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Tutorial I
Einstein relation for the diffusion coefficient

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Einstein relation for the diffusion coefficient

We consider a system of N independent colloidal (dye or tracer) particles in a volume V of a solvent of viscosity $\eta \sim 10^{-3}$ Pa.s. We suppose that the density of these colloidal particles is low, so that they can be considered as independent from each other. We assume these particles are spheres of radius R of mass density $\rho = \rho_s + \Delta\rho$ slightly larger than ρ_s, the mass density of the solvent. The experiment takes place in the gravitational field $\boldsymbol{g}$ on Earth.

Sedimentation

1. Give a quantitative relation on N/V assessing this "low density regime".

   $V/N = v$ is the typical available volume for each colloid, the volume estimation where the colloid will be alone. The *low density regime* means that $v \gg R^3$ where R^3 is the colloid volume scale, thus,

   $$\frac{N}{V} \ll \frac{1}{R^3}$$

   $(V/N)^{1/3}$ is the average distance between one colloid and its nearest neighbor.

2. When the solvent and the colloid are at rest, what is $\boldsymbol{F}$ the total sum of forces exerted on the colloid ?

   $$\vec{F} = \sum \vec{f}$$

   Thus we have,

   $$\vec{P} = m_{\text{cell}}\vec{g}$$

   and the Archimedean pull (or buoyancy),

   $$\vec{\pi} = -m_{\text{fluid}}\vec{g}$$

   with

   $$m_{\text{fluid}} = \frac{4}{3}\pi R^3[\rho_s], \qquad m_{\text{coll}} = \frac{4}{3}\pi R^3[\rho_s + \Delta\rho]$$

   Thus,

   $$\vec{F} = \vec{P} + \vec{\pi} = \frac{4}{3}\pi R^3 \Delta\rho \vec{g}$$

3. When a colloid is moving with a constant velocity $\boldsymbol{v}$, a viscous force $\boldsymbol{F}_{\text{vis}} = -\zeta\boldsymbol{v}$ adds to $\boldsymbol{F}$. How is ζ related to the viscosity η of the fluid ? To which regime of velocity $\boldsymbol{v}$ is this formula adapted ?

We know that (6π is not universal but the R dependence on this regime is),

$$\zeta_{\text{Stokes}} = 6\pi\eta R$$

The Stokes regime (meaning where $\vec{F}_{\text{vis}} = -\zeta\vec{v}$ is valid) occurs when the Reynold number is little compared to 1,

$$\text{Reynolds} \sim \frac{vL}{\eta/\rho_{\text{fluid}}} \ll 1$$

where L is the typical size of the flow, but here it's nothing but R.

> **Example :** If we consider the Navier-Stokes equation,
>
> $$\rho\left[\partial_t\vec{v} + (\vec{v}\cdot\vec{\nabla})\vec{v}\right] = -\vec{\nabla}P + \eta\Delta\vec{v} + \rho\vec{g}$$
>
> this means that we consider that $(\vec{v}\cdot\vec{\nabla})\vec{v}$ is negligible (no quadratic term).

4. For a colloid of radius $\sim 10\ \mu$m, what is the typical time needed for the velocity to relax (*i.e.* to forget the initial condition) ? What is the typical displacement length during this time interval ? Show that acceleration term is negligible if the force is slowly spatially/temporally varying.

$$m\dot{\vec{v}} = \vec{F} - \zeta\vec{v}$$

we assume temporarily $\vec{F}$ constant. The solution to this equation is,

$$\vec{v}(t) = \frac{\vec{F}}{\zeta} + \vec{C}e^{-t/\tau}$$

with $\tau = m/\zeta$ and $\vec{C}$ a vectorial constant. If we impose that $\vec{v}(t=0) = \vec{v}_0$, this leads us to

$$\vec{C} = \vec{v}_0 - \frac{\vec{F}}{\zeta}$$

hence the full solution,

$$\vec{v}(t) = \frac{\vec{F}}{\zeta}\left(1 - e^{-t/\tau}\right)$$

for $t \ll \tau$, we have $\vec{v}(t) \sim \vec{v}_0$. For $t \gg \tau$, the exponential is negligible and thus,

$$\vec{v}(t) = \frac{\vec{F}}{\zeta} = \vec{v}_\infty$$

We see that τ is the crossover time. $t \gg \tau$ means that the initial condition has been forgotten.

