diffusion. *Annalen der Physik*, **170**(1): 59-86, 1855")

[2] R. Krishna and J.A. Wesselingh, The Maxwell-Stefan Approach to Mass Transfer. *Chemical Engineering Science*, **52**(6): 861-911, 1997

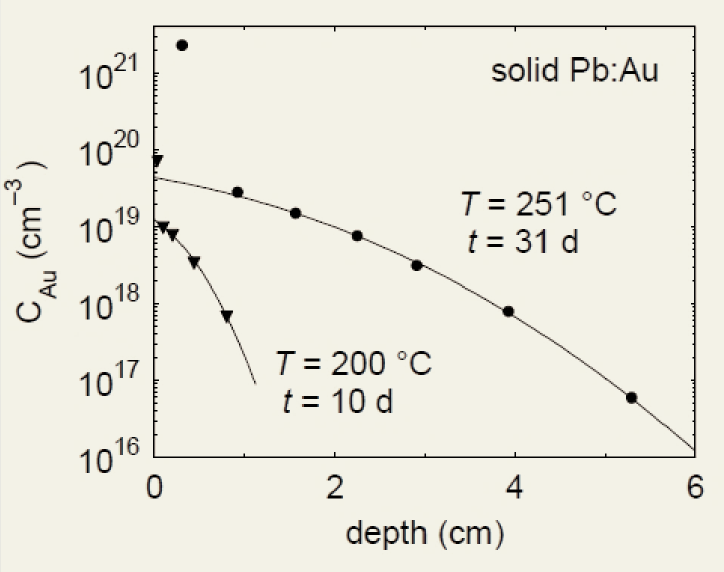
Brief history: solid-state

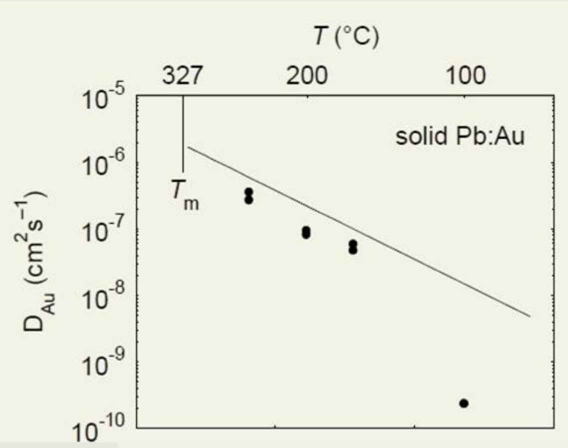
Robert Boyle (1689)

Irving Langmuir (1932)

Nobel Prize in Chemistry (1932)

- Solid-state diffusion
  - Boyle, 1627-1691: First experimental evidence
    - ✓ Phenomena: penetration of zinc (Zn) into a coin of copper (Cu)
  - Roberts-Austen, 1896: Diffusion of gold (Au) in lead (Pb)
  - Dushman & Langmuir, **1922**; Braune, **1924**
    - ✓ Formulation: activation energy theory





$$\frac{D}{D_0} = \exp\left(-\frac{Q}{k_B T}\right)$$

"Arrhenius law"

Brief history: electrolytes

➢ Diffusion in electrolyte solutions


H. van't Hoff — Nobel Prize in Chemistry (1901)

S. Arrhenius — Nobel Prize in Chemistry (1903)

- van't Hoff, 1880s: Principle of mobile equilibrium

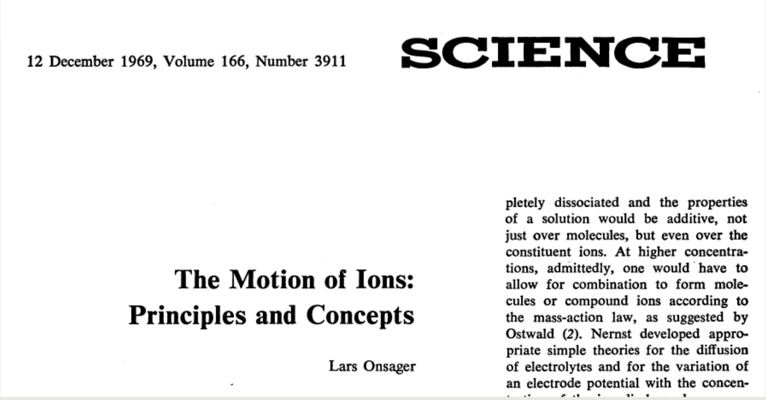
  Theory of osmotic pressure in dilute solution

- Arrhenius, 1884: Electrolytic theory of electrolyte dissociation

- Onsager, **1931**: Formulation of electro-chemical potential driven transport

$$\mathbf{X}_i = \mathbf{F}_i - \nabla \mu_i ,\ i = 1, 2$$
$$\mathbf{j}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2$$
$$\mathbf{j}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2$$

*"for the discovery of the **reciprocal relations bearing his name**, which are fundamental for the **thermodynamics of irreversible processes**"*


12 December 1969, Volume 166, Number 3911 **SCIENCE**

The Motion of Ions: Principles and Concepts

Lars Onsager

pletely dissociated and the properties of a solution would be additive, not just over molecules, but even over the constituent ions. At higher concentrations, admittedly, one would have to allow for combination to form molecules or compound ions according to the mass-action law, as suggested by Ostwald (2). Nernst developed appropriate simple theories for the diffusion of electrolytes and for the variation of an electrode potential with the concen-

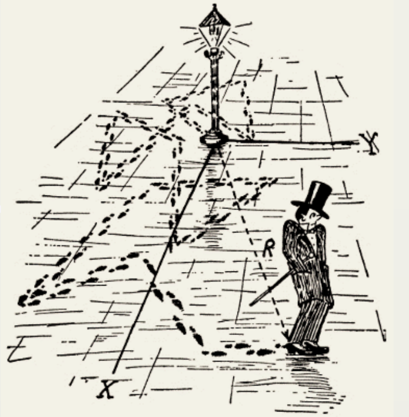
Nobel Prize in Chemistry (1968)

Lars Onsager

[1] L. Onsager and R. M. Fuoss, Irreversible Processes in Electrolytes. Diffusion, Conductance and Viscous Flow in Arbitrary Mixtures of Strong Electrolytes. *J. Phys. Chem.* **36**: 2689, 1931

[2] L. Onsager, The Motion of Ions: Principles and Concepts. *Science* **166**: 1359, 1969

Milestone II: "Triumph of atomism"



Drunkard's walk

- Microscopic picture of diffusion (1905)
  - Brown, 1827: Random motion of pollen in water
  - Einstein, 1905: Theory of Brownian motion and diffusion
    - ✓ Macroscopic measurable quantities ↔ microscopic modelling parameters
    - ✓ How to bridge ? Basic consideration of momentum equation !

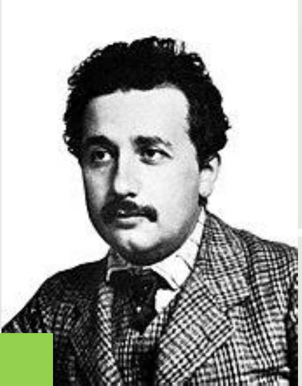
Particle suspension $\overline{x^2(t)} = 2Dt \longrightarrow \frac{1}{6\pi\eta r_P} = \frac{D}{RT / N_A}$

Molecular solution $\frac{\eta^*}{\eta} = 1 + \frac{\rho N_A}{M}\frac{4}{3}\pi r_m^3 \longleftrightarrow \frac{1}{6\pi\eta r_m} = \frac{D}{RT / N_A}$

"Stokes-Einstein relation"

Nobel Prize in Physics (1921)

Albert Einstein (1904)



Nobel Prize in Physics (1926)

Jean Perrin (1908)

- Perrin, 1908: Experimental verification of N_A

"for his work on the ***discontinuous structure of matter****, and especially for his* ***discovery of sedimentation equilibrium****."*

[1] A. Einstein, *Annalen der Physik.* **322** (8): 549–560, 1905. (Translated in 2006)

[2] R. Penrose, **Einstein's Miraculous Year: Five Papers That Changed the Face of Physics.** J. Stachel, T. Lipscombe, A. Calaprice, & S. Elworthy (Eds.), 2005.

[3] G.D. Patterson. Les Atomes: A Landmark Book in Chemistry. *Foundations of Chemistry* **12**: 223–233, 2010

Step 1: Fick's law / Constitutive relation

① Separate diffusion flux from the total: density form

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot (\rho_A \mathbf{v}_A) + \dot{n}_A$$ ***General mass balance equation***

total mass density [kg/m³]

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})$$

ρ_A: mass density of species A

mass fraction of species

$$m_i(\mathbf{r}) = \frac{\rho_i}{\rho}, \quad \sum_i m_i = 1$$

$\dot{n}_A$: mass source term [kg/m³·s]

Absolute flux	$\mathbf{n}''_A = \rho_A \mathbf{v}_A$
Advective + Diffusive	$\mathbf{n}''_A \equiv \rho_A \mathbf{v} + \mathbf{j}_A$
Average velocity	$\mathbf{v} = m_A \mathbf{v}_A + m_B \mathbf{v}_B$
Advection flux	$\rho_A \mathbf{v}$
Relative velocity	$\mathbf{V}_A = \mathbf{v}_A - \mathbf{v}$
Diffusive flux	$\mathbf{j}_A = \rho_A \mathbf{V}_A$

Fick's (first) law $\mathbf{j}_A = -\rho D_{AB} \nabla m_A$

Note. What is the rationale of introducing the (density) average velocity v?

Step 2: Fick's second law / Mass balance

② Rearrange the mass balance equation: density form

$$\frac{\partial \rho_{\mathrm{A}}}{\partial t} = -\nabla \cdot (\rho_{\mathrm{A}} \mathbf{v}_{\mathrm{A}}) + \dot{n}_{\mathrm{A}}$$

General mass balance equation

(law of conservation)

$$\rho_{\mathrm{A}} \mathbf{v}_{\mathrm{A}} = \mathbf{j}_{\mathrm{A}} + \rho_{\mathrm{A}} \mathbf{v}$$

$$\boxed{\mathbf{j}_{\mathrm{A}} = -\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}}$$

Fick's (first) law

(constitutive relation)

$$\boxed{\frac{\partial \rho_{\mathrm{A}}}{\partial t} + \nabla \cdot (\rho_{\mathrm{A}} \mathbf{v}) = \nabla \cdot (\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}) + \dot{n}_{\mathrm{A}}}$$

Fick's second law

(mass advection-diffusion equation (ADE) with Fickian diffusion)

Note. Why not adding an individual momentum equation for species A? When will that equation be necessary?

Discussion: binary diffusivity

- Diffusivity scales in different material states
  - ✓ Gas pair: $D_{\mathrm{AB}} \sim p^{-1}T^{3/2}$ (ideal gas)

Gas pair (*i*–*j*)	*T* (K)	D_{ij} (cm²/s)
Air–ammonia	273	0.198
Air–carbon dioxide	273	0.136
	317.3	0.177

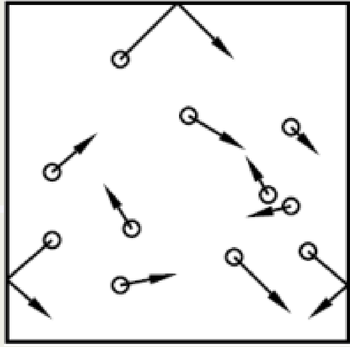
  - ✓ Liquid pair: $\mathrm{d}D_{\mathrm{AB}} / \mathrm{d}T > 0$ (small C_{A})

Liquid pair; solute A (concentration in g mol/l)–solute B	*T* (K)	$D_{\mathrm{AB}} \times 10^5$ (cm²/s)
Ammonia (3.5)–water	278	1.24
Ammonia (1.0)–water	288	1.77

  - ✓ Species in solids: extremely complex

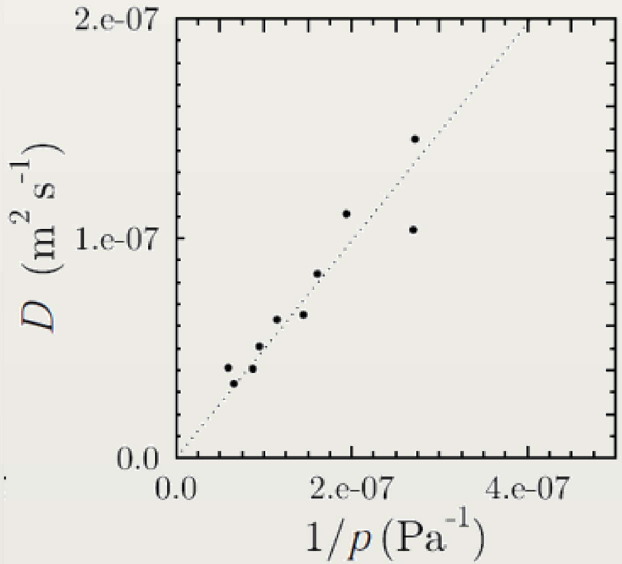
Why? Mechanism?

