What do we mean by fluid transport, self diffusion, transport diffusion, capillary action, osmosis, contact angle, permeability and dynamic equilibrium, Navier-Stokes, ...

Richard Sear

University of Surrey

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Outline

1. Transport of molecules and ions: Getting from A to B. Transport mechanisms: diffusion & flow
2. Flow & Stokes equation. Flow needs forces.
3. Mixing and transport are different: Can have transport without mixing
4. Transport vs. local processes such as reactions: Damköhler numbers
5. Diffusion & flow at higher concentration
6. Flow in pores/porous media: Darcy's and Washburn's laws (diffusion is mostly the same in and out of porous media)

Transport is covered in chem eng textbooks such as *Fundamentals of Thermal-Fluid Sciences* by Çengel and Turner. See also Squires and Quake, Rev. Mod. Phys. (2005)

Learning Objectives

Look at the physics behind how molecules and ions move around

When doing experiments or modelling, we need to measure/calculate things. Here I hope to teach you what properties you need to measure/calculate, what properties you do not need to measure/calculate, and very approximately what values these properties take.

Questions for you at web address: pollev.com/richardsear

Transport of molecules and ions: Getting from A to B. Transport mechanisms: diffusion & flow

Transport of molecules and ions: Getting from A to B

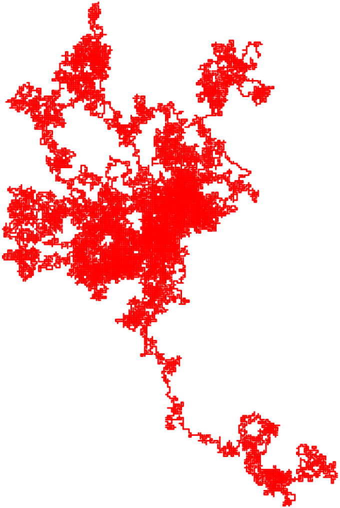
Two basic ways of molecules and ions getting from A to B:

1. Flow/directed movement at speed u. Distance moved $= ut$, when u constant. u the result of a force.
2. Diffusion, with diffusion constant D. Distance moved $= (Dt)^{1/2}$. No force needed.

Distance moved via diffusion only increases as $t^{1/2}$, while for movement at constant u, distance increases as t.

Time to move distance L increases as L^2/D for diffusion, but only as L/u for movement at constant u: In practice, molecules rarely move more than mms by diffusion, movement of cms and above by flow. Exception would be slow processes, eg corrosion that occurs over years. Typically in manufacturing, time is money and you can't wait for diffusion to move molecules $>$ cms.

Diffusion

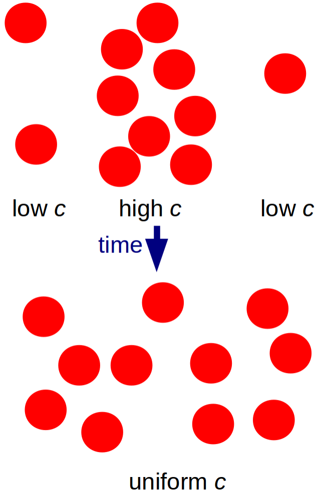


Random walk from Wikimedia

Diffusion is where molecule in a fluid follows a random walk path, with root-mean-square distance increasing as $t^{1/2}$. Does not need forces.

For water molecules in water
$D \sim 10^{-8} \mathrm{m}^2/\mathrm{s}$
For salt ions in water
$D \sim 10^{-9} \mathrm{m}^2/\mathrm{s}$
For water molecules in air
$D \sim 10^{-5} \mathrm{m}^2/\mathrm{s}$

Collective diffusion



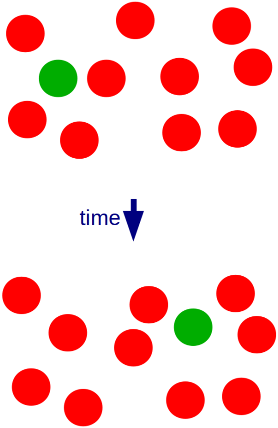
Collective diffusion is where diffusion flattens out concentration gradients, i.e., acts to make concentration uniform in space.

