Thermal Forces and Brownian Motion

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Outline

- Meaning of the Central Limit Theorem
- Diffusion vs Langevin equation descriptions (average vs individual)
- Diffusion coefficient and fluctuation-dissipation theorem

Central Limit Theorem

$$Y = X_1 + X_2 + \ldots + X_N$$

$X_1, X_2, \ldots, X_N$ are random variables

$$\mathrm{E}[Y] = \mathrm{E}[X_1] + \mathrm{E}[X_2] + \ldots + \mathrm{E}[X_N]$$

If $X_1, X_2, \ldots, X_N$ are *independent* random variables:

$$\mathrm{var}[Y] = \mathrm{var}[X_1] + \mathrm{var}[X_2] + \ldots + \mathrm{var}[X_N]$$

Note: $\mathrm{var}[X] = \sigma^2{}_X \equiv \mathrm{E}[\,(X\text{-}\mathrm{E}[X])^2\,]$

If $X_1, X_2, \ldots, X_N$ are *independent* random variables sampled from the *same* distribution:

$$\mathrm{E}[Y] = N\mathrm{E}[X]$$

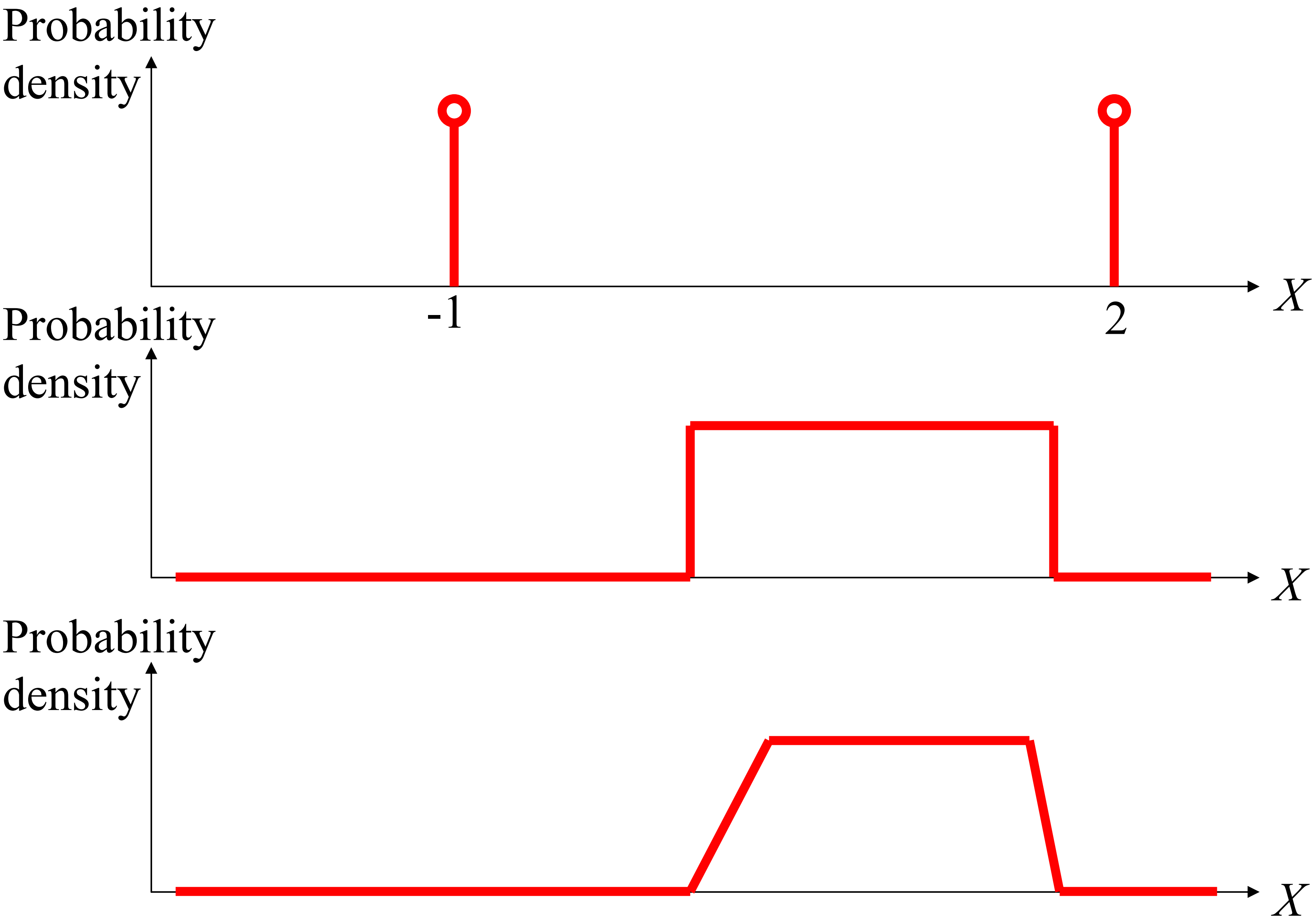
$$\mathrm{var}[Y] = N\,\mathrm{var}[X_1] = N\sigma^2{}_X$$

