# Hydrodynamics and Green-Kubo relation

(free particles)

Conserved quantity $a$

with density $\rho_a(\vec{x},t)$ and current $\vec{J}_a(\vec{x},t)$

continuity
$$\underbrace{\frac{\partial \rho_a(\vec{x},t)}{\partial t} = -\vec{\nabla}\cdot\vec{J}_a(\vec{x},t)}$$

EXACT microscopic law

PHENOMENOLOGICAL constitutive equation

(for weak gradients → local equilibrium)

$$\langle \vec{J}_a(\vec{x},t)\rangle = -\underbrace{D_a}\,\vec{\nabla}\langle \rho_a(\vec{x},t)\rangle$$

Fick's law

non-equilibrium averages

transport coefficient

(transport coefficients derived using kinetic: $D = \langle v\rangle \lambda/3$
$\lambda$ = mean free path)

Continuity eq. + constitutive eq.

→ F. P. eq. for $\langle \rho_a(\vec{x},t)\rangle$

$$\frac{\partial \langle \rho_a(\vec{x},t)\rangle}{\partial t} = D_a \vec{\nabla}^2 \langle \rho_a(\vec{x},t)\rangle$$

$$\underbrace{\langle \rho_a(\vec{x},t)\rangle \propto \langle \rho_a(\vec{x},t)\,\rho_a(\vec{y},t')\rangle_0}$$

spatial homogeneity $\quad C(\vec{x}-\vec{y}, t-t')^{1)} \quad$ time translation invariance

F.P. eq. for $C(\vec{x}-\vec{y}, t-t')$ :

$$\boxed{\frac{\partial C}{\partial t} = D \vec{\nabla}_x^2 C}$$

$$C(\vec{k}, t-t') = \int_V d\vec{x} \exp(-i\vec{k}\cdot(\vec{x}-\vec{y})) \cdot C(\vec{x}-\vec{y}, t-t')$$

$$= \frac{1}{V} \langle \rho(\vec{k},t)\, \rho(-\vec{k},t') \rangle_0$$

F.P. eq. for $C(\vec{k}, t-t')$

$$\boxed{\frac{\partial C}{\partial t} = -D k^2 C}$$ with solution

$$C(\vec{k}, t) = \underbrace{C(\vec{k}, 0)}_{\mathcal{C}} \exp(-D k^2 t) \quad (t > 0)$$

$$\left( \text{for } t < 0 \sim \underline{C(\vec{k}, -t) = C(\vec{k}, t)} \right)$$

from $C(\vec{x}-\vec{y}, t)$ $\shortparallel$ $C(\vec{y}-\vec{x}, t)$

$$\Rightarrow \boxed{C(\vec{k}, t) = \mathcal{C} \exp(-D k^2 |t|)}$$

Time Fourier transform

$$C(\vec{k}, \omega) = \int_{-\infty}^{+\infty} dt \exp(-i\omega t)\, \mathcal{C} \exp(-D k^2 |t|)$$

$$= \mathcal{C} \int_0^{+\infty} dt \exp(-D k^2 t) \left[ \exp(-i\omega t) + \exp(+i\omega t) \right]$$

$$= \mathcal{C} \left[ \frac{1}{D k^2 + i\omega} + \frac{1}{D k^2 - i\omega} \right]$$

$$= \mathcal{C} \frac{2 D k^2}{\omega^2 + (D k^2)^2}$$

Lorentzian with a width $D k^2$

$$\boxed{\lim_{k \to 0} \frac{C(\vec{k}, \omega)}{k^2} = \ell \frac{2D}{\omega^2}} \quad (*)$$

Continuity equation → Fourier Transform ($\vec{k}$)

$$\frac{\partial \rho(\vec{k}, t)}{\partial t} + i \vec{k} \cdot \vec{J}(\vec{k}, t) = 0$$

$$\frac{\partial}{\partial t} \frac{\partial}{\partial t'} C(\vec{k}, t-t') = \frac{1}{V} \left\langle \frac{\partial}{\partial t} \rho(\vec{k}, t) \frac{\partial}{\partial t'} \rho(-\vec{k}, t') \right\rangle_0$$

$$= \frac{1}{V} \sum_{i,j} k_i k_j \langle J_i(\vec{k}, t) J_j(-\vec{k}, t') \rangle_0$$

