

# Paul Langevin 1908

① (kinetic theory of gases)

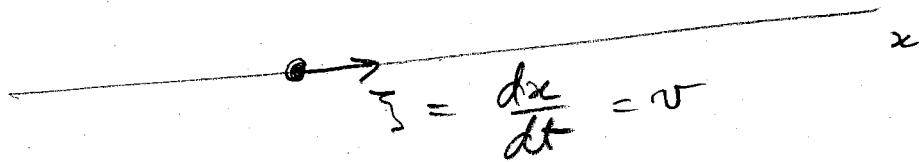
$$E = \frac{1}{2} k_B T$$

$\uparrow$   
 $1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$

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

Universal gas constant  $8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$   
Avogadro's number  $6.02 \cdot 10^{23} \frac{\text{partic}}{\text{mol}}$

② Langevin paper



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

viscous resistance ( $\sim v$ )

random force X

$$= -6\pi \mu a v$$

radius of the particle  
Stokes' formula

$$m a = F_{\text{viscous}} + F_{\text{random}}$$

$$m \frac{dx^2}{dt^2} = -6\pi\mu r \frac{dx}{dt} + X \quad \leftarrow \text{random force}$$

Multiply by  $x$  and integrate

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

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

$$\frac{d}{dt} \left( 2x \frac{dx}{dt} \right)$$

$$2 \left( \frac{dx}{dt} \right)^2 + 2x \frac{d^2x}{dt^2}$$

Take the mean value of (1)

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

Hypothesis

$$\langle Xx \rangle = 0$$

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

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

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

In Einstein's theory

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

We need to find the same time dependence from Langevin approach.

Solve (4)

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

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

The solution is an exponential 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  $\left(\frac{6\pi\mu r}{M}\right)^{-1} \sim 10^{-8}$  seconds so the variable  $z$  reaches a constant value  $\frac{RT}{N_A} \frac{1}{3\pi\mu r}$  very fast

This part is important:

(1) we notice the existence of a relaxation phenomena

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

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

Now we have

$$z_{\text{stationary}} = \frac{RT}{NA} \frac{1}{3\pi\eta r}$$

or

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

then

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

If

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

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

So

$$\langle x^2 \rangle_{\text{stationary}} = \frac{RT}{NA} \frac{1}{3\pi\eta r} t$$

Compare with

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

we get

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

Now we let Einstein speak:

§ 5 from Einstein's paper