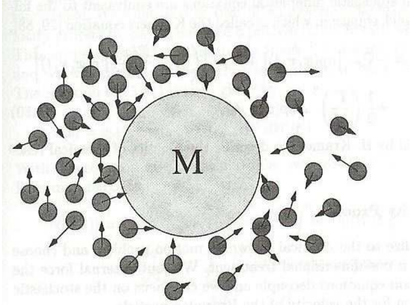
Lecture 28

15.05.2019

Brownian motion
Dissipation-Fluctuation relation

Langevin equation



Brownian particle is moving due to the random collisions with the fluid particles while dissipating energy due to the viscous drag.

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

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

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

- Amplitude of the random force (from random collisions) 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)

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

Langevin equation: Einstein's relation

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

The mean square displacement of the Brownian particles is

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

- $t \gg \frac{m}{\alpha}$ Diffusive Regime: on long timescales, the Brownian particles diffuses like a random walker

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

The diffusivity coefficient is determined by the Fluctuation-Dissipation (Einstein) formula: $D = \frac{kT}{\alpha}$

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

Langevin equation: Ballistic regime

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

The mean square displacement of the Brownian particles is

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

- $t \ll \frac{m}{\alpha}$ Ballistic Regime: on short timescales, the Brownian particles is advected by the fluid with a mean velocity determined by the kinetic energy of the fluid particles

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

$v_{thermal} = \frac{\sqrt{\langle x(t)^2\rangle}}{t} = \frac{kT}{m}$ from the equipartition of energy

Green-Kubo formula

- the mean square displamenent is related to velocity correlation function by

$$\langle x(t)^2 \rangle = \int_0^t dt' \int_0^t dt'' \langle v(t')v(t'') \rangle$$

- Gree-Kubo formula gives a general relationship between diffusion coefficient D and velocity correlation

$$D = \lim_{t \to \infty} \frac{\langle x(t)^2 \rangle}{2t} = \frac{1}{2t} \int_0^t dt' \int_0^t dt'' \langle v(t')v(t'') \rangle$$

$$D = \int_0^\infty d\tau \langle v(0)v(\tau) \rangle$$

Green-Kubo relation: derivation

Stationary process

$\langle v(t')v(t'')\rangle = \langle v(t'-t'')v(0)\rangle = f(|t'-t''|)$
(even function)

$$\langle x(t)^2\rangle = \int_0^t dt' \int_0^t dt''\, f(|t'-t''|)$$

$\tau = t'' - t'$

$$= \int_0^t dt' \int_{-t'}^{t-t'} d\tau\, f(\tau) = \int_0^t dt' \frac{d}{dt'}(t') \int_{-t'}^{t-t'} d\tau\, f(\tau)$$

$$= t' \int_{-t'}^{t-t'} d\tau\, f(\tau)\Big|_0^t + \int_0^t dt'\, t'[f(t-t') - f(t')]$$

$$= t\int_0^t d\tau\, f(\tau) - \int_0^t dt'\,(t-t')f(t-t') + t\int_0^t dt'\, f(t-t') - \int_0^t dt'\, t' f(t')$$

$$= 2t\int_0^t d\tau\, f(\tau) - 2\int_0^t d\tau\, \tau f(\tau)$$

Green-Kubo relation: derivation

$$\langle x(t)^2 \rangle = 2t \int_0^t d\tau\, f(\tau) - 2 \int_0^t d\tau\, \tau f(\tau)$$

$$D = \lim_{t\to\infty} \frac{\langle x(t)^2 \rangle}{2t} = \lim_{t\to\infty} \left[\int_0^t d\tau\, f(\tau) - \frac{1}{t} \int_0^t d\tau\, \tau f(\tau) \right] = \int_0^\infty d\tau\, f(\tau)$$

$$D = \int_0^\infty d\tau\, \langle v(0) v(\tau) \rangle$$

Green-Kubo formula: Brownian motion

$$D = \int_0^\infty d\tau \, \langle v(0)v(\tau)\rangle$$

For the Brownian motion, the velocity correlation function is given by

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

Hence, the diffusivity can be calculated as

$$D = \frac{kT}{m} \int_0^\infty dt \, e^{-\frac{\alpha t}{m}} \rightarrow D = \frac{kT}{\alpha}$$ (Einstein's relation)

Fluctuation-dissipation relation

Green—Kubo formula and Einstein's relation are example of fluctuation-dissipation relations