Flux due to diffusion, i.e., net number of molecules diffusing through unit area per second

$$\mathbf{j} = -D\nabla c$$

for ∇c the concentration gradient. This is Fick's Law.

Self diffusion



molecules move past each other

Self diffusion is where molecules and ions move relative to each other — including diffusing into contact, which is needed for molecules/ions to chemically react.

Self-diffusion essentially stops when a system becomes a glass

Stokes' Flow ($\mathrm{Re} = 0$)

For a slow moving incompressible (water is almost incompressible, air is compressible) fluid, the flow is solution of Stokes' equations

$$-\eta\nabla^2\mathbf{u} + \nabla p + \mathbf{f}_G = 0$$

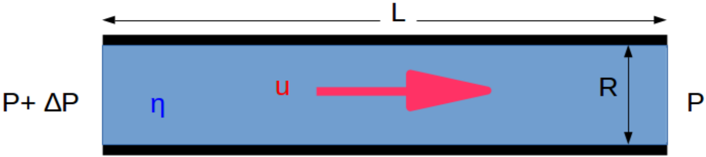
plus the incompressibility condition, which is

$$\nabla.\mathbf{u} = 0$$

Stokes' flows are driven by pressure gradients (∇p), i.e.., flow is away from higher pressure regions of the fluid and towards lower pressure regions, and by gravity ($\mathbf{f}_G$). Here ∇p comes from surface tensions, or is externally imposed.

Stokes' flows are opposed by viscosity($\eta\nabla^2\mathbf{u}$). Viscosity acts to flatten out gradients in velocity $\mathbf{u}$. The kinematic viscosity $\nu = \eta/\rho$ is the diffusion constant for momentum in a fluid; $\rho =$ mass density.

Poiseuille flow



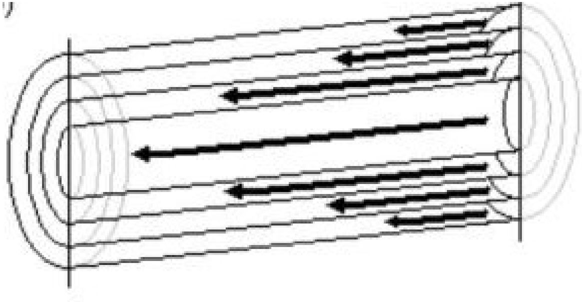
Flow along tube R across and length L can be driven by a pressure gradient. Resisted by viscosity η. Speed u given by

$$u \sim \frac{\Delta P}{L}\frac{R^2}{\eta} \qquad \text{Poiseuille}$$

This is one-phase Poiseuille flow, eg for pore filled with water.

Note that u increases as R^2 — flow very slow in small channels.

Poiseuille flow



Wikimedia

Flow speed maximum at centre, but zero in contact with surface of pore *u* is average speed, it is the velocity gradients here that drive the viscous forces that resist flow

Competition between diffusion and flow: Which is faster? Which one dominates transport?

Over a distance H, diffusion takes a time

$$\tau_D \sim \frac{H^2}{D}$$

If there is flow at speed u, flow takes a time

$$\tau_F \sim \frac{H}{u}$$

If H doubles, τ_D increases by factor of 4.

In practice, this means that transport over distances > 1 mm is almost always via flow — diffusion is too slow.

D of CO_2 in water $= 10^{-9}\text{m}^2/\text{s}$, so to diffuse 1 m takes $10^9\text{s} \simeq 30$ years!

Over lengthscales of micrometers and below, diffusion often dominates but flow can still be important

The Péclet number, Pe

Pe measures which of diffusion or flow dominates transport

$$\mathrm{Pe} = \frac{\text{diffusion time}}{\text{flow time}} = \frac{uL}{D}$$

Pe$\gg 1$ — flow faster
Pe$\ll 1$ — diffusion faster

Dimensionless ratios often determine both the dominant mechanism and the outcome

POLL 1

Jean Claude Eugène Péclet

A comment on dimensionless ratios

Very often there are competing processes, say X and Y, and we want to know which one dominates.