Discussion: binary diffusivity



- Kinetic theory for dilute gases
  - Simple theory of tracer (self-) diffusivity

$$D_{AA^*} = \frac{1}{3}\lambda\bar{c} \xrightarrow[\bar{c} = \sqrt{\frac{8k_B T}{\pi m}}]{\lambda = \frac{k_B T}{\sqrt{2} p \pi d^2}} D_{AA^*} \propto p^{-1} T^{3/2}$$



  - Rigorous theory of binary diffusivity

$$D_{ij}[\mathrm{cm}^2/\mathrm{s}] = \frac{0.0018583\sqrt{T^3(1/M_i + 1/M_j)}}{p[\mathrm{atm}]\sigma_{ij}^2[\mathring{A}^2]\Omega_{ij}}$$

$$\Omega_{ij} = f\left(\frac{k_B T}{\varepsilon_{ij}}\right) \quad \phi_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

Note. How about diffusion in liquids?

Lennard-Jones (L-J) potential

Discussion: from density to molar form

	Density form (质量形式)	Molar form (数量形式)
Fick's law	$\mathbf{j}_{\mathrm{A}} = -\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}$	$\mathbf{J}^*_{\mathrm{A}} = -C D_{\mathrm{AB}} \nabla x_{\mathrm{A}}$
Mass balance	$\frac{\partial \rho_{\mathrm{A}}}{\partial t} + \nabla \cdot (\rho_{\mathrm{A}} \mathbf{v}) = \nabla \cdot (\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}) + \dot{n}_{\mathrm{A}}$	$\frac{\partial C_{\mathrm{A}}}{\partial t} + \nabla \cdot (C_{\mathrm{A}} \mathbf{v}^*) = \nabla \cdot (C D_{\mathrm{AB}} \nabla x_{\mathrm{A}}) + \dot{N}_{\mathrm{A}}$

Note 1. Consistency? Applicability?

x_{A}: molar concentration fraction
$\mathbf{v}^*$: molarity-average velocity

Constant D_{AB} and ρ (C)

$$\mathbf{j}_{\mathrm{A}} = -D_{\mathrm{AB}} \nabla \rho_{\mathrm{A}}$$

$$\frac{\partial m_{\mathrm{A}}}{\partial t} + \mathbf{v} \cdot \nabla m_{\mathrm{A}} = D_{\mathrm{AB}} \nabla^2 m_{\mathrm{A}} + \frac{\dot{n}_{\mathrm{A}}}{\rho}$$

$$\mathbf{J}^*_{\mathrm{A}} = -D_{\mathrm{AB}} \nabla C_{\mathrm{A}}$$

$$\frac{\partial x_{\mathrm{A}}}{\partial t} + \mathbf{v}^* \cdot \nabla x_{\mathrm{A}} = D_{\mathrm{AB}} \nabla^2 x_{\mathrm{A}} + \frac{x_{\mathrm{B}} \dot{N}_{\mathrm{A}} - x_{\mathrm{A}} \dot{N}_{\mathrm{B}}}{C}$$

Total mass transfer

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \dot{n}_{\mathrm{A}} + \dot{n}_{\mathrm{B}} = 0$$

$$\rho \equiv \rho_0 \Rightarrow \nabla \cdot \mathbf{v} = 0$$

$$\frac{\partial C}{\partial t} + \nabla \cdot (C \mathbf{v}^*) = \dot{N}_{\mathrm{A}} + \dot{N}_{\mathrm{B}}$$

$$C \equiv C_0 \Rightarrow \nabla \cdot \mathbf{v}^* = \frac{1}{C_0} (\dot{N}_{\mathrm{A}} + \dot{N}_{\mathrm{B}}) \neq 0$$

Note 2. Why different? Physical insight?

Applications of mass ADE

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (C_A \mathbf{v}^*) = \nabla \cdot (C D_{AB} \nabla x_A) + \dot{N}_A$$

Nonlinear!

- General observation: constant C and D_{AB}

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (\mathbf{v}^* C_A) = D_{AB} \nabla^2 C_A + \dot{N}_A$$

Species adv.-diff. equation (*)

$$\frac{\partial T}{\partial t} + \nabla \cdot (\mathbf{v} T) = \alpha \nabla^2 T + \dot{q}$$

Heat adv.-diff. equation

$$\frac{\partial \mathbf{v}}{\partial t} + \nabla \cdot (\mathbf{v}\mathbf{v}) = \nu \nabla^2 \mathbf{v} + \mathbf{f}$$

Navier-Stokes equation

Lewis number: $Le = \dfrac{\alpha}{D_{AB}}$

Schmidt number: $Sc = \dfrac{\nu}{D_{AB}}$

Thermal diffusivity

Mass diffusivity

“Momentum diffusivity”

“Prandtl” numbers

Applications of mass ADE

◆ Boundary conditions and Source term

- 1^{st}-type boundary (prescribed concentration)
  - Evaporation / sublimation (ideal solution, 理想溶液): $p_A(0) = x_A(0)\, p_{A,sat}$
  - Solubility of gases in liquids and solids: $x_A(0) = \dfrac{p_A(0)}{H}, \quad C_A(0) = S p_A(0)$
- 2^{nd}- and 3^{rd}-type boundary (concentration flux related)
  - Catalytic surface reactions: $N''_{A,x}(0) = N''_A \Rightarrow -C D_{AB} \left.\dfrac{dx_A}{dx}\right|_{x=0} = N''_A$

    or $N''_{A,x}(0) = -k''_1 C_A(0) \Rightarrow -D_{AB} \left.\dfrac{dx_A}{dx}\right|_{x=0} = -k''_1 x_A(0)$
- Source term: order of chemical reaction
  - Zero-order (零级) reaction: $\dot{N}_A = k_0$
  - First-order (一级) reaction: $\dot{N}_A = k_1 C_A$

Note. Compared with heat convection?

Applications of mass ADE

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (C_A \mathbf{v}^*) = \nabla \cdot (C D_{AB} \nabla x_A) + \dot{N}_A$$

a) stationary medium and dilute approx. ($\mathbf{v}_B = 0$, $x_A \ll 1$)

$\mathbf{v}^* \approx \mathbf{v}_B$

$C \approx$ const.

$$\frac{\partial C_A}{\partial t} = \nabla \cdot (D_{AB} \nabla C_A) + \dot{N}_A$$

- Time-independent: steady-state
- Time-dependent: transient
- Source term: chemical reaction

$$N_{A,s} = -D_{AB} \left(\frac{\partial C_A}{\partial y} \right) \Bigg|_{x=x_s}$$

diffusion coefficient

$$=: h_m \left(C_{A,s} - C_{A,\infty} \right)$$

mass transfer coefficient

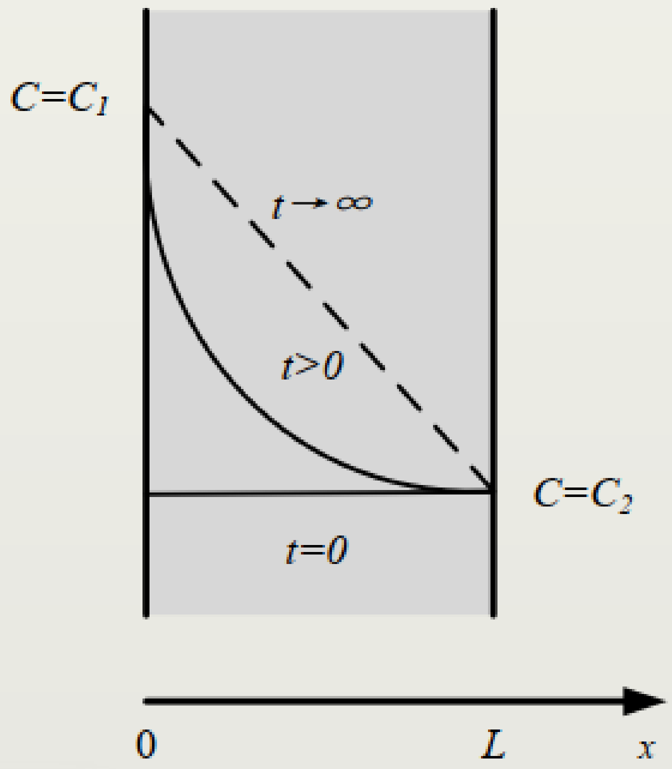
Heat Transfer	Mass Transfer	
$\theta^* = \dfrac{T - T_\infty}{T_i - T_\infty}$	$\gamma^* = \dfrac{C_A - C_{A,s}}{C_{A,i} - C_{A,s}}$	
$1 - \theta^* = \dfrac{T - T_i}{T_\infty - T_i}$	$1 - \gamma^* = \dfrac{C_A - C_{A,i}}{C_{A,s} - C_{A,i}}$	
$Fo = \dfrac{\alpha t}{L^2}$	$Fo_m = \dfrac{D_{AB} t}{L^2}$	mass transfer Fourier number
$Bi = \dfrac{hL}{k}$	$Bi_m = \dfrac{h_m L}{D_{AB}}$	mass transfer Biot number
$\dfrac{x}{2\sqrt{\alpha t}}$	$\dfrac{x}{2\sqrt{D_{AB} t}}$	

Heat-mass transfer analogy

“热质比拟”

Example 1: 1D transient diffusion

➢ Transient without source terms: problem setup



- Governing equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

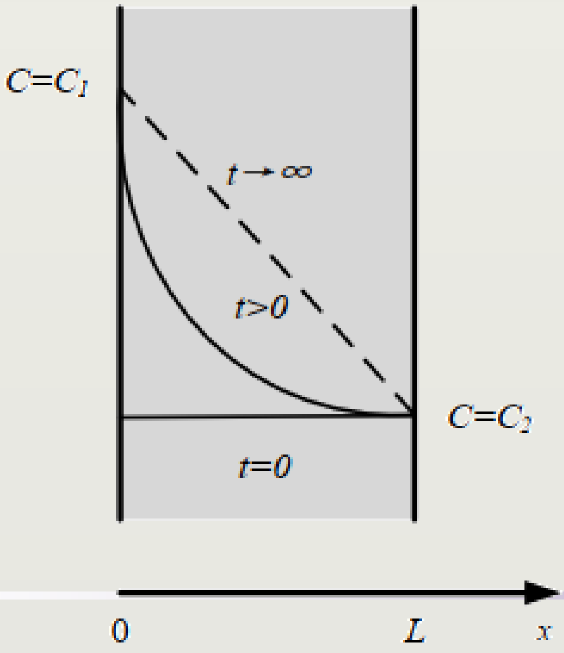
- Initial and boundary conditions

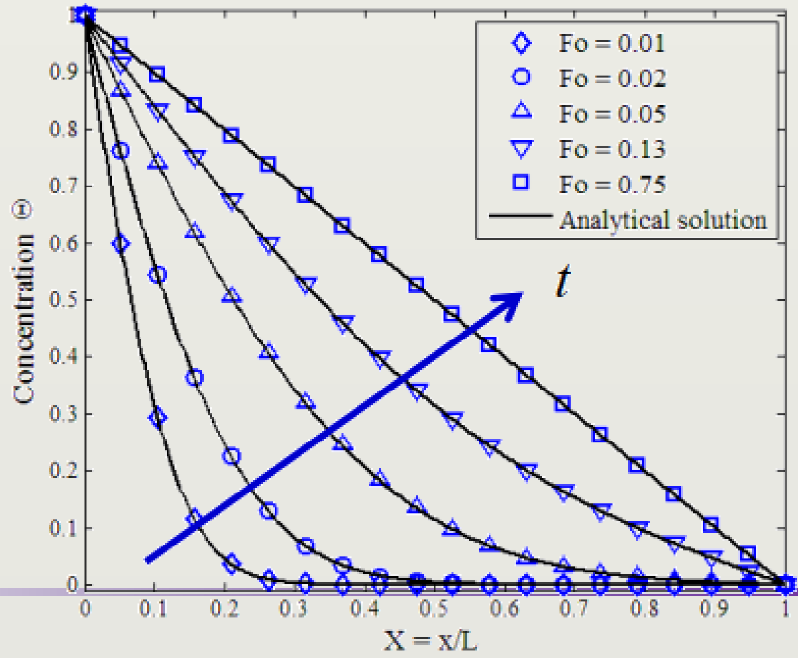
$$0 < x < L,\ \ t = 0:\ \ C = C_2$$
$$x = 0,\ \ t > 0:\ \ C = C_1$$
$$x = L,\ \ t > 0:\ \ C = C_2$$

Example 1: 1D transient diffusion

- Transient without source terms: analytical solution
  - Methods of variable separation $$X=\frac{x}{L},\ \mathrm{Fo}=\frac{Dt}{L^2}$$

$$\Theta \equiv \frac{C(x,t)-C_2}{C_1-C_2}=1-X-\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\sin(n\pi X)}{n}\exp\left[-(n\pi)^2\,\mathrm{Fo}\right]$$





