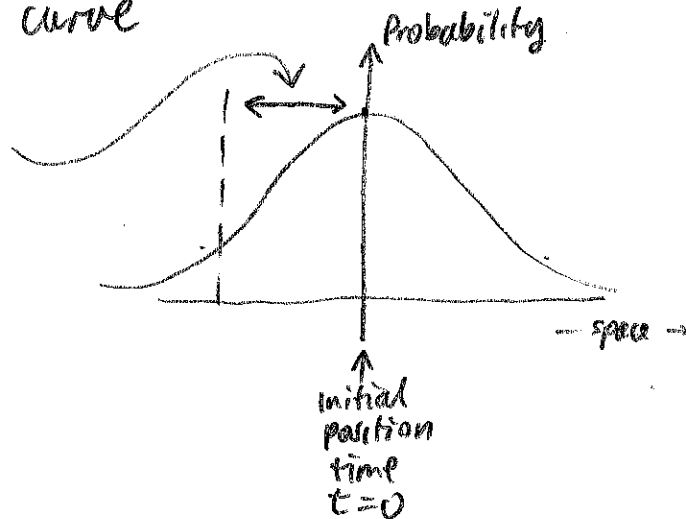


A. Einstein, "On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat"

1905

Principal Result

According to molecular kinetic theory of heat, small particles radius  $P$  (spherical) diffuse through liquid on an error ("bell") curve



