5_Flows_and_Transport_in_Liquids

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0.1 Flows and Transport in Liquids

0.1.1 Diffusion and Brownian Motion

- particles are moving in soft materials all the time→thermal fluctuations, Brownian motion
- in addition flows, friction→hydrodynamics, mechanical properties
- elasticity, rheology

a) Continuity

flux $\vec{j} = \rho\vec{n}$ Consider a volume surrounded by a surface S flow through surface:

$$\int_S \vec{j} \cdot \vec{n} \, \mathrm{d}S \tag{1}$$

material in volume, e.g., particle density:

$$\int_V f \, \mathrm{d}V \frac{\mathrm{d}}{\mathrm{d}t} \int f \, \mathrm{d}V = \int_V \frac{\mathrm{d}f}{\mathrm{d}t} \, \mathrm{d}V \tag{2}$$

conservation of matter:

$$\int_S \vec{j} \cdot \vec{n} \, \mathrm{d}S = -\int_V \frac{\mathrm{d}f}{\mathrm{d}t} \, \mathrm{d}V \tag{3}$$

Due to Gauss's law

$$\int_S \vec{j} \cdot \vec{n} \, \mathrm{d}S = \int_V \operatorname{div} \vec{j} \, \mathrm{d}V \tag{4}$$

and thus

$$\int_V \left(\frac{\mathrm{d}f}{\mathrm{d}t} + \vec{\nabla} \cdot \vec{j} \right) \mathrm{d}V = 0 \tag{5}$$

This yields the continuity equation

$$\frac{\mathrm{d}f}{\mathrm{d}t} + \vec{\nabla} \cdot \vec{j} = 0. \tag{6}$$

For the density $n = f$, $\vec{j} = n \cdot \vec{v}$

$$\frac{\partial n}{\partial t} + \vec{\nabla}(n\vec{v}) = 0 \tag{7}$$

for $n =$ const. it is $\vec{\nabla} \cdot \vec{V} = 0, \vec{\nabla} \cdot \vec{j} = 0$ incompressible

Diffusion

$N(x)$, $N(x + \Delta x)$, $0.5 \cdot N(x)$ to the right, $0.5 \cdot N(x + \Delta x)$ to the left net number $-1 \,/\, 2(N(x + \Delta x) - N(x))$ thus

$$j = \frac{-\frac{1}{2}(N(x+\Delta x) - N(x))}{A\,\tau} \tag{8}$$

With the number density of particles $n(x) \equiv N(x) \,/\, A\tau$ one obtains

$$j = -\frac{1}{2}\frac{n(x+\Delta x)\,A\,\Delta x - n(x)\,A\,\Delta x}{A\,\tau} = -\frac{1}{2}\frac{(\Delta x)^2}{\tau}\frac{n(x+\Delta x) - n(x)}{\Delta x} \tag{9}$$

For $\Delta x \to 0$ it is

$$j = -D\frac{\partial n}{\partial x} \tag{10}$$

with $D = (\Delta x)^2/2\tau$. In 3d, this is

$$\vec{j} = -D\vec{\nabla}n \tag{11}$$

This is Fick's first law (1855, Fick, empirical). flux from a gradient is due to fluctuations in the velocity, diffusion max. entropy to vanish the gradient

Combination with the continuity equation

in 1d:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\partial j}{\partial x}\frac{\partial j}{\partial x} = -D\frac{\partial^2 n}{\partial x^2} = -\frac{\partial n}{\partial t} \tag{12}$$

Fick's second law:

$$\frac{\partial n}{\partial t} = D\nabla^2 n \tag{13}$$

n f could be different quantities

flux	transport property	gradient
particles	diffusivity	particle density
charge	conductivity	potential
liquid	permeability	pressure

flux	transport property	gradient
momentum	viscosity	momentum density
energy	heat conductivity	temperature