Example 1: 1D transient diffusion

➢ Transient without source terms: result analysis

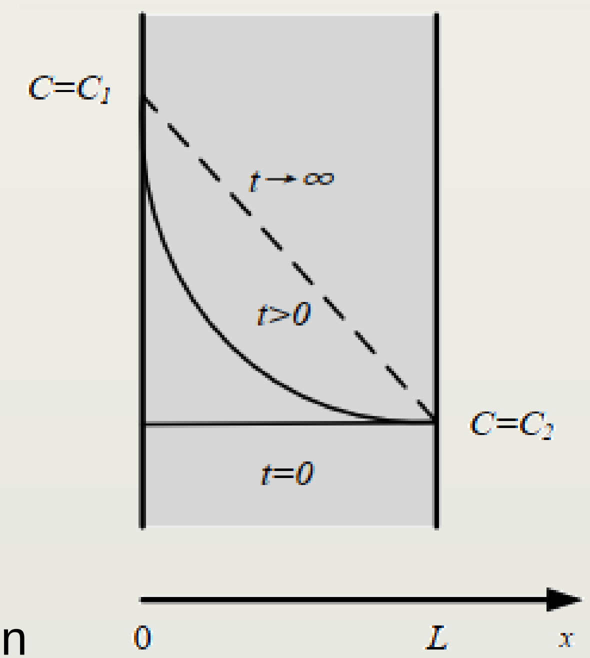
- Final steady-state
  - Linear concentration distribution:

$$C(x,t) = C_2 + \left(1 - \frac{x}{L}\right)(C_1 - C_2)$$

  - Molar flux:

$$N = -D\frac{\mathrm{d}C}{\mathrm{d}x} = \frac{C_1 - C_2}{L/D}$$

Diffusion resistance



Example 2: 1D diffusion with source

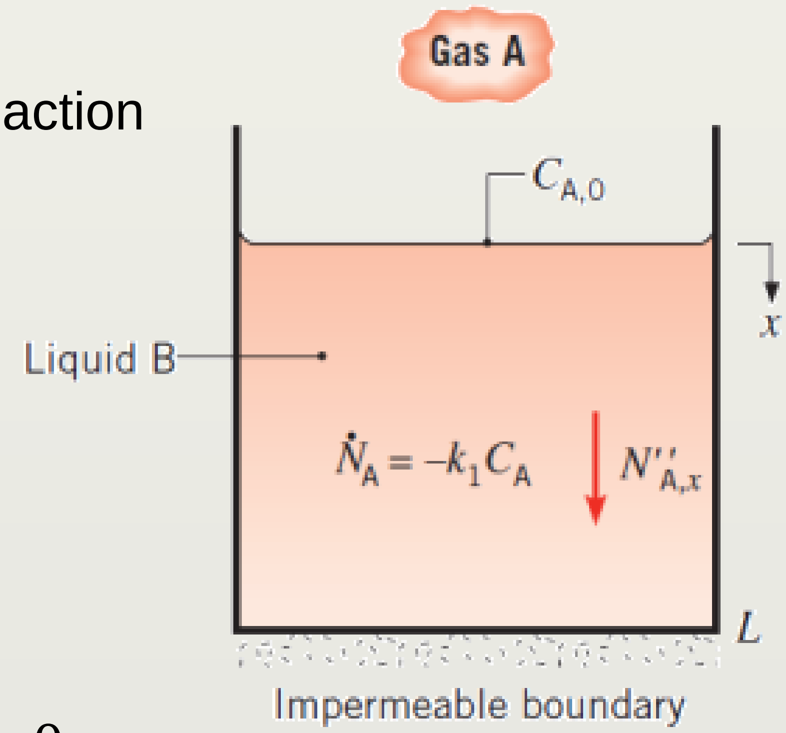
➤ Steady-state with source term: problem setup

- 1D steady state diffusion
  - Homogeneous chemical reaction
  - First-order reaction
  - Constant D_{AB}, C

$$D_{AB}\frac{d^2C_A}{dx^2}+\dot{N}_A=0$$

- Boundary conditions

$$C_A(0)=C_{A,0},\quad \left.\frac{dC_A}{dx}\right|_{x=L}=0$$



Example 2: 1D diffusion with source

- Steady-state with source term: analytical solution

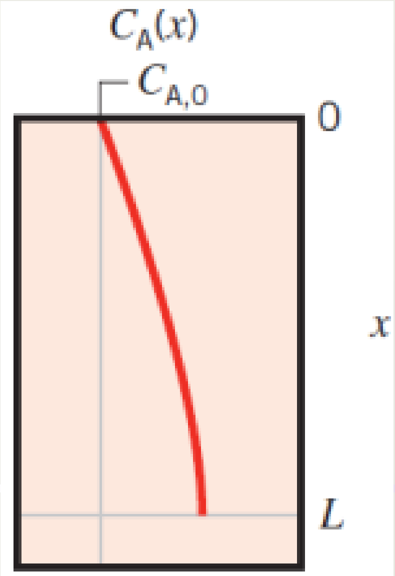
$$D_{AB}\frac{d^2C_A}{dx^2}-k_1C_A=0,\quad m=\sqrt{k_1/D_{AB}}$$

What if $\dot{N}_A=k_0$?

- General solution: $C_A(x)=C_1\exp(mx)+C_2\exp(-mx)$

- With the B.C. s:

$$C_A(x)=C_{A,0}\frac{\cosh[m(L-x)]}{\cosh(mL)}$$



$$C_A(L)=\frac{C_{A,0}}{\cosh(mL)}$$

"End concentration"

$$N_{A,x}(0)=-D_{AB}\frac{dC_A(x)}{dx}\bigg|_{x=0}=D_{AB}C_{A,0}m\tanh(mL)$$

"Interfacial molar flux"

Other orthogonal curvilinear coordinates

$$\frac{\partial C_A}{\partial t} = \nabla\cdot(CD_{AB}\nabla x_A) + \dot{N}_A$$

- Cylindrical coordinate **1D, steady-state**

$$\frac{1}{r}\frac{\partial}{\partial r}\left(CD_{AB} r \frac{\partial x_A}{\partial r}\right) + \dot{N}_A = 0$$

$$\frac{\partial C_A}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(CD_{AB} r \frac{\partial x_A}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial \phi}\left(CD_{AB}\frac{\partial x_A}{\partial \phi}\right) + \frac{\partial}{\partial z}\left(CD_{AB}\frac{\partial x_A}{\partial z}\right) + \dot{N}_A$$

- Spherical coordinate **1D, steady-state**

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(CD_{AB} r^2 \frac{\partial x_A}{\partial r}\right) + \dot{N}_A = 0$$

$$\frac{\partial C_A}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(CD_{AB} r^2 \frac{\partial x_A}{\partial r}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial}{\partial \phi}\left(CD_{AB}\frac{\partial x_A}{\partial \phi}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(CD_{AB}\sin\theta\frac{\partial x_A}{\partial \theta}\right) + \dot{N}_A$$

Applications of mass ADE

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (C_A \mathbf{v}^*) = \nabla \cdot (C D_{AB} \nabla x_A) + \dot{N}_A$$

b) convection mass transfer in dilute sol. ($x_A \ll 1$) $\mathbf{v}^* \approx \mathbf{v}_B$, $C \approx \text{const.}$

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (C_A \mathbf{v}_B) = \nabla \cdot (C D_{AB} \nabla x_A) + \dot{N}_A$$

$$\frac{\partial C_A}{\partial t} + \mathbf{v}_B \cdot \nabla C_A = D_{AB} \nabla^2 C_A + \dot{N}_A$$

constant D_{AB}, incompressible fluid B

$$N_{A,s} := -D_{AB} \left(\frac{\partial C_A}{\partial y} \right)\bigg|_{x=x_s} =: h_m \left(C_{A,s} - C_{A,\infty} \right) \Rightarrow h_m = \frac{-D_{AB} \left(\partial C_A / \partial y \right)\big|_{x=x_s}}{C_{A,s} - C_{A,\infty}}$$

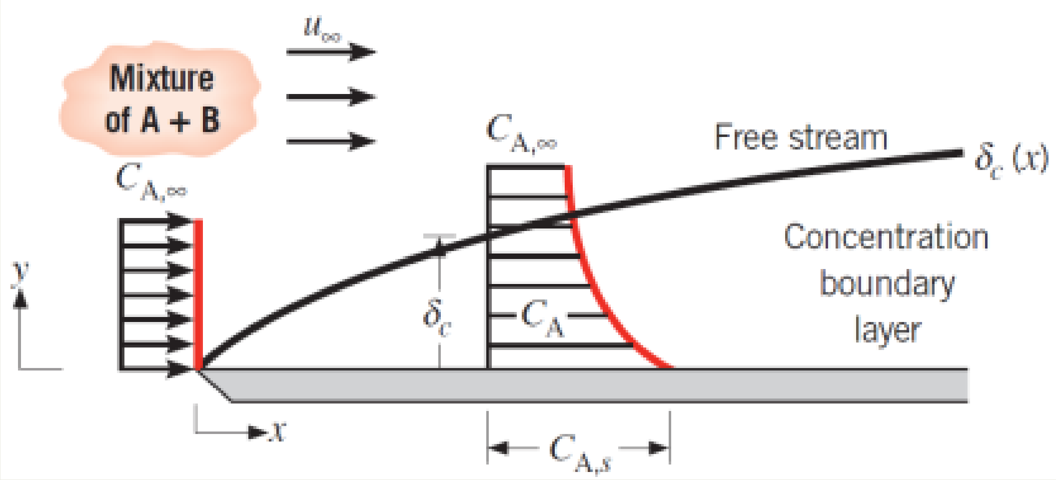
Surface molar flux

Diffusion coefficient (fundamental, physical)

Mass transfer coefficient (phenomenological, engineering)

Example 3: convection mass transfer

- Concentration boundary layer: differential equation



- Species balance equation: $$\frac{\partial C_A}{\partial t} + \mathbf{v}_B \cdot \nabla C_A = D_{AB}\nabla^2 C_A + \dot{N}_A$$

- Steady-state boundary layer differential equation:

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} = D_{AB}\frac{\partial^2 C_A}{\partial y^2} + \dot{N}_A$$

Example 3: convection mass transfer

➢ Concentration boundary layer: empirical correlation

Heat Transfer		Mass Transfer	
$T^* = f\left(x^*, y^*, Re_L, Pr, \frac{dp^*}{dx^*}\right)$	(6.47)	$C_A^* = f\left(x^*, y^*, Re_L, Sc, \frac{dp^*}{dx^*}\right)$	(6.51)
$Nu = \frac{hL}{k} = +\frac{\partial T^*}{\partial y^*}\Big\vert_{y^*=0}$	(6.48)	$Sh = \frac{h_m L}{D_{AB}} = +\frac{\partial C_A^*}{\partial y^*}\Big\vert_{y^*=0}$	(6.52)

Nusselt number Sherwood number

- Laminar flow over a flat plate with a constant surface C

$$Sh_x = 0.332\,\mathrm{Re}_x^{1/2} Sc^{1/3},\ \overline{Sh}_x = 0.664\,\mathrm{Re}_x^{1/2} Sc^{1/3},\quad Sc \geq 0.6$$

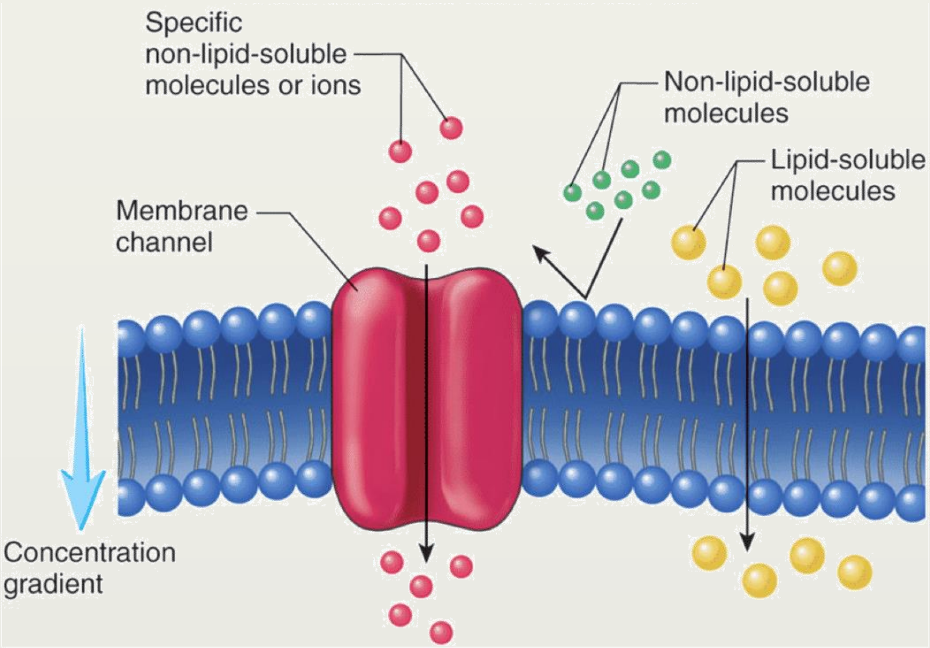
- Fully-dev flow in a circular tube with a constant surface C

