$$\bar{A} = \langle A \rangle + \beta f_0 \underbrace{\int_0^\infty dt \, \langle \delta A(t) \, \delta \dot{B}(0) \rangle}_{\text{transport coefficient}}$$

$\mathcal{H} = \mathcal{H}_0 - fB$ NESS

Green-Kubo formula

<u>Example 1:</u> Electrical conductivity

$$\mathcal{H} = \mathcal{H}_0 - E \sum_i q_i x_i$$

x_i: x-coord. of p. i

q_i: charge " " "

E: electric field in x direction

$$f \equiv E \quad , \quad B \equiv \sum_i q_i x_i$$

$$\langle B \rangle = 0 \qquad \dot{B} = \sum_i q_i \dot{x}_i = \sum_i q_i v_{ix}$$

Current density : $\bar{j} = \sum_i q_i \, \delta(\bar{r} - \bar{r}_i(t)) \, \dot{\bar{r}}_i$

$$\bar{J} := \int d^3\bar{r} \, \bar{j}(\bar{r}, t) = \underline{\sum_i q_i \dot{\bar{r}}_i} \Rightarrow \dot{B} = J_x$$

Set $A = \dot{B} = J_x \qquad \langle A \rangle = 0$

$$\bar{J}_x = \beta E \int_0^\infty dt \, \langle J_x(t) J_x(0) \rangle$$

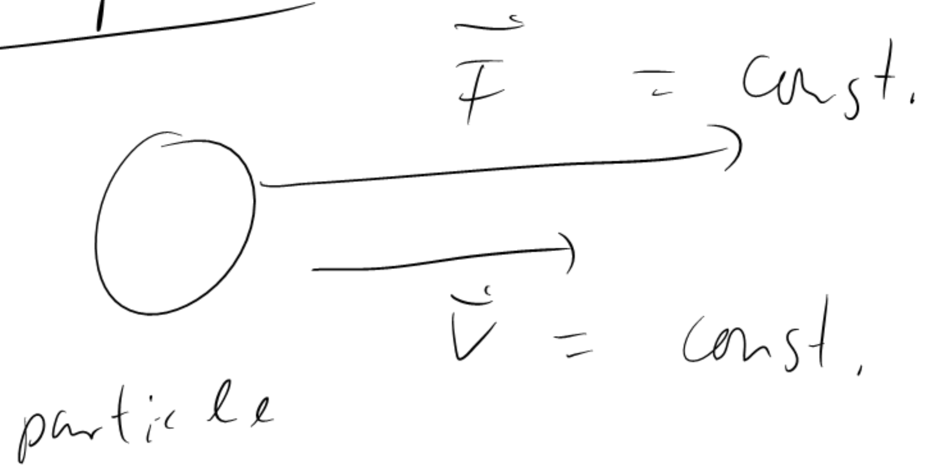
$$\bar{j}_x = \frac{1}{V}\bar{J}_x = \frac{\beta E}{V}\int_0^\infty dt \, \langle J_x(t)\, J_x(0)\rangle$$

$$j_x \doteq \sigma E$$ conductivity (def.)

$$\boxed{\sigma = \frac{1}{VT}\int_0^\infty dt \, \langle J_x(t)\, J_x(0)\rangle}$$

Green-Kubo formula for the conductivity

Example 2:



mobility μ:

$$\vec v = \mu \vec F \quad (F \to 0)$$

friction coefficient ξ

$$\vec F = \xi \vec v \,, \quad \xi = \frac{1}{\mu}$$

$$\mathcal{H} = \mathcal{H}_0 - F x$$

x → coordinate of the particle

$f \equiv F \qquad B \equiv x \qquad \langle x \rangle = 0 \qquad \dot B = \dot x = v$

(in x direct.)

