

# Lecture 4: Time-correlation functions.

①

## Outline

- \* Introduction to TCFs.
- \* Properties of Quantum TCFs.
- \* Example:

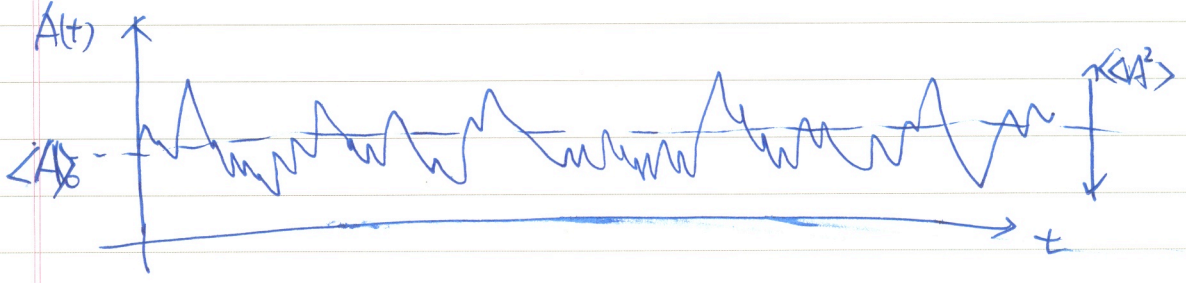
\* Statistical properties of dynamical fluctuations are captured by time-correlation functions.

Fluctuations are critical in everyday physical phenomena  $\Rightarrow$  practically they are the source of all physical transitions.

No fluctuation  $\rightarrow$  everything in ~~equilibrium~~/eigenstate  $\rightarrow$  dead world  $\sim$ .

"Fluctuations" ← change of <sup>Law</sup> ~~dyn~~ observables around  $\langle A \rangle$  mean, equilibrium value.

← TS are "equilibrium" phenomena.  
← induced by "environment", open system.



"stochastic",  
random  
variables

We can not predict the value of  $A(t)$  at a precise time, but we can measure the statistical ~~stochastic~~ properties of  $A(t)$ .

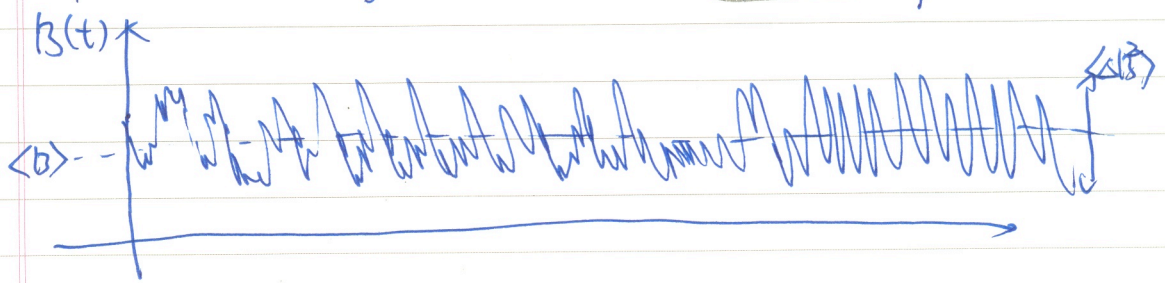
mean :  $\langle A \rangle$

variance :  $\langle (A - \langle A \rangle)^2 \rangle$

co-variance :  $C_{AB} = \langle AB \rangle - \langle A \rangle \langle B \rangle \dots$

} "statistics"

However, these "static" measures are not enough to describe  $A(t)$ , since <sup>another stochastic</sup> a process can exhibit the same mean, variance ... etc, yet be very different "dynamically".



It is necessary to consider "statistics of dynamics".

⇒ time-correlation functions.

~~$C_{AA}(t)$~~

measure value @  $t_1$   
measure value @  $t_2$ .

$$C_{AA}(t_1, t_2) = \langle A(t_1) A(t_2) \rangle$$

eg: ← average over equilibrium & ensemble, i.e. many traces.

↑ auto-correlation function.

