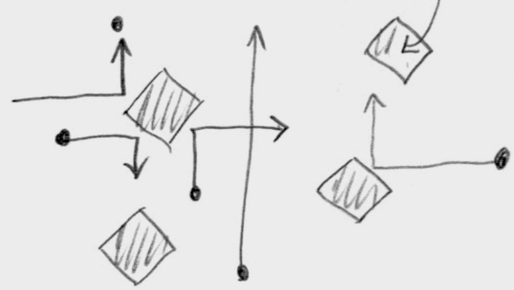
Ehrenfests' "Wind Tree" model

shows how a time reversible dynamics can lead to a unidirectional approach to equilibrium

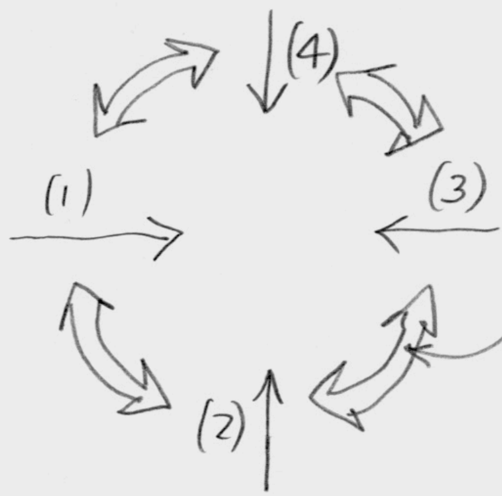
System is a plane



fixed "Q-molecules"

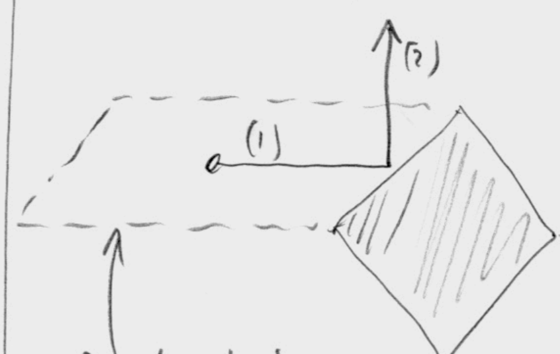
"P-molecules" bounce elastically Q-molecules

P-molecules initially & always confined to four directions of motion



One collision changes of direction possible

Collision dynamics



P molecules in this area will collide & move from (1) to (2)

$$\text{Area} = \underbrace{k}_{\text{constant}} \underbrace{dt}_{\text{time interval}}$$

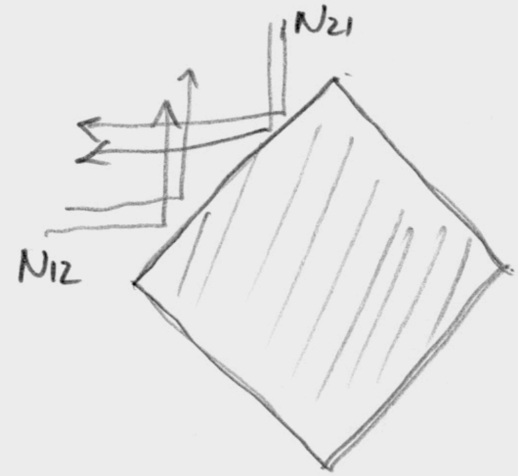
Stosszahl ansatz

$$\underbrace{N_{12}\Delta t}_{\text{Number of transitions}} = f_1 \cdot \underbrace{k\Delta t}_{\text{area}}$$

f_1: number of P molecules moving with motion (1)

Approach to Equilibrium

Typical interchange mechanism



without Stosszahlansatz this equilibrating mechanism is not available

Net rate transfer (1) → (2) by this mechanism $= N_{12} - N_{21} = k(f_1 - f_2)$

∴ Transfer rate (1) → (2) is positive when $f_1 > f_2$

is negative when $f_1 < f_2$

Hence mechanism drives numbers towards limit $f_1 = f_2$

Same for all interchange mechanisms

∴ Collisions drive system towards $f_1 = f_2 = f_3 = f_4$

Dynamics

$$\frac{df_1}{dt} = (\underbrace{-N_{12} - N_{14}}_{\text{Rate reduction (1) motions}} + \underbrace{N_{21} + N_{41}}_{\text{Rate creation (1) motions}})$$

$$= k(-2f_1 + f_2 + f_4)$$

similarly

$$\frac{df_2}{dt} = k(-2f_2 + f_1 + f_3)$$

$$\frac{df_3}{dt} = k(-2f_3 + f_4 + f_2)$$

$$\frac{df_4}{dt} = k(-2f_4 + f_1 + f_3)$$

$\Downarrow$ sum

$$\frac{d}{dt}(f_1+f_2+f_3+f_4) = k\big(-2(f_1+f_2+f_3+f_4) + (f_2+f_4) + (f_1+f_3) + (f_2+f_4) + (f_1+f_3)\big) = 0$$

As expected $f_1+f_2+f_3+f_4 = N$

$\uparrow$ total number of P-molecules

Compare f_1, f_3

$$\frac{1}{K}\frac{d}{dt}(f_1 - f_3) = -2f_1 + f_2 + f_4 + 2f_3 - f_2 - f_4 = -2(f_1 - f_3)$$

$$f_1(t) - f_3(t) = [f_1(0) - f_3(0)]\exp(-2Kt)$$

$$f_1(t) \to f_3(t) \text{ as } t \to \infty$$

Similarly f_2, f_4

$$f_2(t) - f_4(t) = [f_2(0) - f_4(0)]\exp[-2Kt]$$

$$f_2(t) \to f_4(t) \text{ as } t \to \infty$$

Still need: show $f_1(t) \to f_2(t)$ when $t \to \infty$

Otherwise we cannot preclude oscillations in $f_1 \approx f_3$ counterbalanced by oscillations in $f_2 \approx f_4$

$\boxed{\text{Compare } (f_1+f_3) \text{ with } (f_2+f_4)}$

$$\frac{1}{k}\frac{d}{dt}(f_1+f_3) = -2(f_1+f_3) + 2(f_2+f_4)$$

$$-\frac{1}{k}\frac{d}{dt}(f_2+f_4) \quad -\left[-2(f_2+f_4)+2(f_1+f_3)\right]$$

$$= -4\left[(f_1+f_3) - (f_2+f_4)\right]$$

Hence solving

$$\{(f_1+f_3)-(f_2+f_4)\} = (f_1(0)+f_3(0)) - \{f_2(0)+f_4(0)\}\exp(-4kt)$$

$\boxed{\text{i.e. } f_1(t)+f_3(t) \longrightarrow f_2(t)+f_4(t) \quad \text{as } t\to\infty}$

Combining

All $f_1(t), f_2(t), f_3(t), f_4(t) \longrightarrow$ same value $= \frac{N}{4}$

as $t\to\infty$