$$\tau = \frac{m}{\zeta} \sim \frac{\frac{4}{3}\pi R^3 \rho_{\text{coll}}}{6\pi\eta R} \sim \frac{2}{9}\frac{\rho_{\text{coll}} R^2}{\eta} \sim 10^{-5}\ \text{s}$$

usually in soft-condensed matter physics, we often use $\rho_{\text{coll}} = 10^3$ kg.m^3.
We look for the typical displacement of a colloid. We need a velocity, we have two candidates for that, either v_∞, or the thermal velocity that is $v_{\text{th}} \sim \sqrt{k_B T/m_{\text{coll}}}$.

$$v_\infty = \frac{\frac{4}{3}\pi R^3 \Delta\rho g}{6\pi\eta R} \sim \frac{2}{9}\frac{R^2 \Delta\rho g}{\eta} \sim 10^{-5}\ \text{m.s}^{-1}$$

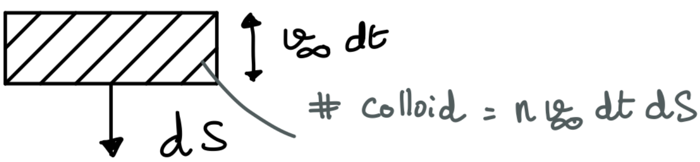
$$v_{\text{th}} = \sqrt{\frac{k_B T}{m_{\text{coll}}}} \sim \sqrt{\frac{10^{-23} \times 300}{\frac{4}{3}\pi R^3 \times 10^3}} \sim 10^{-5}\sqrt{10}\ \text{m.s}^{-1}$$

So we see that the two velocities are of the same order of magnitude. Thus the typical length visited by the colloid before reaching the asymptotic velocity (meaning loss of initial conditions) is

$$\text{typical length} = 10^{-5} \times \tau \sim 10^{-10}\ \text{m} = 1\ \text{Å}$$

This is of atomic scale. Clearly the inertia phenomena occurs on extremely small length-scale. If the particle experience a (slow) change of force, the acceleration will go to non-zero value, and thus changing the velocity. But it is at a such reduced scale that we can **neglect this acceleration** on the range of forces we are considering on this study.

5. Give the mesoscopic colloidal particle current $\boldsymbol{j}_{\text{drift}}(\boldsymbol{r}, t)$ resulting from the gravitational drift in terms of $n(\boldsymbol{r}, t)$ the colloid number density and a velocity $\boldsymbol{v}_\infty$ that will be precised.



$|\vec{j}_{\text{drift}}| \mathrm{d}S \mathrm{d}t$ is the number of particles crossing $\mathrm{d}\vec{S}$ pointing downwards during $\mathrm{d}t$,

$$|\vec{j}_{\text{drift}}| \mathrm{d}S \mathrm{d}t = n v_\infty \mathrm{d}t \mathrm{d}S$$

Thus,

$$\vec{j}_{\text{drift}} = n\vec{v}_\infty$$

6. If the mechanical actions on the colloid considered in this paragraph are all taken into account, the colloid particles settle at the bottom of the beaker. Estimate the sedimentation time if $\rho = 1.1\rho_s$.

   We can estimate it using a 10 cm beaker,

$$t_{\text{solution}} \sim \frac{10^{-1}}{10^{-5}} \sim 10^4 \text{ s}$$

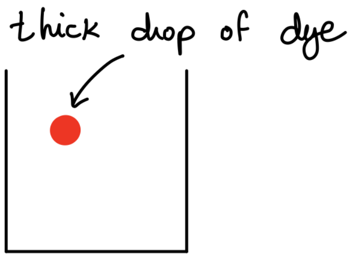
Fick's law and Einstein relation

In the XIXth century, Fick showed that an excess concentration of dispersed colloidal dye particles gives rise to a particle current given by the phenomenological law

$$\boldsymbol{j}_{\text{diff}} = -D\boldsymbol{\nabla} n$$

where D is called the diffusion coefficient.