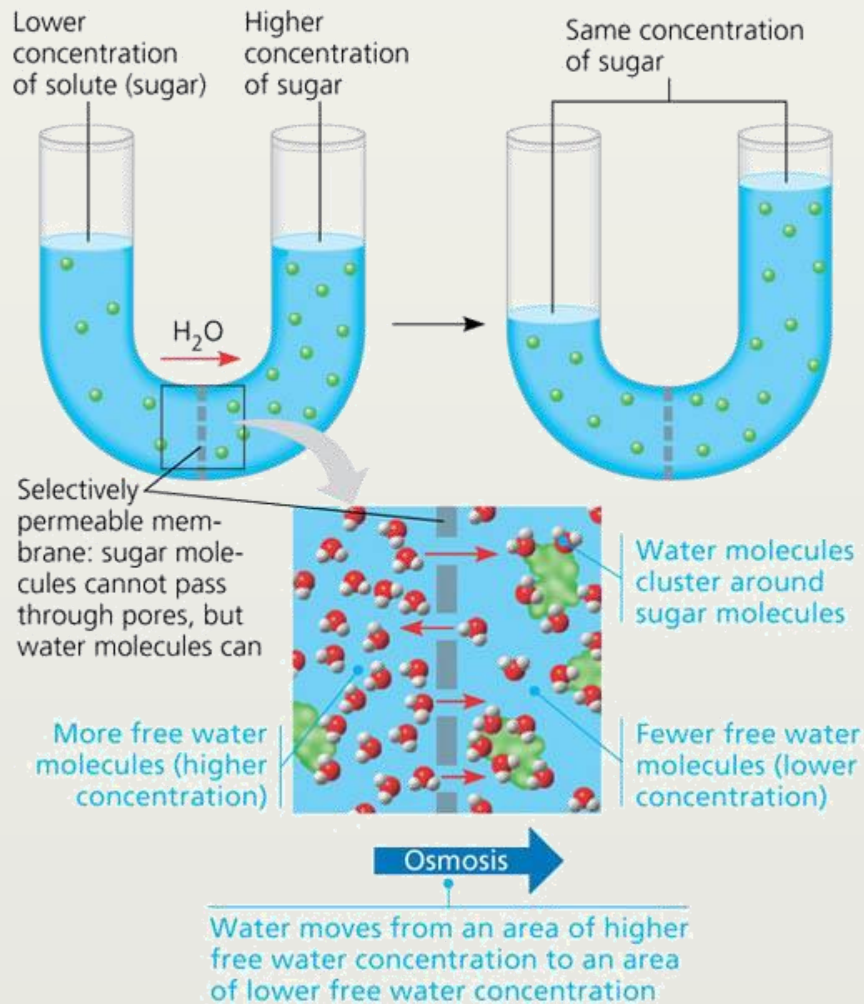
$$Sh_{D,\text{laminar}} = 3.66 \qquad Sh_{D,\text{turbulent}} = 0.023\,\mathrm{Re}_D^{4/5} Sc^{0.4}$$

Outline

- Fundamentals
  - ☺ Mass diffusion: historical review and physical origin
  - ☺ Fick’s law, diffusivity, and mass balance equation
  - ☺ Examples of mass advection-diffusion
- Beyond Fick’s law
  - ◆ Mass transfer: advanced applications and retrospect of Fick’s law
  - ◆ Ions in electrolytes: multi-component, non-ideal and multi-physical effect
  - ◆ Micro-/nano-pores: geometry, history and confinement effect

Bio-membrane and BioE

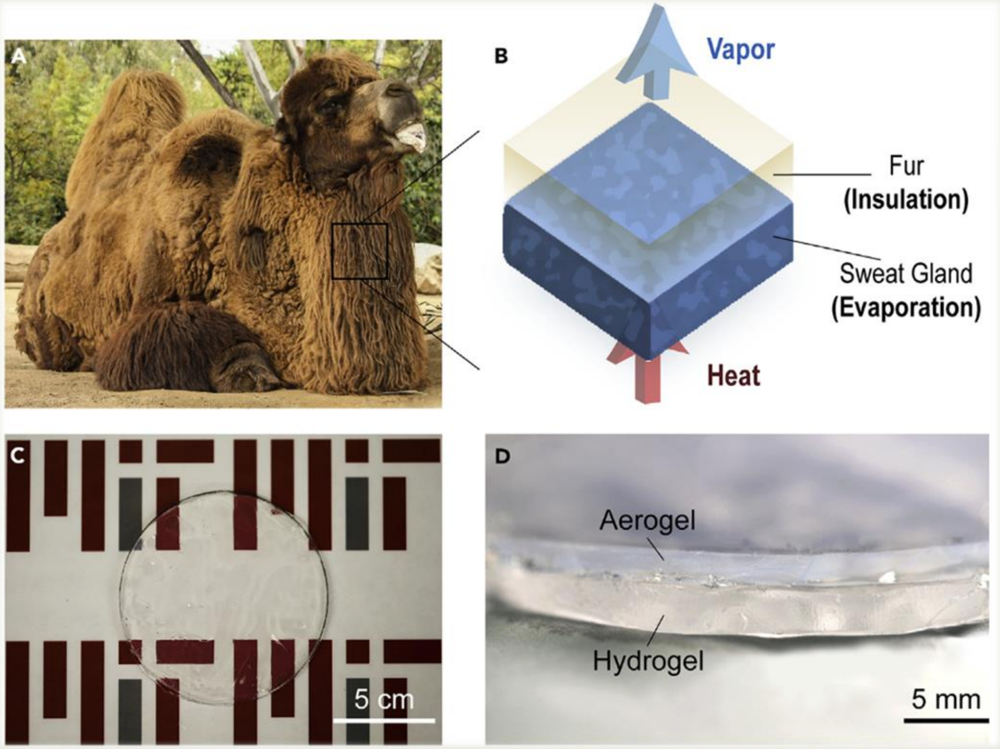




Selective permeability of bio-membrane
(molecule and electrolyte)

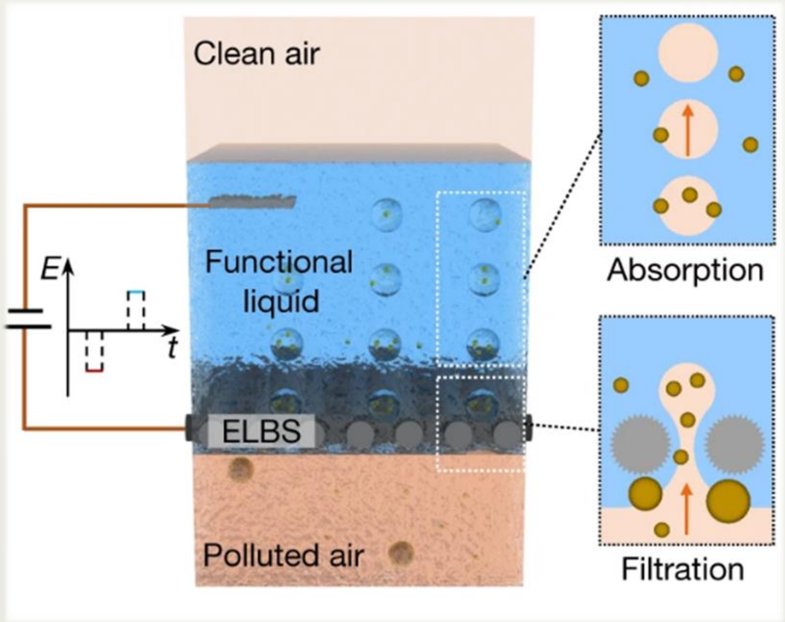
Multi-component, membrane permeability,
bio-chemical selectivity

Water resource and CEE



Overall concepts of hydrogel-aerogel cooling (water and air)

Porous media, heat-mass coupled transfer

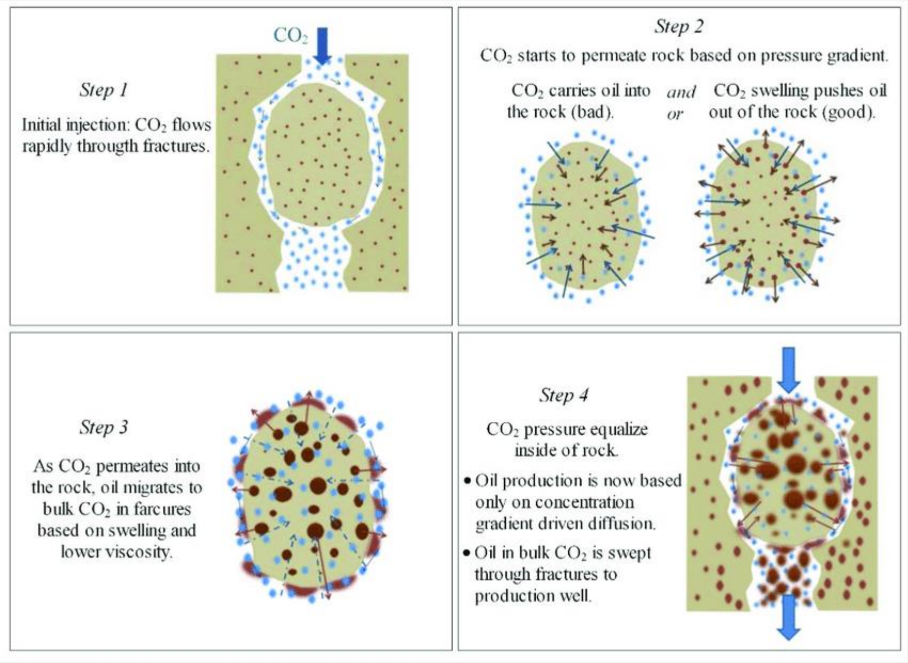


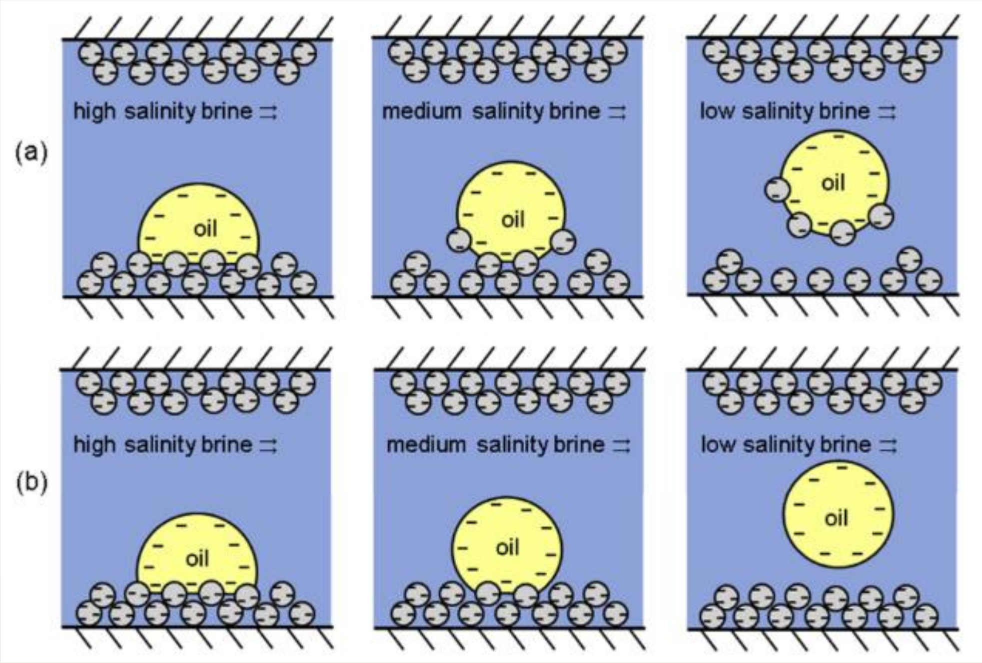
Air purification with functional liquid (air mixture and functional liquid)

Multi-component, surface force, flow-mass coupled transfer

Y. Zhang, *et al.* Continuous Air Purification by Aqueous Interface Filtration and Absorption. *Nature* **610**: 74-80, 2022

Enhanced oil recovery and PE





Conceptual steps of CO_2-based EOR (gas and oil)

One mechanism of low-salinity waterflooding (electrolyte and particle)

Multi-component, porous media, multiphase with phase change

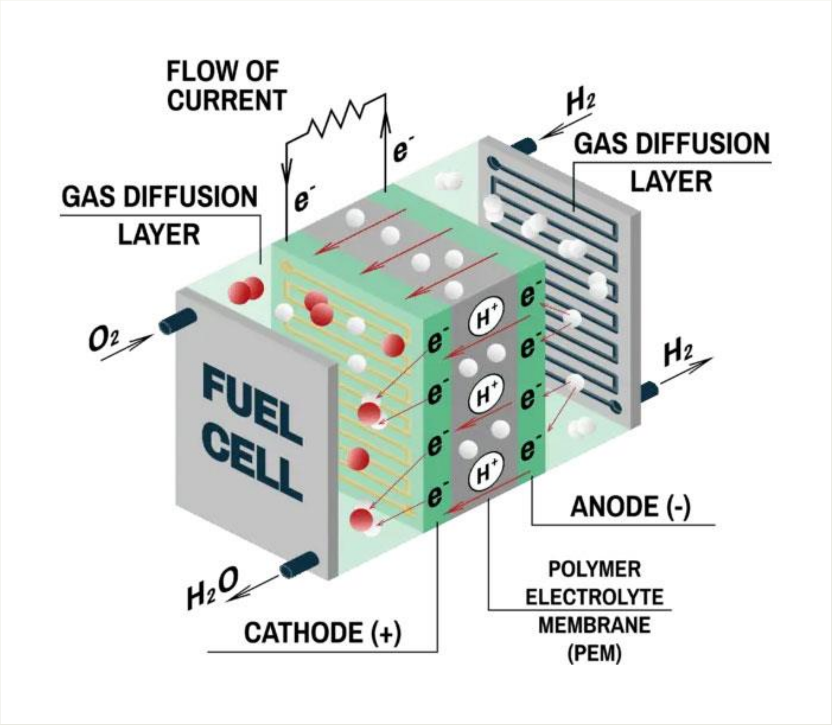
Multi-component, electrical/surface force, ion–tuned wettability

H. Tian and M. Wang. Electrokinetic Mechanism of Wettability Alternation at Oil-water-rock Interface. *Surface Science Reports* **72**(6): 369-391, 2017

Advanced power/energy and MAE

Diffusion and premixed combustion
(gas mixture)