- In general, **Fluctuation-Dissipation relation** connects equilibrium correlation functions (measure of spontaneous equilibrium fluctuations) $C(r-r',t)$ with response functions (measure of dissipation), $\chi(r-r',t)$

$$\chi(r,t) = \begin{cases} -\beta \dfrac{\partial}{\partial t} C(r,t), & t > 0 \\ 0, & t \leq 0 \end{cases} \leftrightarrow \int_t^{\infty} d\tau \; \chi(r,t) = \beta C(r,t)$$

Assumptions:

- **Linear response**: a perturbation due an applied, external field is *linearly proportional* to the applied field
- **Time-Causality**: a perturbation cannot occur before the system is perturbed.
- **Onsager regression hypothesis**

Fluctuation-dissipation relation: Brownian motion

- Consider a Brownian motion under an externally applied force
- The system is brought of out of equilibrium by switching off the force at $t = 0$ and we want to understand how does the system relaxes back to equilibrium

$$m\,\dot{v} = -\alpha v + R(t) + F(t)$$
$$\langle R(t)\rangle = 0$$
$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

- *Average over different trajectories:* $m\frac{d}{dt}\langle v\rangle = -\alpha\langle v\rangle + F(t)$
- *Fourier transform the average equation of motion* $\left(\langle v\rangle = \frac{1}{2\pi}\int d\omega\, e^{-i\omega t}\hat{v}(\omega)\right)$

$(-im\omega + \alpha)\hat{v}(\omega) = \hat{F}(\omega)$

$$\hat{v}(\omega) = \hat{\chi}(\omega)\hat{F}(\omega), \qquad \hat{\chi}(\omega) = \frac{\alpha + im\omega}{\alpha^2 + m^2\omega^2} \quad (\mathit{response\ function})$$

- **Linear response**: *The average velocity at a given time t is linearly related to the external force applied to the system at a time $t' < t$*

$$\langle v\rangle(t) = \int_{-\infty}^{\infty} dt'\,\chi(t-t')F(t')$$

Fluctuation-dissipation relation: Brownian motion

- Consider a Brownian motion under an externally applied force

$$\hat{v}(\omega) = \hat{\chi}(\omega)\hat{F}(\omega), \qquad \hat{\chi}(\omega) = \frac{\alpha + im\omega}{\alpha^2 + m^2\omega^2}$$

  - $\hat{\chi}'(\omega) = \mathrm{Re}[\hat{\chi}(\omega)] = \frac{\alpha}{\alpha^2+m^2\omega^2}, \quad \hat{\chi}''(\omega) = Im[\hat{\chi}(\omega)] = \frac{m\omega}{\alpha^2+m^2\omega^2}$

- **Causality**: $\chi(t) = 0, t < 0 \rightarrow Kramers - Krönig\ relations\ for\ \hat{\chi}'(\omega)\ and\ \hat{\chi}''(\omega)$

$$\hat{\chi}'(\omega) = \frac{1}{\pi}\mathrm{PV}\int_{-}^{+} d\omega' \frac{\hat{\chi}''(\omega')}{\omega'-\omega}$$

$$\hat{\chi}''(\omega) = -\frac{1}{\pi}\mathrm{PV}\int_{-}^{+} d\omega' \frac{\hat{\chi}'(\omega')}{\omega' - \omega}$$

Brownian motion: response function and damping coefficient (measure of dissipation)

- Consider a Brownian motion under an externally applied force

$$\hat{v}(\omega) = \hat{\chi}(\omega)\hat{F}(\omega), \qquad \hat{\chi}(\omega) = \frac{1}{-im\omega + \alpha}$$

Response function: $\chi(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \hat{\chi}(\omega) e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{-im\omega+\alpha}$