Variance =  $2Dt$

$\lambda_c$  = root mean square displacement  
 $= \sqrt{2Dt}$

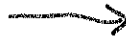
Diffusion coefficient

$$D = \frac{RT}{N 6\pi k P}$$

↑ ideal gas constant  
 ↑ Avogadro's number  
 ↑ viscosity water

Uses: Test of kinetic theory

particles size 0.001mm



Predict Displacement in one minute 6 microns

Determine  $N$

observe displacement in time  $t$

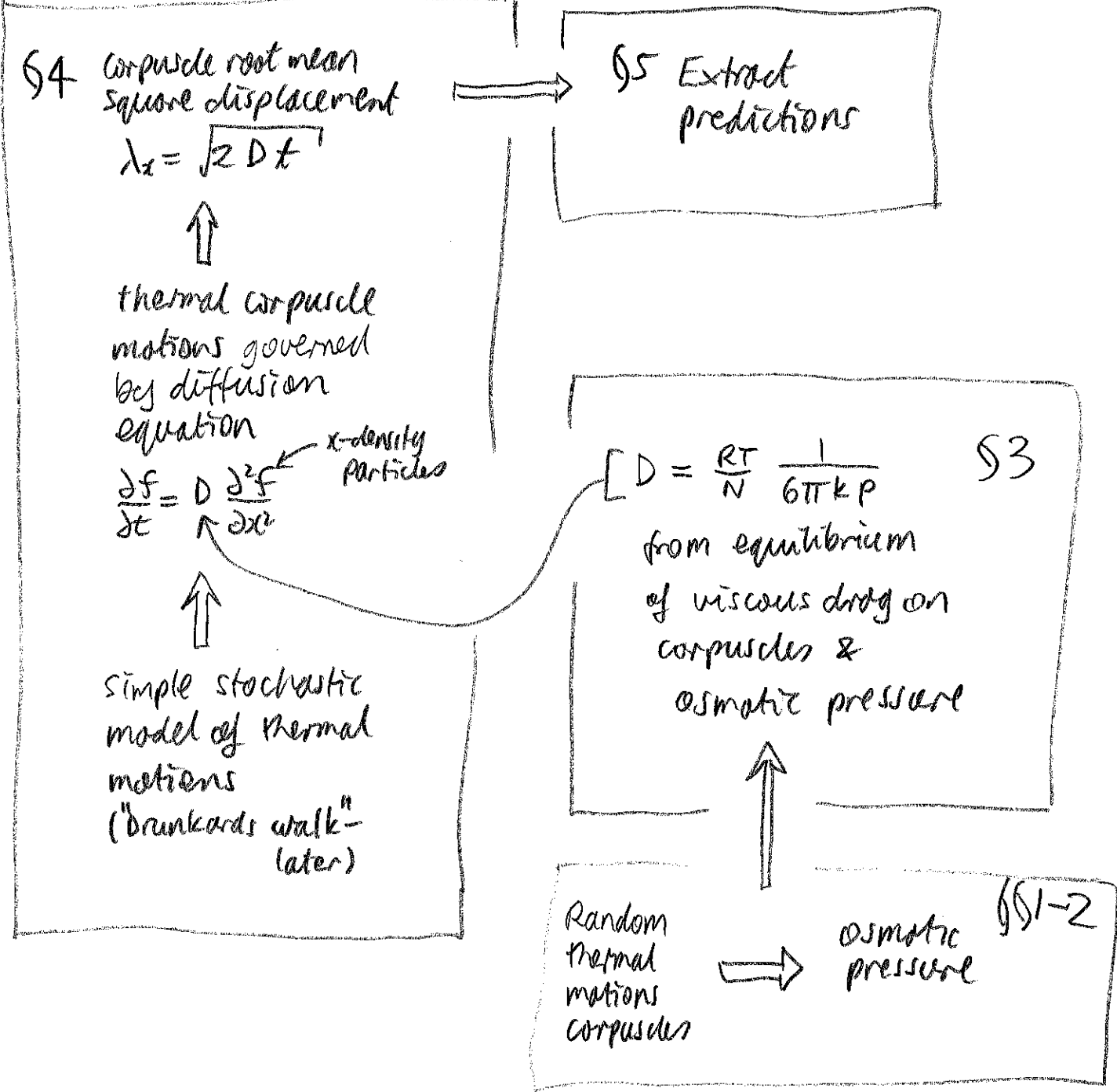


$$N = \frac{t}{\lambda_c^2} \cdot \frac{RT}{3\pi k P}$$

NB Displacement  $\propto \sqrt{\text{time}}$   $\Rightarrow \lim_{\text{time} \rightarrow \infty} \left( \frac{\text{displacement}}{\text{time}} \right) \rightarrow 0$

Average velocity over long time not useful

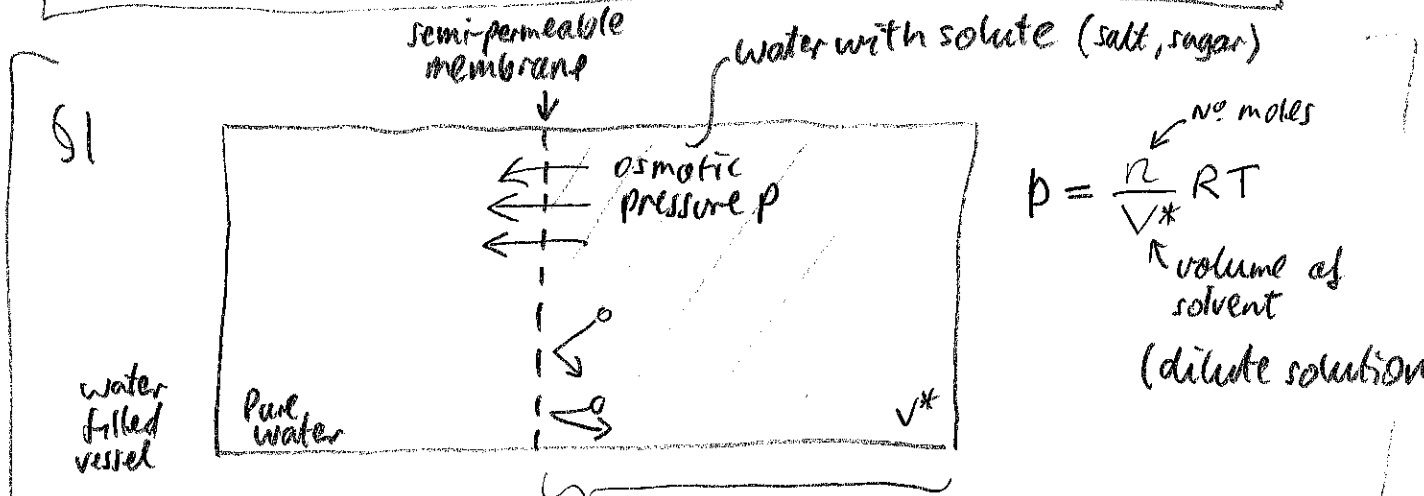
# Structure of Paper



Hidden treasure of paper

000  
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# Osmotic Pressure



$$p = \frac{n}{V^*} RT$$

no moles

volume of solvent

(dilute solutions)

solute = v. small molecules bouncing around

Expect slightly larger corpuscles to do same

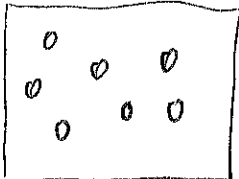
↓

Exercise osmotic pressure obeying same law

$$p = \frac{n}{V^*} RT$$

Q2 Very general demonstration that covers ideal gases, solutes, suspended particles

Result shown in §2



n corpuscles in volume V\*

Each configuration equally likely

corpuscles exert pressure

$$p = \frac{n}{V^*} RT$$

From earlier work in statistical mechanics:

Entropy of system of n corpuscles

$$S = \frac{\bar{E}}{T} + k \ln \int \exp(-E/kT) dp_1 \dots dp_l$$

mean energy

k = Boltzmann's constant  
 = R/N  
 = Einstein's 2k

p<sub>1</sub> ... p<sub>l</sub> are variables of state of corpuscles

Free energy  $F = E - TS = -kT \ln \int \exp(-E/kT) dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n$

x<sub>i</sub>, y<sub>i</sub>, z<sub>i</sub> = Cartesian coords of centers mass of corpuscles



Each configuration equally likely

uniform distribution of probability over x<sub>i</sub>, y<sub>i</sub>, z<sub>i</sub> space

$$J = \exp(-E/kT)$$

independent of x<sub>i</sub>, y<sub>i</sub>, z<sub>i</sub>

statistical physics: canonical probability density.

