II.1.4 Green-Kubo Relations

earlier example: diffusion coefficient (a transport, i.e. out-of-equilibrium, quantity) can be calculated by only knowing the equilibrium correlation function VACF

Is this finding more general? Yes!

consider motion of a sphere in a fluid with drag and random forcing

$$\boxed{\partial_t \vec{v} + \zeta \vec{v} = \vec{F}_{rand}}$$ Langevin equation

generalisation leads to history-dependent friction force expressed as

$$\boxed{\partial_t \vec{v} + \int_0^t dt' \, \zeta(t-t') \, \vec{v}(t') = \vec{F}_{rand}(t)}$$

generalized Langevin equation

also for many other variables $A(t) \leftrightarrow v(t)$

$$\frac{dA(t)}{dt} + \int_0^t dt' \, K(t-t') \, A(t') = F(t)$$

assuming $\langle A(0) \, F(t) \rangle = \langle A(t_0) \, F(t_0+t) \rangle = 0 \quad \forall t, t_0$

multiplication by complex conjugate $A(0)^*$ and canonical averaging produces equation for correlation function $C(t) = \langle A(t) A^*(0) \rangle = \langle A^*(t) A(0) \rangle$

as $$\boxed{\partial_t C(t) + \int_0^t dt' \, K(t-t') \, C(t') = 0}$$

reminiscent of equations derived by MZ projections

expression of dynamics of $A(t)$ through MZ

projection operator $P = |A\rangle\langle A|$

$$Q = \mathbb{1} - P$$

$$\frac{d}{dt} A(t) = e^{i\mathcal{L}t} i\mathcal{L} A = e^{i\mathcal{L}t} i(P+Q)\mathcal{L} A$$

NB: Dyson decomposition of operators A, B

$$\boxed{e^{(A+B)t} = e^{At} + \int_0^t dt' \, e^{At'} B \, e^{(A+B)(t-t')}}$$

for A, B without explicit time dependence

proof: exponential function for operators

application for $A = iQ\mathcal{L}$

$$B = iP\mathcal{L}$$

$$\boxed{e^{i\mathcal{L}t} = e^{iQ\mathcal{L}t} + \int_0^t dt' \, e^{i\mathcal{L}(t-t')} \, iP \, e^{iQ\mathcal{L}t'}}$$

$$e^{i\mathcal{L}t}\, i\mathcal{P}\mathcal{L} A(t) = i\,\Omega\, A(t)$$

definition of MZ-frequency matrix

Hence,

$$\boxed{\frac{d}{dt} A(t) = i\,\Omega\, A(t) + e^{i\mathcal{L}t}\, i\mathcal{Q}\mathcal{L} A(t)}$$

i.e., dynamics of $A(t)$ driven by deterministic part, Ω, and random force $F(t) = e^{i\mathcal{Q}\mathcal{L}t}\, i\mathcal{Q}\mathcal{L} A$, with $\langle F \,|\, A\rangle = 0$

↳ Dyson decomposition

$$\frac{d}{dt} A(t) = i\,\Omega\, A(t) + \int_0^t dt'\, e^{i\mathcal{L}(t-t')}\, i\mathcal{P}\mathcal{L}\, e^{i\mathcal{Q}\mathcal{L}t'}\, i\mathcal{Q}\mathcal{L} A$$
$$+ e^{i\mathcal{Q}\mathcal{L}t}\, i\mathcal{Q}\mathcal{L} A$$

note: random force driven by $e^{i\mathcal{Q}\mathcal{L}t}$ not full dynamics $e^{i\mathcal{L}t}$

$$i\mathcal{P}\mathcal{L}\, e^{i\mathcal{Q}\mathcal{L}t}\, i\mathcal{Q}\mathcal{L} A = \underbrace{-\langle F(t) \,|\, \underbrace{i\mathcal{Q}\mathcal{L} A^*}_{F(0)} \rangle}_{\text{correlator for fluctuating forces}} A = -K(t) A$$

and

$$\frac{dA(t)}{dt} - i\,\Omega\, A(t) + \int_0^t dt'\, e^{i\mathcal{L}(t-t')}\, K(t') A = F(t)$$

or equivalently

$$\boxed{\frac{dA(t)}{dt} - i\Omega A(t) + \int_0^t dt'\, K(t')A(t-t') = F(t)}$$

generalized Langevin equation as exact(!) consequence of MZ EOM as random force is orthogonal to A

respective MZ eom for correlation fct

$$\boxed{\frac{dC(t)}{dt} - i\Omega C(t) + \int_0^t dt'\, K(t')C(t-t') = 0}$$

notes

① memory kernel $K(t)$ is equivalent to transport coefficient

② Onsager regression hypothesis (1931)

equilibrium fluctuations in phase variable $A(t)$ governed by identical transport coefficients as relaxation of that variable to zero (non equilibrium)