Dimensionless ratios help here

$$\text{Dimensionless ratio} = \frac{\textsf{timescale for X}}{\textsf{timescale for Y}}$$

Then if ratio $\gg 1$, often X limits rate of a process $\rightarrow$ varying rate of Y will have little effect, while rate of X controls the rate

Calculating this number told us which process we need to control — very useful!

Flow & Stokes equation. Flow needs forces.

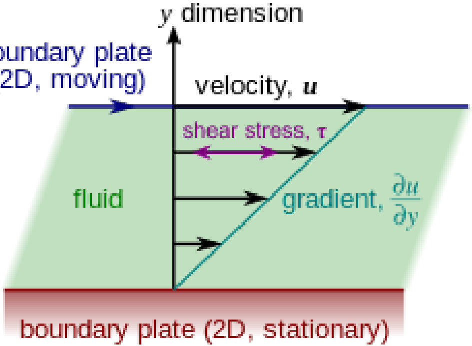
Viscous forces

Fluids such as water have viscosity, η (units = Pa s), which resists, by generating forces, non-uniform flow.

Shear stress τ equals fluid's viscosity times gradient in velocity. So if velocity is along x and varying with y

$$\text{shear stress} = \tau = \eta \frac{\partial u_x}{\partial y}$$

for water $\eta \sim 10^{-3}$Pa s
for air $\eta \sim 10^{-5}$Pa s



sheared fluid

NB shearing is by definition when the fluid's velocity varies along an axes perpendicular to the velocity.

Surface tension — surfaces exert forces

When porous medium has two phases in it, eg water and air, surfaces often drive behaviour

At the interface between any two phases, eg water and air, surface tension exerts a force per unit length of the interface, eg for water/air ~ 70 mN/m.

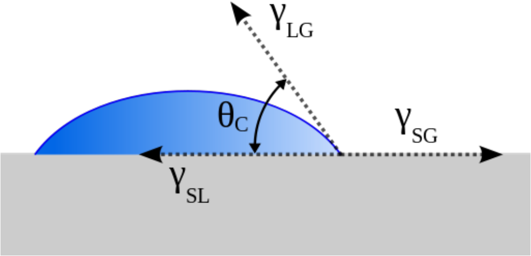
Insects called water striders/pond skaters can walk on water, as force of surface tension stronger than gravity

Wikimedia

Surface tension — surfaces exert forces

At the interface between any two phases, eg water and air, there is a surface tension that exerts a force per unit length of the edge of the interface, eg for water/air ∼ 70 mN/m.

For a liquid droplet on a surface there are three surface tensions: γ_{LG}, γ_{SL} and γ_{SG}



As all three surfaces exert forces, line where they meet will move unless forces balance, when Young's equation

$$\gamma_{SG} - \gamma_{SL} - \gamma_{SG}\cos(\theta_C) = 0$$

is satisfied

Wikimedia

When surface is not-uniform, stresses will drive flow

Previous slide was for uniform surfaces. If a surface is non-uniform, eg, solute more concentrated at one point than at another, then stresses at surface will drive flow

For a fluid/fluid interface this resulting motion is called the Marangoni effect. Movie!

For a fluid/solid interface this resulting motion is called the diffusioosmosis.

Flows require Forces

Forces can come from:

1. Inertia: $\rho L^2 u^2$ for mass density ρ
2. Viscosity: $u\eta L$, for viscosity η
3. Surface tension: γL, for surface tension γ
4. Gravity: $mg = \rho L^3 g$, for mass m, mass density ρ, and $g = 10$ m/s^2 the acceleration due to gravity

to move at speed u a force is needed.

