II. 1. G Single-Particle Dynamics

selected ('s') or tagged particle or single ('s') particle, trajectory $\vec{R}(t)$

homogeneity in time: $\vec{R}(t-t_0)$ has properties similar to $\vec{R}(t)$

homogeneity in space: $\vec{R}(t)+\vec{R}_0$ has similar properties as $\vec{R}(t)$

stationary process $\Delta\vec{R}(t-t_0)=\vec{R}(t)-\vec{R}(t_0)$

$\langle \Delta \vec{R}(\tau)\rangle$, mean drift

$\langle \Delta \vec{R}(\tau)^2\rangle$, mean-squared displacement

τ, lag time

Definition: van Hove self correlation function

$$\boxed{\mathbb{P}(\vec{r},\tau) := \langle \delta(\vec{r}-\Delta\vec{R}(\tau))\rangle \geq 0}$$

probability of finding a displacement $\vec{r}$ after lag time τ

mean drift and mean-squared displacement are moments of the van Hove function

$$\langle \Delta \vec{R}(\tau)\rangle = \int d\vec{r}\, \vec{r}\, \mathbb{P}(\vec{r},t)$$

$$\langle \Delta \vec{R}(\tau)^2\rangle = \int d\vec{r}\, \vec{r}^2\, \mathbb{P}(\vec{r},t)$$

$\mathbb{P}$ can be measured experimentally (particle tracking, microscopy...) and in computer simulations

Definition: Incoherent (or Self-intermediate) Scattering Function

$$\boxed{\begin{aligned} F^s(\vec{q},\tau) &= \langle \exp[-i\vec{q}\cdot\Delta\vec{R}(\tau)] \rangle \\ &= \int d\vec{r}\; \hat{n}(\vec{r},\tau)\, \exp[-i\vec{q}\cdot\vec{R}(\tau)] \end{aligned}}$$

$F^s(\vec{q},\tau)$ is the characteristic function of the random variable $\Delta\vec{R}(t)$

$F^s(\vec{q},\tau)$ measured in incoherent scattering experiment with photons (light, X-ray) or particles (e.g. neutrons)

Definition: Single-Particle Density

$$\rho^s(\vec{r},t) = \delta(\vec{r}-\vec{R}(t))$$

Fourier transform $\rho^s_q(t) = e^{i\vec{q}\cdot\vec{R}(t)}$

Incoherent scattering function is the autocorrelation function of the single-particle density

$$\boxed{F^s(\vec{q},\tau) = \langle \rho^s_q(t)^* \rho^s_q(t_0) \rangle, \quad \tau = t - t_0}$$

averages $\langle \rho^s_q(t) \rangle = 0$ for $\vec{q} = 0$

$$F^s_{q=0}(t) = 1, \quad |F^s_q(t)| \leq 1$$

Definition: Incoherent Dynamic Structure Factor

$$\boxed{\hat{F}^s_q(z) = i\int_0^\infty dt\, e^{izt}\, F^s(\vec{q},t)\,,\quad z\in\mathbb{C}_+}$$

$\mathrm{Im}[\hat{F}^s_q(z=\omega+i0)]$ measured in scattering experiments

Examples

1) drift / directed motion $\vec{R}(t) = \vec{R}_0 + \vec{v}t$

$\vec{R}_0$ is averaged out, consider only

$$\Delta\vec{R} = \vec{R}(t) = \vec{v}t \to P(\vec{r},\tau) = \delta(\vec{r}-\vec{v}\tau)$$

$$\boxed{F^s(\vec{q},\tau) = \exp(-i\vec{q}\cdot\vec{v}\tau)}$$ complex! does not decay, too!

↳ particle with fixed velocity is not in equilibrium

2) Brownian motion

$\Delta R(\tau)$ are independent Gaussian variables, i.e., a random walk with non-trivial cumulants

$$\langle\Delta R_\alpha(\tau)\rangle = 0\,,\quad \langle\Delta R_\alpha(\tau)\,\Delta R_\beta(\tau)\rangle = 2D\tau\,\delta_{\alpha\beta}$$

$\alpha,\beta = x,y,z$

$$\boxed{P(\vec{r},\tau) = \frac{1}{\sqrt{4\pi D\tau}^{\,d}}\, e^{-\frac{\vec{r}^2}{4D\tau}}}$$

$$\boxed{F^s(q,\tau) = e^{-Dq^2\tau}}$$

3) Brownian motion with drift

$$\vec{R}(t) = \vec{v}\,t + \xi(t)$$

drift term — Brownian noise term

$$\boxed{P(\vec{r},\tau) = 1/\sqrt{4\pi D t}^{\,d} \exp[-(\vec{r}-\vec{v}t)^2/(4Dt)]}$$