0.1.2 Smoluchowski-diffusion in an external potential

Smoluchowski-diffusion in an external potential

$$F = -\frac{\mathrm{d}U}{\mathrm{d}x} \tag{14}$$

velocity of the particle

$$v = -\frac{1}{\xi}\frac{\partial U}{\partial x} \tag{15}$$

$\xi$is the friction coefficient. For a sphere $\xi = 6\pi\eta R$. flux due to flow with v, $j_v = nv$

$$j = -D\frac{\partial n}{\partial x} - \frac{n}{\xi}\frac{\partial U}{\partial x} \tag{16}$$

in steady state $j = 0$ and

$$n = n_0 \exp\left(-\frac{U}{k_\mathrm{B}T}\right) 0 = -D\frac{\mathrm{d}}{\mathrm{d}x}\left(n_0 \exp\left(-\frac{U}{k_\mathrm{B}T}\right)\right) - \frac{1}{\xi}\frac{\mathrm{d}U}{\mathrm{d}x} n_0 \exp\left(-\frac{U}{k_\mathrm{B}T}\right) + \frac{D}{k_\mathrm{B}T}\frac{\mathrm{d}U}{\mathrm{d}x} n_0 \exp\left(-\frac{U}{k_\mathrm{B}T}\right) = -\frac{1}{\xi}\frac{\mathrm{d}U}{\mathrm{d}x} r \tag{17}$$

With the diffusion coefficient $D = k_B T/\xi$ one has

$$j = -\frac{1}{\xi}\left(k_\mathrm{B}T\frac{\partial n}{\partial x} + n\frac{\partial U}{\partial x}\right) = -\frac{1}{\xi} n \frac{\partial}{\partial x}(k_\mathrm{B}T \cdot \ln(n) + U), \tag{18}$$

since

$$\frac{\mathrm{d}}{\mathrm{d}x}\ln(n(x)) = \frac{1}{n}\frac{\mathrm{d}u}{\mathrm{d}x} \tag{19}$$

and thus

$$\frac{\mathrm{d}u}{\mathrm{d}x} = n \cdot \ln(n). \tag{20}$$

Here, $k_B T \cdot \ln n + U$ is the chemical potential.

$$j = -\frac{1}{\xi} n \frac{\partial \mu}{\partial x} \tag{21}$$

The chemical potential is constant in equilibrium, extend potential for ?? $\mu = \mathrm{const}$.

$$U = -k_\mathrm{B}T \ln(n(x)) + \mathrm{const.} \tag{22}$$

With Fick's second law

$$\frac{\partial n}{\partial t} = -\frac{\partial j}{\partial x} = \frac{1}{\xi}\frac{\partial}{\partial x}\left(k_{\mathrm{B}}T\frac{\partial U}{\partial x} + n\frac{\partial U}{\partial x}\right)\frac{\partial n}{\partial t} = \vec{\nabla}\left(D\vec{\nabla}n + \frac{\vec{F_{\mathrm{ext}}}}{\xi}n\right) \tag{23}$$

This is the Smoluchowski equation. More general: Fokker—Planck equation

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{1}{\xi(x,t)}p(x,t)\right] + \frac{\partial^2}{\partial x^2}\left[D(x,t)p(x,t)\right] \tag{24}$$

$D = k_B T/\xi$ gives a connection between thermal position fluctuations and viscous friction (fluctuation—dissipartion) $D = k_B T/6\pi\eta R$ for sphere, e.g., protein: $R \equiv 3\,\mathrm{nm}$, D = 100 m^2/s, = 0.7 mPas. Solution of the diffusion equation

$$\frac{\partial}{\partial t}n(\vec{r},t|\vec{r_0},t_0) = D\nabla^2 n(\vec{r},t|\vec{r_0},t_0) \tag{25}$$

initial condition $n(\vec{r},t\to t_0|\vec{r_0},t_0) = \delta(\vec{r}-\vec{r_0})$

solution:

$$n(\vec{r},t|\vec{r_0},t_0) = \frac{1}{(4\pi D(t-t_0))^{\frac{3}{2}}}\exp\left(-\frac{(\vec{r}-\vec{r}_0)^2}{4D(t-t_0)}\right) \tag{26}$$

This is the Green's function for the diffusion equation for the given boundary conditions. It propagates the initial conditions through the ??? space. solution for any initial condition can be found

$$n(\vec{r},t\to 0) = f(\vec{r_0})n(\vec{r},t) = \int \mathrm{d}^3 r_0\, n(\vec{r},t|\vec{r_0},t_0)\, f(\vec{r_0}) \tag{27}$$

properties: e.g., particle initially at x_0 in 1D, initial distribution $\delta(x_0)$

$$\langle x\rangle = \int_{-\infty}^{\infty} x\frac{1}{\sqrt{4\pi D(t-t_0)}}\exp\left(-\frac{(x-x_0)^2}{4D(t-t_0)}\right)\mathrm{d}x \tag{28}$$