$A \equiv v \qquad \langle A \rangle = 0$

$$\bar{v} = \beta F \int_0^\infty dt \, \langle v(t) \, v(0) \rangle$$

velocity autocorrelation function

$$\boxed{\mu = \frac{1}{T} \int_0^\infty dt \, \langle v(t) \, v(0) \rangle}$$

Green - Kubo relation for μ

$$\Rightarrow \zeta = \frac{T}{\int_0^\infty dt \, \langle v(t) \, v(0) \rangle}$$

Green - Kubo relation for ζ = ??

relation to the diffusion coefficient?

in thermal equilibrium, particle performs Brownian motion

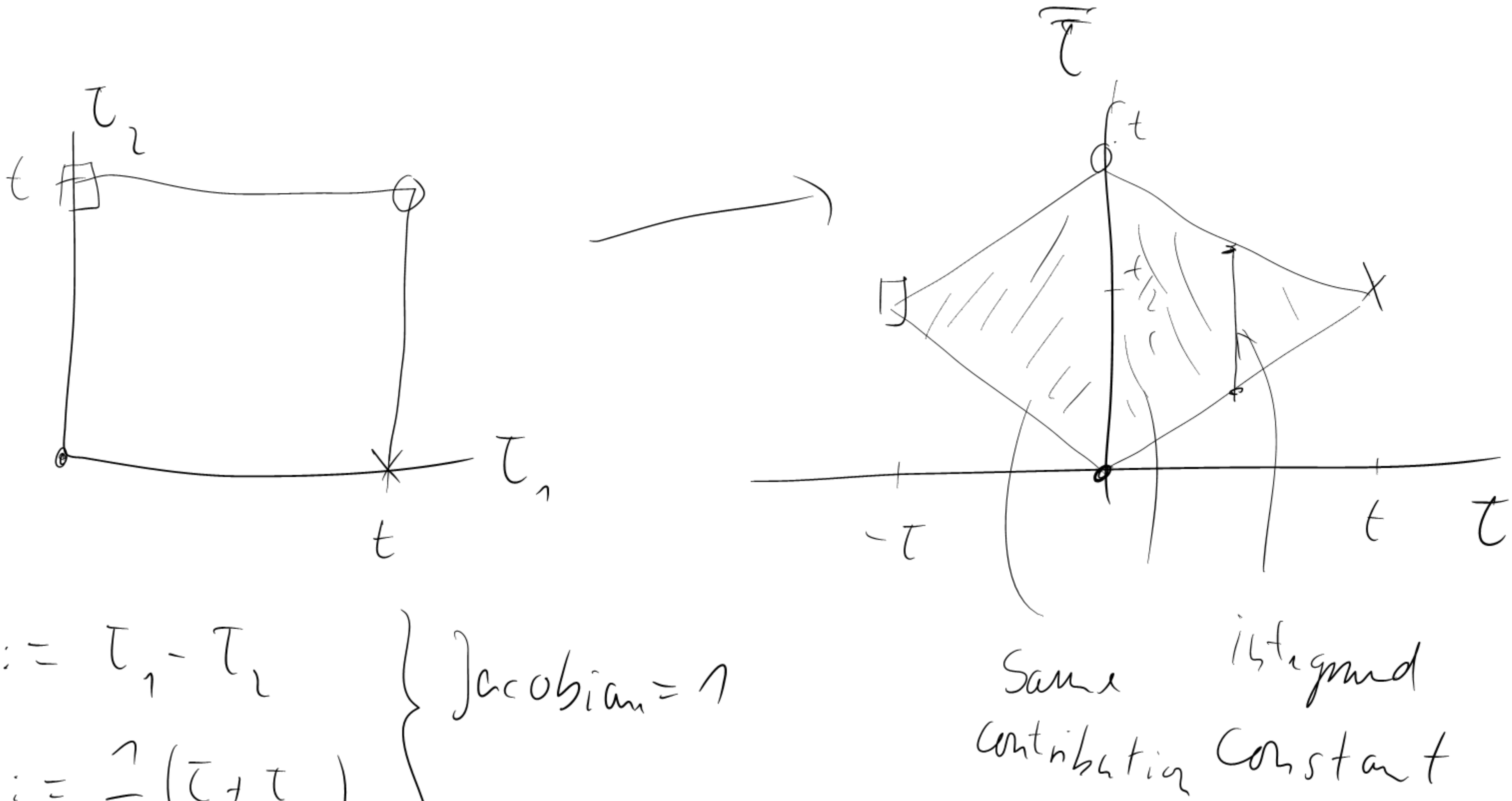
$$\langle \Delta x^2 \rangle = 2D\,t$$

$$\langle \Delta \vec{r}^{\,2} \rangle = \langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle + \langle \Delta z^2 \rangle = 6Dt$$