1. Explain qualitatively why the Fick's term will counteract the gravitational drift.



Fick observed that the imbalance of dye concentration is responsible for the diffusion,

$$\vec{j}_{\text{diff}} = \vec{f}(\vec{\nabla} n)$$

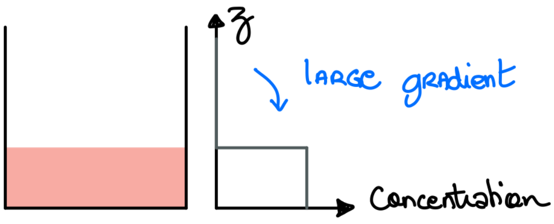
if there is no gradient, this current must vanish : $\vec{f}(\vec{\nabla} n = 0) = 0$. So if $\vec{\nabla} n$ is small we can expect a regular first order Taylor expansion of $\vec{f}$,

$$\vec{f}(\vec{\nabla} n) \overset{|\vec{\nabla} n| \ll 1}{\sim} \text{constant} \times \vec{\nabla} n$$

With only this phenomenological argument ; Fick arrived to

$$\vec{j}_{\text{diffusion}} = -D\vec{\nabla} n$$

the minus sign comes from the fact that the dye diffuse from large concentration region towards diluted region, so that $D > 0$. Pay attention to the fact that dye do not go far apart from each others due to repulsive interaction : they do not see each others in the dilute limit ($N/V \ll R^{-3}$ limit).



$\vec{j}_{\text{drift}}$ tends to build up concentration gradients (at the bottom), and diffusion replies by developing a diffusion current $\vec{j}_{\text{diffusion}}$ as vertical flux opposing $\vec{j}_{\text{drift}}$.

2. Assuming that the total particle current is $\boldsymbol{j} = \boldsymbol{j}_{\text{drift}} + \boldsymbol{j}_{\text{diff}}$ (why ?), find the equilibrium profile $n_{\text{eq}}(z)$.

   Why ? because the total current can be seen as a function $f(\rho\vec{v}_{\text{drift}}, -D\vec{\nabla}n)$ which, when we make a linear approximation will lead to $\alpha\rho\vec{v}_{\text{drift}} - \beta D\vec{\nabla}n$ and thus, by considering alone drift and diffusion, we get $\alpha = \beta = +1$.
   To find the equilibrium profile we say that $\vec{j} = \vec{0}$ and we find that,

   $$-D\vec{\nabla}n_{\text{eq}} + n_{\text{eq}}\vec{v}_{\infty} = \vec{0}$$

   We assume that $n_{\text{eq}} = n_{\text{eq}}(z)$ and thus,

   $$n_{\text{eq}}(z) = n_{\text{eq}}(0)\exp\left(-\frac{v_{\infty}}{D}z\right) = n_{\text{eq}}(0)\exp\left(-\frac{\frac{F}{\zeta}}{D}z\right)$$

3. Deduce the **Einstein relation**

   $$D = \frac{k_B T}{\zeta}$$

   which makes a connection between two phenomenological coefficients of different origins.

   It is related to the Boltzmann distribution. Signature of the equilibrium $k_B T$. Fluctuation-dissipation.

Microscopic origin of the diffusion

In the previous derivation, there is a slight apparent glitch in the reasoning. We assumed throughout that the velocity of the colloid is constant, but the Fickian diffusion shows that there must be an overlooked mechanical action at the level of colloids which changes their velocity and leads to diffusion.

Langevin proposed the dynamical equation

$$m\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \boldsymbol{F} - \zeta\boldsymbol{v} + \boldsymbol{F}_{\text{fluct}}$$

where the last term is a rapidly varying force of zero temporal average, different and uncorrelated for two distant colloids. This term accounts for the fluctuations of the force of the solvent due to the molecular nature of the fluid.

1. Find the dynamical equation obeyed by $\langle\boldsymbol{v}\rangle$, the mesoscopic local mean over the colloids.

   $\vec{F}$ is the external potential force where $-\zeta\vec{v} + \vec{F}_{\text{fluct}}$ is the total action of the fluid on the colloid. $\vec{F}_{\text{fluct}}$ is a zero mean, very rapidly varying and not space correlated. Clearly, the only possible microscopic mechanism for the diffusion is from $\vec{F}_{\text{fluct}}$.