$\langle x\rangle = x_0$,does not depend on time, particles do not change their initial position on average

$$\langle (x-x_0)^2\rangle = \int_{-\infty}^{\infty}(x-x_0)^2\, n(x,t)\,\mathrm{d}x \tag{29}$$

$\langle (x-x_0)^2\rangle = 2Dt$ in 1D

$\langle r^2\rangle = 6Dt$ in 3D

mean squared displacement=ˆwidth of the probability distribution increases linearly in time

$\langle r^2\rangle = 2dDt$,d is the dimension in more complex diffusion scenarios: $\langle r^2\rangle = cDt^\alpha$ with $\alpha < 1$ for subdiffusion and $\alpha > 1$ for superdiffusion Application: fluorescence recovery after photobleaching

Molecules are photophysically/chemically bleached in a spatial region with high intensity layer. Diffusion causes fluorescent molecules to diffuse in again, ?? bleached come out The “hole” is filling up and the dynamics is determined by the diffusion coefficient. initial distribution after the bleach is $w(x, t_0)$

$$n(x, t_0) = \Theta(-a - x) + \Theta(x - a) \tag{30}$$

Heaviside step function

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \geq 0 \end{cases} \tag{31}$$

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} n(x, t) \tag{32}$$

boundary condition $\lim_{x \to \infty} n(x, t) = 0$ solution with Green’s function

$$n(x, t | x_0, t_0) = \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left(-\frac{(x - x_0)^2}{4D(t - t_0)}\right) \tag{33}$$

$$\begin{aligned} n(x, t) &= \int_{-\infty}^{\infty} \mathrm{d}x_0 \, n(x, t|x_0, t_0) \, [\Theta(-a - x) + \Theta(x - a)] \\ &= \int_{-\infty}^{-a} \mathrm{d}x_0 \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left(-\frac{(x - x_0)^2}{4D(t - t_0)}\right) + \int_{a}^{\infty} \mathrm{d}x_0 \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left(-\frac{(x - x_0)^2}{4D(t - t_0)}\right) \end{aligned} \tag{34}$$

$$\mathrm{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^{x} \exp\left(-t^2\right) \, \mathrm{d}t = \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp\left(-t^2\right) \, \mathrm{d}t \tag{35}$$

solution:

$$n(x, t) = 1 + \frac{1}{2} \left(\mathrm{erf}\left[\frac{\mathrm{x + a}}{2\sqrt{\mathrm{D(t - t_0)}}}\right] - \mathrm{erf}\left[\frac{\mathrm{x - a}}{2\sqrt{\mathrm{D(t - t_0)}}}\right] \right) N(t, t_0) = c_0 \int_{-a}^{a} \mathrm{d}x \, n(x, t) \tag{36}$$

if there is a concentration of c_0 fluorescent molecules

$$N(t, t_0) = \frac{\sqrt{D(t - t_0)}}{a\sqrt{\pi}} \left(\exp\left[-\frac{a^2}{D(t - t_0)}\right] - 1 \right) + 1 + \mathrm{erf}\left[\frac{a}{\sqrt{D(t - t_0)}}\right] \tag{37}$$

Extension

Diffusion can also occur on a spherical surface ?? to a point ?? surface is ?? doing rotational diffusion

$$\frac{\partial n(\vec{r},t|\vec{r_0},t_0)}{\partial t} = D\nabla^2 n(\vec{r},t|\vec{r_0},t_0) \tag{38}$$

with $|\vec{r_0}| = |\vec{r}| = 1$ so no radial ??

$$\frac{\partial n(\Omega,t|\Omega_0,t_0)}{\partial t} = D_{\text{rot}}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right] n(\Omega,t,\Omega_0,t_0) \tag{39}$$

The eigenfunctions of the operator on the right are sperical harmonics and the solution may be expressed in terms of Y_l^m.

