Paul Langevin 1908

(1) (kinetic theory of gases)

$$E = \frac{1}{2} k_B T$$

$1,38 \cdot 10^{-23} \frac{J}{K}$

$$E = \frac{1}{2} m \overline{v^2}$$

$$k_B = \frac{R}{N_A}$$

R — universal gas constant 8.314 J/mol.K

N_A — Avogadro's number $6.02 \cdot 10^{23} \frac{\text{partic}}{\text{mol}}$

(2) Langevin paper

$$\xi = \frac{dx}{dt} = v$$

$$\frac{1}{2} m \overline{\xi^2} = \frac{1}{2} \frac{R}{N_A} T$$

viscous resistence $(\sim v)$ $= -6\pi \mu r \xi$ Stokes' formula

r — radius of the particle.

random force X

$$ma = F_{viscous} + F_{random}$$

random force

$$m\frac{d^2x}{dt^2} = -6\pi\mu r\frac{dx}{dt} + X$$

Multiply by x and integrate

$$m\,x\frac{d^2x}{dt^2} = -6\pi\mu r\,x\frac{dx}{dt} + Xx$$

$$(1)\quad \frac{m}{2}\underbrace{\frac{d^2}{dt}(x^2)}_{\underbrace{\frac{d}{dt}\left(2x\frac{dx}{dt}\right)}_{2\left(\frac{dx}{dt}\right)^2+2x\frac{d^2x}{dt^2}}} - m\left(\frac{dx}{dt}\right)^2 = -3\pi\mu r\frac{d(x^2)}{dt} + Xx$$

Take the mean value of (1)

$$(2)\quad \frac{m}{2}\frac{d^2}{dt^2}\langle x^2\rangle - m\langle\xi^2\rangle = -3\pi\mu r\frac{d}{dt}\langle x^2\rangle + \langle Xx\rangle$$

Hypothesis $\langle Xx\rangle = 0$

$$(3)\quad \frac{m}{2}\frac{d^2}{dt^2}\langle x^2\rangle + 3\pi\mu r\frac{d}{dt}\langle x^2\rangle = \overset{m}{\cancel{\mu}}\langle\xi^2\rangle$$

$$(4)\quad \boxed{\frac{m}{2}\frac{d^2}{dt^2}\langle x^2\rangle + 3\pi\mu r\frac{d}{dt}\langle x^2\rangle = \frac{R}{N_A}T}$$

Equation for $\langle x^2\rangle$ as a function of time.

In Einstein's theory

$$(5) \qquad \langle x^2 \rangle = 2Dt$$

We need to find the same time dependance from Langevine approach.

<u>Solve (4)</u>

Denote $\quad z = \dfrac{d\langle x^2 \rangle}{dt}$

$$(6) \quad \frac{m}{2}\frac{dz}{dt} + 3\pi\mu r\, z = \frac{R}{N_A} T$$

The solution is an exponetial plus a constant

$$z = C e^{-bt} + B$$

The coefficients A, B and b are found from (6). C is indetermined because we do not know the initial condition (z at time t=0).

$$z = c e^{-\frac{6\pi\mu r}{m} t} + \frac{RT}{N_A}\frac{1}{3\pi\mu r}$$

Now $\left(\dfrac{6\pi\mu r}{m}\right)^{-1} \sim 10^{-8}$ seconds so the variable z recheas a <u>constant</u> value $\dfrac{RT}{N_A}\dfrac{1}{3\pi\mu r}$ very fast

This part is important:

(1) we notice the existence of a relaxation phenomena

$$e^{-\frac{6\pi\mu r}{m}t}$$

(2) we neglect it; that is the particles reaches a <u>stationary</u> distribution very fast

Now we have

$$z_{\text{stationary}} = \frac{RT}{N_A} \frac{1}{3\pi\mu r}$$

or

$$\frac{d}{dt}\langle x^2\rangle_{\text{stationary}} = \frac{RT}{N_A} \frac{1}{3\pi\mu r}$$

Then

$$\langle x^2\rangle_{\text{stationary}} = \langle x_0^2\rangle_{\text{stationary}} + \frac{RT}{N_A} \frac{1}{3\pi\mu r} t$$

If all particles were at the origin at time $t=0$

$$\langle x_0^2\rangle_{\text{stationary}} = 0$$

So

$$\boxed{\langle x^2\rangle_{\text{stationary}} = \frac{RT}{N_A} \frac{1}{3\pi\mu r} t}$$

Compare with

$$\langle x^2 \rangle_{\text{EINSTEIN}} = 2Dt$$

we get

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

Now we let Einstein speak:

§5 from Einstein's paper