$$\Delta x(t) = \int_0^t d\tau\, v(\tau)$$

$$\langle \Delta x(t)^2 \rangle = \int_0^t d\tau_1 \int_0^t d\tau_2 \langle v(\tau_1)\, v(\tau_2) \rangle$$

depends only on $\tau_1 - \tau_2$



$$\left.\begin{aligned} t &:= \tau_1 - \tau_2 \\ \tilde{\tau} &:= \frac{1}{2}(\tau_1 + \tau_2) \end{aligned}\right\} \text{Jacobian} = 1$$

$$\langle \Delta x(t)^2 \rangle = 2 \int_0^t d\tau \underbrace{\int_{\tau/2}^{t-\tau/2} d\tilde{\tau}}_{\to (t-\tau)} \langle v(0)\, v(\tau) \rangle$$

$$\frac{\langle \Delta x^2(t) \rangle}{2t} = \int_0^t d\tau \left(1 - \frac{\tau}{t}\right) \underbrace{\langle v(\tau)\, v(0) \rangle}_{\text{decays quickly}}$$

$t \to \infty$:

$$\underbrace{\int_0^\infty d\tau \, \langle v(\tau)\, v(0) \rangle} - \underbrace{\frac{1}{t} \underbrace{\int_0^t d\tau \, \tau \, \langle v(\tau)\, v(0) \rangle}_{\to \text{ const. for } t \to \infty}}_{\to 0}$$

$$\Rightarrow \boxed{D = \int_0^\infty dt \, \langle v(t)\, v(0) \rangle}$$

Green-Kubo for the diffusion const

$$\Rightarrow \mu = \beta D \,, \quad D = T\mu = \frac{T}{\xi}$$

Einstein relation

The Mori-Zwanzig Projection Operator Formalism

Γ phase space, $A(\Gamma)$, $B(\Gamma)$ observables, function on phase space

complex conjugate

Scalar product:

$$(A|B) = \int d\Gamma \, A^*(\Gamma) \, B(\Gamma)$$

operator $\mathcal{J}$: $A(\Gamma) \longrightarrow \mathcal{J} A(\Gamma)$

linear

$$(A|\mathcal{T}B) = (A|\mathcal{T}B)$$

adjoint operator $\mathcal{T}^+$; $(A|\mathcal{T}B) = (\mathcal{T}^+A|B)$

Self-adjoint op.: $\mathcal{T}^+ = \mathcal{T}$

Hamilton's eq. of motion: q_i coord, p_i mom.

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

dynamics of an observable:

$$\frac{d}{dt} A = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) =$$

$$= \underbrace{\sum_i \left(\frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial}{\partial p_i} \right)}_{i\mathcal{L}} A = i\mathcal{L} A$$

$\mathcal{L}$: Liouville operator

$$\boxed{A(t) = \exp(i\mathcal{L}t)\, A(0)}$$

$\mathcal{L}$ is self-adjoint:

$$\mathcal{L} = \frac{1}{i} \underbrace{iL}_{\text{real}}$$

$$L^* = -L$$

$$(A|\mathcal{L}B) = \int d\Gamma \, A^*(\Gamma) \, \mathcal{L} \, B(\Gamma) =$$

$$= \frac{1}{i} \int d\Gamma \, A^*(\Gamma) \sum_i \left(\frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial}{\partial p_i} \right) B(\Gamma) =$$

$$= -\frac{1}{i} \int d\Gamma \, B(\Gamma) \sum_i \left(\frac{\partial}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) A^*(\Gamma) =$$

$$= -\frac{1}{i} \int d\Gamma \, B(\Gamma) \underbrace{\sum_i \left(\frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial}{\partial p_i} \right)}_{iL} A^*(\Gamma)$$