Now we perform a mesoscopic space average, meaning we take a very small intermediate volume, meaning we have a large number of colloids $N \gg 1$, but the size is small enough such that $\vec{F}$ can be considered as a constant.
We perform an instantaneous average of the Langevin equation over such a mesoscopic $\mathrm{d}^3\tau$ volum,

$$m\frac{\mathrm{d}\langle\vec{v}\rangle}{\mathrm{d}t} = \vec{F} - \zeta\langle\vec{v}\rangle + \underbrace{\langle\vec{F}_{\text{fluct}}\rangle}_{\mathcal{O}(1/\sqrt{N})\sim 0}$$

Which is the same equation we consider on the first part of this exercise sheet. This explain why it was correct to neglect the noise contribution in that first part.
Now, we can also perform a *modest* time average and consider that,

$$\langle\bar{v}\rangle(t) = \frac{1}{\tau}\int_t^{t+\tau} \mathrm{d}t\langle v\rangle(t)$$

with this modest sliding average the high-frequency features associated to acceleration disappears. And thus,

$$\langle\bar{v}\rangle \approx \frac{\vec{F}}{\zeta}$$

2. Show that the inertia (*i.e.* all phenomena associated to the term "mass×acceleration" in the Newton's law) is as surmised before negligible for $\langle\boldsymbol{v}\rangle$. What about the individual velocities ?

3. Conclude about the possible origin of the Fick's diffusion term.

   The only reasonable candidate is $\vec{F}_{\text{fluct}}$,

4. The Einstein relation is called a "fluctuation-dissipation relation". Why ?

   D is associated with the dissipation, and ζ is the friction term, it shows how energy is degraded, the possible kinetic energy of the colloid, which is mesoscopic ordered energy, a low-entropy energy. This energy is sucked out of the colloid and disperse into thermal degree of freedom.

   $$D = \frac{k_B T}{\rho}$$

   They both speak about the interaction of the colloid with the solvent.

Non-stationary state : the Smoluchowski equation

1. In the non-stationary regime the total current $\boldsymbol{j} = j_z \boldsymbol{e_z}$ does not vanish. Show that j_z can be written in the following form (with $U = (\frac{4}{3}\pi R^3 \Delta\rho) g z$)

$$j_z(z,t) = \rho(z,t) v_f(z,t) \quad \text{with} \quad v_f(z,t) = -\frac{1}{\zeta}\frac{\partial}{\partial z}\left[k_B T \ln \rho(z,t) + U(z)\right]. \tag{1}$$

Here, $v_f(z,t)$ is sometimes called "current velocity". To which thermodynamic quantity does the expression in the angular brackets $[\cdots]$ correspond ?

In this regime, since we are out-of-equilibrium,

$$\vec{j}_{\text{tot}} = \vec{j}_{\text{drift}} + \vec{j}_{\text{diff}} \neq \vec{0}$$

$$\vec{j}_{\text{drift}} = \rho(\vec{r},t)\langle\bar{v}\rangle(\vec{r}) = \rho(\vec{r},t)\frac{\vec{F}(\vec{r},t)}{\zeta}$$

$$\vec{j}_{\text{diff}} = -D\vec{\nabla}\rho = -\frac{k_B T}{\zeta}\rho\vec{\nabla}(\ln\rho)$$

Thus,

$$\vec{j}_{\text{tot}} = \rho\left[\frac{\vec{F}}{\zeta} - \frac{k_B T}{\zeta}\vec{\nabla}(\ln\rho)\right]$$

$\vec{F} = -\vec{\nabla}U$ and so,

$$\vec{j} = -\frac{\rho}{\zeta}\vec{\nabla}\left[U + k_B T \ln\rho\right]$$

The quantity $k_B T \ln\rho + U$ correspond to the excess of chemical potential of the colloids particles.

2. Utilize now the continuity equation relating ρ and $\boldsymbol{j}$ to derive the Smoluchowski equation

$$\frac{\partial\rho(z,t)}{\partial t} = -\frac{\partial}{\partial z}\left[\left\{-\frac{1}{\zeta}\frac{\partial U(z)}{\partial z}\right\}\rho(z,t)\right] + D\frac{\partial^2\rho(z,t)}{\partial z^2}. \tag{2}$$

This equation is of general validity (*i.e.* whatever $U(z)$) and describes the evolution of the density of a low-density population of colloids or (equivalently) the probability of a single tracer, via the ergodic hypothesis.

We have also the conservation equation,

$$\frac{\partial\rho}{\partial t} + \text{div}(\vec{j}) = 0$$

and this leads to Eq. (2).