$$Y_l^m = N\exp(im\varphi)\; P_l^m(\cos\theta) p(\Omega,t|\Omega_0,t_0) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} A_{lm}(t,\Omega_0,t_0)Y_l^m(\Omega) \tag{40}$$

insert into diffusion equation

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\frac{\partial A_{lm}}{\partial t}Y_l^m = -\sum_{l=0}^{\infty}\sum_{m=-l}^{l} l(l+1)\frac{1}{\tau_R}A_{lm}Y_l^m \tag{41}$$

with orthonormality

$$\frac{\partial A_{lm}}{\partial t} = -l(l{+}1)\,\tau_R^{-1}\,A_{lm}A_{lm}(t|\Omega_0,t_0) = \exp\left(-l(l+1)\frac{t-t_0}{\tau_R}\right)\,a_{lm}(\Omega_0)p(\Omega,t|\Omega_0,t_0) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\exp\left(-l(l+1)\frac{t-}{\tau}\right. \tag{42}$$

a_{lm} from $p(\Omega,t_0|\Omega_0,t_0) = \delta(\Omega-\Omega_0)$ and

$$\delta(\Omega-\Omega_0) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_l^m(\Omega_0)\,Y_{lm}(\Omega) \tag{43}$$

$$a_{lm}(\Omega_0) = Y_{lm}^*(\Omega_0)p(\Omega,t|\Omega_0,t_0) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\exp\left(-\frac{l(l+1)}{\tau_R}\right)\,Y_{lm}^*(\Omega_0)\,Y_{lm}(\Omega) \tag{44}$$

for example projection on z-direction (NMR/diel.)

$$P_3 = P_0\cos(\theta),\; l = 1\langle P_3\rangle = \frac{1}{4\pi}\int \mathrm{d}\Omega\, P_0\cos(\theta) \to 0 \tag{45}$$

?? correlation:

$$\begin{aligned}\langle P_3(t)P_3^*(t_0)\rangle &= P_0^2\int\mathrm{d}\Omega\int\mathrm{d}\Omega_0\cos(\theta)\cos(\theta_0)\,p(\Omega,t|\Omega_0,t_0)\,p_0(\Omega_0)\\ &= \frac{4\pi}{3}P_0^2\sum_{m=-l}^{l}\exp\left(-l(l+1)\frac{t-t_0}{\tau_r}\right)|C_{10lm}|^2\end{aligned} \tag{46}$$

$$C_{10lm} = \int \mathrm{d}\Omega\, Y^*_{10}(\Omega)\, Y_{lm}(\Omega) = \delta_{l1}\delta_{m0}\langle P_3(t)P^*_3(t_0)\rangle = \frac{4\pi}{3}\, P_0^2 \exp\left(-\frac{2(t-t_0)}{\tau_r}\right) \tag{47}$$

application in dielectric spectroscopy or NMR for example, $A_l m \rightarrow C_l m\, exp(-t/\tau_l)$ rotational diffusion of Janus particles

$$P_3 = P_0 \cos(\vartheta) \tag{48}$$

$l = 1$,Legendre projection on z-axis, NMR, DS

$$\langle P_3(t)P^*_3(t_0)\rangle = \frac{4\pi}{3}\, P_0^2 \exp\left(-\frac{2(t-t_0)}{\tau_r}\right) \tau_l = \frac{D_1}{D_{\mathrm{rot}} l(l+1)} n(\vartheta,\varphi,t) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}\, Y_l^m(\vartheta,\varphi) \exp\left(-\frac{t}{\tau_l}\right) \tag{49}$$

quadratic angular displacement

$$\langle|\hat{u}(t) - \hat{u}_0|^2\rangle = 2 - 2\langle\cos(\theta)\rangle \tag{50}$$

uˆis a unit vector

$$\frac{\mathrm{d}}{\mathrm{d}t} p(\theta,t) = D_r \nabla^2 p(\theta,t) 2\pi \int_0^{\pi} p(\theta,t)\sin(\theta)\,\mathrm{d}\theta = 1 \langle\cos(\theta)\rangle = 2\pi\int_0^{\pi} p\sin(\theta)\cos(\theta)\,\mathrm{d}\theta \tag{51}$$

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\langle\cos(\theta)\rangle &= 2\pi\int_0^{\pi}\frac{\partial p}{\partial t}\sin(\theta)\cos(\theta)\,\mathrm{d}\theta \\ &= 2\pi D_r \int_0^{\pi}\frac{1}{\sin(\theta)}\left[\frac{\partial}{\partial t}\left(\sin(\theta)\frac{\partial p}{\partial \theta}\right)\right]\sin(\theta)\cos(\theta)\,\mathrm{d}\theta \end{aligned} \tag{52}$$

0.1.3 Hydrodynamics