Multi-component, chemical reaction,
heat-mass coupled transfer

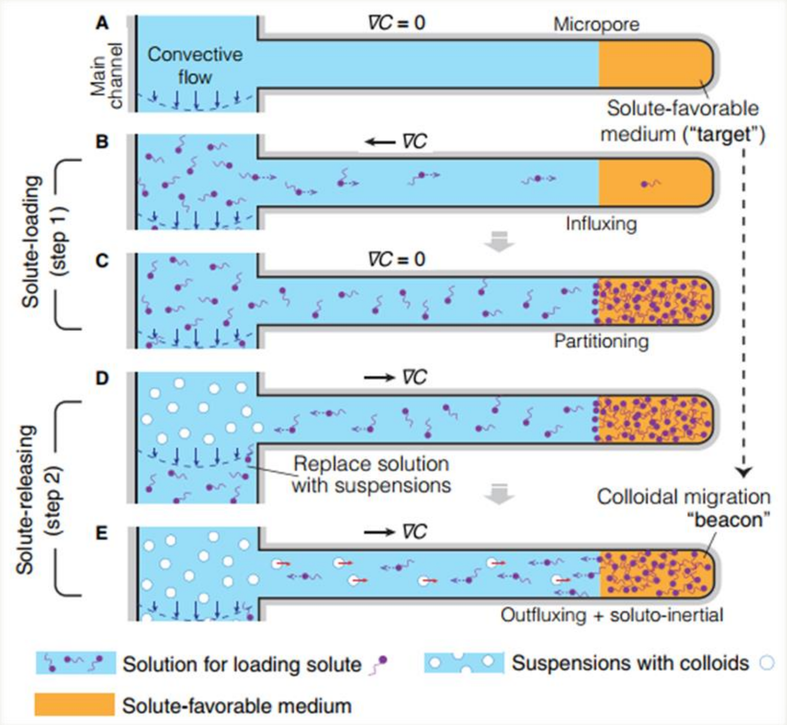


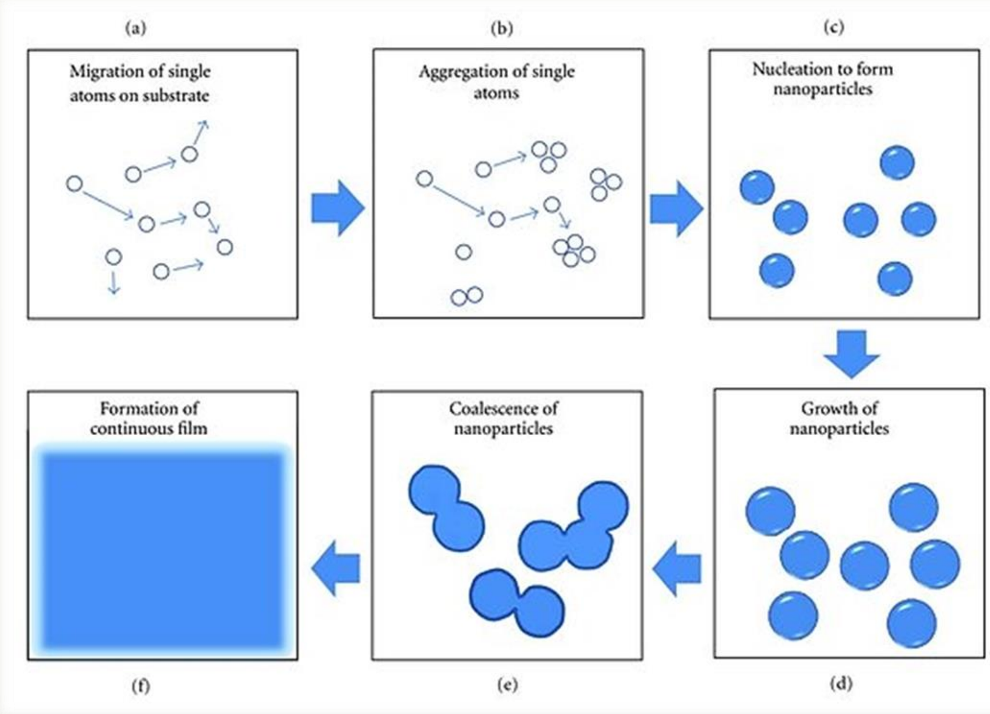
Schematics of fuel cell
(gas and electrolyte)

Multi-component, chemical reaction,
porous media, electro-chemistry

M.N. Nasharudin, *et al*. Mass Transfer and Performance of Membrane-less Micro Fuel Cell: A Review. *International Journal of Hydrogen Energy*, **39**: 1034-1055, 2014

Advanced manufacturing and ChemE





Marangoni-driven targeted colloidal delivery (solute and colloid particle)

Thin-film growth based on DC sputtering (atom and nanoparticle)

Multi-component, surface force, multiphase interface

Multi-scale evolution, surface force, low-dimensional transport

H. Tan, *et al.* A Two-step Strategy For Delivering Particles to Targets Hidden Within Microfabricated Porous Media. *Science Advances* **7**(33): eabh0638, 2021

General consideration

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_i) = 0 \quad \text{or} \quad \frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{u}_i) = 0$$

Essential equations to describe mass transfer? Is the above enough?

☺ **binary dilute mixture – mass diffusion fundamentals**

- dry air (gas), liquor (liquid), doped semiconductor (solid) …

✓ multi-component, non-ideal and multi-physical effect

- crossing, interaction (e.g. crowding), electric | temperature field …

✓ geometry, history and confinement (surface) effect

- pore | network, flow | dead-end, surface diffusion | relaxation …

◘ more complex: inertia/scattering, dispersity, correlation

- fluidized bed, ink | foam, polymer solution | liquid crystal …

Complex fluid (复杂流体) / Soft matter (软物质)

Assumption of Fick's law

- Rethinking Fick's law

$$\mathbf{J}_A^* = -CD_{AB}\nabla x_A$$

- Diffusion in binary mixture, especially in dilute solutions
  → Non-ideal & multicomponent effect: activity? crossing?
- Concentration-fraction-gradient force v.s. viscous force
  → Multi-physical effect: electric field/temperature?

} Diffusion in electrolytes

- Bulk diffusion dominated molecular-boundary interaction
  → Geometry, history & confinement effect: pores?

— Diffusion in micro-/nano-pores

Ion diffusion in electrolytes – multi-component

➢ From Fick's law to Maxwell-Stefan equation

Fick's law $\mathbf{J}_A^* = -CD_{AB}\nabla x_A \Leftrightarrow x_A x_B(\mathbf{v}_A - \mathbf{v}_B) = -D_{AB}\nabla x_A$

Maxwell-Stefan eqn. $\mathbf{J}_A^* = -C\hat{D}_{AB} x_A \dfrac{\nabla \mu_A}{k_B T} \Leftrightarrow x_A x_B(\mathbf{v}_A - \mathbf{v}_B) = -\hat{D}_{AB} x_A \nabla \ln a_A$

Chemical potential of A in a binary mixture (A B) $\mu_A(T, p, \varphi_A, x_A) \equiv \left(\dfrac{\partial g}{\partial C_A}\right)_{\overline{C_A}} = \mu_A^0(T, p) + k_B T \ln a_A + z_A F \varphi_A$

$a_A = \gamma_A x_A$

activity (coefficient)

Comparison:

$$D_{AB} = \hat{D}_{AB}\left(\frac{\ln a_A}{\ln x_A}\right)_{T,p,\varphi_A} \equiv \hat{D}_{AB}\left(1 + \left(\frac{\ln \gamma_A}{\ln x_A}\right)_{T,p,\varphi_A}\right)$$

For ideal solution (no interaction between molecules, such as dilute solution):

$$\gamma_A = 1 \Rightarrow D_{AB} = \hat{D}_{AB}$$

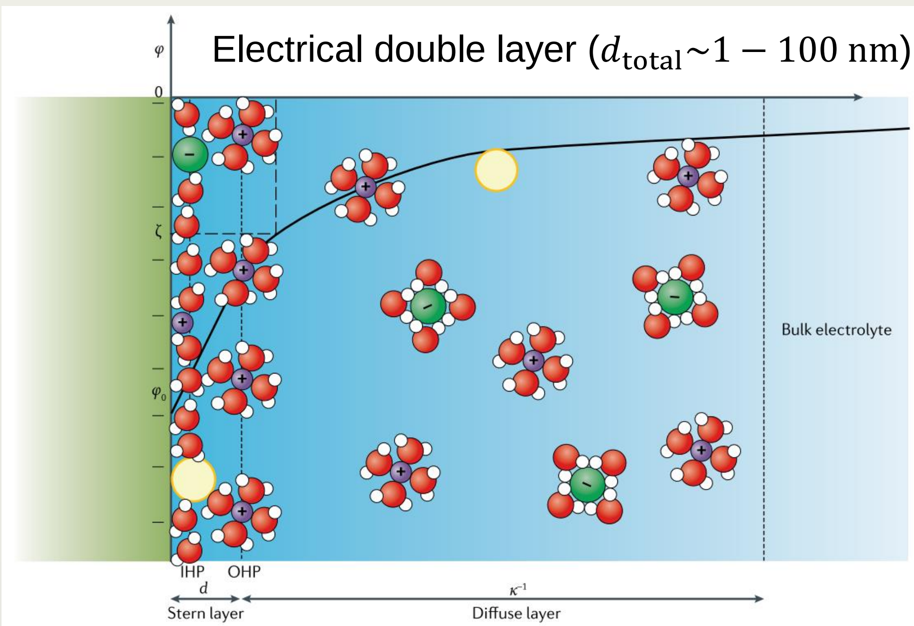
L. Onsager, Activity Coefficients and Mass-Action Law in Electrolytes. *J. Phys. Chem.*, **32**(10): 1461-1466, 1928

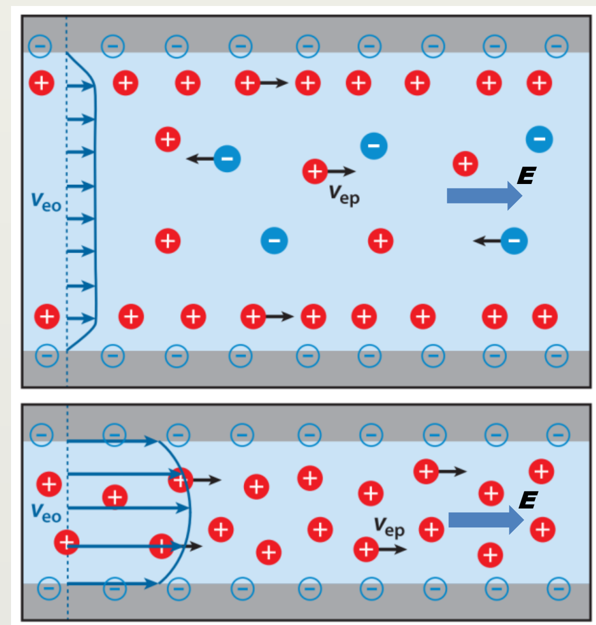
Ion diffusion in electrolytes – multi-physics

➢ Electro-chemical diffusion of charged species

charged species (e.g. ion) transfer influenced by the local electrical potential and chemical reaction[1]

$$\mathbf{j}_{\mathrm{A}} = -c_{\mathrm{A}} \tilde{D}_{\mathrm{AB}} \frac{\nabla \mu_{\mathrm{A}}(\varphi_{\mathrm{A}}, x_{\mathrm{A}})}{k_{\mathrm{B}} T}$$





Electrokinetic effects: ion-fluid coupling transport near charged surfaces, especially in micro-/nanoscales

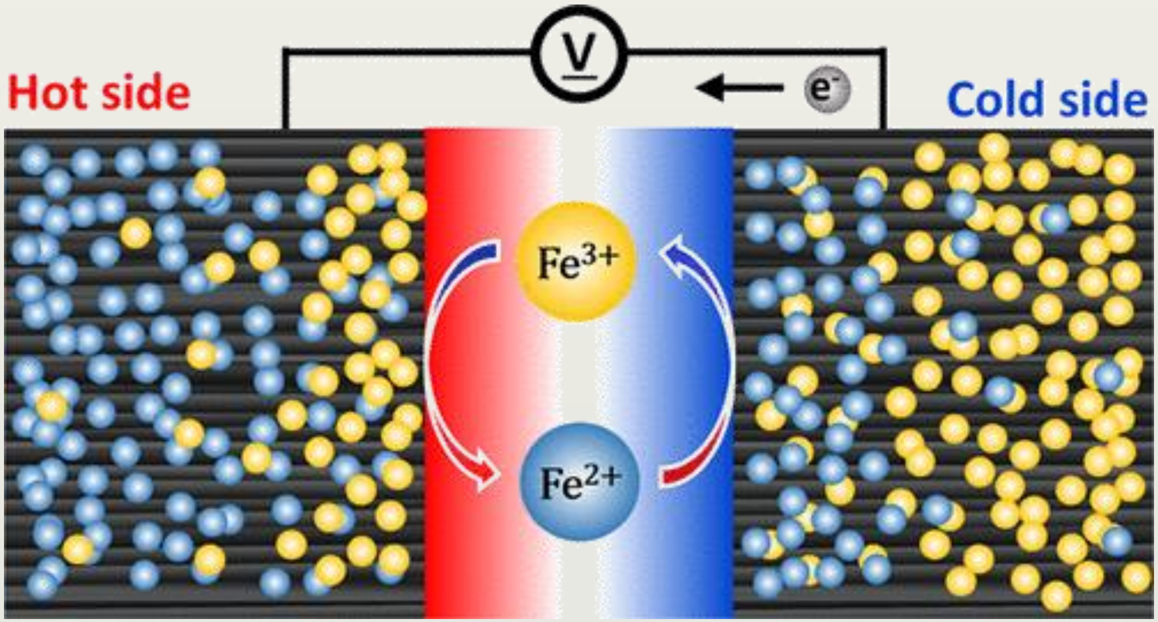
[1] L. Onsager, On the Theory of Electrolytes. II. *Physikalische Zeitschrift*, **28**: 277-298, 1927.
[2] A. Alizadeh, *et al*. Electroosmotic Flow: From Microfluidics to Nanofluidics. *Electrophoresis* **42**(7-8): 834-868, 2021.
[3] G. Gonella, *et al.*, Water at Charged Interfaces. *Nature Reviews Chemistry*, **5**(7): 466-485, 2021.
[4] N. Kavokine, *et al*, Fluids at the Nanoscale. *Annual Review of Fluid Mechanics*, **53**(1): 377-410, 2021.