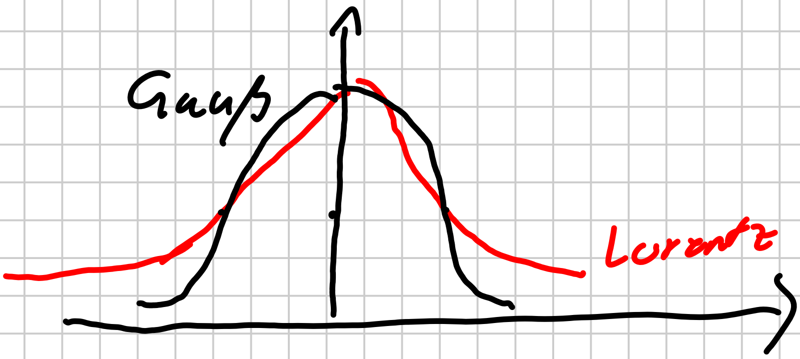
$$\boxed{F^s(q,\tau) = \exp[-i\vec{q}\cdot\vec{v}t - q^2 D t]}$$

and $\boxed{\hat{F}^s_q(z) = \dfrac{-1}{z - \vec{q}\cdot\vec{v} + i D q^2}}$

$$\mathrm{Im}[\hat{F}^s_q(z)] = \frac{-\mathrm{Im}[(z-\vec{q}\cdot\vec{v}) - iDq^2]}{(z-\vec{q}\cdot\vec{v})^2 + D^2 q^4} = \frac{Dq^2}{(z-\vec{q}\cdot\vec{v})^2 + D^2 q^4}$$

spectral line shape is a Lorentzian

with maximum at $\omega = \vec{v}\cdot\vec{q}$



4) general case

$$F^s(\vec{q},\tau = t-t') = \langle \exp[-i\vec{q}[\vec{R}(t) - R(t')]] \rangle$$

$$F^s(\vec{q},\tau=0) = 1$$

$$\dot{F}^s(\vec{q},\tau=0) = -i\vec{q}\cdot\langle \dot{\vec{R}}(0)\rangle = -i\vec{q}\cdot\vec{v}\ \text{, drift}$$

usually not present

$$\ddot{F}^s(\vec{q}, \tau=0) = -\frac{d}{dt}\frac{d}{dt'}F^s(\vec{q}, t-t')\Big|_{t=t'=0}$$

$$= -\langle \vec{q}\cdot\dot{\vec{R}}(t)\, q\cdot\dot{\vec{R}}(t')\exp[-iq\{\vec{R}(t)-\vec{R}(t')\}]\rangle$$

Definition: tagged current density

$$\boxed{\vec{j}^s_q(t) = \dot{\vec{R}}(t)\exp[i\vec{q}\cdot\vec{R}(t)]}$$

$$\ddot{F}^s(\vec{q}, t) = -q_\alpha q_\beta\langle j^s_\alpha(\vec{q}, t)^* j^s_\beta(\vec{q})\rangle =$$

$$= -q^2\underbrace{\langle j^{sL}(\vec{q}, t)^* j^{sL}(\vec{q})\rangle}_{\text{current-curent correlation function for longitudinal self-currents}}$$

Mori-Zwanzig projector $\mathcal{P} = |\rho^s_q)(\rho^s_q|$

particle conservation $\partial_t \rho^s_q(t) = i\mathcal{L}\rho^s_q(t) = iq\, j^{sL}_q(t)$

frequency matrix

$$\langle \rho^s_q|\mathcal{L}|\rho^s_q) = (\rho^s_q|j^{sL}_q) = 0, \text{ parity}$$

memory kernel

$$\langle \mathcal{Q}\mathcal{L}\rho^s_q|\frac{1}{\mathcal{Q}\mathcal{L}\mathcal{Q}-z}|\mathcal{Q}\mathcal{L}\rho^s_q) =$$

$$= q^2\langle j^{sL}_q|\frac{1}{\mathcal{Q}\mathcal{L}\mathcal{Q}-z}|j^{sL}_q) \text{ as } \mathcal{Q}|j^{sL}_q) = |j^{sL}_q)$$

Definition diffusion kernel

$$\boxed{\hat{D}(q,z) := \langle j^{sL}_q|\frac{1}{\mathcal{Q}\mathcal{L}\mathcal{Q}-z}|j^{sL}_q)}$$

→ general eom

$$\boxed{\hat{F}^s(q,z) = \frac{-1}{(z-\vec{q}\cdot\vec{v}) + q^2 \hat{D}(q,z)}}$$

or in the time domain

$$\boxed{\dot{F}^s(q,t) - i\vec{q}\cdot\vec{v}\, F^s(q,t) + \int_0^t dt'\, q^2 D(\hat{q}, t-t') F^s(q,t') = 0}$$

NB: approximating D is a safer alternative to approximating F^s directly, e.g.

$$\hat{D}(q,z) = \underbrace{(\hat{q}\cdot\hat{v})^2 D_{\parallel}}_{\text{parallel to drift}} + \underbrace{[1-(\hat{q}\cdot\hat{v})^2]\, D_{\perp}}_{\text{perpendicular to drift}}$$

diffusion coefficient D from $\hat{D}(q,z)$:

velocity $v^s(t) = \lim_{q\to 0} j^{sL}_q(t)$ in q direction

$$D = \lim_{z\to 0} \lim_{q\to 0} \frac{1}{i} \hat{D}(q,z) =$$

$$= \lim_{q\to 0} \int_0^\infty dt \, \langle v^s | e^{-iQ\mathcal{L}Qt} | v^s \rangle$$

$$Q = 1 - P = 1 - |\rho^s_q\rangle\langle\rho^s_q|$$

$$\mathcal{L}Q = \mathcal{L} - \mathcal{L}|\rho^s_q\rangle\langle\rho^s_q| \longrightarrow \mathcal{L} \text{ as } q\to 0$$

since ρ^s_q is conserved

$$\hookrightarrow \boxed{D = \frac{1}{d}\int_0^\infty dt \, \langle v^s | e^{-i\mathcal{L}t} | v^s \rangle}$$

Green-Kubo relation