The function actually measures the "memory" of the process, or "interdependence" of two events.



very often, we care more about the auto-correlation of "fluctuations" !

$$C_{\delta A \delta A}(t_1, t_2) = \langle (A(t_1) - \langle A \rangle) (A(t_2) - \langle A \rangle) \rangle$$

$$= \langle \delta A(t_1) \delta A(t_2) \rangle$$

Note that when  $|t_1 - t_2| \rightarrow \infty$ , then the two becomes independent.

independence  
 $\downarrow$   $\langle AB \rangle = \langle A \rangle \langle B \rangle$

$$1) \lim_{|t_1 - t_2| \rightarrow \infty} C_{\delta A \delta A}(t_1, t_2) = \overbrace{\langle A(t_1) - \langle A \rangle \rangle} = 0 \times \overbrace{\langle A(t_2) - \langle A \rangle \rangle} = 0$$

$\therefore$  TCF of fluctuations always decays to "0",

It is also easy to prove that

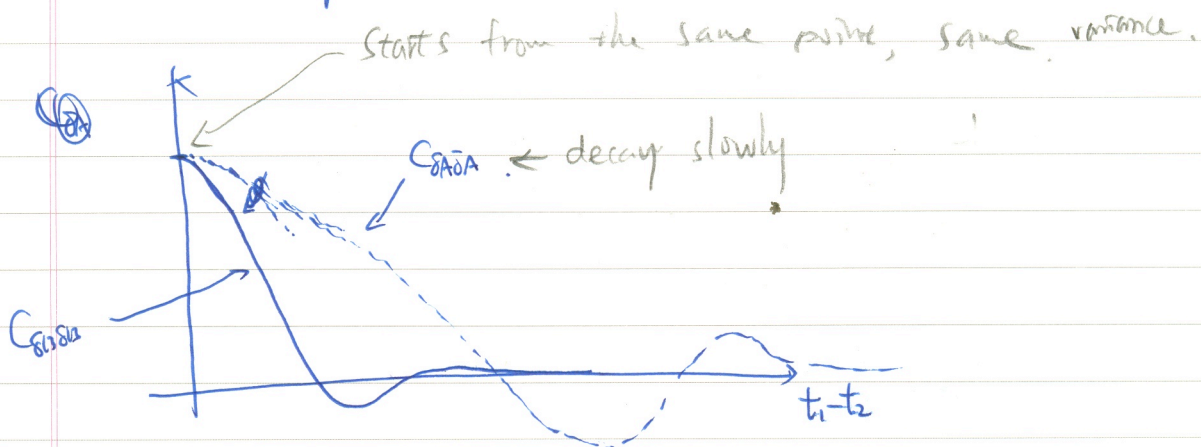
$$\left| \frac{\langle A(t_1) A(t_2) \rangle}{\langle A^2(0) \rangle} \right| \leq 1$$

- TCF:
- ① averaged / ensemble quantity.
  - ② describes fluctuations  $\Rightarrow$  equilibrium quantities
  - ③ statistics of dynamical variables.



for example; the two processes mentioned

before might look like:



We can then distinguish the two processes from their different TCFs.

Time-correlation functions play central role in statistical mechanics & many physical processes:

spectroscopy  $\rightarrow \langle \mu(t) \mu(0) \rangle$   
relaxation/dephasing  $\rightarrow \langle \sigma_w(t) \sigma_w(0) \rangle$   
diffusion  $\rightarrow \langle v(t) v(0) \rangle$

⋮ many many more!!

\* Quantum TCFs

can be done by definition.

In quantum mechanics (we assume  $\langle A \rangle = 0$ ):

~~$C_{AA}(t) = \langle A(t) A \rangle$~~   $C_{AA}(t) = \langle A(t) A \rangle$   
 a scalar

variables in the Heisenberg picture.

$C_{AA}(t_1, t_2) = \langle A(t_1) A(t_2) \rangle_{eq}$

equilibrium distribution

$= \text{Tr} \{ A(t_1) A(t_2) \cdot \rho_{eq} \}$

trace everything here assume "A" time-independent

$= \text{Tr} \{ U^\dagger(t_1) A_S \cdot U(t_1) U^\dagger(t_2) A_S \cdot U(t_2) \cdot \rho_{eq} \}$

From here we can derive many useful properties

of  $C_{AA}(t_1, t_2)$ :

① ~~maximally~~ stationary:

$C_{AA}(t_1, t_2) = \text{Tr} \{ U^\dagger(t_1) A U(t_1) U^\dagger(t_2) A U(t_2) \rho_{eq} \}$

trace invariant

$= \text{Tr} \{ U(t_2) U^\dagger(t_1) A U(t_1) U^\dagger(t_2) A \rho_{eq} \}$

since

$[U(t), \rho_{eq}] = 0$

Why??