Average of the sum: $y \equiv Y/N$

$$\mathrm{E}[y] = \mathrm{E}[X], \quad \mathrm{var}[y] = \mathrm{var}[Y]/N^2 = \sigma^2{}_X / N$$

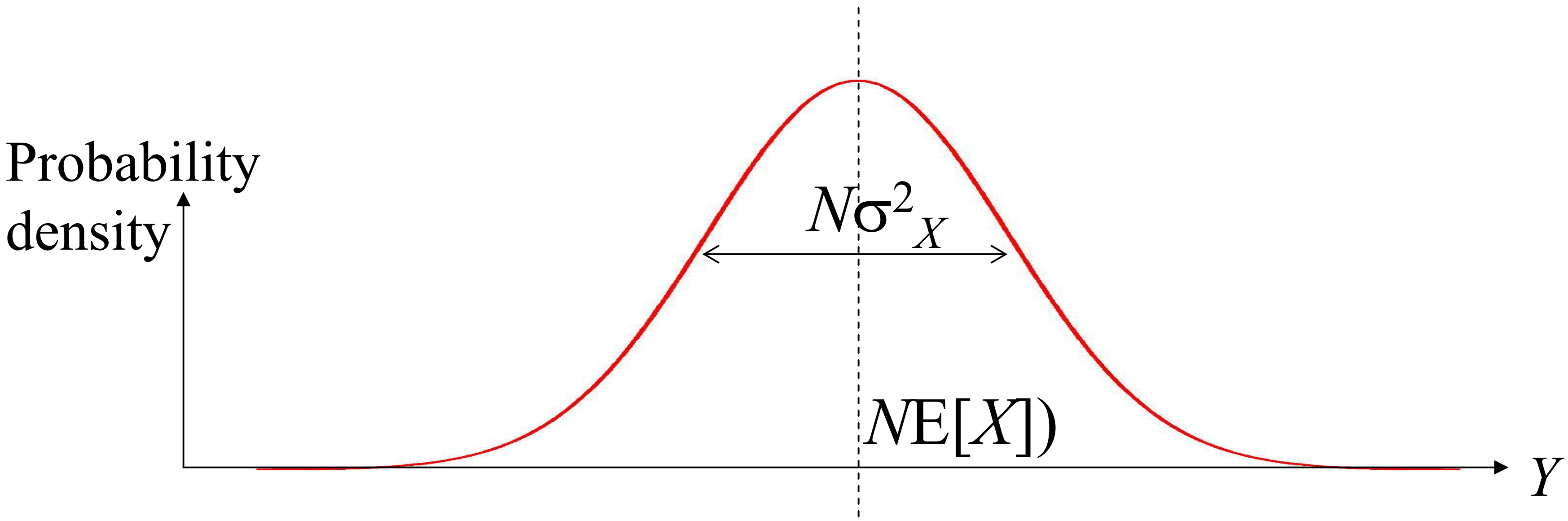
Law of large numbers: as N gets large, the average of the sum becomes more and more deterministic, with variance $\sigma^2{}_X / N$.

$X_1, X_2, \ldots, X_N$ may be sampled from



We know the probability distribution of Y is shifting ($N\mathrm{E}[X]$), as well as getting fat ($N\sigma^2_X$). But how about its *shape* ?

