

## Diffusion & Mobility

(1-dimension)

$f$  = force of gravity

Viscous drag

$$= 6\pi\eta r v_0 \leftarrow \text{"Stokes law"}$$

When this external force  $f$

balances the viscous drag, then  
the particle moves with the  
constant velocity  $v_0$

If  $\nu$  is the number of particles  
per unit volume, then  $\nu v_0 \rightarrow$  no. of  
particles passing through a unit area per unit time

○ Spherical particle of radius  $r$   
is moving under the force  
of gravity in a liquid.

↓  
Coefficient of  
viscosity " $\eta$ "

$$f = 6\pi\eta r v_0$$

$$v_0 = \frac{f}{6\pi\eta r}$$

$$\Rightarrow \frac{\nu f}{6\pi\eta r}$$

$-D \frac{\partial v}{\partial x} \rightarrow$  Fick's law (first law)  
 ↳ "Diffusion flux"  
 ↳ no. of particles per unit area per unit time

$$-D \frac{\partial v}{\partial x} = \frac{f}{6\pi\eta r}$$

$$-\int_{v_0}^v \frac{dv'}{v'} = \frac{f}{(6\pi\eta r D)} \int_{x_0}^x dx'$$

$$\Rightarrow \ln(v/v_0) = -\frac{f}{6\pi\eta r D} (x - x_0)$$

$$\Rightarrow v = v_0 e^{-\frac{f(x-x_0)}{6\pi\eta r D}} \quad \dots \text{II}$$

$D \rightarrow$  "Diffusion coefficient"  
 $f \rightarrow$  force due to gravity  
 Boltzmann distribution of  $v$  (Density)

$$v = v_0 \exp \left[ -\frac{f(x-x_0) N_A}{RT} \right] \quad \dots \text{I}$$

Comparing I & II

$$\frac{N_A}{RT} = \frac{1}{6\pi\eta r D}$$

$$B = \frac{1}{6\pi\eta r} \rightarrow \text{Mobility}$$

$$D = \frac{RT}{N_A} \cdot B$$

$$D = k_B T B$$

$$D = \frac{k_B T}{6\pi\eta r} \downarrow \text{Stokes-Einstein relation}$$

## Determination of Avagadro's number:

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta r}$$

$$\lambda_x = \sqrt{2Dt}$$

$$\lambda_x = \sqrt{2t} \left( \frac{RT}{N_A} \right)^{\frac{1}{2}} \left( \frac{1}{6\pi\eta r} \right)^{\frac{1}{2}}$$

↳ to find  $N_A$

$$\begin{aligned}\langle x^2 \rangle &= 2Dt \\ \sqrt{\langle x^2 \rangle} &= \sqrt{2Dt} \\ &\downarrow \\ \lambda_x &\end{aligned}$$

Experimentally

can be measured

$\eta \rightarrow$  known for liquids

At the single particle level



$$m \frac{dv}{dt} = -6\pi\eta r v \quad \text{Force} \quad (\text{Newton's equation})$$

$$v = v_0 e^{-\frac{6\pi\eta r}{m} t}$$

$$\ln(v/v_0) = -\frac{6\pi\eta r}{m} t$$

$$t_{1/10} \equiv v/v_0 = \frac{1}{10}$$

$$\ln 10 = \frac{6\pi\eta r}{m} t_{1/10}$$

$$\Rightarrow t_{1/10} = 3.3 \times 10^{-7} \text{ sec}$$

$$\sim 10^{-7} \text{ sec}$$

Within very short time the particle nearly  
completely loses its original velocity ]  $\rightarrow$  In reality it  
does not happen!!