Scalings with parameters: — note different forces scale as L, L^2 and L^3, so on large lengthscales gravity (L^3) dominates, while viscosity and surface tension dominate at small L

POLL 2

Dimensionless ratios of forces

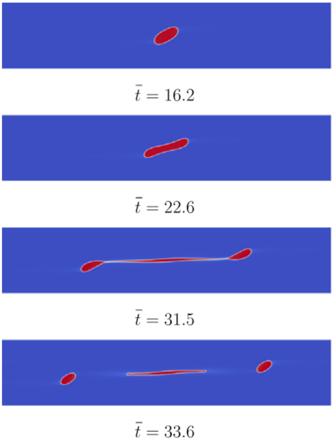
4 forces: inertia, surface, viscous and gravity, and so we have the dimensionless ratios:

1. Reynolds number Re $=\frac{\text{inertial forces}}{\text{viscous forces}}$
2. Weber number We $=\frac{\text{inertial forces}}{\text{surface forces}}$
3. Capillary number Ca $=\frac{\text{viscous forces}}{\text{surface forces}}$
4. Bond or Eötvös number Bo or Eo $=\frac{\text{gravity forces}}{\text{surface forces}}$
5. Grashof number Gr $=\frac{\text{gravity forces}}{\text{viscous forces}}$

large Re → turbulence, large We → splashing, large Ca → shear breaks up droplets, large Bo/Eo → flattened droplets

Capillary number Ca

Droplet (red) in sheared fluid, at 4 successive times



$$\text{Ca} = \frac{\text{viscous forces}}{\text{surface forces}}$$

$$\text{Ca} = \eta u/\gamma$$

For Ca > 1, shear forces larger than surface tension (which holds droplets together) so can shear droplets apart.

Komrakova et al.,
Chem. Eng. Sci. (2015)

Transport and Mixing are different:
Can have transport without mixing

Laminar flow

Laminar Flow movie

Mixing is not transport

We often need to mix two miscible liquids, eg two solutions with different solutes. Start with separate solutions and want to end up well-mixed, i.e., uniform concentrations of all solutes. Physics of mixing not at all trivial, typically flow on long lengthscales, then diffusion on smaller lengthscales.

Mixing two miscible liquids on lengthscales of cms, note turbulent mixing (= swirls).

Wikimedia

Mixing combination of Re $>$ 1 flow and diffusion

Elisa95 (flickr)

Flow in mixing: turbulent and laminar

Reynolds number

$$\mathrm{Re} = \frac{\rho u L}{\eta}$$

$\rho =$ mass density
$u =$ velocity
$L =$ lengthscale $\eta =$ viscosity

$\mathrm{Re} < 1$: laminar flow — no mixing
$\mathrm{Re} > 1$: mixing
$\mathrm{Re} \gg 1$: turbulence — mixing

$\mathrm{Re} \gg 1$ possible for water with lengthscales of cms and above, eg, for $L = 1$ cm, and $u = 1$ cm/s

$$\mathrm{Re} = 100 \gg 1$$

so flow can drive mixing
But for lengthscales mm or less, it is hard to achieve $\mathrm{Re} \gg 1$, then have laminar flow — no swirls and so no mixing.

Laminar flow does not mix, so on smaller lengthscales need diffusion to mix

As flows with lengthscale $L \lesssim 1$ mm are laminar (at reasonable speeds), so mixing at lengthscales $L \lesssim 1$ mm is typically via diffusion.

For salt $D \sim 10^{-9}\text{m}^2/\text{s}$

$$\text{diffusion timescale for } 1 \text{ mm} \sim \frac{(10^{-3})^2}{10^{-9}} \sim 10^3 \text{ s} \sim 10 \text{ min}$$

In systems using microfluidics can push L down to 0.1 mm → 1 s mixing times, but very hard to mix quicker than that

Impossible to mix instantly, typically takes minutes plus

Transport vs. local processes such as reactions: Damköhler numbers

Local processes that form or erode the cement

Chemical reactions occur locally but may rely on transport into or out of the cement.
For example, if cement requires a chemical reaction

$$X + Y \xrightarrow{k} Z$$

with k the reaction rate constant for the chemical reaction.