The central limit theorem says that *irrespective* of the shape of X,



Why Gaussian ?

$$\rho(Y) \xrightarrow{\text{large } N} \frac{1}{\sqrt{2\pi N\sigma_X^2}} \exp\left(\frac{(Y - NE[X])^2}{2N\sigma_X^2} \right)$$

Gaussian is special
(Maxwellian velocity distribution, etc).

While proof is involved,
here we note that Gaussian is an invariant shape (attractor in shape space) in the mathematical operation of convolution.

Diffusion Equation in 1D

$$\partial_t \rho = -\partial_x \overbrace{(-D\partial_x \rho)}^{J} = D\partial_x^2 \rho$$

Random walker view of diffusion: imagine

(a) We release the walker at x=0 at t=0,

(b) Walker makes a move of $\pm a$, with equal probability, every $\Delta t = 1/\nu$ from then on.

Mathematically, we say $\rho(x, t=0) = \delta(x)$.

$$\text{Then, } x(t) = \overbrace{\Delta x_1 + \Delta x_2 + \ldots + \Delta x_{t/\Delta t}}^{N = \frac{t}{\Delta t} = \nu t \text{ independent random steps}}$$

When $N = \nu t >> 1$,

the central limit theorem applies:

$$E[x(t)] = 0, \quad \mathrm{var}[x(t)] = \nu t \,\mathrm{var}[\Delta x] = \nu t a^2$$

So we can directly write down $\rho(x(t))$ as

$$\rho_{\mathrm{G}}(x,t) = \frac{1}{\sqrt{2\pi \nu a^2 t}} \exp\left(\frac{x^2}{2\nu a^2 t}\right)$$

It is the probability of finding the walker at x at time t, knowing he was at 0 at time 0.

By plugging in, we can directly verify

$\rho_{\mathrm{G}}(x,t)$ satisfies

$$\partial_t \rho = D\partial_x^2 \rho, \;\; \rho(x,0) = \delta(x).$$

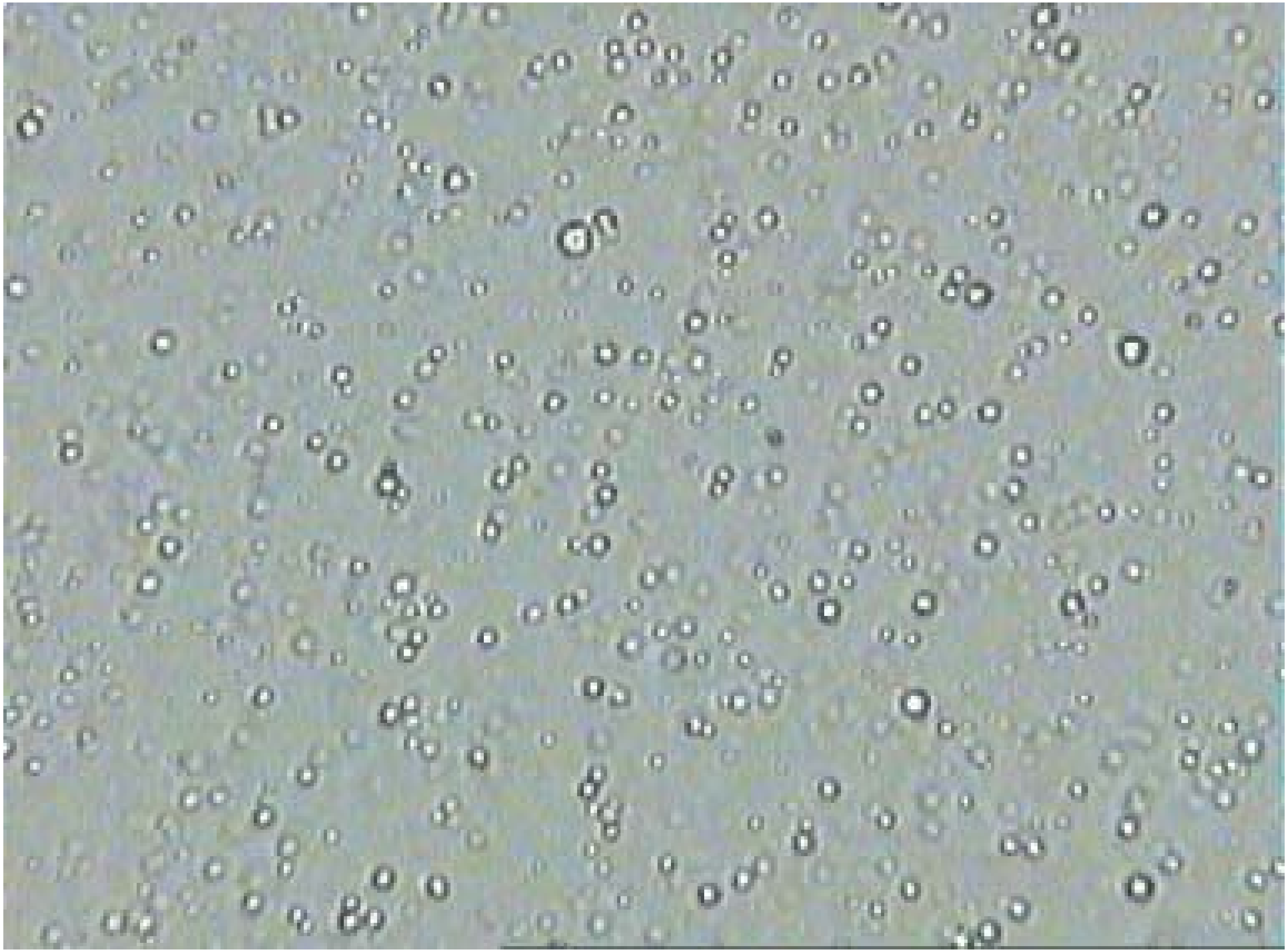
with macroscopic D identified as $\dfrac{va^2}{2}$.