$$= - \int d\Gamma \; B(\Gamma) \; \mathcal{L} A^*(\Gamma) = \int d\Gamma \; B(\Gamma) \; \mathcal{L}^* A^*(\Gamma)$$

$$= \int d\Gamma \; (\mathcal{L} A)^* B = (\mathcal{L} A | B)$$

$\rightsquigarrow$ $\mathcal{L}$ is self-adjoint

$\rightsquigarrow$ $\exp(i \mathcal{L} t)$ is UNITARY

$\rightarrow$ Liouville theorem

yet another scalar product:

$$\langle A | B \rangle = \int d\Gamma \, \underbrace{\rho(\Gamma)}_{>0} \; A^*(\Gamma) \, B(\Gamma)$$

$$\rho(\Gamma) = \frac{\exp(-\beta \mathcal{H}(\Gamma))}{\int d\Gamma \exp(-\beta \mathcal{H}(\Gamma))}$$

$$= \left(A^* B \right)_{\text{thermal}}$$

$$\left(A^*(0) \, B(t) \right)_{\text{thermal}} = \left\langle A^* e^{iLt} B \right\rangle_{tL} =$$

$$= \langle A | e^{iLt} | B \rangle \qquad (e^{iLt})^+ = e^{-iLt}$$

Claim: $\mathcal{L}$ is ALSO self-adjoint wrt. $\langle | \rangle$

$$\langle A | \mathcal{L} B \rangle = \int d\Gamma\, \rho(\Gamma)\, A^*(\Gamma)\, \mathcal{L}\, B(\Gamma) =$$

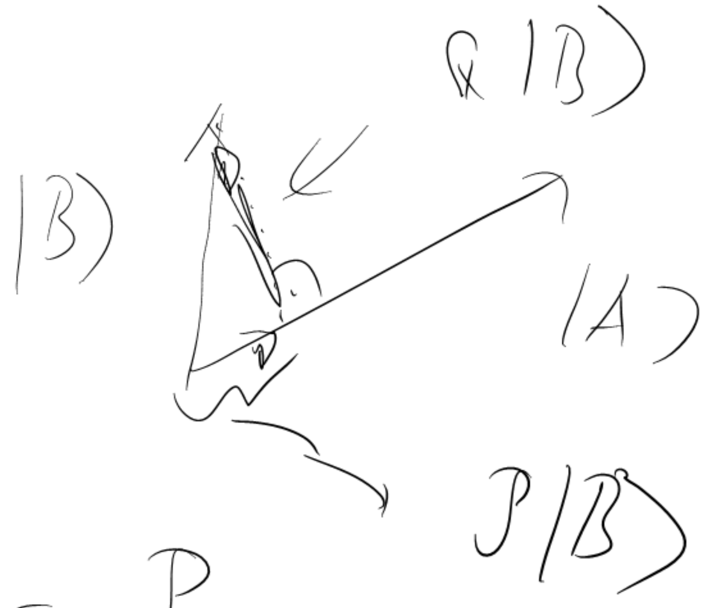
$$= \frac{1}{i} \int d\Gamma\, B(\Gamma)\, i\mathcal{L} \left(\rho(\Gamma) A^*(\Gamma) \right) \overset{\text{product rule}}{=} \dots$$

$$= \pm \frac{1}{i} \int d\Gamma\, B(\Gamma)\, A^*(\Gamma)\, \underbrace{i\mathcal{L}\, \rho(\Gamma)}_{=0} \pm \frac{1}{i} \int d\Gamma\, B(\Gamma)\, \rho(\Gamma)\, i\mathcal{L}\, A^*(\Gamma)$$

$$= \langle \mathcal{L} A | B \rangle$$

$|A\rangle$ "slow"

all the rest "fast"



$$P := \frac{|A\rangle\langle A|}{\langle A|A\rangle} \qquad P^2 = P$$

$$P^2 = \frac{1}{\langle A|A\rangle^2} |A\rangle\langle A|A\rangle\langle A| = P$$

$$\langle B|A\rangle = 0$$

$$Q = 1 - P$$