③ assume $K(t) \propto e^{-t/\tau}$, relaxation time τ:

observation of equilibrium system on time scale τ

↳ ⓐ system is out of equilibrium and relaxes back to equilibrium

ⓑ system is in equilibrium and experiences a fluctuation

ⓐ and ⓑ cannot be decided on timescale τ

example: shear viscosity

$$A(t) = j_q^{\perp}(t) \text{ , transverse momentum current}$$

assume $j^{\perp} \parallel x$ and $q \parallel y$

$$j_q^{\perp}(t) = i q \, P_{yx}(q,t) \text{ , pressure tensor shear stress}$$

$$\langle j_q^{\perp} | j_q^{\perp} \rangle = N m k_B T$$

$$\Omega = \langle i\mathcal{L} j_q^{\perp} | j_q^{\perp} \rangle = 0 \text{ , due to parity}$$

for any variable B in the Dyson equation, one has

$$i\mathcal{P}\mathcal{L}B = \langle j_q^{\perp} | i\mathcal{L}B \rangle \frac{1}{N m k_B T} | j_q^{\perp} \rangle =$$

$$= -\langle B \, (i\mathcal{L} j_q^{\perp})^{*} \rangle \frac{1}{N m k_B T} | j_q^{\perp} \rangle =$$

$$= -iq \langle B \, P_{yx}(-q) \rangle \frac{1}{N m k_B T} | j_q^{\perp} \rangle$$

↳ substitution into Dyson equation

$$\left(e^{i\mathcal{L}t} - e^{i\mathcal{QL}t} \right) B = \int_0^t dt' \, e^{i\mathcal{L}(t-t')} \cdot \mathcal{PL} e^{i\mathcal{QL}t'} B$$

→ difference between full propagator $e^{i\mathcal{L}t}$ and $e^{i\mathcal{QL}t}$ is of order $\mathcal{O}(q)$ and vanishes for $q \to 0$ (BUT only then!)

memory kernel for $q \to 0$

$$K(t) = q^2 \frac{1}{Vmk_BT} \langle P_{yx}(q,t) | P_{yx}(q,0) \rangle$$

autocorrelation function for pressure tensor

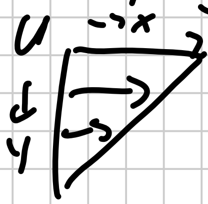
$\to$ GLE for transverse currents

$$\boxed{\lim_{q\to 0} \partial_t j_q^\perp(t) = -q^2 \frac{1}{Vmk_BT} \int_0^t dt' \langle P_{yx}(q,t') | P_{yx}(q,0) \rangle j_q^\perp(t-t') + iq P_{yx}(q,t)}$$

reminder: for simple Newtonian fluids, shear stress given by strain rate

$\dot{\gamma} = \partial_y u_x$ and viscosity η by

$$P_{yx} - \sigma = \eta \dot{\gamma}$$



we can identify $iq j_q^\perp$ with a wave-vector dependent strain rate $\dot{\gamma}_q$ and $\langle P_{yx}(q,t) | P_{yx}(q,0) \rangle$ with a wave-vector dependent generalized viscosity η_q. for $q \to 0$ we have

$$\boxed{\eta(t) = \frac{V}{k_BT} \langle P_{yx}(t) | P_{yx}(0) \rangle}$$ Green-Kubo relation

and the constitutive equation

$$\lim_{q\to 0} P_{yx}(q,t) = \boxed{\sigma = -\int_0^t dt' \eta(t-t') \dot{\gamma}(t')}$$

notes

1. generalization of Newtons viscosity to viscoelastic fluids

2. derivation of constitutive relations from first principles