Ion diffusion in electrolytes – multi-physics

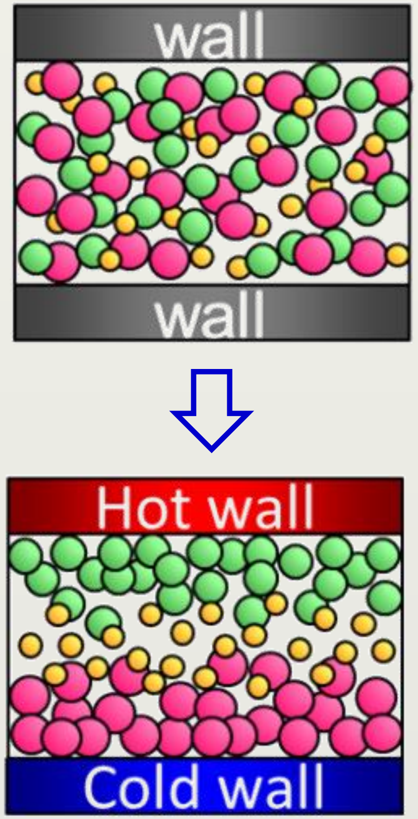
- Thermo-diffusion effect of charged species

coupling transport between mass/heat flow and molecules/ions transport (including thermal transpiration)

$$\mathbf{j}_A = -D_A^T \nabla \ln T$$



Thermo-electrochemical cells



Isotope separation

[1] W.H. Furry, R.C. Jones, and L. Onsager. On the Theory of Isotope Separation by Thermal Diffusion. *Phys. Rev.*, **55**: 1083, 1939
[2] 杨元凯. 致密多孔介质内多场作用下离子扩散的多尺度模拟与分析, 博士学位论文. 清华大学, 2019.
[3] Y. Yang, *et al*. Ionic Thermodiffusion in Nanoconfined Aqueous Electrolytes. *J. Colloid Interface Sci*. **619**: 331-338, 2022

Ion diffusion in electrolytes – symmetry

Lars Onsager

- Onsager's reciprocal relation (昂萨格倒易关系)

$$\mathbf{X}_i = \mathbf{F}_i - \nabla\mu_i,\ i = 1,2$$
$$\mathbf{j}_1 = L_{11}\mathbf{X}_1 + L_{12}\mathbf{X}_2$$
$$\mathbf{j}_2 = L_{21}\mathbf{X}_1 + L_{22}\mathbf{X}_2$$

$\rightarrow L_{12} = L_{21}$

Reciprocal relations? Only definition!

$$\mathbf{X}_i = \mathbf{F}_i - \nabla\mu_i,\ i = 1,2,3$$
$$\mathbf{j}_1 = L_{11}(\mathbf{X}_1 - \mathbf{X}_3) + L_{12}(\mathbf{X}_2 - \mathbf{X}_3)$$
$$\mathbf{j}_2 = L_{21}(\mathbf{X}_1 - \mathbf{X}_3) + L_{22}(\mathbf{X}_2 - \mathbf{X}_3)$$
$$\mathbf{j}_3 = -\mathbf{j}_1 - \mathbf{j}_2$$

$\rightarrow \boxed{L_{12} = L_{21}}$

Used for prediction

$$\mathbf{j}_A = \rho_A \mathbf{V}_A = \rho_A(\mathbf{v}_A - \mathbf{v})$$
$$\mathbf{j}_B = \rho_B \mathbf{V}_B = \rho_B(\mathbf{v}_B - \mathbf{v})$$
$$\mathbf{v} = m_A\mathbf{v}_A + m_B\mathbf{v}_B$$

$$\mathbf{j}_A + \mathbf{j}_B = 0$$

$$\mathbf{j}_A = -\rho D_{AB}^{(AA)}\nabla m_A$$
$$\mathbf{j}_B = -\rho D_{AB}^{(BB)}\nabla m_B$$

$$D_{AB}^{(AA)}\nabla m_A = -D_{AB}^{(BB)}\nabla m_B$$

$$m_A + m_B = 1$$
$$\nabla m_A = -\nabla m_B$$

$$D_{AB}^{(AA)} = D_{AB}^{(BB)} \Leftrightarrow D_{AB}^{(AB)} = D_{AB}^{(BA)}$$

$$\text{Defs}: \begin{cases} D_{AB}^{(xx)} = \text{mixture components (A B)} \\ D_{xx}^{(AA)} = \text{related quantities } (\mathbf{j}_A, m_A) \end{cases}$$

L. Onsager, *Physical Review* **37**: 405, 1931; L. Onsager, *Physical Review* **38**: 2265, 1931.

Diffusion in micro-/nano-pores

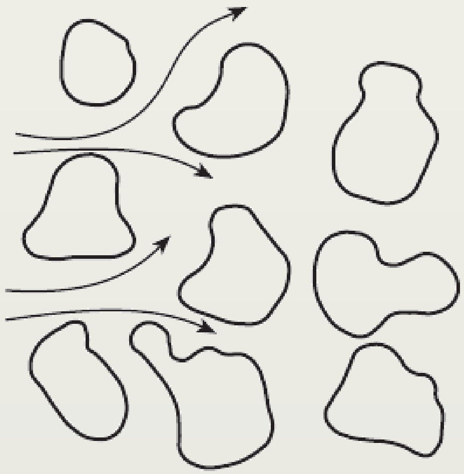
- Complexity of mass transfer in porous media
  - Geometry effect inside macro-pores – Fick's law is still valid (in general)
  - Confinement effect at the micro-/nano-scales – Fick's law is invalid

Molecule-boundary interaction ↑ ~ **sub-continuum** diffusion

Spatial effect		Temporal effect
high Kn	high Du	large τ
non-equilibrium transport w rarefied/ballistic effect	surface diffusion, molecular sieving	inertia of species vs. capillary potential effect

Geometry effect: porous diffusion

- Empirical description of transport in porous media



Pore-scale bulk property (binary diffusivity) D_b

$$D_{\text{eff}} \simeq D_b \frac{\varepsilon}{\tau}$$

Void fraction, i.e. porosity

Tortuosity

Effective average property (binary diffusivity)

$$D_{\text{eff}} := \frac{\int J_A'' dA}{A \Delta C / L}$$

Note. Applicability? Flow path? Dead-end pores?

How to validate/evaluate the empirical description?

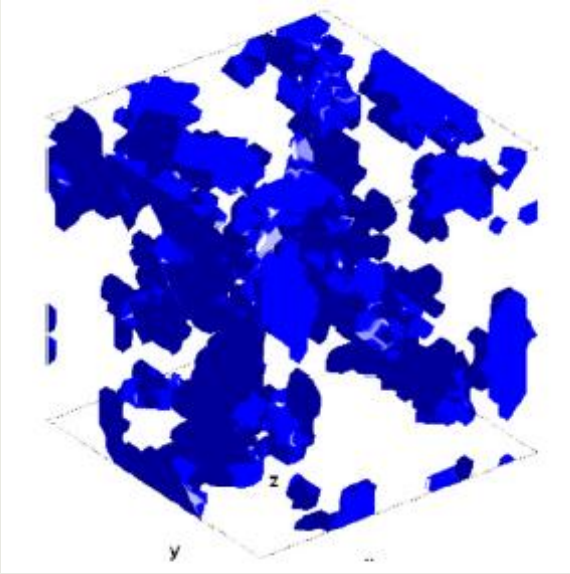
Experiment? Modeling and simulation!

[1] D. M. Tartakovsky and M. Dentz. Diffusion in Porous Media: Phenomena and Mechanisms. *Transp. Porous Media* **130**: 105–127, 2019.
[2] F.A. Oliveira, *et al.*, Anomalous Diffusion: A Basic Mechanism for the Evolution of Inhomogeneous Systems. *Front. Phys.* **7**, 2019.

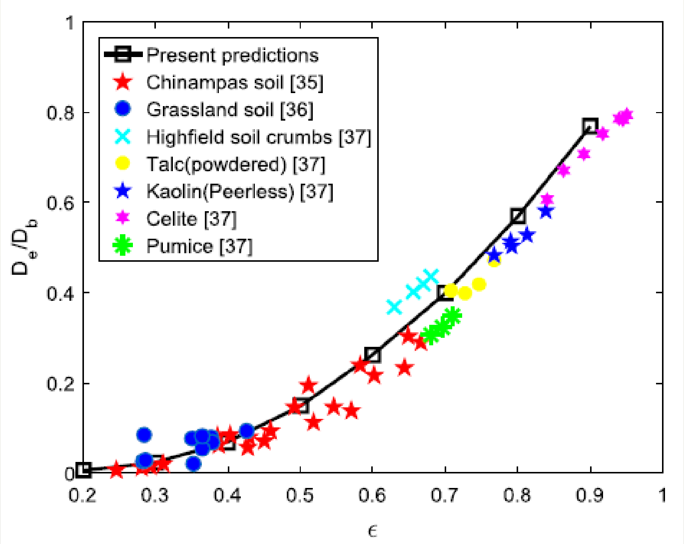
Geometry effect: porous diffusion

- Numerical simulation paradigm (CT/RGG & LBM/PNM)

Real porous media → Numerical reconstruction → Solution of local Fick's law → Get D_{eff}



Regenerated porous structure



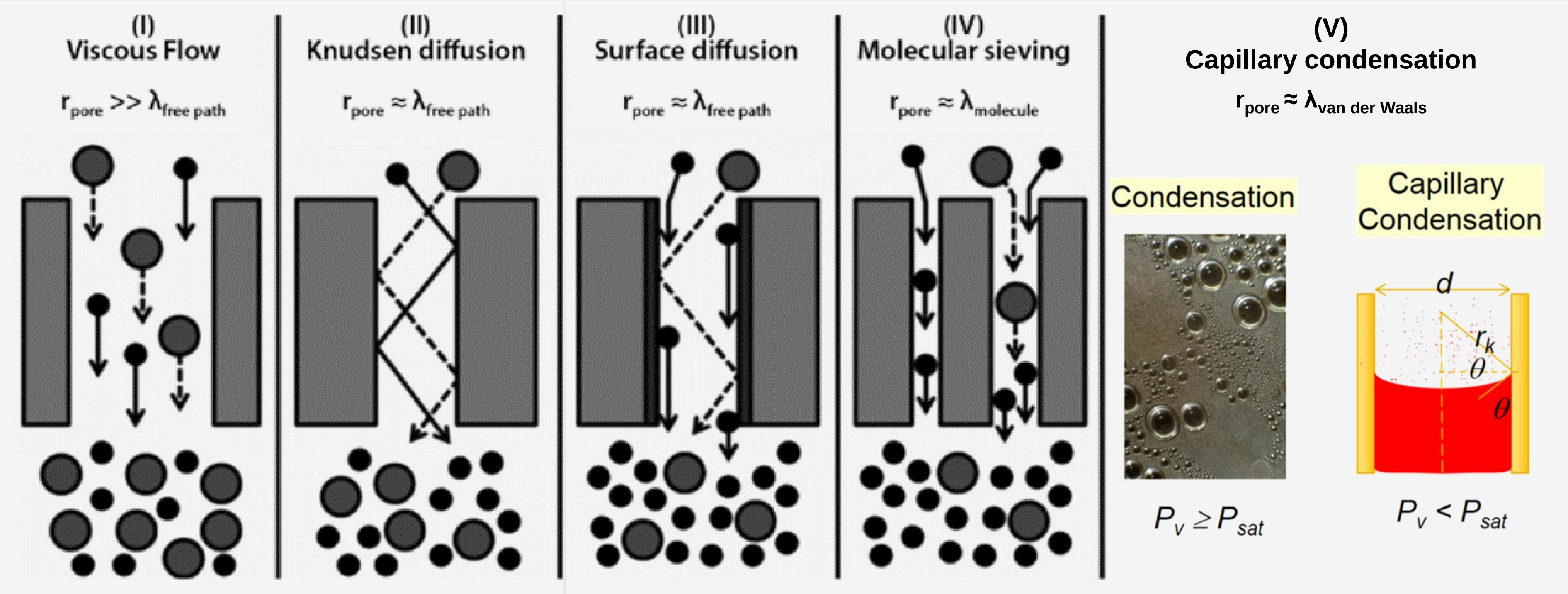
D_{eff} versus porosity (granular porous media)

