II. 1. D Correlation Functions

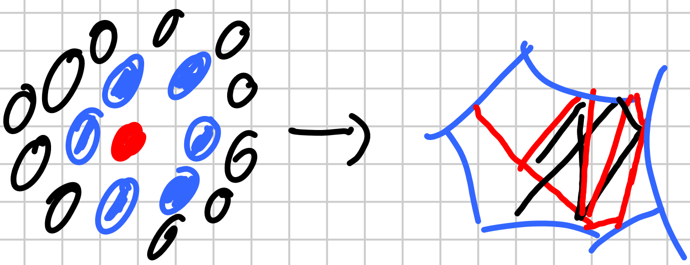
Why consider correlation functions and not trajectories in phase or configuration space?

① in atomic/molecular systems, trajectories cannot be measured experimentally, but correlation functions can. However, computer simulation can produce trajectories, as can mesoscopic model systems

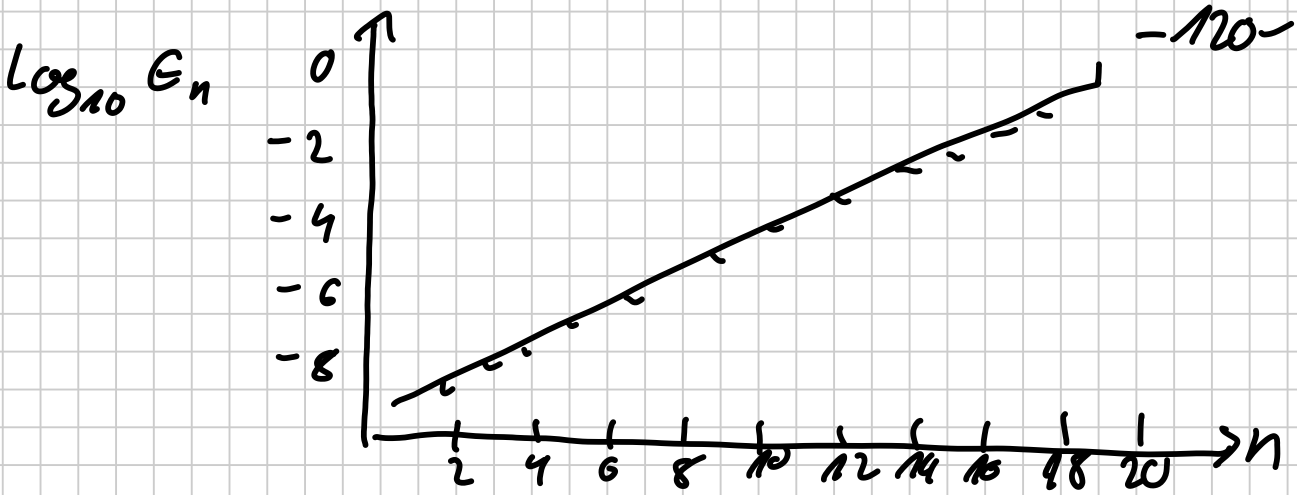
② integrable Hamiltonians are rare: solution of equations of motion depend sensitively on initial conditions (e.g. positive Lyapunov exponent)
↳ initial deviations of trajectories, say $r_0 - r_0' = \delta_0$ grow exponentially with time t

$$\delta(t) = \delta_0 \, e^{\gamma t / \bar{t}}$$

consider fluid particle in dense environment



typical orbits typically diverge quickly with number n of collisions



unstable orbits already for single particle
↳ it is NOT the many-particle property that makes statistical description necessary

NB1: proof for special case by Ya. Sinai for hard-sphere billiard system

NB2: All trajectories from computer simulations are wrong, only pseudo trajectories are calculated

NB3: most pseudo trajectories are arbitrarily close to a true trajectory ('shadowing lemma')

Conclusion: Trajectories have no meaning any more; correlation function carries meaningful information

general correlator between dynamical variable A and B, expressed by linear combination of four autocorrelators

$$C_{AB}(t) = \langle A| e^{-i\mathcal{L}t} |B) =$$

$$= [C_{X_+}(t) - C_{X_-}(t)] - i\,[C_{Y_+}(t) - C_{Y_-}(t)]$$

with $X_{\pm} = \frac{A \pm B}{2}$, $Y_{\pm} = \frac{A \pm iB}{2}$

hence: general correlation functions inherit properties from autocorrelation functions

now goal: determine all matrix elements of operator $e^{-i\mathcal{L}t}$

for bounded operators, knowing all matrix elements means knowing the operator

knowing all correlation functions means knowing the time evolution operator $e^{-i\mathcal{L}t}$

> Set of all correlators provides complete statistical description of the dynamics

spectrum of Liouville operator may be discrete, then sum of exponentials is solution, e.g. harmonic oscillator, cf. last lecture

$$C_{AA}(t) = \sum_{\lambda} |\langle A|\lambda\rangle|^2 e^{-i\lambda t}$$

typically, the space of dynamical variables is not finite dimensional

→ description in terms of infinite-dimensional Hilbert space necessary

basis for Hilbert space given by set of dynamical variables

more details: Akhiezer/Glazmann, Theory of Linear Operators in Hilbert Space

Correlation functions in space and time

consider N particles in box $V = L^d$

coordinates $\vec{R}_i(t) \in V$, momenta $\vec{P}_i(t)$

Def: Local variable

$$A(\vec{r}, t) = \sum_{i=1}^{N} a_i(\Gamma_t)\, \delta(\vec{r} - \vec{R}_i(t))$$

with $a_i(\Gamma_t)$ a property (mass, momenta, energy, ...) of a particle

finite box with periodic boundary

$$A(\vec{r}, t) = A(\vec{r} + \vec{G}, t), \quad \vec{G} \in (L\mathbb{Z})^d$$

(important especially for computer simulations)