$$\rho_{\mathrm{G}}(x,t) \; = \; \frac{1}{\sqrt{2\pi(2Dt)}} \exp\left(\frac{x^2}{2(2Dt)} \right)$$

is called Green's function solution

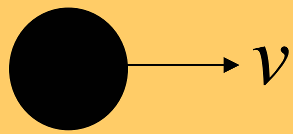
to diffusion equation.

Brownian Motion



Fat droplets suspended in milk (from Dave Walker).
The droplets range in size from about 0.5 to 3 μm.

viscous oil



Stokes' law:

$F = -6\pi r \eta v = -\lambda v$

$$m\dot{v} = F = -\lambda v, \quad v(t=0) = v_0$$

$$\rightarrow \quad v(t) = v_0 e^{-\frac{\lambda}{m}t}$$

Einstein's Explanation of Brownian Motion

Also, equi-partition theorem: $\left\langle \frac{mv^2}{2} \right\rangle = \frac{k_B T}{2}$

In addition to dissipative force, there must be another, stimulative force.

$$m\dot{v} = F_{\text{dissipative}} + F_{\text{stimulative/fluctuation}} = -\lambda v + F_{\text{fluc}}(t)$$

$$\langle F_{\text{fluc}}(t) \rangle = 0$$

$$\langle F_{\text{fluc}}(t) F_{\text{fluc}}(t') \rangle = b(t - t')$$

If $b(t - t') = B\delta(t - t')$: white noise

Exact Green's function solution of $v(t)$:

$$v(t) = \frac{1}{m} \int_{-\infty}^{t} dt' F_{\text{fluc}}(t') e^{-\frac{\lambda}{m}(t-t')}$$

$$\left\langle v(t)v(\tilde{t})\right\rangle$$

$$= \frac{1}{m^2}\left\langle \int_{-\infty}^{t} dt' F_{\text{fluc}}(t') e^{-\frac{\lambda}{m}(t-t')} \int_{-\infty}^{\tilde{t}} d\tilde{t}' F_{\text{fluc}}(\tilde{t}') e^{-\frac{\lambda}{m}(\tilde{t}-\tilde{t}')} \right\rangle$$

$$= \frac{1}{m^2}\int_{-\infty}^{t} dt' e^{-\frac{\lambda}{m}(t-t')} \int_{-\infty}^{\tilde{t}} d\tilde{t}' e^{-\frac{\lambda}{m}(\tilde{t}-\tilde{t}')} \left\langle F_{\text{fluc}}(t') F_{\text{fluc}}(\tilde{t}') \right\rangle$$

$$= \frac{1}{m^2}\int_{-\infty}^{t} dt' e^{-\frac{\lambda}{m}(t-t')} \int_{-\infty}^{\tilde{t}} d\tilde{t}' e^{-\frac{\lambda}{m}(\tilde{t}-\tilde{t}')} B\delta(t'-\tilde{t}')$$

$$= \frac{1}{m^2}\int_{-\infty}^{t} dt' e^{-\frac{\lambda}{m}(t-t')} H(\tilde{t}-t') e^{-\frac{\lambda}{m}(\tilde{t}-t')} B$$