So at a point in space in setting cement, the reaction requires:
a) the molecules/ion X and Y have to be transported to that point
b) the reaction needs to occur
These two processes effectively occur in series and so one or both may limit the rate of cement setting. A Damköhler number compares these processes

Damköhler number: transport versus reaction

Ratio of transport to reaction time defines a type of Damköhler (dimensionless) number:

$$\text{Damköhler number} \quad \mathrm{Da} = \frac{\tau_{TRANS}}{\tau_{REAC}}$$

We expect whichever process is slower to be the one that sets the rate of setting

$\mathrm{Da} \gg 1$ transport to growing limits rate of setting

$\mathrm{Da} \ll 1$ reaction limits rate of setting

Also applies if transport and reaction both needed for cement erosion

Damköhler number: transport versus reaction

$$\text{Damköhler number} \quad \text{Da} = \frac{\tau_{TRANS}}{\tau_{REAC}}$$

We expect whichever process is slower to be the one that sets the rate of setting

$\text{Da} \gg 1$ transport to growing limits rate of setting

$\text{Da} \ll 1$ reaction limits rate of setting

For diffusion: $\tau_{TRANS} = L^2/D$

For reaction: $\tau_{REAC} = 1/k$

POLL 3

Diffusion & flow at higher concentration

Diffusion at higher concentrations & in mixtures

For species i if it is alone in dilute solution, then flux $\mathbf{j}_i$, i.e., number of molecules crossing unit area in unit time is

$$\mathbf{j}_i = -D_{ii}\nabla c_i \qquad \text{Fick's law}$$

D_{ii} a diffusion constant and c_i the concentration of i.

In concentrated multicomponent solution

$$\mathbf{j}_i = -\sum_j M_{ii}(c_1, c_2, \ldots,)\nabla\mu_j + q_i M_{iE}\mathbf{E} - M_{iT}\nabla T$$

with μ_j the chemical potential of species j, and M_{ij} are mobilities. q_i is charge on species i, $\mathbf{E}$. NB, when salts (NaCl etc) diffuse they create local $\mathbf{E}$ fields.

Diffusion at higher concentrations & in mixtures

In concentrated multicomponent solution

$$\mathbf{j}_i = -M_{ii}(c_1, c_2, \ldots,)\nabla\mu_i - \sum_{j\neq i} M_{ij}(c_1, c_2, \ldots,)\nabla\mu_j + q_i M_{iE}\mathbf{E} - M_{iT}\nabla T$$

1. Self term: $M_{ii}(c_1, c_2, \ldots,)\nabla\mu_i$. This is for collective diffusion, i.e., relaxation of non-uniform concentration profiles. M_{ii} often increases as c_i increases: roughly speaking interactions often speed up relaxation of concentration profiles. But they can also slow motion of one molecule relative to surrounding molecules — extreme example is glasses where relative motion essentially stops.
2. Other terms: a gradient in anything will drive diffusion of everything, although sometimes effect will be small and can be ignored. For example, if species j attracts i then molecules of i will move up a concentration gradient in j.

Viscosity of concentrated solutions

The viscosity η is essentially a constant for air and water — examples of what are called Newtonian fluids. But concentrated solutions, especially those with nanoscale structure can have viscosities that depends sensitively on the concentrations of the molecules and the ions, and on shear.

At high concentrations of solute in water, viscosity $\eta \gg 10^{-3}$Pa s, it can even diverge — then you have a glass. Also, can be shear thinning $\rightarrow$ flow reduces η or shear thickening $\rightarrow$ shear increases η

Flow in pores/porous media: Darcy's and Washburn's laws

Diffusion & flow on porous media

Diffusion mostly unaffected in all but the smallest pores.