[1] M. Wang and N. Pan, Predictions of Effective Physical Properties of Complex Multiphase Materials. *Mat. Sci. Eng. R* **63**: 1-30, 2008
[2] X. He, *et al.*, Effective Gas Diffusion Coefficient of Fibrous Materials by Mesoscopic Modeling. *Int. J. Heat. Mass. Trans*. **107**: 736-746, 2017
[3] Y. Liu, *et al.*, A Pore-scale Numerical Framework for Solute Transport and Dispersion in Porous Media. *Adv. Water. Res.* **183**: 104602, 2024

Confinement effect: classification

- Types of enhanced molecular-boundary interaction

Ordinary　　high Kn　　high Du　　large τ

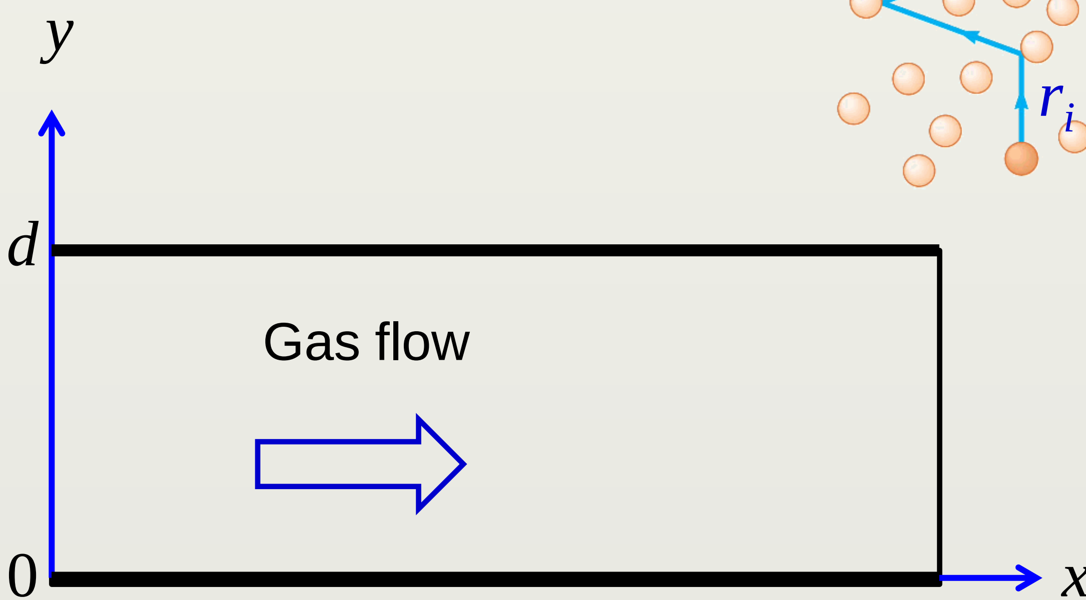


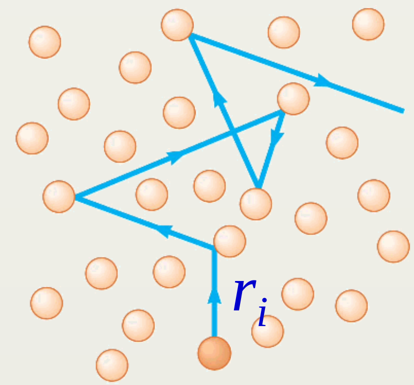
[1] K. Ghasemzadeh, *et al*. Progress in Modeling of Silica-Based Membranes and Membrane Reactors for Hydrogen Production and Purification. *ChemEngineering*, **3**(1): 2, 2019

[2] De Meis, *et al*. Microporous Inorganic Membranes for Gas Separation and Purification. *Interceram-International Ceramic Review*, **67**(4): 16-21, 2018

Confinement effect: high Kn

- Knudsen diffusion
  - Knudsen number





$$\lambda \equiv \frac{\sum_i r_i n_i}{\sum_i n_i}$$

Mean free path

$$\mathrm{Kn} = \frac{\lambda}{d}$$

Characteristic size

Applicability of NSE-ADE when d << 1?

M. Knudsen, *Journal of Membrane Science* **100**(1): 23-25, 1995. (Translated from "Knudsen, M. Die Gesetze der Molekularstromung und der inneren Reibungsstromung der Gase durch Rohren, *Annalen der Physik*, **28**: 75-130, 1909".)

Confinement effect: high Kn

- Knudsen diffusion: microscale gas flow

$$\mathrm{Kn} = \frac{\lambda}{d}$$

λ — Mean free path

d — Channel width

Range	Regime	Model
$\mathrm{Kn} < 10^{-3}$	Continuum regime	N-S eqn.
$10^{-3} < \mathrm{Kn} < 10^{-1}$	Slip regime	N-S eqn. + slip boundary
$10^{-1} < \mathrm{Kn} < 10$	Transition regime	Boltzmann eqn.
$\mathrm{Kn} > 10$	Free molecular flow regime	Boltzmann eqn.

H.-S. Tsien, Superaerodynamics, Mechanics of Rarefied Gases. *Journal of the Aeronautical Sciences* **13**(12): 653-664, 1946.

Confinement effect: high Kn

➢ Knudsen diffusion: statistical description

- Boltzmann transport equation

$$\mathrm{d}N\left(t, x_\alpha, c_\alpha\right) \equiv f\left(t, x_\alpha, c_\alpha\right)\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{c}$$

f : particle number distribution function

x_α : spatial position in phase space

c_α : molecular velocity in phase space

F_α : external force per phase element

$$\rho(\mathbf{x}) = \int mf\,\mathrm{d}\mathbf{c}$$

$$\rho(\mathbf{x})u_\alpha(\mathbf{x}) = \int mc_\alpha f\,\mathrm{d}\mathbf{c}$$

$$\rho(\mathbf{x})e(\mathbf{x}) = \int \frac{1}{2}m\left(c_\alpha - u_\alpha\right)^2 f\,\mathrm{d}\mathbf{c}$$

$$\underbrace{\frac{\partial f}{\partial t}}_{\text{Transient term}} + \underbrace{c_\alpha \frac{\partial f}{\partial x_\alpha} + F_\alpha \frac{\partial f}{\partial c_\alpha}}_{\text{Advection term}} = \underbrace{C(f) =: -\frac{f - f_{\mathrm{eq}}}{\tau}}_{\text{Collision term: BGK model}}$$

$$f_{\mathrm{eq}} \propto \exp\left(-\frac{mc^2}{2k_{\mathrm{B}}T}\right)$$

Transient term   Advection term   Collision term: BGK model

How to obtain the rigorous solution?   Analytical, DSMC, LBM, …

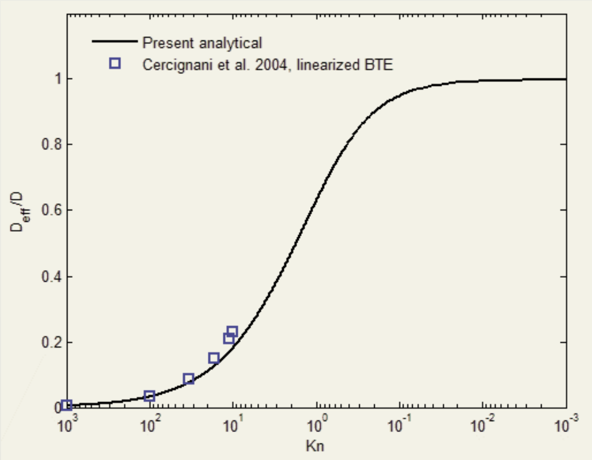
[1] P. L. Bhatnagar, *et al*. A Model for Collision Processes in Gases. I. Small Amplitude Processes in Charged and Neutral One-Component Systems. *Phys*. *Rev*. **94**: 511–525, 1954.
[2] 王沫然. 微纳尺度气体流动和换热的 Monte Carlo 模拟, 博士学位论文. 清华大学, 2004.

Confinement effect: high Kn

- Knudsen diffusion: numerical results

$$\mathrm{Kn} > 10$$

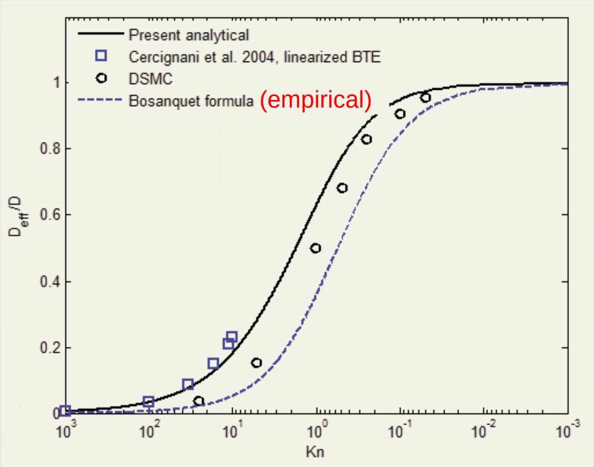
Free molecular flow regime
(Knudsen diffusion)



$$D_{\mathrm{Kn}} = \frac{d}{3}\sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}}$$

$$10^{-1} < \mathrm{Kn} < 10$$

Transition regime
(bulk diffusion "+" Knudsen diffusion)



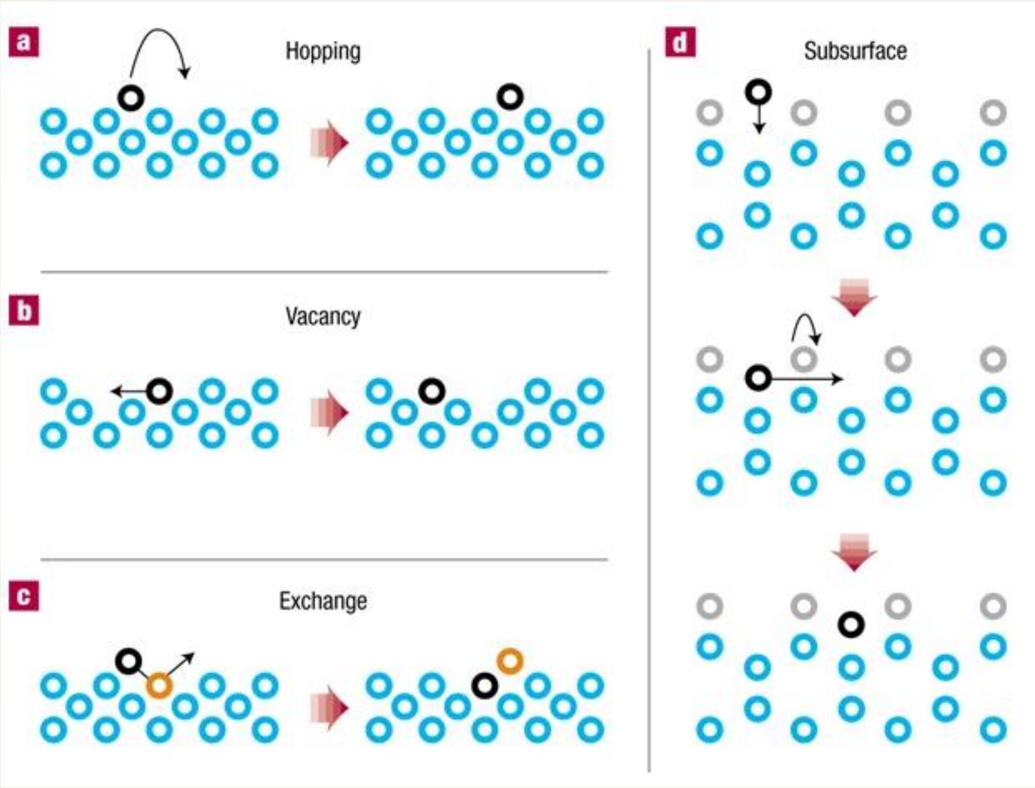
$$\frac{1}{D_{\mathrm{eff}}} = \frac{1}{D_{\mathrm{b}}} + \frac{1}{D_{\mathrm{Kn}}}$$

[1] S-H Kim *et al*., Lattice Boltzmann Modeling of Multicomponent Diffusion in Narrow Channels. *Phys. Rev. E.* **79**: 016702, 2009

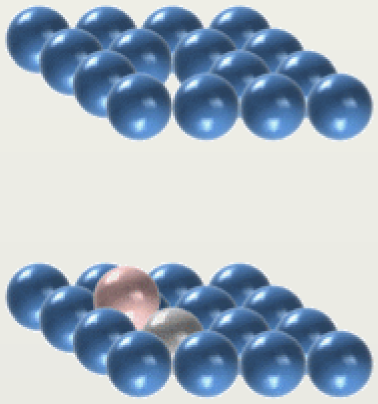
[2] Y. Guo, *et al*. Microstructure Effects on Effective Gas Diffusion Coefficient of Nanoporous Materials. *Transp. Porous Media* **126**(2): 431-453, 2019.