↓

$$F = -kT \ln \left[ J \int \overbrace{dx_1 \dots dx_n}^{\text{volume } (V^*)^n} \right] = -kT [\ln J + n \ln V^*]$$

↑  $R/N$



Pressure  $p = -\frac{\partial F}{\partial V} \Big|_T$  since:

For a reversible, iso thermal expansion

$$dF = dE - Tds = \underbrace{dQ - PdV}_{\text{heat-work}} - \underbrace{Tds}_{\substack{\text{Reversible process} \\ \frac{dQ}{T} = ds}} = -pdV$$

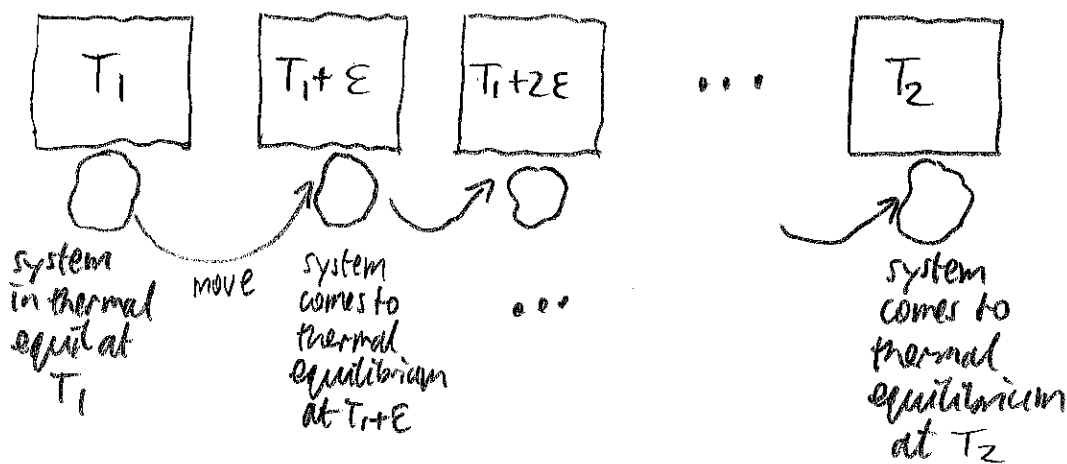
$$\begin{aligned} \text{Pressure } p &= -\frac{\partial F}{\partial V} \Big|_T = +kT \frac{\partial}{\partial V} (\ln + n \ln V^*) = +kT \frac{n}{V^*} \\ &= \frac{RT}{V^*} \left( \frac{n}{N} \right) \leftarrow \begin{matrix} \text{No} \\ \text{moles} \end{matrix} \end{aligned}$$

↑  $R/N$

\* Derivation of  $S = \frac{E}{T} + k \ln \int e^{-E/kT} dp_1 \dots dp_l$   
 after the manner of Einstein's 1902-1904  
 papers in foundations of statistical  
 mechanics.

NB  
 Boltzmann  
 $k$   
 $=$   
 Einstein's  
 $2k$

Entropy change in reversible heating:



Series of large  
 heat baths v.  
 close in temp.  
 span temp  
 range  $T_1$  to  $T_2$

Overall effect = reversible heating of  
 system from  $T_1$  to  $T_2$

By definition, entropy change  $ds = \frac{dQ}{T}$  (heat added = energy gained)

At any moment  
 in process

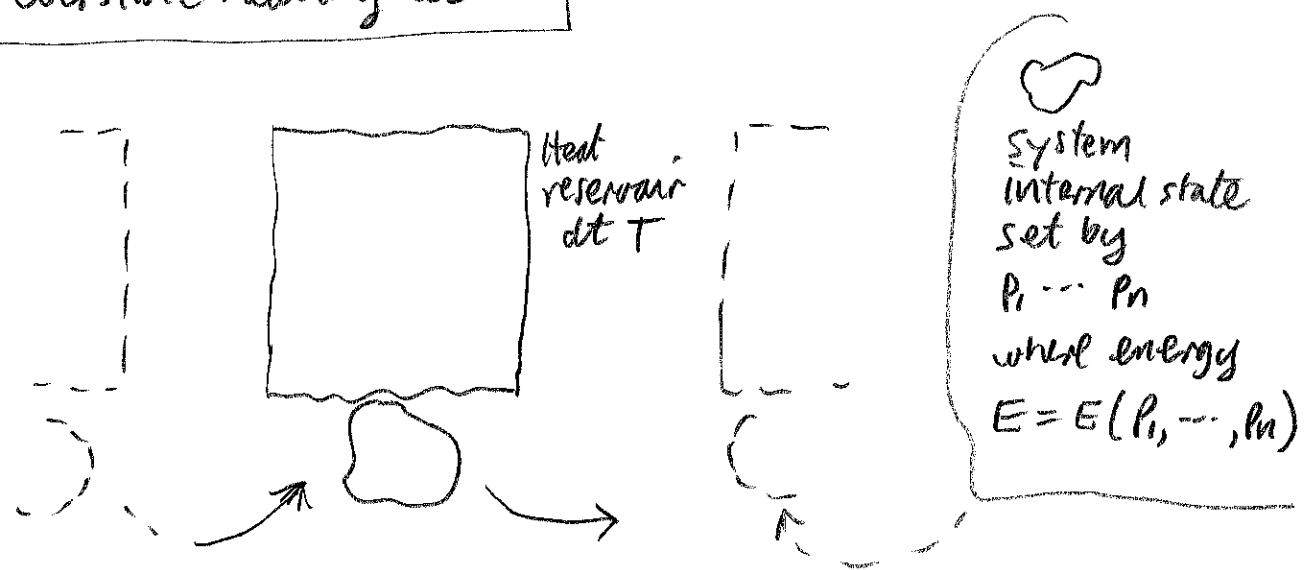
$$\frac{ds}{dt} = \frac{1}{T} \frac{dQ}{dt} = \frac{1}{T} \frac{d(\text{Energy system})}{dt}$$

↑  
time



Oops! Proof incomplete: To assure generality, must take process in  
 which both heat transfer & work done. See standard  
 derivation in textbooks!

model reversible heating as:



system comes to equilibrium.