Time Fourier transform $\int_{-\infty}^{+\infty} d(t-t') \exp(-i\omega(t-t'))\, \square$

$$\omega^2 C(\vec{k}, \omega) = \frac{1}{V} \int_{-\infty}^{+\infty} d(t-t') \cdot \sum_i k_i k_j \langle J_i(\vec{k}, t) J_j(-\vec{k}, t') \rangle_0 \cdot \exp(-i\omega(t-t'))$$

$$\lim_{\omega \to 0} \lim_{k \to 0}$$

$$J_i^T(t) = \lim_{k \to 0} J_i(\vec{k}, t) = \int_V d\vec{x}\, J_i(\vec{x}, t)$$

total current

$$\lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega^2 C(\vec{k}, \omega)}{k^2} = \frac{1}{V} \int_{-\infty}^{+\infty} d(t-t') \lim_{k \to 0} \frac{\sum_{ij} k_i k_j}{k^2} \cdot \langle J_i^T(t) J_j^T(t') \rangle_0$$

isotropy

$$\frac{\delta_{ij}}{d} \langle \vec{J}^T(t) \cdot \vec{J}^T(t') \rangle_0$$

$$\lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2 C(\vec{k},\omega)}{k^2} = \frac{1}{dV}\int_0^{+\infty} dt\, \langle \dot{\vec{J}}^T(t)\cdot\dot{\vec{J}}^T(0)\rangle_0$$

$$\left(\dot{\vec{J}}^T(t) = \dot{\vec{J}}^T(-t)\right)$$

Together with (*)

$$\boxed{\underset{\text{transport coefficient}}{\underline{D}} = \frac{1}{dV\,\mathcal{C}}\lim_{\varepsilon\to 0^+}\int_0^{\infty} dt\, \exp(-\varepsilon t)\,\langle \dot{\vec{J}}^T(t)\cdot\dot{\vec{J}}^T(0)\rangle_0}$$

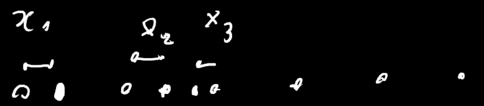
eq. average of current-current autocorrelation function

$$\boxed{\mathcal{C} = C(0,0) = \int_V d\vec{x}\, C(\vec{x},0)}$$

general Green-Kubo relation

Example for 1d system of $N$ particles with mass $m$, interacting through n-n potential

$V(x_{n+1} - x_n)$ $\quad x_n$ = displacement from lattice site (eq. position)




With PBC and the constraint $v_{cm} = 0$

$$\eta_B = \frac{1}{NT}\int_0^{\infty} dt\, \langle J_p(t)\, J_p(0)\rangle_0$$

bulk viscosity

$$J_p(t) = \sum_{n=1}^{N} F_n(t)$$

Total momentum flux

eq. of motion

$$m\ddot{x}_n = -F_n + F_{n-1}$$

$$F_n = -V'(x_{n+1} - x_n)$$

$$K = \frac{1}{NT^2}\int_0^{\infty} dt\, \langle J_E(t)\, J_E(0)\rangle_0$$

thermal conductivity

$$J_E(t) = \frac{1}{2}\sum_{n=1}^{N} F_n(t)\left[\dot{x}_{n+1} + \dot{x}_n\right]$$

total heat flux

Generalized Linear Response Function

different pairs of conjugated variables $h_k X_k$

$$\mathcal{H}' = \mathcal{H} - \sum_k h_k(t) X_k$$

Perturbation $h_j(t) \Rightarrow$ response in the observable $X_i$ $(i \neq j)$

$(\langle X_k \rangle_0 = 0 \quad \forall k)$

$$\langle X_i(t) \rangle = \int_{-\infty}^{+\infty} dt' \underbrace{\chi_{ij}(t-t')}_{\text{Response of } X_i \text{ to the perturbation } h_j} h_j(t')$$

non-equilibrium average

$$\chi_{ij}(t) = -\beta\, \theta(t) \frac{d}{dt} \langle X_i(t) X_j(0) \rangle_0$$

In Fourier space (frequency domain)

$$\langle X_i(\omega) \rangle = \chi_{ij}(\omega) h_j(\omega)$$

$$\chi_{ij}(\omega) = -\beta \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \theta(\omega-\omega')\, i\omega' C_{ij}(\omega')$$

