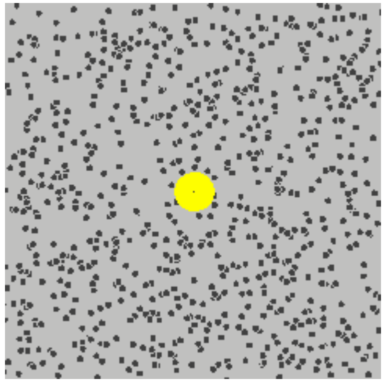
Lecture 27

10.05.2019

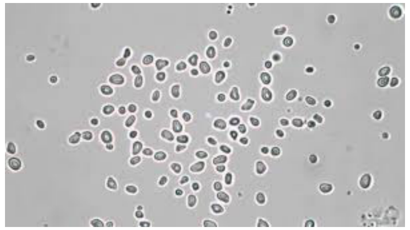
Brownian motion, Einstein relation

Brownian motion and Brownian particle



- Random motion of particles suspended in a fluid. These are also called **colloidal particles** and are much bigger in size than the fluid particles

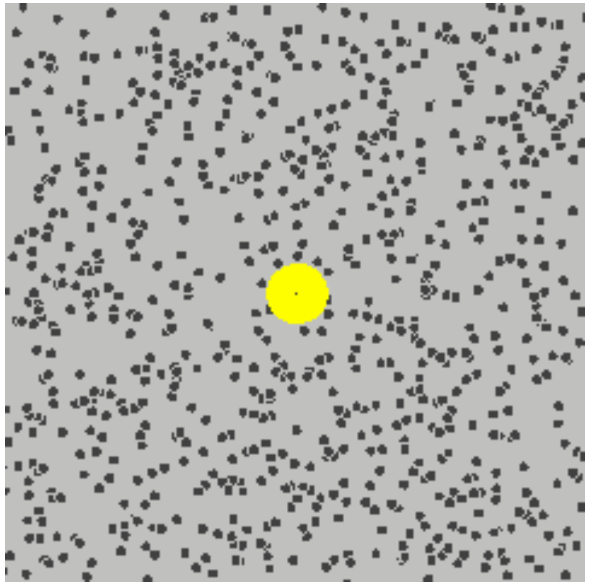
- Discovered by biologist Robert Brown (1827)
  - observed pollen grains from a flowering plant through a microscope.
  - tiny particles of the grain suspended within the fluid, moved in a randomly
  - He found that other non-living particles suspended in fluids executes a similar random motion, e.g. dust in the air.