But flow is typically slower in porous media than in bulk fluids — lots of pore walls where fluid is forced to be stationary by friction with wall

I will focus on flow driven by pressure gradients that come for surface tension

Surface tension & porous media — Wicking

Liquids can be pulled into porous media, eg when you use a paper towel to soak up water

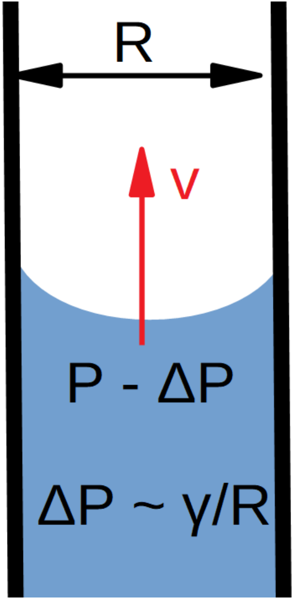
Paper towels and other porous media are full of tiny pores, $R \sim$ nm to $100\mathrm{\mu m}$.

thegreywaterguide.com

Surface tension & porous media — Wicking

The surface tension of water creates a pressure when the interface is curved: the Laplace pressure

$$\Delta p_{LAPLACE} \sim \frac{\gamma}{R}$$



Flow in porous media: Darcy's Law

Darcy's Law is the flux of fluid $\mathbf{Q} =$ volume of fluid flowing through unit area of the porous media is proportional to the pressure gradient ∇p

$$\frac{\mathbf{Q}}{A} = -\frac{k}{\eta} \nabla p$$

the proportionality constant is a property (mostly) of the porous media, the permeability k (units of m^2), divided by the viscosity of the fluid.

The ratio $\mathbf{Q}/A$ has dimensions of m/s, and so is effective velocity: $\mathbf{u}_{\text{DARCY}}$ — Darcy velcocity. So,

$$\mathbf{u}_{\text{DARCY}} \sim -\frac{k}{\eta} \nabla p$$

Flow in porous media: Poiseuille flow and Darcy's Law

Darcy's Law:

$$\mathbf{u}_{\text{DARCY}} \sim -\frac{k}{\eta} \nabla p$$

Note similarity to Poiseuille flow, for flow through tube R across

$$\mathbf{u} \sim -\frac{R^2}{\eta} \nabla p$$

If porous media is network of pores of typical radius R, then permeability $k \sim R^2$, i.e., permeability of porous medium expected to scale as roughly the square of the typical pore radius. Darcy's and Poiseuille's Laws roughly are the same.

Washburn equation for fluid being pulled into porous media

We assume:

1. A fixed pressure at outside of porous media
2. $L(t)$ is distance water has penetrated into the porous medium
3. porous media of pores of radius R
4. The pressure gradient pulling the water into the porous medium is a Laplace pressure $\Delta p \sim \gamma/R$

Then want to calculate

$$\frac{\mathrm{d}L}{\mathrm{d}t} = u$$

Washburn equation for fluid being pulled into porous media

Darcy/Poiseuille

$$u \sim \frac{k}{\eta} \times \frac{\Delta p}{L} \qquad \text{when } \Delta p \text{ Laplace} \qquad u \sim \frac{k}{\eta} \times \frac{\gamma}{LR}$$

Putting $k \sim R^2$

$$\frac{\mathrm{d}L}{\mathrm{d}t} \sim \frac{\gamma R}{\eta} \frac{1}{L(t)}$$

Solution is

$$L \sim \left(\frac{\gamma R}{\eta}\right)^{1/2} t^{1/2} \qquad \text{Washburn}$$

note that due to pressure drop decreasing with time $u \sim 1/t^{1/2}$ and so t dependence of distance travelled is $L \sim t^{1/2}$ — which same as for diffusion. But physics very different!

Movie!

Conclusion for transport

1. A chemical reaction occuring at a point in space (eg in drying cement) may rely on flow for transport over distances $>$ mms, diffusion for mixing, and a local reaction rate — Good starting point is to ask which of 3 is rate limiting?
2. If we compare bulk fluids with porous media, then in pores flow slower, but also surface forces at walls of pores can drive flow — wicking. Diffusion is relatively weakly affected unless pores nanoscale.

Transport is covered in chem eng textbooks such as *Fundamentals of Thermal-Fluid Sciences* by Çengel and Turner
Nanoscale motion covered by review of Bocquet and Charlaix, Chem. Soc. Rev. 39, 1073 (2010)