Energy is canonically distributed:

$$\left( \begin{array}{l} \text{Probability system} \\ \text{in state} \\ p_1 \dots p_n \text{ to} \\ p_1 + dp_1 \dots p_n + dp_n \end{array} \right) \propto \exp(-E/k) dp_1 \dots dp_n$$

Hence show for reversible heating (see over)

↙ mean energy

$$\frac{1}{T} \frac{d\bar{E}}{dt} = \frac{d}{dt} \left( \frac{\bar{E}}{T} + k \ln \left( \exp(-E/kT) dp_1 \dots dp_n \right) \right) \quad \dots \dots \quad (1)$$

$$\underbrace{\frac{ds}{dt}}$$

$$\therefore S = \frac{\bar{E}}{T} + k \ln \left( \exp(-E/kT) dp_1 \dots dp_n \right) + \underbrace{\text{constant}}_{\substack{\text{set to zero since} \\ \text{defined up to} \\ \text{additive} \\ \text{constant}}}$$

Proof of (1)

For canonical distribution of system internal states

$$1 = \int \exp(C - E/kT) dp_1 \dots dp_n \quad (\text{normalization of probability})$$

↑  
normalization  
constant

↓  
 $d/dt$

$$0 = \frac{d}{dt} \left( \int \exp(C - E/kT) dp_1 \dots dp_n \right) = \int \frac{d}{dt} \exp(C - E/kT) dp_1 \dots dp_n$$

$$= \int \left( \frac{dC}{dt} - E \frac{d}{dt} \left( \frac{1}{kT} \right) \right) \exp(C - E/kT) dp_1 \dots dp_n$$

since  $E = E(p_1, \dots, p_n)$   
 $\downarrow$   
 $\frac{dE}{dt} = 0$   
 But - beware! -  $\frac{d\bar{E}}{dt} \neq 0$

$$\therefore 0 = \frac{dC}{dt} \underbrace{\left( \int \exp(C - E/kT) dp_1 \dots dp_n \right)}_1 - \frac{d}{dt} \left( \frac{1}{kT} \right) \underbrace{\left( \int E \exp(C - E/kT) dp_1 \dots dp_n \right)}_{\bar{E}}$$

$$0 = \frac{dC}{dt} - \bar{E} \frac{d}{dt} \left( \frac{1}{kT} \right)$$

$$\therefore \frac{1}{kT} \frac{d\bar{E}}{dt} = \frac{1}{kT} \frac{d\bar{E}}{dt} + \bar{E} \frac{d}{dt} \left( \frac{1}{kT} \right) - \frac{dC}{dt}$$

$$\frac{1}{k} \frac{d}{dt} \left( \frac{\bar{E}}{T} \right)$$

$$\therefore \frac{1}{T} \frac{d\bar{E}}{dt} = \frac{d}{dt} \left( \frac{\bar{E}}{T} - kC \right)$$

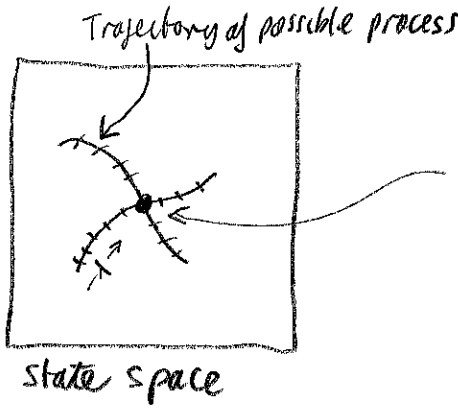
$$= \frac{d}{dt} \left( \frac{\bar{E}}{T} + k \ln \int \exp(-E/kT) dp_1 \dots dp_n \right)$$

$1 = \int \exp(C - E/kT) dp_1 \dots dp_n$   
 $= \exp(C) \int \exp(-E/kT) dp_1 \dots dp_n$   
 $\therefore 0 = C + \ln \int \exp(-E/kT) dp_1 \dots dp_n$   
 $\therefore C = -\ln \int \exp(-E/kT) dp_1 \dots dp_n$



# Free Energy $F$ & conditions for equilibrium

condition for equilibrium



For ISOLATED process

Reversible  $\Rightarrow$  entropy  $S$  is constant  $\Rightarrow dS = 0$  or  $\frac{dS}{d\lambda} = 0$

$\lambda$  path parameter for possible process

For process in heat bath kept at temperature  $T$

Reversible  $\Rightarrow dS = \frac{dQ_{rev}}{T} \Rightarrow dE - TdS = 0$

$dQ_{rev} = dE$  (change in energy)