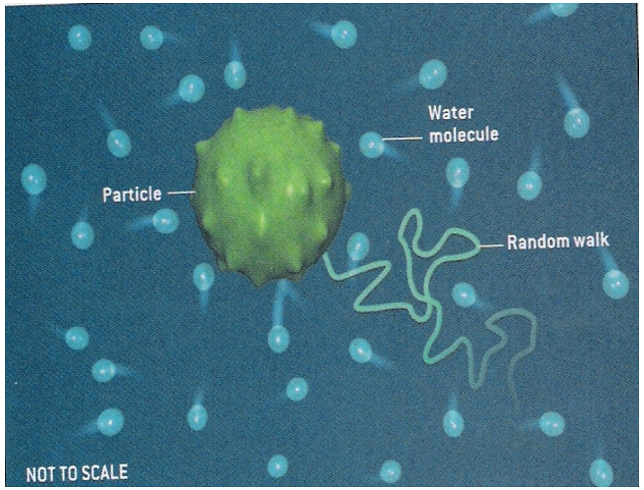


Enstein explanation of Brownian motion

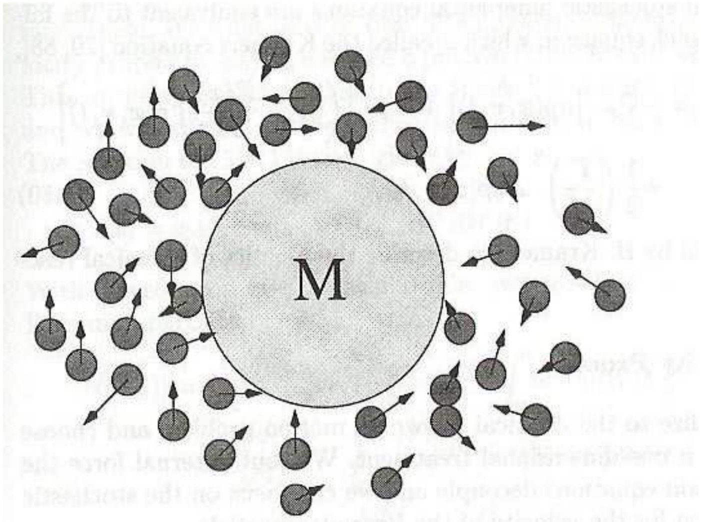
- Molecular theory of Brownian motion as thermal motion

- Brownian motion as the microscopic process responsible for diffusion on a macroscopic scale.





Random force from thermal motion



The Brownian motion is described by a stochastic dynamics of the colloidal particle. The evolution equation of the Brownian particle position is known as the Langevin equation. It is a generalization of the Newton's law of motion when the Brownian particle experiences a random force.

Net momentum exchange ΔP between fluid particles and Brownian particle in a time interval Δt is a superposition of random collisions due to thermal motion of fluid particles

$$\Delta P = \sum_{i=1}^{N} \delta p_i$$

$$\langle \delta p_i \rangle = 0$$

$$\left\langle \delta p_i^2 \right\rangle = \sigma$$

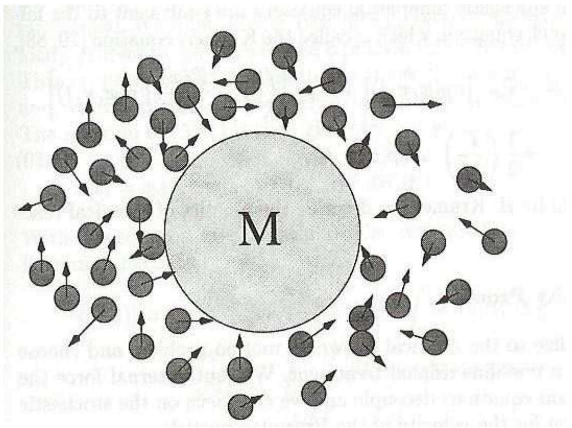
From the central limit theorem, ΔP is Gaussian distributed with zero mean and standard deviation increases as the square root of time

$$\langle \Delta P \rangle = 0$$

$$\langle \Delta P^2 \rangle = N\sigma \sim \Delta \mathrm{t}$$

Random force

Brownian particle is moving under the random force $R(t)$ induced by the collisions with the fluid particles



$$m\frac{dv}{dt} = R$$

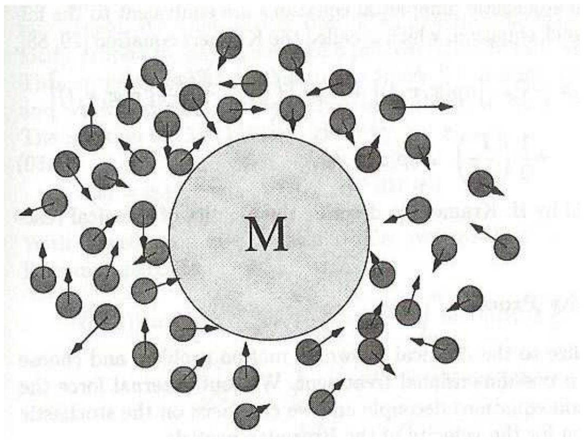
The force fluctuates around a zero mean

$$\langle R \rangle \sim \left\langle \frac{\Delta P}{\Delta \mathrm{t}} \right\rangle = 0$$