Platinum  
particles

$$r = 2.5 \times 10^{-6} \text{ cm}$$

$$\eta = 0.01 \text{ poise}$$

(water)

$$m = 2.5 \times 10^{-15} \text{ g}$$

$$m \frac{dv}{dt} = -6\pi\eta r v + F(t)$$

random kicks  
 ↘ random function  
 of time = Noise

$$\langle F(t) \rangle = 0$$

$$\langle F(t) F(t') \rangle = 2C' \delta(t-t')$$

1908

Langevin eqn

"Paul Langevin"

$$m \ddot{x} = -6\pi\eta r \dot{x} + F(t)$$

Multiplying both sides by  $x$

$$\begin{aligned}\dot{x} &= v \\ \ddot{x} &= \dot{v} = \frac{dv}{dt}\end{aligned}$$

$$m x \ddot{x} = -6\pi\eta r x \dot{x} + x F(t)$$

$$\Rightarrow x \ddot{x} = -\frac{6\pi\eta r}{m} x \dot{x} + \frac{1}{m} x F(t)$$

$$x \ddot{x} = -\Gamma x \dot{x} + \frac{1}{m} x F(t)$$

$$\frac{1}{2} \ddot{x^2} - (\dot{x})^2 = -\Gamma x \dot{x} + \frac{1}{m} x F(t)$$

$$\Rightarrow \ddot{x^2} - 2(\dot{x})^2 = -2\Gamma x \dot{x} + \frac{2}{m} x F(t)$$

$$\Rightarrow \ddot{x^2} - 2(\dot{x})^2 = -\Gamma \dot{x^2} + \frac{2}{m} x F(t) \Rightarrow \frac{d^2(x^2)}{dt^2} - 2\left(\frac{dx}{dt}\right)^2 = \dots \dots$$

Taking the averages on both sides

$$\frac{d^2}{dt^2} \langle x^2 \rangle - 2 \langle \dot{x}^2 \rangle = -\Gamma \frac{d}{dt} \langle x^2 \rangle + \frac{2}{m} \langle x F(t) \rangle$$

↓
{
} zero (position  
and the  
random  
force are  
uncorrelated)

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and the  
random  
force are  
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$$\dot{x^2} = \frac{d}{dt} (x^2)$$

$$= 2x\dot{x}$$

$$\ddot{x^2} = \frac{d^2}{dt^2} (x^2)$$

$$= \frac{d}{dt} (2x\dot{x})$$

$$\ddot{x^2} = 2(\dot{x})^2 + 2x\ddot{x}$$

$$\Rightarrow x \ddot{x} = \frac{1}{2} \ddot{x^2} - (\dot{x})^2$$

$$\frac{d}{dt} \langle x^2 \rangle + \Gamma \frac{d}{dt} \langle x^2 \rangle - 2 \frac{k_B T}{m} = 0$$

$$\dot{y} + \Gamma y - c = 0$$

Let,  $\Gamma y - c = y'$  (not derivative)

$$\dot{y} = -y' \Rightarrow \dot{y} = \frac{1}{\Gamma} \dot{y}'$$

$$\dot{y}' = \Gamma \dot{y} + 0$$

$$\dot{y}' = \Gamma \dot{y}$$

$$\dot{y}' = -\Gamma y' \quad (\text{as } \dot{y} = -y')$$

$$\Rightarrow \frac{dy'}{dt} = -\Gamma y'$$

$$\Rightarrow \int \frac{dy'}{y'} = -\Gamma \int dt$$

$$y'(t=0) \Rightarrow$$

Let,  $\frac{d}{dt} \langle x^2 \rangle = y$

$$\frac{2k_B T}{m} = c$$

$$\dot{x} = -\Gamma x$$

$$y' = A e^{-\Gamma t}$$

$$A = y'(t=0)$$

$$\gamma - c = \gamma' = A e^{-\Gamma t}$$

$$y = \frac{d}{dt} \langle x^2 \rangle$$

$$\Rightarrow y = \frac{c}{\Gamma} + \frac{A}{\Gamma} e^{-\Gamma t}$$

$$\frac{d}{dt} \langle x^2 \rangle = \frac{c}{\Gamma} + \frac{A}{\Gamma} e^{-\Gamma t}$$