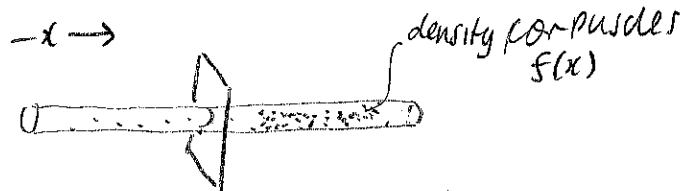
$\therefore d(E - TS) = 0$   $T$  constant

$\therefore dF = 0$   $F = E - TS$

or  $\frac{dF}{d\lambda} = 0$

# Diffusion

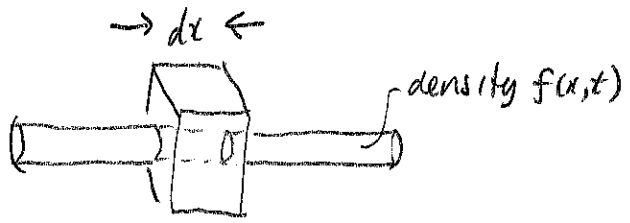
(one dimensional) law of diffusion



$$(\text{Rate transport corpuscles}) = -D \left( \text{gradient of corpuscle density} \right)$$

$$\frac{\partial f}{\partial x}$$

(one dimensional) diffusion equation



Rate accumulation corpuscles in  $dx$  = Rate corpuscles enter at  $x+dx$  - Rate corpuscles leave at  $x$

$$\frac{\partial}{\partial t} \{ f(x,t) dx \} = D \frac{\partial}{\partial x} f(x+dx,t) - D \frac{\partial f(x,t)}{\partial x}$$

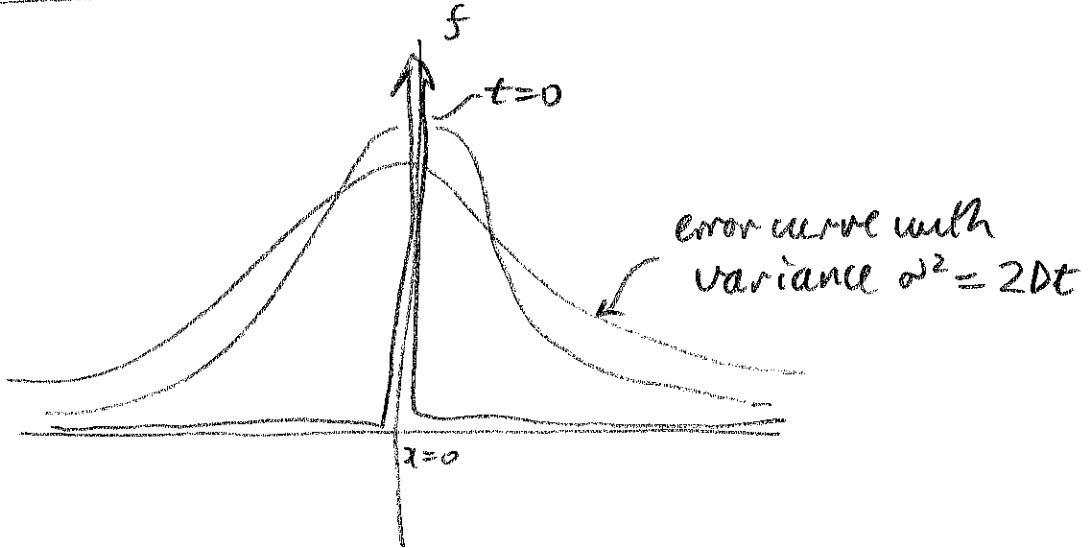
$$\frac{\partial f(x,t)}{\partial t} = D \frac{1}{dx} \left( \frac{\partial f(x+dx,t)}{\partial x} - \frac{\partial f(x,t)}{\partial x} \right) \rightarrow D \frac{\partial^2 f}{\partial x^2}$$

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

Physical contingency

The linearity of this relation is a physical assumption that must be established.

Diffusion equation  $\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}$  solved by  $f(x,t) = n \cdot \frac{1}{\sqrt{2\pi t}} \cdot \frac{1}{\sqrt{2Dt}} e^{-\frac{x^2}{2(2Dt)}}$



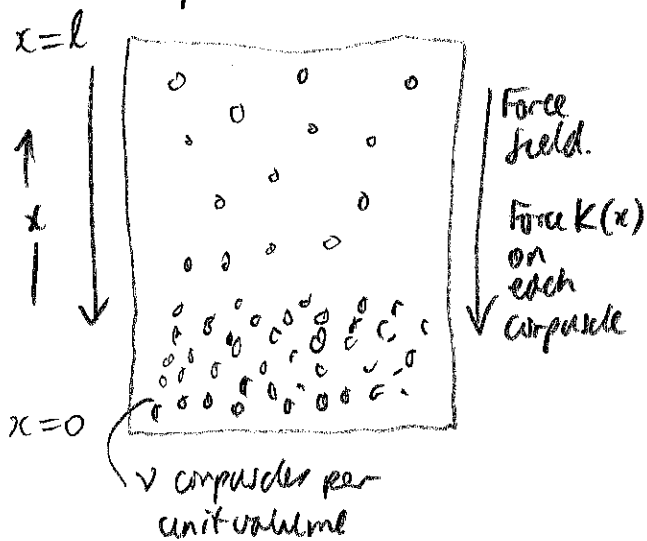
$\frac{\partial f}{\partial t} = \dots$

Left as editing exercise!