And is δ-correlated in time

$$\langle R(t)R(t+\Delta t) \rangle \sim \left\langle \frac{\Delta P^2}{\Delta \mathrm{t}} \right\rangle \sim \frac{1}{\Delta t} \to \delta(\Delta t)$$

Random motion



Brownian particle is moving under the random force R induced by the collisions with the fluid particles

$$m\frac{dv}{dt} = R(t)$$

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

$$\langle R(t)R(t') \rangle = a\delta(\mathrm{t} - \mathrm{t}')$$

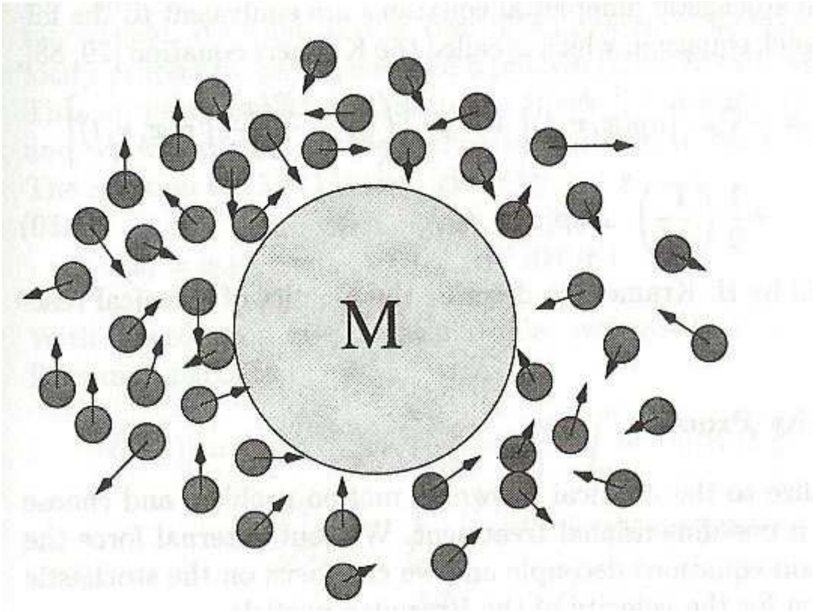
Langevin equation includes a drag force and random force

Brownian particle dissipates some of its kinetic energy by viscous drag

$$m\frac{dv}{dt} = -\alpha v + R(t)$$

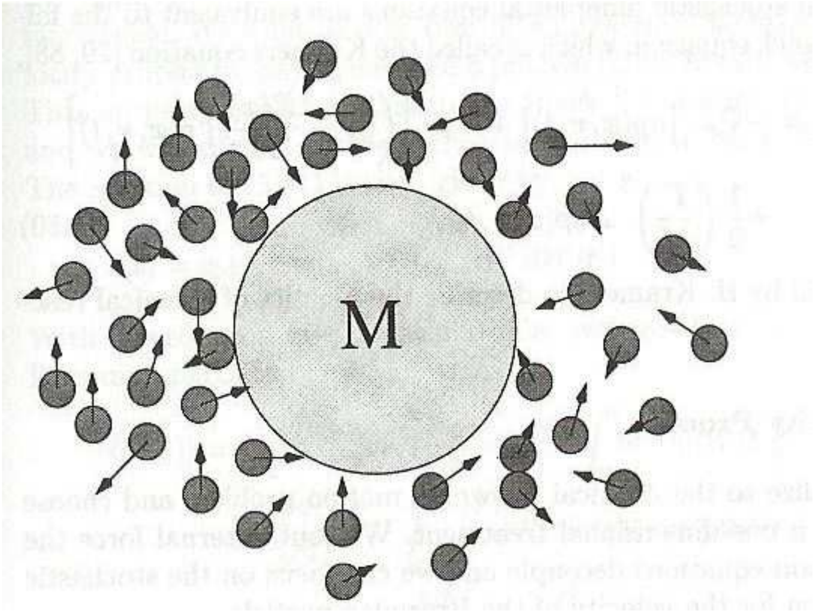
$$\langle R(t) \rangle = 0$$

$$\langle R(t)R(t') \rangle = a\delta(\mathrm{t} - \mathrm{t}')$$



- strength of the random force is set by the assumption that the Brownian particle is at thermal equilibrium with the fluid particles