$U(t_2) U^\dagger(t_1) = U^\dagger(t_1 - t_2) U(t_2)$   
 $= U^\dagger(t_1 - t_2) U(t_2)$   
 $= U^\dagger(t_1 - t_2)$

$= \text{Tr} \{ U^\dagger(t_1 - t_2) A \cdot U(t_1 - t_2) A \cdot \rho_{eq} \}$

$= \langle A(t) A(0) \rangle_{eq}$

timeless

$\therefore C_{AA}(t_1, t_2) = C_{AA}(t_1 - t_2)$ , only dependent on the time difference.

$\Rightarrow$  this is ~~due to~~ reasonable since  $C_{AA}(t)$  is a "equilibrium" property, thus does not depend on the choice of time "zero".

② maximum @  $t=0$  and  $\rightarrow 0$  when  $t \rightarrow \infty$ ,  
"memory effect"

③ Characteristic time-scale of a stochastic process:

$$\tau_c = \frac{1}{\langle \delta A^2 \rangle} \int_0^{\infty} \langle \delta A(t) \delta A(0) \rangle dt = \frac{1}{C(0)} \times \int_0^{\infty} C(t) dt$$

plug in  $C(t) = C_0 \cdot e^{-t/\tau_c}$

$\tau_c$ : correlation time, describes the time scale for TCF to decay to zero. This definition is self-evident for exponentially decaying TCFs.



$C(t) \equiv C_{AA}(t)$ , will drop  $[AA]$  later - (8)

(4)  $C(t)$  is complex for Hermitian operator:

$$\begin{aligned} (\langle A(t)A(s) \rangle)^* &= \text{Tr} \left\{ U^\dagger(t) A U(t) A P_{\text{eq}} \right\}^* \\ &= \text{Tr} \left\{ \underbrace{P_{\text{eq}}^*}_{=A} A^\dagger \underbrace{U^\dagger(t) A^\dagger U(t)}_{=A} \right\} \leftarrow \text{Hermitian} \\ &= \text{Tr} \left\{ A \cdot U^\dagger(t) A \cdot U(t) \cdot P_{\text{eq}} \right\} \\ &= \langle A(s)A(t) \rangle = \langle A(-t)A(s) \rangle \end{aligned}$$

Therefore  $C(t)^* = C(-t)$ .

if we define real & imaginary parts:

$$C(t) = \overset{\text{real}}{C'(t)} + i \cdot \overset{\text{imag.}}{C''(t)}$$

$$\therefore C'(t) = \frac{1}{2} [C(t) + C(-t)]$$

$$C''(t) = \frac{1}{2i} [C(t) - C(-t)]$$

Note that

real part  $C'(t)$  is even in time:  $C'(t) = C'(-t)$   
imag. part  $C''(t)$  is odd in time:  $C''(t) = -C''(-t)$

Actually the real-part & imaginary part of the QM time correlation function is related by the "fluctuation-dissipation" theorem:

$$C''(t) = \tan\left(\frac{\beta\hbar}{2} \cdot \frac{d}{dt}\right) \cdot C'(t)$$

In particular, at high temperatures  $\beta \ll 1$ , then

$$\tan\left(\frac{\beta\hbar}{2} \cdot \frac{d}{dt}\right) \approx \frac{\beta\hbar}{2} \cdot \frac{d}{dt}$$

therefore  $C''(t) \approx \frac{\beta\hbar}{2} \cdot \frac{d}{dt} C'(t)$

Furthermore, the real part determines "correlation, fluctuations", whereas the imaginary part determines "response" of

~~copy~~ the system, thus the name fluctuation-dissipation theorem.   
  $\Rightarrow$  out of ~~copy~~ scope, will not go into details here,

\* Examples of quantum time correlation functions:

Now lets' compute a time-correlation function. Consider a Harmonic oscillator !!

$$\Rightarrow H = \left(n + \frac{1}{2}\right) \hbar \omega \cdot b^\dagger b \equiv \hbar \omega \cdot b^\dagger b$$

We want to compute position-position TCF.