$D \frac{\partial^2 f}{\partial x^2} = \dots$

§3  $D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta R}$  for spherical corpuscles of radius  $R$  in fluid of viscosity  $\eta$

Equilibrium distribution of corpuscles



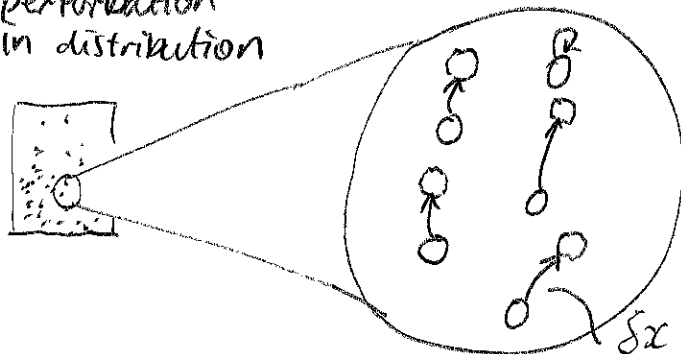
Treat corpuscle density distribution  $\nu$  as a thermodynamic quantity.

condition for equilibrium

$$\delta F = \delta E - T\delta S = 0$$

Free energy  $F = E - TS$

any isothermal perturbation in distribution



$$\delta E = - \int_0^l K \nu \delta x \, dx$$

since energy change for each corpuscle is  $-K\delta x$

$$\delta S = \int_0^l R \frac{\nu}{N} \frac{\partial}{\partial x} (\delta x) \, dx = \frac{R}{N} \int_0^l \frac{\partial}{\partial x} (\nu \delta x) \, dx - \frac{R}{N} \int_0^l \frac{\partial \nu}{\partial x} \cdot \delta x \, dx = - \int_0^l \frac{R}{N} \frac{\partial \nu}{\partial x} \cdot \delta x \, dx$$

JON WHY?

$\frac{R}{N} (\nu \delta x) \Big|_0^l = 0$   
since  $\delta x = 0$  at  $x=0, x=l$

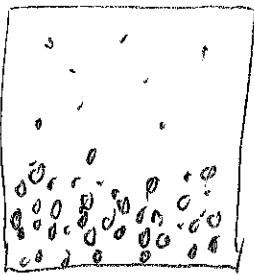
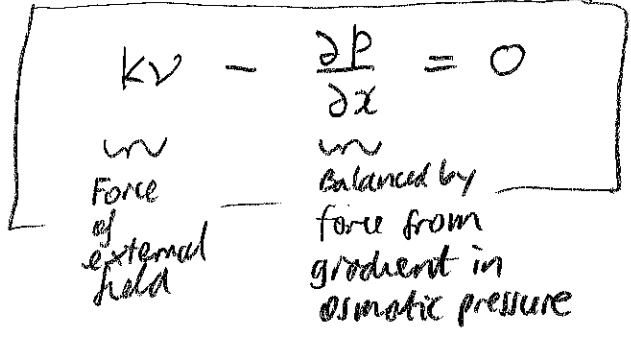
Combining:

$$0 = \delta F = \delta E - T \delta S = - \int_0^l K v \delta x dx + \int_0^l \frac{RT}{N} \frac{\partial v}{\partial x} \delta x$$

$$= \int_0^l \left( -Kv + \frac{RT}{N} \frac{\partial v}{\partial x} \right) \delta x dx$$

$\therefore -Kv + \frac{RT}{N} \frac{\partial v}{\partial x} = 0$  --- (1)

$p = \frac{RTv}{N}$



- Particle flux due to  $K$

$$\frac{vK}{6\pi k p}$$

= Particle flux due to diffusion

$$= -D \frac{\partial v}{\partial x}$$

caused by random thermal motion

--- (2)

Stokes law:

$$K = 6\pi k p v$$

$\uparrow$   
velocity of particle

Eliminate  $\frac{\partial v}{\partial x}$  from (1) & (2)

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi k p}$$

§4 simple stochastic model for thermal motions  $\longrightarrow$  root mean displacement of corpuscles  $= \sqrt{2Dt}$

In time interval  $\tau$  large enough so successive displacements are probabilistically independent

probability density corpuscle x-coordinate changes by  $\Delta = \varphi(\Delta)$  where  $\int_{-\infty}^{\infty} \varphi(\Delta) d\Delta = 1$   
 $\varphi(\Delta) = \varphi(-\Delta)$

$f(x,t)$  = density particles at  $x$  at time  $t$ .  
 show it is governed by diffusion equation  $\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}$

Density at  $t+\tau$  satisfies  $f(x, t+\tau) = \int_{-\infty}^{+\infty} f(x+\Delta, t) \cdot \varphi(\Delta) d\Delta$  more natural to say  $\varphi(-\Delta)$ . But  $\varphi(\Delta) = \varphi(-\Delta)$ .