Fourier transformation

$$\hat{A}(\vec{q}, t) = \int_V d^d\vec{r}\, e^{i\vec{q}\vec{r}} A(\vec{r}, t)$$

on discrete lattice $q \in \left(\frac{2\pi}{L}\mathbb{Z}\right)^d$

inverse Fourier transformation

$$A(\vec{r}, t) = \frac{1}{V} \sum_{\vec{q}} \hat{A}(\vec{q}, t)\, e^{-i\vec{q}\vec{r}}$$

proof
$$\frac{1}{V}\int_V d^d\vec{r}\, e^{i(\vec{q}-\vec{q}')\vec{r}} = \delta_{\vec{q},\vec{q}'} \quad \text{orthonormal}$$

$$\frac{1}{V}\sum_{\vec{q}} e^{i\vec{q}(\vec{r}-\vec{r}')} = \delta(\vec{r} - \vec{r}') \quad \text{complete}$$

time-translational invariance, spatial homogenity

$$C_{AB}(\vec{r} - \vec{r}', t - t') = \frac{V}{N}\langle A(\vec{r}, t) \,|\, B(\vec{r}', t')\rangle$$

$$\hat{C}_{AB}(\vec{q},t) = \frac{V}{N}\int d(\vec{r}-\vec{r}')\, e^{-i\vec{q}(\vec{r}-\vec{r}')}\langle A(\vec{r},t)|B(\vec{r}',0)\rangle$$

$$= \frac{1}{N}\int d\vec{r}\, d\vec{r}'\, e^{-i\vec{q}(\vec{r}-\vec{r}')}\langle A(\vec{r},t)|B(\vec{r}',0)\rangle$$

$$\boxed{\hat{C}_{AB}(\vec{q},t) = \frac{1}{N}\langle A(\vec{q},t)^{*} B(\vec{q},0)\rangle}$$ for finite system

thermodynamic limit

$$\boxed{C_{AB}(\vec{r},t) = \frac{1}{(2\pi)^d}\int d^d q\, \hat{C}_{AB}(\vec{q},t)\, e^{i\vec{q}\vec{r}}}$$

$a_1 = 1 \rightarrow$ number density $\rho(\vec{r},t) = \sum_{i=1}^{N}\delta(\vec{r}-\vec{R}_i(t))$

defines van-Hove correlation function

$$\boxed{G(r,t) = \frac{V}{N}\langle \rho(\vec{r}',t)|\rho(\vec{r}'',0)\rangle\,,\quad \vec{r} = (\vec{r}'-\vec{r}'')}$$

probability density to find <u>any particle</u> after a lag time t at a distance $\vec{r}$ from a known particle

$$G(r,t) = \frac{V}{N}\Big\langle \sum_{i,j=1}^{N}\delta(\vec{r}'-\vec{R}_i(t))\,\delta(\vec{r}'-\vec{r}-\vec{R}_j(0))\Big\rangle$$

$$= \frac{V}{N}\Big\langle \sum_{i,j=1}^{N}\delta(\vec{r}-\vec{R}_i(t)+\vec{R}_j(0))$$

$$\delta(\vec{r}'-\vec{r}-\vec{R}_j(0)\Big\rangle$$

$$\hookrightarrow \boxed{G(r,t) = \frac{1}{N}\Big\langle \sum_{i,j=1}^{N}\delta(\vec{r}-\vec{R}_i(t)-\vec{R}_j(0))\Big\rangle}$$

independent of $\vec{r}'$

splitting into 2 parts

$$\boxed{\begin{aligned} G(r,t) &= G_s(r,t) + G_d(r,t) \quad \text{with} \\ \text{self part} \quad G_s(r,t) &= \frac{1}{N}\sum_{i=1}^{N} \langle \delta(\vec{r} - [\vec{R}_i(t) - \vec{R}_i(0)]) \rangle \\ \text{distinct part} \quad G_d(r,t) &= \frac{1}{N}\sum_{i\neq j}^{N} \langle \delta(\vec{r} - [\vec{R}_i(t) - \vec{R}_j(0)]) \rangle \end{aligned}}$$

for $t=0$

$$G(r,t=0) = \delta(\vec{r}) + \frac{1}{N}\sum_{i\neq j} \langle \delta(\vec{r} - [\vec{R}_i - \vec{R}_j]) \rangle$$

$$= \delta(\vec{r}) + n\, g(r), \quad \text{particle density } n = \frac{N}{V}$$

pair distribution function $g(r)$

in wave-vector space: coherent intermediate scattering function

$$\boxed{S(q,t) = \frac{1}{N}\langle \hat{\rho}_{\vec{q}}(t)^{*}\, \hat{\rho}_{\vec{q}}(0) \rangle = \int d^d r\, G(\vec{r},t)\, e^{i\vec{q}\vec{r}}}$$

in frequency space: coherent dynamic structure factor

$$\boxed{\hat{S}(q,z) = i\int_0^{\infty} dt\, e^{izt}\, S(q,t)}$$

static structure factor

$$S_q = S(q, t=0) = \frac{1}{N}\langle |\rho_{\vec{q}}|^2 \rangle$$

$$= \int d^d\vec{r}\,[\delta(\vec{r}) + n g(r)]\, e^{i\vec{q}\vec{r}}$$

$$\boxed{S_q = 1 + n\int d^d\vec{r}\,[g(r)-1]\, e^{i\vec{q}\vec{r}} + n(2\pi)^d \delta(\vec{q})}$$