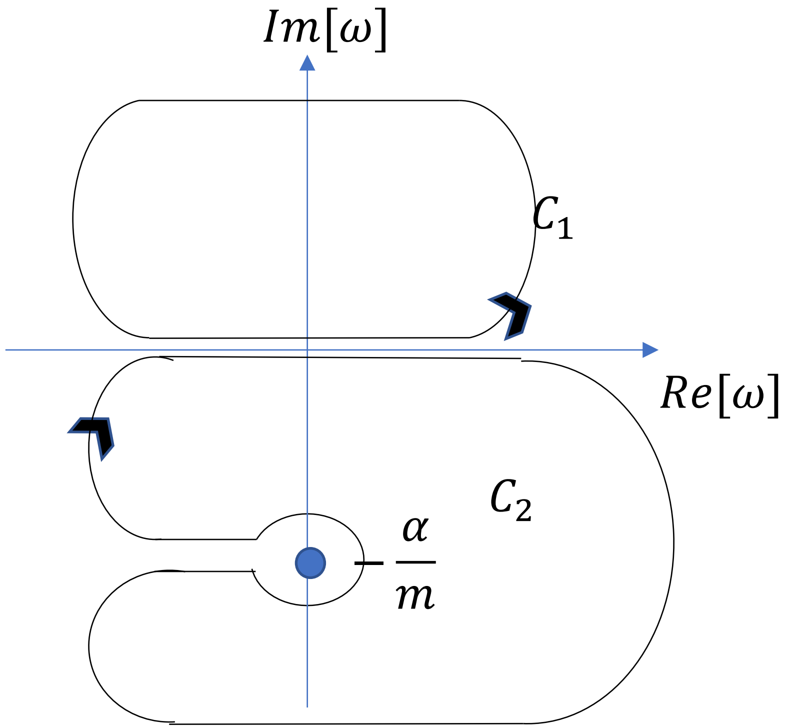
$$\chi(t) = -\frac{1}{2\pi i m}\int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{\omega + \frac{i\alpha}{m}} \rightarrow \boldsymbol{\chi(t) = \frac{1}{m} e^{-\frac{\alpha t}{m}} Heaviside[t]}$$

- $t < 0,\ \int d\omega e^{-i\omega t} < \infty\ for\ Im(\omega) > 0$

$$\oint_{C_1} d\omega \frac{e^{-i\omega t}}{\omega + i\alpha/m} = 0 \text{ (no poles)}$$

- $t > 0, \int d\omega e^{-i\omega t} < \infty\ for\ Im(\omega) < 0$

$$\oint_{C_2} d\omega \frac{e^{-i\omega t}}{\omega + i\alpha/m} = 2\pi i\, e^{-i\omega t}\Big|_{\omega = -\frac{i\alpha}{m}} = 2\pi i\, e^{-\frac{\alpha t}{m}}$$



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Response function: $\chi(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \hat{\chi}(\omega) e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{-im\omega+\alpha}$

$$\chi(t) = -\frac{1}{2\pi i m}\int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega t}}{\omega + \frac{i\alpha}{m}} \rightarrow \boldsymbol{\chi(t)} = \begin{cases} \frac{\mathbf{1}}{\boldsymbol{m}} \boldsymbol{e}^{-\frac{\boldsymbol{\alpha t}}{\boldsymbol{m}}}, & t > 0 \\ 0, & t \leq 0 \end{cases}$$

Integrated response function equals mobility: $\int_0^\infty dt\, \chi(t) = \frac{1}{\alpha}$

Brownian motion: Dissipation-fluctuation

- Consider a Brownian motion under an externally applied force

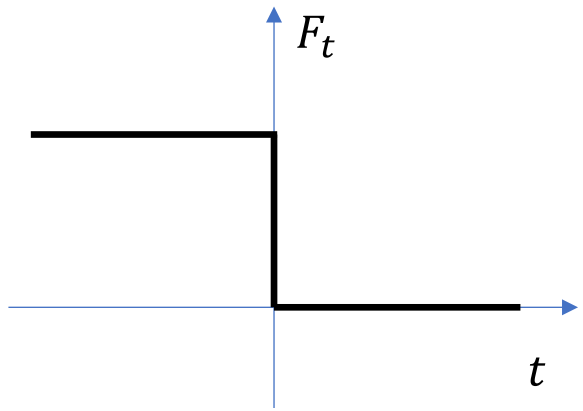
$$\hat{v}(\omega) = \hat{\chi}(\omega)\hat{F}(\omega), \qquad \hat{\chi}(\omega) = \frac{1}{-im\omega + \alpha}$$

  - **Linear response**: $\langle v\rangle(t) = \int_{-\infty}^{\infty} dt'\, \chi(t-t')F(t')$
  - **Causality** : $\chi(t) = \boldsymbol{\chi(t)} = \begin{cases} \frac{\mathbf{1}}{\boldsymbol{m}}\boldsymbol{e}^{-\frac{\boldsymbol{\alpha t}}{\boldsymbol{m}}}, & t > 0 \\ 0, & t \leq 0 \end{cases}, \int_0^{\infty} dt\, \chi(t) = \frac{1}{\alpha}$
  - **Regression hypothesis**: noise averages along different trajectories equal ensemble averages with the equilibrium Maxwell-Boltzmann distribution during the relation from an initial perturbation