power series in  $\tau$   $\downarrow$

$f(x, t)$   
 $+$   
 $\frac{\partial f(x, t)}{\partial t} \cdot \tau$   
 $+$   
 $\vdots$

power series in  $\Delta$   $\downarrow$

$f(x, t) \int_{-\infty}^{\infty} \varphi(\Delta) d\Delta = 1$   
 $+$   
 $\frac{\partial f(x, t)}{\partial x} \int_{-\infty}^{\infty} \Delta \varphi(\Delta) d\Delta = 0$   
 $+$   
 $\frac{\partial^2 f(x, t)}{\partial x^2} \cdot \int_{-\infty}^{\infty} \frac{1}{2} \Delta^2 \varphi(\Delta) d\Delta$   
 $+$   
 $\vdots$

Setting lowest order terms equal

$$f(x,t) + \frac{\partial f(x,t)}{\partial t} \cdot \tau = f(x,t) + \frac{\partial^2 f(x,t)}{\partial x^2} \underbrace{\left( \frac{1}{2} \int_{-\infty}^{\infty} \Delta^2 \varphi(\Delta) d\Delta \right)}_{\text{DEFINE as } D}$$

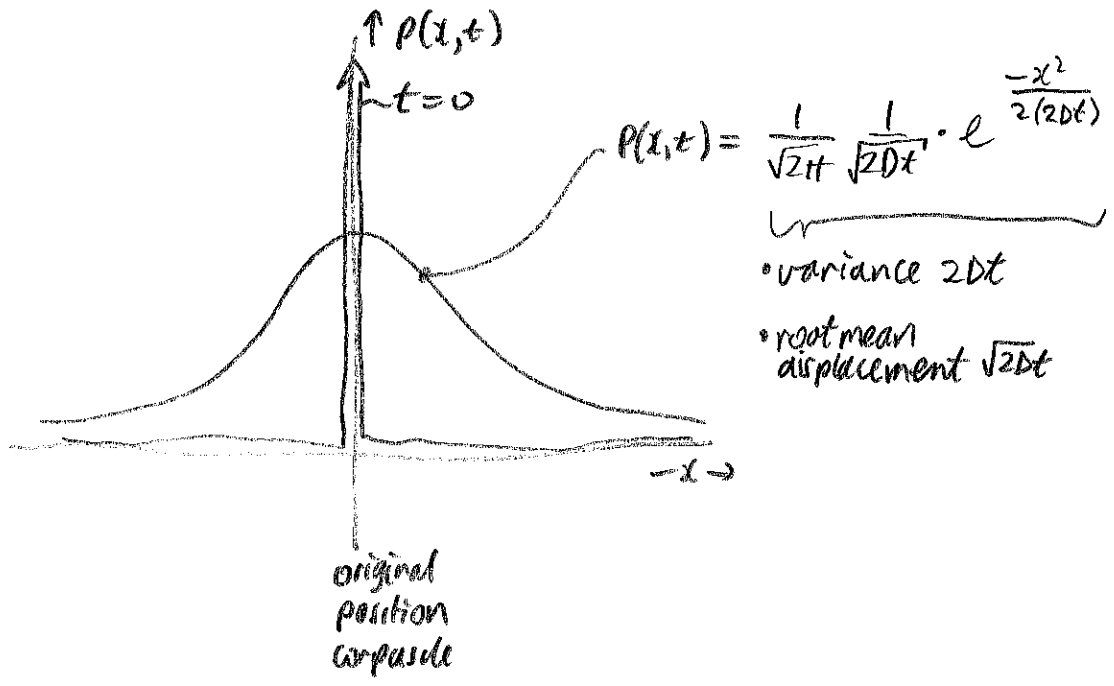
Hence  $\boxed{\frac{\partial f(x,t)}{\partial t} = D \frac{\partial^2 f(x,t)}{\partial x^2}}$

Probability density  $p(x,t)$  for position of individual corpuscle

$$p(x,t) = \frac{1}{n} f(x,t)$$

↑  
Total number corpuscles

solve diffusion equation:



# Assumptions in derivation

and, while  $\Delta$  is integrated over  $\Delta = -\infty$  to  $\Delta = +\infty$ , actual values are small enough to warrant power series in  $\Delta$ .

- \* These are values of  $\tau$  that are
  - big enough so that successive positions are probabilistically independent
  - small enough so that power series expansion is viable

\* Einstein's recovery of diffusion equation depends on correctness of assumption that terms in power series expansion must match

$$f(x, t) + \left[ \frac{\partial f}{\partial t} \tau + \frac{\partial^2 f}{\partial x^2} \frac{1}{2!} \tau^2 + \frac{\partial^3 f}{\partial x^3} \frac{1}{3!} \tau^3 \right]$$

$$= f(x, t) + \left[ \frac{\partial^2 f}{\partial x^2} \frac{1}{2!} \int \Delta^2 \phi(\Delta) d\Delta + \frac{\partial^4 f}{\partial x^4} \frac{1}{4!} \int \Delta^4 \phi(\Delta) d\Delta + \dots \right]$$

↑ AE assumes these terms match rather than ↑ rise or something else

↓  
OK as long as

$$\tau \sim \int \Delta^2 \phi(\Delta) d\Delta = \text{Variance of wave generated in } \tau \text{ by spike at } \Delta=0$$

But  $\sigma^2 \sim \tau$  is signature property of Bell curve!