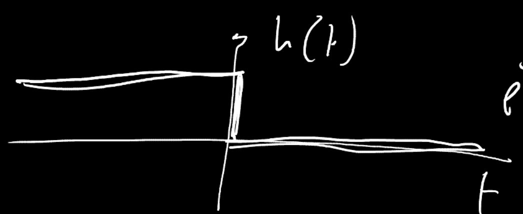
with $C_{ij}(\omega) = \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \langle X_i(t) X_j(0) \rangle$

$$= \lim_{T\to\infty} \frac{1}{T} \langle | X^*_{i,T}(\omega) X_{j,T}(\omega) | \rangle_0$$

$C_{ij}(\omega) \geq 0$ !

$$\chi^I_{ij}(\omega) = -\frac{\beta\omega}{2} C_{ij}(\omega) \; ; \; \chi^R_{ij}(\omega) = PV\left[\int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\chi^I_{ij}(\omega')}{\omega-\omega'}\right]$$

for $h_i(t) = h\,\theta(-t)$




SMALL PERTURBATION!

$$\langle X_i(t)\rangle = \beta h \langle X_i(t)\, X_j(0)\rangle_0$$

non-equilibrium relaxation to the equilibrium value

equilibrium decay of the correlation function

ONSAGER REGRESSION RELATION

Time reversal properties of $\Xi_{ij}(t)$

$\mathcal{T}$ = time reversal operator

$\{q_k(t), p_k(t)\}_{t=0,T}$

Trajectory solving the Hamilton equations with initial conditions $q_k(0), p_k(0)$

$$\mathcal{T}\,(q_k(t), p_k(t)) = (q_k(t), -p_k(t))$$

Reversibility (DB in stochastic processes) implies

if $(q_k(t), p_k(t))$ trajectory with initial conditions $q_k(0), p_k(0)$

$\Rightarrow$ time-reversed trajectory $\mathcal{T}(q_k(t), p_k(t))$ is also a solution with initial conditions $\mathcal{T}(q_0(t), p_0(t))$


forward trajectory

backward trajectory (explicit time inversion)

going backward in time

Assume that $X_i(t)$ eigenfunctions of $\mathcal{T}$ + i eigenvalues?

$$X_i(-t) = \mathcal{T} X_i(t) = X_i(\mathcal{T}(q_x(t), p_x(t))) \stackrel{!}{=} X_i(q_x(t), -p_x(t)) \stackrel{!}{=} \varepsilon_i X_i(t)$$

eigenvalues $\varepsilon_i$

$$\boxed{\varepsilon_i = \pm 1}$$

$\mathcal{H} = \mathcal{T}\mathcal{H}$ — at equilibrium Boltz. distrib. $\exp(-\beta\mathcal{H})$ is the same for forward and the time-reversed trajectories

$$\langle X_i(t) X_j(0)\rangle_0 = \langle \mathcal{T} X_i(-t)\, \mathcal{T} X_j(0)\rangle_0 \stackrel{!}{=} \varepsilon_i \varepsilon_j \langle X_i(-t) X_j(0)\rangle_0 \stackrel{!}{=} \varepsilon_i \varepsilon_j \langle X_j(t) X_i(0)\rangle_0$$

time translation invariance →

$$\tilde{\Gamma}_{ij}(t) = -\beta\, \theta(t) \frac{d}{dt} \langle X_i(t) X_j(0)\rangle_0 \stackrel{!}{=} -\beta\, \varepsilon_i \varepsilon_j\, \theta(t) \frac{d}{dt} \langle X_j(t) X_i(0)\rangle_0$$

$$\Rightarrow \boxed{\tilde{\Gamma}_{ij}(t) = \varepsilon_i \varepsilon_j \tilde{\Gamma}_{ji}(t)}$$

response function may be symmetric or antisymmetric

observables with the same parity under time-reversal

observables with different parities under time reversal

Entropy Production, Thermodynamic forces, fluxes
(Affinities)