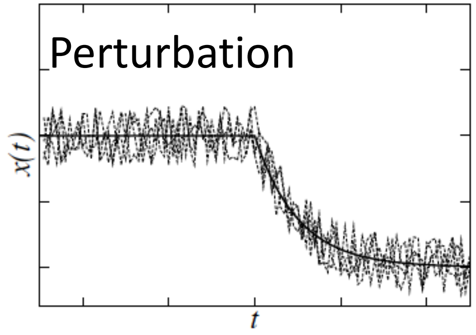
$$\langle x\rangle(t) \equiv \frac{1}{Z}\int d\omega_{eq} x_t\, e^{-\beta(H - x_t F_t)}$$

Brownian motion: Regression hypothesis

- Regression hypothesis: noise averages along different trajectories equal ensemble averages with the equilibrium Maxwell-Boltzmann distribution during the relation from an initial perturbation

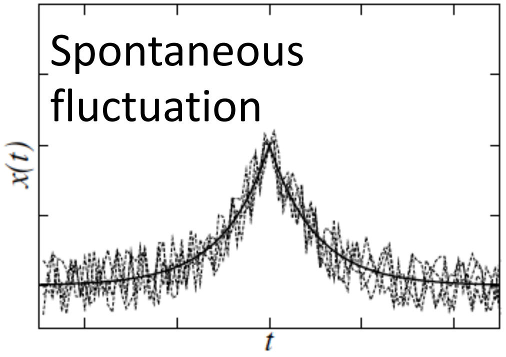


$$\langle x\rangle(t) \equiv \frac{1}{Z}\int d\omega_{eq} x_t\, e^{-\beta(H - x_t F_t)} \approx \frac{1}{Z}\int d\omega_{eq} x_t\, e^{-\beta H}(1 + \beta x_0 F_0)$$

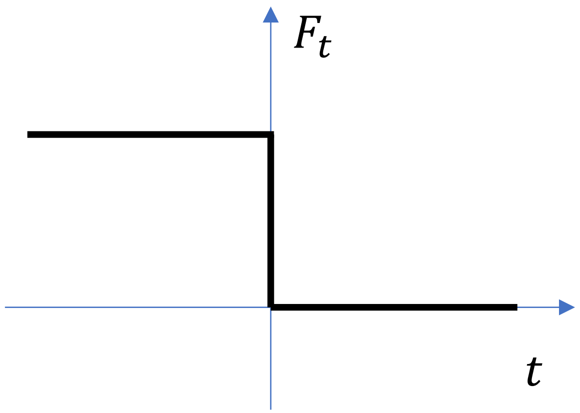


$$\langle x\rangle_F(t) \equiv \langle x\rangle_{F=0} + \beta\langle x_t x_0\rangle_{F=0} F$$

$$\langle x\rangle(t) \equiv \beta\langle x_t x_0\rangle_{F=0} F$$



Brownian motion: Regression hypothesis



- Regression hypothesis:

$$\langle x\rangle(t) \equiv \beta\langle x_t x_0\rangle_{F=0} F \qquad (1)$$

- Linear response: $\langle \dot{x}\rangle(t) = \int_{-\infty}^{\infty} dt'\,\chi(t-t')F(t') \to \langle x\rangle(t) = \int_0^t dt_1 \int_{-\infty}^{\infty} dt'\,\chi(t_1-t')F(t')$

$$\langle x\rangle(t) = \int_{-\infty}^{\infty} dt'\,\kappa(t-t')F(t'), \qquad \kappa(t-t') = \int_0^t dt_1\,\chi(t_1-t')$$

Hence using Eq. (1): $\langle x\rangle(t) = F\int_{-\infty}^{0} dt'\,\kappa(t-t') = \beta\langle x_t x_0\rangle_{F=0}F$

$$\int_{-\infty}^{0} dt'\,\kappa(t-t') = \beta\langle x_t x_0\rangle_{F=0}$$

$\tau = t - t'$

$$\int_t^{\infty} d\tau\,\kappa(\tau) = \beta\langle x_t x_0\rangle_{F=0}$$

Response function is $\kappa(t) = -\beta\frac{d}{dt}\langle x_t x_0\rangle_{F=0}, \qquad t > 0$