Langevin equation



Brownian particle dissipates some of its kinetic energy by viscous drag

$$m\frac{dv}{dt} = -\alpha v + R(t)$$

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

$$\langle R(t)R(t')\rangle = a\delta(t - t')$$

- strength of the random force is determined by the assumption that the Brownian particle (BP) is at thermal equilibrium with the fluid particles
  - Mean kinetic energy of BP equal to the average kinetic energy per fluid particle

$$\frac{m\langle v^2\rangle}{2} = \frac{m_f\langle v_f^2\rangle}{2} = \frac{kT}{2} \quad (1D)$$

Determine $\langle v^2 \rangle$ from $\langle v(t)v(0) \rangle$

$$\frac{e^{\frac{\alpha t}{m}}}{m} m \frac{dv}{dt} = [-\alpha v + R(t)] \frac{e^{\frac{\alpha t}{m}}}{m} \rightarrow \frac{d}{dt}\left[v\, e^{\frac{\alpha t}{m}}\right] = \frac{R}{m} e^{\frac{\alpha t}{m}}$$

$$v(t) = \int_{-\infty}^{t} dt' \frac{R(t')}{m} e^{-\frac{\alpha(t-t')}{m}}$$

Autocorrelation function $\langle v(t)v(0) \rangle = \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt''\, e^{-\frac{\alpha(t-t'-t'')}{m}} \frac{\langle R(t')R(t'') \rangle}{m^2} = \frac{a}{2m\alpha} e^{-\frac{\alpha}{m}t}$

$$\langle v(t)v(0) \rangle = \frac{a}{m^2} \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt''\, e^{-\frac{\alpha(t-t'-t'')}{m}} \delta(t'-t'')$$

$$\langle v(t)v(0) \rangle = \frac{a}{m^2} \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt''\, e^{-\frac{\alpha(t-t'-t'')}{m}} \delta(t'-t''), \qquad t > 0$$

$$\langle v(t)v(0) \rangle = \frac{a}{m^2} \int_{-\infty}^{0} dt''\, e^{-\frac{\alpha(t-2t'')}{m}} = \frac{a}{2m\alpha} e^{-\frac{\alpha}{m}t}$$

BP at thermal equilibrium with the fluid
Fluctuation-dissipation relation

$$\frac{m}{2}\langle v(t)^2\rangle = \frac{m}{2}\langle v(0)^2\rangle = \frac{kT}{2}$$

$$\langle v(t)v(0)\rangle = \frac{a}{2m\alpha}e^{-\frac{\alpha}{m}t}$$

$$a = 2\alpha kT$$

- Amplitude of the random force increases with:
  - the temperature of the fluid (more energetic particles, more collusions)
  - the viscous drag coefficient (the higher the damping, the more energy is dissipated into the fluid)

Langevin equation:

$$m\frac{dv}{dt} = -\alpha v + R(t)$$

$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

- Find the mean square displacement and the diffusion coefficent (1D)

Langevin equation: mean square displacement

$$m\frac{dv}{dt} = -\alpha v + R(t)$$
$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