$2^{nd}$ law: for isolated systems $\underline{\underline{dS \geq 0}}$

- in out-of-equilibrium (irreversible) processes $\to dS > 0$
- in equilibrium $dS = 0 \to S$ is maximum

universe = system + reservoir

$d\mathcal{S} = dS + dS_r$ $\qquad$ $2^{nd}$ law: $\boxed{d\mathcal{S} \geq 0}$

(entropy is extensive) $\qquad$ $dS, dS_r$ may be $< 0$

For example: - adiabatic process $\to dS_r = 0 \; (dQ = 0)$

$\Rightarrow \quad dS = d\mathcal{S} \geq 0$

- isothermal process $\Big($ $dQ > 0 \Rightarrow$ heat absorbed by the system and lost by the reservoir $\Big)$

$dS_r = -\frac{dQ}{dt}$

$\Rightarrow dS = d\mathcal{S} - dS_r \geq 0 + dQ/dt = + dQ/dt$

$\underline{dS \geq dQ/dt}$ (at equilibrium $dS = dQ/dt$)

Relation between ENTROPY PRODUCTION and THERMODYNAMIC FORCES (causing entropy production)

$S = S(\{X_i\})$ $\qquad$ $X_i$ = extensive thermodynamic observables

$\mathbb{X}_i = X_i + X_i^{(r)}$ $\qquad$ $\underline{X_i \text{ conserved quantity}}$

$d\mathbb{X}_i = 0 \Rightarrow dX_i = -dX_i^{(r)}$

Thermodynamic force: (entropy is the thermodyn. potential for an isolated system)

$$\mathbb{F}_i = \frac{\partial \mathcal{S}}{\partial X_i}$$

( $-S$ )

$$= \frac{\partial S}{\partial X_i} - \frac{\partial S_r}{\partial \cancel{X}_i^{(r)}} \qquad \left( dX_i = - dX_i^{(r)} \right)$$

$$= F_i - F_i^{(r)}$$

$$F_i = \frac{\partial S}{\partial \cancel{X}_i} \; ; \; F_i^{(r)} = \partial S_r / \partial X_i^{(r)}$$

AFFINITY

at equilibrium: $d\mathcal{S} = 0$ ; $\mathcal{S}$ is maximum

$$\Rightarrow \mathbb{F}_i = 0 \quad \forall i$$

$( X_i^* = 0 \; \forall i )$

$\mathbb{F}_i \neq 0 \Rightarrow$ irreversible processes to restore equilibrium

Example: $\underline{T\,dS = dU} + \underline{P\,dV} - \underline{\sum_j \mu_j\, dN_j}$

pressure

chemical potential for species $j$

(local equilibrium)

quasi-reversible processes

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \; ; \; \left(\frac{\partial S}{\partial V}\right)_{T,N_j} = \frac{P}{T} \; ; \; \left(\frac{\partial S}{\partial N_j}\right)_{T,V} = -\frac{\mu_j}{T}$$

affinities: $\mathbb{F}_U = \frac{1}{T} - \frac{1}{T_r}$ ; $\mathbb{F}_V = \frac{P}{T} - \frac{P_r}{T_r}$

$$\mathbb{F}_{N_j} = -\frac{\mu_j}{T} + \frac{\mu_j^{(r)}}{T_r}$$

at equilibrium: $\mathbb{F}_U = \mathbb{F}_V = \mathbb{F}_{N_j} = 0 \Rightarrow T, P, \mu_i$ are the same in the system and in the reservoir

if $T_r \neq T$

heat flows from/to the reservoir to/from the system

$\Rightarrow U$ changes in the system

In general: Flux: $J_i = \frac{dX_i}{dt}$

$$\underbrace{(J_i \neq 0 \Leftarrow \mathbb{F}_i \neq 0)}_{\text{non-equilibrium process}}$$

$$\frac{dS}{dt} = \sum_i \underbrace{\left(\frac{\partial S}{\partial X_i} - \frac{\partial S_r}{\partial X_i^{(r)}}\right)}_{\frac{\partial S}{\partial X_i} = \mathbb{F}_i} \underbrace{\frac{dX_i}{dt}}_{J_i}$$

$$\boxed{\frac{dS}{dt} = \sum_i \mathbb{F}_i J_i \geq 0}$$

universe entropy production rate

- equilibrium: $(J_i = 0)$ $\mathbb{F}_i = 0$ $dS/dt = 0$
- non-equilibrium $\mathbb{F}_i, J_i \neq 0$ $dS/dt > 0$