Integrating

$$\langle x^2 \rangle = \frac{c}{\Gamma} t + \frac{A}{\Gamma} \int_0^t e^{-\Gamma t'} dt'$$

$$\langle x^2 \rangle = \frac{c}{\Gamma} t + \frac{A}{\Gamma} \left[ \frac{e^{-\Gamma t'}}{-\Gamma} \right]_0^t = \frac{c}{\Gamma} t + \frac{A}{\Gamma^2} (1 - e^{-\Gamma t})$$

$$\langle x^2 \rangle = \frac{c}{\Gamma} t + \frac{A}{\Gamma^2} (1 - e^{-\Gamma t})$$

$$y'(0) = A$$

$$\Gamma y(0) - c \leq A$$

$$y(0) = \left( \frac{d}{dt} \langle x^2 \rangle \right)_{t=0} = 0$$

$$A = -c$$

$$\langle x^2 \rangle = \frac{c}{\tau} t + \frac{(-c)}{\tau \nu} (1 - e^{-\tau t})$$

$$c = \frac{2k_B T}{m}$$

$$\langle x^2 \rangle = \frac{2k_B T}{m \tau} t - \frac{2k_B T}{m \tau^2} (1 - e^{-\tau t})$$

general expression  
for the mean  
square displacement  
of a Brownian  
particle suspended  
in a fluid  
(no external force)

When  $t \rightarrow \infty$  (long time limit)

$$\langle x^2 \rangle = \frac{2k_B T}{m \tau} t - \frac{2k_B T}{m \tau^2} (1 - 0)$$

$$\langle x^2 \rangle \approx \frac{2k_B T}{m \tau} t = \frac{2k_B T}{m \frac{6\pi r}{m}} t = 2 \left( \frac{k_B T}{6\pi r m} \right) t$$

$$\langle x^2 \rangle = 2 D t$$

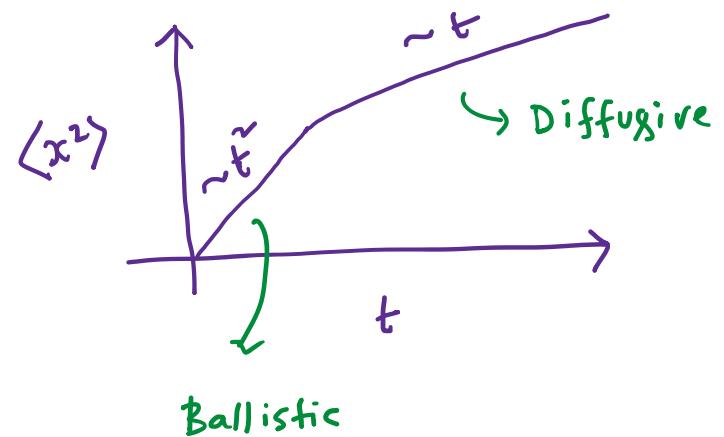
$$\langle x^2 \rangle = \frac{2k_B T}{m \tau} t - \frac{2k_B T}{m \tau^2} \left( 1 - \left( 1 - \tau t + \frac{\tau^2 b^2}{2!} + \dots \right) \right)$$

$t \rightarrow 0$  (short time limit)

$$\langle x^2 \rangle = \frac{2k_B T}{m\gamma} t - \frac{2k_B T}{m\gamma^2} \left( x - \gamma + \Gamma t - \frac{\Gamma^2 t^2}{2} \dots \right)$$

$$= \cancel{\frac{2k_B T}{m\gamma} t} - \cancel{\frac{2k_B T}{m\gamma^2} \left( x - \gamma \right)} + \frac{k_B T}{m} t^2 \dots$$

$$\langle x^2 \rangle = \frac{k_B T}{m} t^2 \rightarrow \text{Ballistic} \rightarrow \text{inertia driven}$$



A Langevin description without inertia (large viscosity limit).

$$6\pi\eta r \dot{x} = F(t) \rightarrow \langle x^2 \rangle \sim t$$

"no ballistic"