- $x(t) = \int_0^t dt_1\, v(t_1) = \int_0^t dt_1 \int_{-\infty}^{t} dt'\, \frac{R(t')}{m} e^{-\frac{\alpha}{m}(t_1-t')}$

$$\langle x(t)^2\rangle = \int_0^t dt_1\, v(t_1) \int_0^t dt_2\, v(t_2)$$

$$\langle x(t)^2\rangle = \int_0^t dt_1 \int_0^t dt_2 \int_{-\infty}^{t_1} dt' \int_{-\infty}^{t_2} dt''\, e^{-\frac{\alpha(t_1+t_2-t'-t'')}{m}} \frac{\langle R(t')R(t'')\rangle}{m^2}$$

Langevin equation: mean square displacement

$$m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + R(t), \qquad (1)$$
$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

Mean square displacement is obtained from the integration of eq (1)

$$\langle x(t)^2\rangle = \int_0^t dt_1 \int_0^t dt_2 \int_{-\infty}^{t_1} dt' \int_{-\infty}^{t_2} dt''\, e^{-\frac{\alpha(t_1+t_2-t'-t'')}{m}} \frac{\langle R(t')R(t'')\rangle}{m^2}$$

$$\langle x(t)^2\rangle = \frac{2\alpha kT}{m^2}\int_0^t dt_1 \int_0^t dt_2 \int_{-\infty}^{t_1} dt' \int_{-\infty}^{t_2} dt''\, e^{-\frac{\alpha(t_1+t_2-t'-t'')}{m}} \delta(t'-t'')$$

$$\langle x(t)^2\rangle = \frac{2\alpha kT}{m^2}\int_0^t dt_1 \int_0^t dt_2 \int_{-\infty}^{\min(t_1,t_2)} dt'\, e^{-\frac{\alpha(t_1+t_2-2t')}{m}}$$

$$\langle x(t)^2\rangle = \frac{\alpha kT}{m}\int_0^t dt_1\, e^{-\frac{\alpha}{m}t_1} \int_0^t dt_2\, e^{-\frac{\alpha}{m}t_2}\, e^{\frac{2\alpha}{m}\min(t_1,t_2)}$$

Langevin equation: mean square displacement

(continued–)

$$\langle x(t)^2\rangle = \frac{\alpha kT}{m}\int_0^t dt_1\, e^{-\frac{\alpha}{m}t_1}\int_0^t dt_2\, e^{-\frac{\alpha}{m}t_2}\, e^{\frac{2\alpha}{m}\min(t_1,t_2)}$$

$$\langle x(t)^2\rangle = \frac{\alpha kT}{m}\int_0^t dt_1\, e^{-\frac{\alpha}{m}t_1}\left[\int_0^{t_1} dt_2\, e^{-\frac{\alpha}{m}t_2}\, e^{\frac{2\alpha}{m}t_2} + \int_{t_1}^t dt_2\, e^{-\frac{\alpha}{m}t_2}\, e^{\frac{2\alpha}{m}t_1}\right]$$

$$\langle x(t)^2\rangle = \frac{\alpha kT}{m}\int_0^t dt_1\left[2 - e^{-\frac{\alpha}{m}t_1} - e^{-\frac{\alpha}{m}(t-t_1)}\right] = \frac{2kT}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-\frac{\alpha}{m}t}\right)\right]$$

Langevin equation: Einstein's relation

$$m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + R(t), \qquad (1)$$
$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(t-t')$$

$$\langle x(t)^2\rangle = \frac{2kT}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-\frac{\alpha t}{m}}\right)\right]$$

- $t \gg \frac{m}{\alpha}$ (diffusion limit)

$$\langle x(t)^2\rangle = 2\frac{kT}{\alpha}t = 2Dt$$

Fluctuation-Dissipation (Einstein) formula provides a relation between the diffusivity of the Brownian particle due to thermal motion and the drag coefficient for a viscous (dissipative) fluid

$$\boldsymbol{D = \frac{kT}{\alpha}}$$

In 3D: $\langle \boldsymbol{r}(t)^2\rangle = 3\langle x(t)^2\rangle = 6\frac{kT}{\alpha}t \to D_{3D} = \frac{3kT}{\alpha}$