$$X = \sqrt{\frac{\hbar}{2m\omega}} (b + b^\dagger)$$

$$C(t) = \langle X(t) X(0) \rangle$$

$$b^\dagger(t) = b^\dagger \cdot e^{i\omega t}$$

$$b(t) = b \cdot e^{-i\omega t}$$

$$= \frac{\hbar}{2m\omega} \times \text{Tr} \{ [b^\dagger(t) + b(t)] [b^\dagger + b] \cdot \rho_{eq} \}$$

$$\langle b^\dagger b \rangle = \bar{n} = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Planck distribution

$$= \frac{\hbar}{2m\omega} \times \langle [b^\dagger b^\dagger e^{i\omega t} + b^\dagger b e^{i\omega t} + b b^\dagger e^{-i\omega t} + b b e^{-i\omega t}] \rangle$$

$$= \frac{\hbar}{2m\omega} \times \{ \bar{n} \cdot e^{i\omega t} + (\bar{n} + 1) \cdot e^{-i\omega t} \}$$

$$= \frac{\hbar}{2m\omega} \times [ (2\bar{n} + 1) \cdot \cos(\omega t) - i \cdot \sin(\omega t) ]$$

$$= \frac{\hbar}{2m\omega} \times \left[ \coth\left(\frac{\beta \hbar \omega}{2}\right) \cdot \cos(\omega t) - i \sin(\omega t) \right]$$

"oscillatory" function ← of course.

timeless



Very important model in condensed phase quantum dynamics!!

if we look at "collective coordinate" of many modes?

$$q = \sum_{\alpha} g_{\alpha} \cdot \omega_{\alpha} \cdot (b_{\alpha}^{\dagger} + b_{\alpha})$$

~~gg(t) = ...~~

Very often we assume modes are "normal modes" and thus uncorrelated,

$$\langle gg(t) \rangle = \left\langle \sum_{\alpha} g_{\alpha} \cdot \omega_{\alpha} \cdot [b_{\alpha}^{\dagger}(t) + b_{\alpha}(t)] \cdot \sum_{\beta} g_{\beta} \cdot \omega_{\beta} \cdot [b_{\beta}^{\dagger} + b_{\beta}] \right\rangle$$

$\langle b_{\alpha}^{\dagger} b_{\beta} \rangle = \langle b_{\alpha}^{\dagger} \times b_{\beta} \rangle = 0$

Independent modes

$$= \sum_{\alpha} g_{\alpha}^2 \cdot \omega_{\alpha}^2 \cdot \langle [b_{\alpha}^{\dagger}(t) + b_{\alpha}(t)] [b_{\alpha}^{\dagger} + b_{\alpha}] \rangle$$

done in previous page

$$= \sum_{\alpha} g_{\alpha}^2 \cdot \omega_{\alpha}^2 \cdot \left[ \cosh\left(\frac{\beta \hbar \omega_{\alpha}}{2}\right) \cdot \cos(\omega_{\alpha} t) - i \sinh(\omega_{\alpha} t) \right]$$

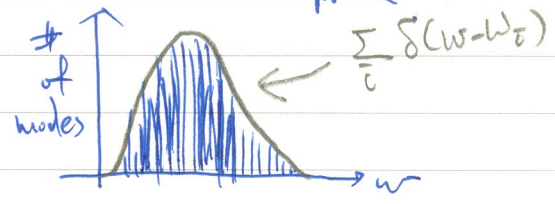
Note that for a condensed-phase system,

the number of modes are vast, therefore we do not sum over states carry out

gas phase.



Condensed phase.



In condensed-phase system, the number of modes are huge and ~~become~~ become a continuous distribution, therefore it is suitable to use a continuous function to describe  $\Rightarrow$  spectral density.

define  $J(\omega) = \sum_{\alpha} g_{\alpha}^2 \omega_{\alpha}^2 \cdot \delta(\omega - \omega_{\alpha})$ .

We can re-write  $C_{gg}(t)$  as integral over frequency  $\omega$ :

$$C_{gg}(t) = \int_0^{\infty} d\omega \cdot \left[ \underbrace{\cosh\left(\frac{\beta \hbar \omega}{2}\right) \cdot \cos(\omega t) \cdot J(\omega)}_{\text{real part}} - i \cdot \underbrace{\sinh(\omega t) \cdot J(\omega)}_{\text{imag. part}} \right]$$

This is a very useful formula.

timeless.

Let's assume :

$$J(\omega) = \omega \cdot e^{-\omega/\omega_c}$$

cut-off freq  $\swarrow$

at small  $\omega$ ,  $J(\omega) \sim \omega$  ~~Ohmic~~

"ohmic spectral density"

ohmic-st, mws

$$\omega_c = 100 \text{ cm}^{-1}$$

$$T = 77 \text{ K.}$$