Confinement effect: high Du

➢ Surface diffusion



$$\mathrm{Du} = \frac{j_{\mathrm{surf}}}{j_{\mathrm{bulk}}}$$



- Adsorption: Physical / Chemical
- Diffusion along surface

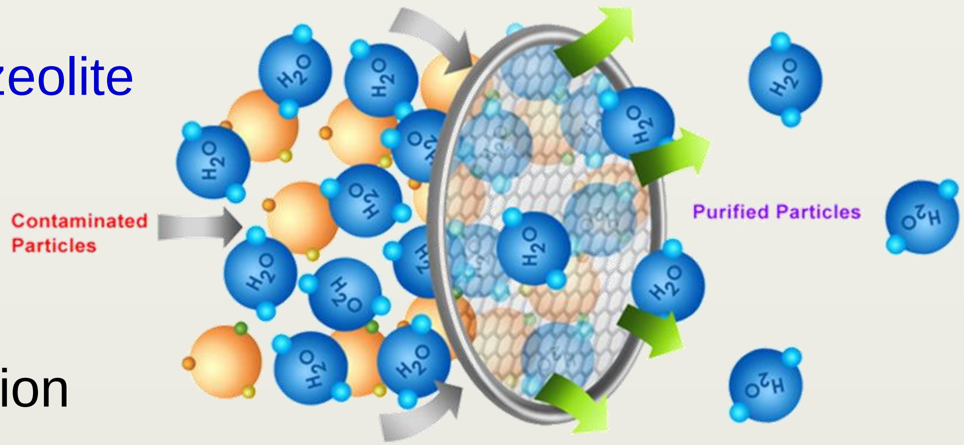
R. Tromp, Atoms Go Underground. *Nat. Mat.* **2**: 212-213, 2003

Confinement effect: high Du

- Molecular sieving (configurational diffusion)

  - water purification through zeolite

  pore size ~ molecular size

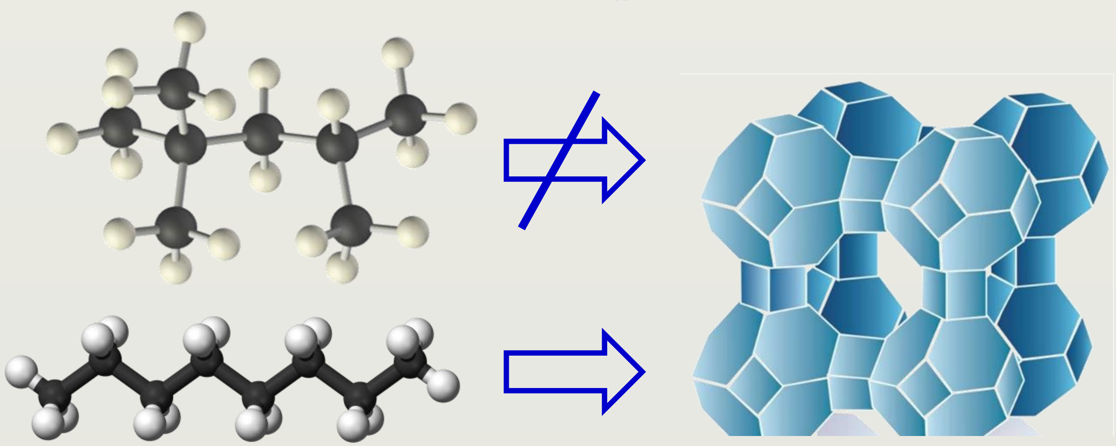


  - organic compound separation

Branched alkane:

(C_8H_{18})

Linear alkane:



K. Ghasemzadeh, *et al*. H_2 Production by Low Pressure Methanol Steam Reforming in a Dense Pd–Ag Membrane Reactor in Co-current Flow Configuration: Experimental and Modeling Analysis. *Chem Engineering*, **3**(1): 2, 2019.

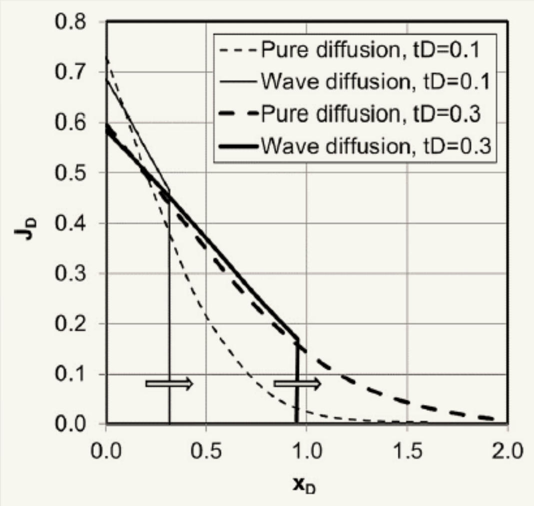
Confinement effect: large τ

- Capillary potential effect (τ: diffusion relaxation time)

Fick's law $$\mathbf{J}_{\mathrm{A}} = -D_{\mathrm{AB}} \nabla C_{\mathrm{A}}$$

Instantaneous response ignoring the inertia

Telegraph equation $$\tau \frac{\partial \mathbf{J}_{\mathrm{A}}}{\partial t} + \mathbf{J}_{\mathrm{A}} = -D_{\mathrm{AB}} \nabla C_{\mathrm{A}}$$



Jeffreys-type equation $$\tau \frac{\partial \mathbf{J}_{\mathrm{A}}}{\partial t} + \mathbf{J}_{\mathrm{A}} = -D_{\mathrm{AB}} \left(\tau_2 \frac{\partial \nabla C_{\mathrm{A}}}{\partial t} + \nabla C_{\mathrm{A}} \right)$$

Time delay ("inertia") due to surface effect

[1] A. V. Luikov, Application of Irreversible Thermodynamics Methods to Investigation of Heat and Mass Transfer. *Int. J. Heat Mass Transf.*, **9**(2): 139-152, 1966.
[2] S. A. Rukolaine and A. M. Samsonov, Local Immobilization of Particles in Mass Transfer Described by a Jeffreys-type Equation. *Phys. Rev. E.* **88**: 062116, 2013.

Summary

- ☺ Basic concepts of mass diffusion and historical review
  - ✓ Analogy between linear transport phenomena
- ☺ Fick’s law: density and molar forms
  - ✓ Definition of diffusivity and physical origins
- ☺ Fick’s second law and typical examples
  - ✓ Analogy between heat and mass diffusive transfer
- ◆ Diffusion beyond Fick’s law (*non-Fickian diffusion*)

Homework: 14.7, 14.34

Figure investigation: Lars Onsager

Additional question: Will mass diffusion happen in a binary mixture with uniform concentration fraction under ∇p? Think about the high pressure gradient limit.

Do a literature review on *methods of separation of isotopes*, such as thermal diffusion, centrifugal force, *et al*.

Supplemental Materials

Details: comparisons of the two forms

	density form	molar form
Absolute flux	$\mathbf{n}''_{\mathrm{A}} = \rho_{\mathrm{A}} \mathbf{v}_{\mathrm{A}}$	$\mathbf{N}''_{\mathrm{A}} = C_{\mathrm{A}} \mathbf{v}_{\mathrm{A}}$
Average velocity	$\mathbf{v} = m_{\mathrm{A}} \mathbf{v}_{\mathrm{A}} + m_{\mathrm{B}} \mathbf{v}_{\mathrm{B}}$	$\mathbf{v}^{*} = x_{\mathrm{A}} \mathbf{v}_{\mathrm{A}} + x_{\mathrm{B}} \mathbf{v}_{\mathrm{B}}$
Advection flux	$\rho_{\mathrm{A}} \mathbf{v}$	$C_{\mathrm{A}} \mathbf{v}^{*}$
Relative velocity	$\mathbf{V}_{\mathrm{A}} = \mathbf{v}_{\mathrm{A}} - \mathbf{v}$	$\mathbf{V}^{*}_{\mathrm{A}} = \mathbf{v}_{\mathrm{A}} - \mathbf{v}^{*}$
Diffusive flux	$\mathbf{j}_{\mathrm{A}} = \rho_{\mathrm{A}} \mathbf{V}_{\mathrm{A}}$	$\mathbf{J}^{*}_{\mathrm{A}} = C_{\mathrm{A}} \mathbf{V}^{*}_{\mathrm{A}}$
Diffusive + Advective	$\mathbf{n}''_{\mathrm{A}} \equiv \rho_{\mathrm{A}} \mathbf{v}_{\mathrm{A}} = \mathbf{j}_{\mathrm{A}} + \rho_{\mathrm{A}} \mathbf{v}$	$\mathbf{N}''_{\mathrm{A}} \equiv C_{\mathrm{A}} \mathbf{v}_{\mathrm{A}} = \mathbf{J}^{*}_{\mathrm{A}} + C_{\mathrm{A}} \mathbf{v}^{*}$
Property of diffusive flux	$\mathbf{j}_{\mathrm{A}} + \mathbf{j}_{\mathrm{B}} = 0$	$\mathbf{J}^{*}_{\mathrm{A}} + \mathbf{J}^{*}_{\mathrm{B}} = 0$
Fick's law	$\mathbf{j}_{\mathrm{A}} = -\rho D_{\mathrm{AB}} \nabla m_{\mathrm{A}}$	$\mathbf{J}^{*}_{\mathrm{A}} = -C D_{\mathrm{AB}} \nabla x_{\mathrm{A}}$

$$C(\mathbf{r}) = \sum_i C_i(\mathbf{r}) \qquad x_i(\mathbf{r}) = \frac{C_i}{C}, \quad \sum_i x_i = 1 \qquad \rho_i = M_i C_i$$

C_i : molar concentration [mol/m³] x_i: molar concentration fraction M_i: molar mass

Extension: models of binary diffusivity

- Microscopic models of binary Fickian diffusivity
  - **Dilute gas mixture**: mesoscopic kinetic theory
  - **Solid solution**: transition state theory
  - **Liquid / dense gas**: activated state theory
  - **Colloidal mixture**: Stokes-Einstein relation

- Related concepts on molecular mass diffusion
  - **Mutual diffusion** (i.e. inter-diffusion): $\mathbf{J}_{\mathrm{A}}^{*} = -CD_{\mathrm{AB}}\nabla x_{\mathrm{A}}$
    - ≥ **Self-diffusion** (i.e. intra-diffusion): limits of mutual diffusion

$$D_{\mathrm{A}} = \lim_{x_{\mathrm{A}}\to 0} D_{\mathrm{AB}}$$

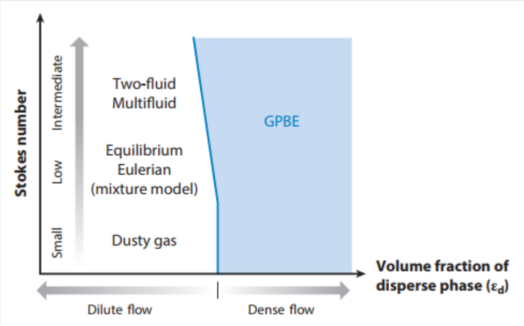
      - ≥ **Tracer diffusion**: a special case for chemical identical species

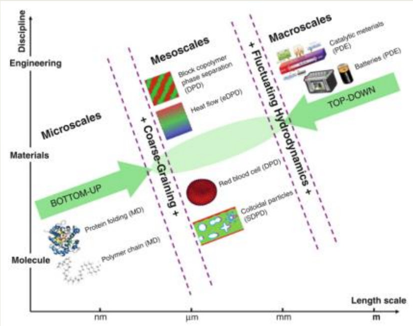
[1] M. Schoen, C. Hoheisel. *Molecular Physics*, **52**(1): 33-56, 1984 [Section 2]
[2] J.H. Kim and T.J. Kang. *ACS Appl. Mater. Interfaces*, **11**(32): 28894–28899, 2019

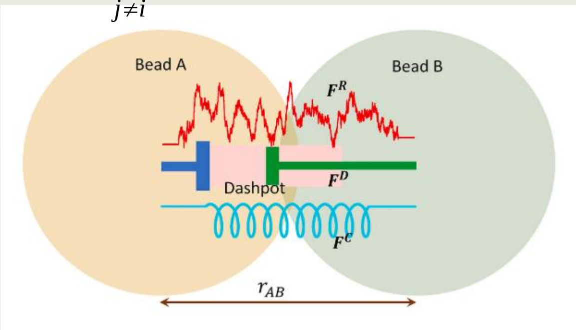
Extension: models of mass balance

Paul Langevin

- Mass balance models for general systems
  - **Multiple components** with simple dynamics
    - Non-ideal mixture: mass ADE with Maxwell-Stefan equation
    - Poly-disperse / dense flow: general population balance equation
  - **Complex dynamics** of individual species
    - Brown dynamics (random walk): $\dot{\mathbf{x}} = \mathbf{v}_{\text{background}} + (i\Omega - \gamma)\mathbf{x} + \boldsymbol{\eta}(t)$
    - Langevin dynamics: $m\ddot{\mathbf{x}}_i = -\lambda\dot{\mathbf{x}}_i + \mathbf{F}_{\text{ext}}(\dot{\mathbf{x}}_{j\neq i}, \mathbf{x}_{j\neq i}) + \boldsymbol{\eta}(t)$ (Langevin, 1908)
    - Dissipative particle dynamics: $m\ddot{\mathbf{x}}_i = \mathbf{f}_i^{\text{int}} + \mathbf{f}_i^{\text{ext}}, \mathbf{f}_i^{\text{int}} = \sum_{j\neq i} \mathbf{F}_{ij}^{\text{C}} + \mathbf{F}_{ij}^{\text{D}} + \mathbf{F}_{ij}^{\text{R}}$







[1] M. Shiea, *et al.*, *Annual Review of Chemical and Biomolecular Engineering* **11**: 339, 2020.
[2] H. Mori, *Progress of Theoretical Physics* **33**: 423, 1965.
[3] X. Li, … G. E. Karniadakis, *Encyclopedia of Nanotechnology*. Dordrecht: Springer, 2015.
[4] K. P. Santo and A. V. Neimark, *Advances in Colloid and Interface Science* **298**: 102545, 2021.