Langevin equation: Ballistic regime

$$m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + R(t), \qquad (1)$$

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

$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

$$\langle x(t)^2\rangle = \frac{2kT}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-\frac{\alpha t}{m}}\right)\right]$$

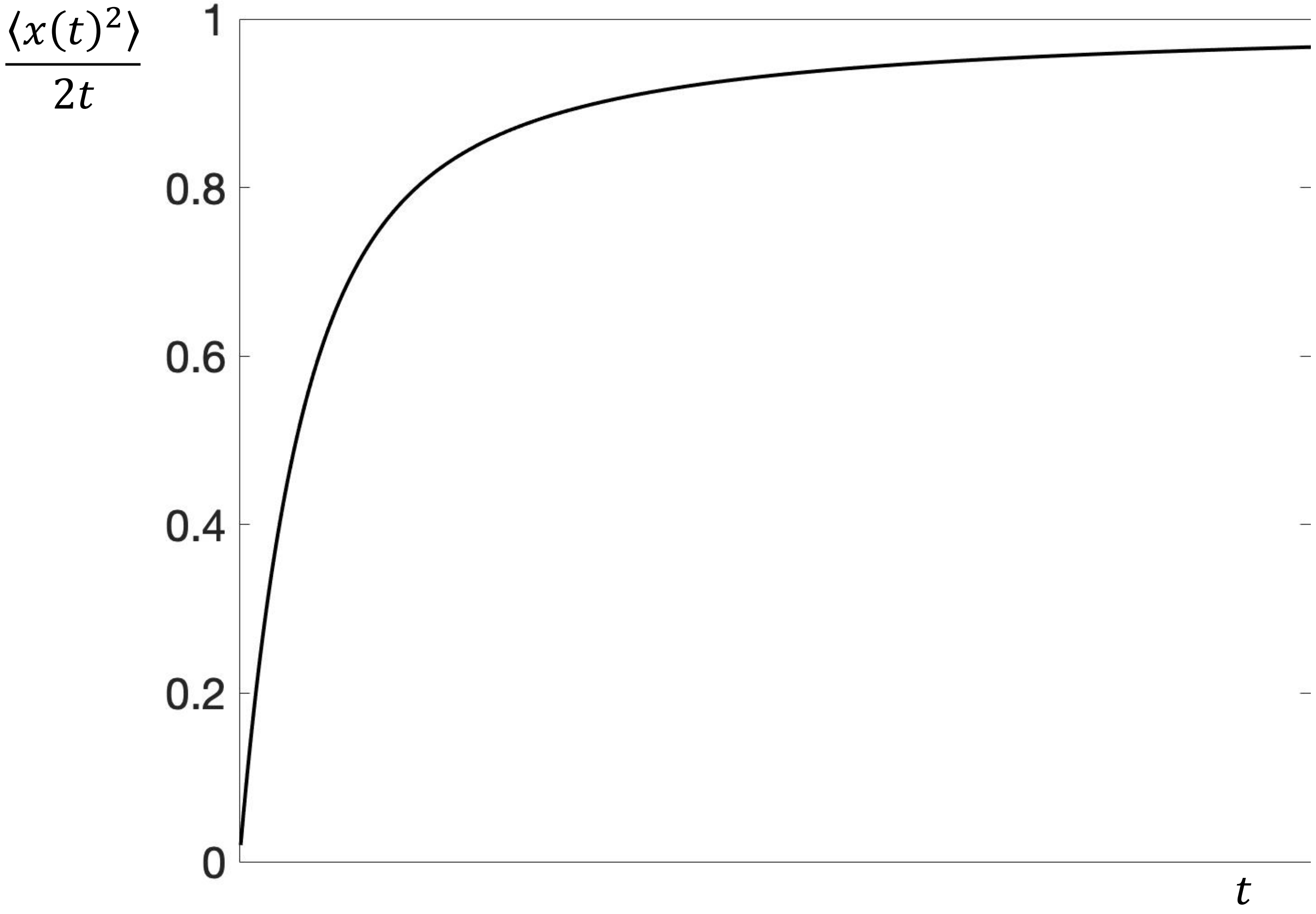
- $t \ll \frac{m}{\alpha}$ (ballistic regime)

$$\langle x(t)^2\rangle = \frac{kT}{m}\,t^2$$

$$v_{thermal} = \frac{\sqrt{\langle x(t)^2\rangle}}{t} = \frac{kT}{m} \quad (equiparti on\ of\ energy)$$