← simplest solution of diffusion equation

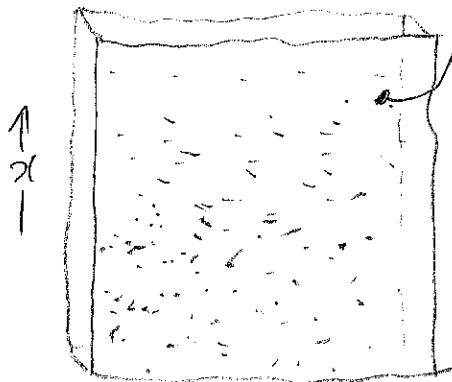
How much are we assuming of what is to be shown?!



# Short cut derivation of

$$-Kv + \frac{RT}{N} \frac{\partial v}{\partial x} = 0$$

NOT EINSTEIN'S!



mean particle density at  $x$  is  $v(x)$

At thermal equilibrium

$$v(x) \propto \exp\left(-\frac{\phi(x)}{\frac{RT}{N}}\right)$$

i.e.

$$v(x) = A \exp\left(-\frac{\phi(x)}{\frac{RT}{N}}\right)$$

↑ some constant A

independence of molecules assumed here. Energy  $\sim \phi(x)$ . No interaction with other molecules

External field  $\phi(x)$

Force  $K_x = -\frac{\partial \phi(x)}{\partial x}$

↑ write "K"

$$\therefore \frac{\partial v}{\partial x} = \underbrace{A \exp\left(-\frac{\phi(x)}{\frac{RT}{N}}\right)}_v \cdot \underbrace{-1}_{\frac{RT}{N}} \cdot \frac{\partial \phi}{\partial x}$$

↓  
-K

i.e.  $\frac{\partial v}{\partial x} = v \cdot \frac{N}{RT} \cdot K$

$$\therefore Kv - \frac{RT}{N} \frac{\partial v}{\partial x} = 0$$

JDN: Hence  
DEDUCE ideal  
gas law

& INVERT & deduce  
Boltzmann dist.  
from ideal gas  
(dw!)

Assume  
external  
force  
density  
 $Kv$

balanced  
by gradient  
is osmotic/  
kinetic  
pressure

←  $\frac{\partial p}{\partial x}$  -- by definition

$$\therefore \frac{\partial p}{\partial x} = \frac{RT}{N} \frac{\partial v}{\partial x} = \frac{\partial}{\partial x} \frac{RT}{N} v$$

set to  
zero since  
 $v=0 \Rightarrow p=0$

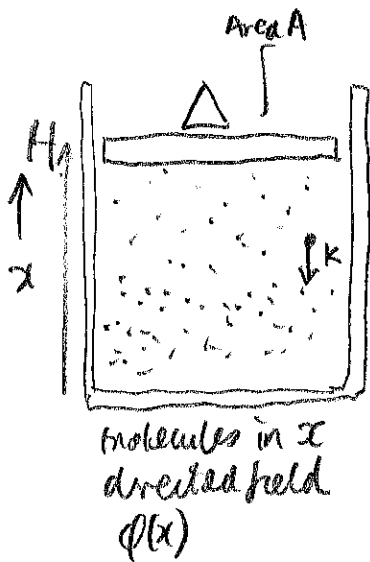
Ideal  
gas law



$$p = \frac{RT}{N} v + \text{constant}$$

The longer derivation of  $-kT + \frac{RT}{N} \frac{\partial V}{\partial x} = 0$

Assume  $n$  molecules each with phase space coordinates  $p_x, p_y, p_z, x, y, z$



$$E = E_{\text{kinetic}}(p_x, p_y, p_z) + \phi(x)$$

Partition function for one molecule is

$$Z_1(T) = \iiint_{x=0}^H \exp\left(-\frac{E_{\text{kinetic}} + \phi(x)}{kT}\right) dp_x dp_y dp_z dx dy dz$$

All  $n$  molecules alike; hence partition function for all is  $Z(T) = (Z_1(T))^n$

Free energy  $F = -kT \ln Z = -nkT \ln Z_1$

isothermal

Reversible expansion of gas that lift piston  $H \rightarrow H + dH$

$$dF = d(E - TS) = dE - TdS - SdT \rightarrow 0$$

$$-PdV \text{ at piston} = -P_x(x=H) dH \cdot A$$

$$\therefore -P_x(x=H) = -\frac{1}{A} \frac{\partial F}{\partial H} \Big|_T = +\frac{n kT}{A} \frac{\partial}{\partial H} \left[ \ln \left( \int_0^H \exp\left(-\frac{\phi(x)}{kT}\right) dx \right) + \ln \left( \text{Terms without } H \right) \right]$$

$$+ \frac{n kT}{A} \frac{\partial}{\partial H} \ln \int_0^H \exp\left(-\frac{\phi(x)}{kT}\right) dx = +kT \frac{n}{A} \cdot \frac{\exp(-\phi(H)/kT)}{\int_0^H \exp(-\phi(x)/kT) dx}$$

To see that consider layer of thickness  $dx$  at  $x=H$

$\nu(H) \leftarrow$  Particle density at  $x$

$$\nu(H) = \frac{\text{Portion of } n \text{ in layer}}{\text{Volume of layer}} = \frac{n \cdot \exp(-\phi(H)/kT) dx}{\int_0^H \exp(-\phi(x)/kT) dx \cdot A dx}$$

Hence  $P_x = \nu(H) kT$  at  $x=H$

what about  $p_y, p_z$ ?