$H(x)$ is Heaviside step function:

$$H(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x \le 0 \end{cases}$$

$$= \frac{B}{2m\lambda} e^{-\frac{\lambda}{m}\left|t-\tilde{t}\right|}$$

In particular: $\left\langle v(t)v(t)\right\rangle = \dfrac{B}{2m\lambda}$

However, from equilibrium statistical mechanics:

equi-partition theorem:

$$m\left\langle v(t)v(t)\right\rangle = k_{\mathrm{B}}T$$

$$\rightarrow \quad \frac{B}{2\lambda} = k_{\mathrm{B}}T$$

The ratio between *square* of stimulative force and dissipative force is fixed, $\propto T$

$$\langle v(t)v(\tilde{t})\rangle = \frac{k_B T}{m} e^{-\frac{\lambda}{m}|t-\tilde{t}|}$$

Previously, from the Gaussian solution to

$$\partial_t \rho = D\partial_x^2 \rho, \ \ \rho(x,0) = \delta(x):$$

$$\rho_G(x,t) = \frac{1}{\sqrt{2\pi(2Dt)}} \exp\left(\frac{x^2}{2(2Dt)}\right)$$

we know if the particle is released at $x = 0$ at $t = 0$:

$$\langle x(t)x(t)\rangle = 2Dt$$

$$x(t) = 0 + \int_0^t dt' v(t'), \qquad \dot{x}(t) = v(t)$$

$$\frac{d}{dt}\left\langle x(t)x(t)\right\rangle = 2\left\langle x(t)\dot{x}(t)\right\rangle = 2\left\langle x(t)v(t)\right\rangle$$

$$= \frac{d}{dt}(2Dt) = 2D$$

$$D = \left\langle x(t)v(t)\right\rangle = \left\langle \left(\int_0^t dt'v(t')\right)v(t)\right\rangle$$

$$= \int_0^t dt'\left\langle v(t')v(t)\right\rangle$$

$$= \int_0^t dt'\left\langle v(t')v(0)\right\rangle$$

Velocity auto-correlation function: $g(t) \equiv \left\langle v(t)v(0)\right\rangle$

Actually, the onset of macroscopic diffusion

($\partial_t \rho = D\partial_x^2 \rho$) is only valid only when

$$t \gg \text{ intrinsic timescale of } g(t) \propto \frac{m}{\lambda}$$

(Same as central limit theorem in random walk)

So the correct formula is

$$D = \int_0^\infty dt' \langle v(t')v(0) \rangle$$

The above is one of the *fluctuation-dissipation* theorems.

Thermal conductivity: $\kappa = \frac{1}{\Omega k_B T^2} \int_0^\infty \langle J_q(t) J_q(0) \rangle dt$

Electrical conductivity: $\sigma = \frac{1}{\Omega k_B T} \int_0^\infty \langle J(t) J(0) \rangle dt$

Shear viscosity: $\eta = \frac{\Omega}{k_B T} \int_0^\infty \langle \tau_{xy}(t) \tau_{xy}(0) \rangle dt$

Fluctuation-dissipation theorem (Green-Kubo formula) is one of the most elegant and significant results of statistical mechanics. It relates *transport properties* (system behavior if linearly perturbed from equilibrium) to the time-correlation of *equilibrium fluctuations*.

Coming back to diffusion (mass transport):

$$\left\langle v(t)v(\tilde{t})\right\rangle = \frac{k_B T}{m} e^{-\frac{\lambda}{m}|t-\tilde{t}|}$$

So $$D = \int_0^\infty dt' \left\langle v(t')v(0)\right\rangle = \frac{k_B T}{\lambda}.$$

$\frac{1}{\lambda}$ is actually the mobility of the particle, when driven by external (non-thermal) force.

$\frac{D}{1/\lambda} = k_B T$ is called the Einstein relation, first derived in 1905.

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