(on short timescales, the Brownian particles is «advected» by the fluid with a mean velocity determined by the kinetic energy of the fluid particles)

Brownian motion



Random walk of *fluid particles*
Brownian motion of *suspended particles*

Random walk of fluid particles:

$X = \sum_{i=1}^{N} \Delta \mathrm{x_i} \rightarrow \langle X^2 \rangle = N \langle \Delta \mathrm{x}^2 \rangle \leftrightarrow \langle X^2 \rangle = 2 \frac{\lambda^2}{2\tau} t$

- Diffusion coefficient of fluid particles (ideal gas approx.) $D_{FP} = \frac{\lambda^2}{2\tau}$ is determined by the mean-free path (mean path between successive collisions) and the scattering time (mean time between successive collisions)
- Thermal velocity of the gas particles $v_{th}^{(3D)} = \sqrt{3kT/m} \sim \frac{\lambda}{\tau}$

Brownian motion of suspended particles:

$$m \frac{dv}{dt} = -\alpha v + R(t)$$

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

$$\langle R(t) R(t') \rangle = 2\alpha k T \delta(\mathrm{t} - \mathrm{t}')$$

$$\langle x(t)^2 \rangle = \frac{2kT}{\alpha} \left[t - \frac{m}{\alpha} \left(1 - e^{-\frac{\alpha t}{m}} \right) \right] \rightarrow_{t \gg \frac{m}{\alpha}} 2 \frac{kT}{\alpha} t$$

- Diffusion cofficient of suspended particles $D^{3D} = \frac{3kT}{\alpha}$, depends on the fluid temperature and the damping coefficient

Dynamic equilibrium of Brownian motion (Einstein 1905)

Concentration of independent Brownian particles

$$\frac{\partial C}{\partial t} + \nabla \cdot J_C = 0, \qquad J_c = Cv - D\nabla \mathrm{C}$$

At equilibrium: $J_c = 0 \rightarrow Cv = \ D\nabla \mathrm{C}$

Brownian particle in a uniform gravitational field: $\mu v_z = -mg$

$$\mathrm{D}\frac{\mathrm{dC}}{\mathrm{dz}} = -\mu mgC \rightarrow C(z) \sim e^{-\frac{\mu}{D}mgz}$$

Maxwell-Bolztmann equilibrium distribution for the concentration of particles in a gravitational potential $U(z) = mgz$

$$C(z) \sim e^{-\beta U(z)} \rightarrow D = \mu kT = \frac{kT}{\alpha}$$

Brownian motion and the determination of the Avogadro's number (Einstein 1905)

Brownian motion:

$$m\frac{dv}{dt} = -\alpha v + R(t)$$
$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

$$\langle x(t)^2\rangle = \frac{2kT}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-\frac{\alpha t}{m}}\right)\right] \rightarrow_{t \gg \frac{m}{\alpha}} 2\frac{kT}{\alpha}\,t$$

- Diffusion cofficient of suspended particles $D = \frac{3kT}{\alpha} = 3\lim_{t\to\infty}\frac{\langle x(t)^2\rangle}{2t}$, depends on the fluid temperature and the damping coefficient. Since the Boltzmann's factor relates to the Avocado number by $k = \frac{R}{N_A}$, we can determine N_A as

$$N_A = \frac{3RT}{\alpha\, D}$$