Brownian motion: Fluctuation-Dissipation relation

- *How do we obtain Einstein's formula for the diffusivity?*

Fluctuation-Dissipation relation

$$\kappa(t) = -\beta \frac{d}{dt}\langle x_t x_0 \rangle_{F=0}, \qquad t > 0 \quad (*)$$

Use that $\langle x(t)x(0)\rangle = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \hat{S}_x(\omega) e^{-i\omega t}$, $\hat{S}_x(\omega) = |\tilde{x}(\omega)|^2$ power spectrum of position fluctuations

Similarly, $\langle v(t)v(0)\rangle = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, \hat{S}_v(\omega) e^{-i\omega t}$, $\hat{S}_v(\omega) = |\tilde{v}(\omega)|^2$ power spectrum of velocity fluctuations

Relation between power spectrum:

$$\boldsymbol{\hat{S}_v(\omega) = \omega^2 \hat{S}_x(\omega)}$$

Then, the FT of the Fluctuation-Dissipation relation (*)

$$\hat{\kappa}(\omega) = i\beta\omega \hat{S}_x(\omega)$$

Brownian motion: Fluctuation-Dissipation relation

Fluctuation-Dissipation relation

$$\kappa(t) = -\beta \frac{d}{dt} \langle x_t x_0 \rangle_{F=0}, \qquad t > 0$$

With the FT

$$\hat{\kappa}(\omega) = i\beta\omega \hat{S}_x(\omega)$$

Relation between power spectrum:

$$\hat{S}_v(\omega) = \omega^2 \hat{S}_x(\omega) \rightarrow \hat{\kappa}(\omega) = -\frac{\beta}{i\omega} \hat{S}_v(\omega)$$

- Relate it with velocity response function $\chi(t) = \frac{d}{dt}\kappa(t) \rightarrow \hat{\chi}(\omega) = -i\omega\hat{\kappa}(\omega)$
- Fluctuation-Dissipation relation for the velocity fluctuations:

$$\hat{\chi}(\omega) = \beta \hat{S}_v(\omega) \rightarrow$$

$$\chi(t) = \beta \langle v(t) v(0) \rangle, \qquad t > 0$$

Brownian motion: Fluctuation-Dissipation relation

- Fluctuation-Dissipation relation for position fluctuations:

$$\kappa(t) = -\beta \frac{d}{dt}\langle x_t x_0 \rangle_{F=0}, \qquad t > 0$$

- Fluctuation-Dissipation relation for the velocity fluctuations:

$$\chi(t) = \beta \langle v(t)v(0) \rangle, \qquad t > 0$$

Recall: $\int_0^\infty dt\, \chi(t) = \frac{1}{\alpha}$ and Green-Kobo formula $D = \int_0^\infty dt\, \langle v(t)v(0) \rangle$

$$\int_0^\infty dt\, \chi(t) = \beta \int_0^\infty dt\, \langle v(t)v(0) \rangle$$

$$\frac{1}{\alpha} = \beta D \rightarrow \boldsymbol{D = \frac{kT}{\alpha}}$$

Fluctuation-Dissipation relations

- FT of the Langevin equation:

$$\tilde{\mathrm{v}}(\omega) = \frac{\hat{R}(\omega)}{-i\omega m + \alpha} = \hat{\chi}(\omega)\hat{R}(\omega)$$

- Power spectrum of the velocity fluctuations:

$$\hat{\mathrm{S}}_{\mathrm{v}}(\omega) = |\tilde{v}(\omega)|^2 = \frac{\left|\hat{R}(\omega)\right|^2}{|-i\omega m + \alpha|^2} = \frac{2\alpha kT}{|-i\omega m + \alpha|^2}$$

Using Green-Kobo formula $\mathrm{D} = \int_0^\infty dt\,\langle \mathrm{v(t)v(0)}\rangle = \hat{\mathrm{S}}_{\mathrm{v}}(0)$

$$\boldsymbol{D = \hat{S}_v(0) \leftrightarrow D = \frac{kT}{\alpha} \leftrightarrow D = kT\hat{\chi}(0) \leftrightarrow D = -kT \lim_{\omega\to 0}(\omega\hat{\kappa}(\omega))}$$