TIME-CORRELATION FUNCTIONS

> T.C.F.s are statistical measures of the time-evolution of an observable under equilibrium conditions. → They describe an ensemble.

> T.C.F.s can be used to describe spectroscopy and other time-dependent phenomena.

> They are generally applicable to any time-dependent process for an ensemble, but are commonly used to describe random or stochastic processes in condensed phases.

Qualitatively:

- A correlation function describes how long a given property of a system persists until it is averaged out by microscopic motions of system.
- It describes how and when a statistical relationship has vanished.
- T.C.F.s describes the dynamics associated with a dynamical variable A(t), averaged over the ensemble.

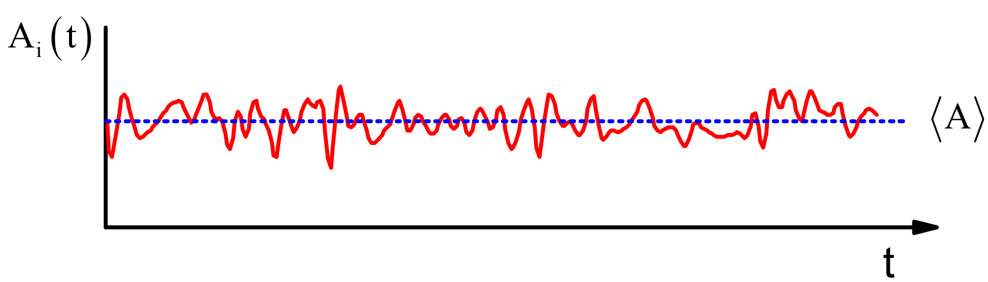
A: Microscopic variable

$\langle A \rangle$: Equilibrium ensemble average

Classical: $\langle A \rangle \equiv \int d\bar{p} \int d\bar{q}\; A(p,q;t)\, f(p,q)$ f: equil. Prob. distribution function

Quantum: $\langle A \rangle = \sum_n p_n \langle n|A|n \rangle$ $p_n = e^{-\beta E_n}/Z$

$A_i(t)$: Expectation value of A for a member of ensemble as a function of time.



If we look at this behavior there seems to be little information in the random fluctuations of *A*, but there are characteristic time scales and amplitudes to these changes. We can characterize these by comparing the value of *A* at time *t* with the value of *A* at time *t'* later.

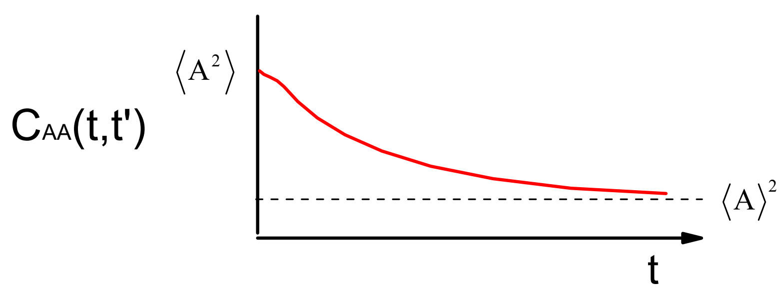
Correlation functions are defined as a time-dependent quantity, $A(t)$, multiplied by that quantity at some later time, $A(t')$, and averaged over ensemble:

$$C_{AA}(t,t') \equiv \langle A(t)A(t') \rangle \qquad \leftarrow \text{auto-correlation function}$$

$$C_{AB}(t,t') \equiv \langle A(t)B(t') \rangle \qquad \leftarrow \text{cross-correlation function}$$

These are products of a pair of dynamical variables.

Properties of Correlation Functions



1. $C_{AA}(t,t) = \langle A(t)A(t) \rangle = \langle A^2(t) \rangle \geq 0$

   $= \langle A^2 \rangle$ (mean square value of A – independent of time)

2. $C_{AA}(t,t') = C_{AA}(t+\tau, t'+\tau) = C_{AA}(t-t')$ ← for $\tau = -t'$

   ↗ Stationary random process.
   Time average = Ensemble average

   Just express in time separation C(t)

3. $\lim_{t \to \infty} C_{AA}(t) = \langle A(t) \rangle \langle A(0) \rangle = \langle A \rangle^2$

   Processes lose all correlation at infinite time separation .

4. For classical mechanics:

$$\langle A(t)A(t')\rangle = \langle A(t')A(t)\rangle$$

$$C_{AA}(t) = C_{AA}(-t) \qquad \text{Even in time}$$

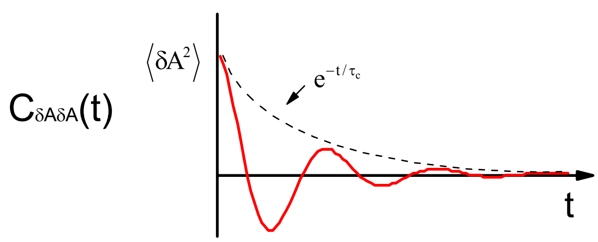
5. If we are observing fluctuations about an average position:

Redefine $\delta A \equiv A - \langle A\rangle$ deviation from average

$$C_{\delta A\delta A}(t) = \langle \delta A(t)\delta A(0)\rangle = C_{AA}(t) - \langle A\rangle^2$$

Properties: $\lim_{t\to\infty} C_{\delta A\delta A}(t) = 0$ all correlation lost at $t = \infty$

$$C_{\delta A\delta A}(0) = \langle \delta A^2\rangle = \langle A^2\rangle - \langle A\rangle^2 \qquad \text{(variance)}$$



6. τ_c : Correlation time is characteristic time for decay to zero.

There may be several time scales over which the correlation vanishes, so we can define

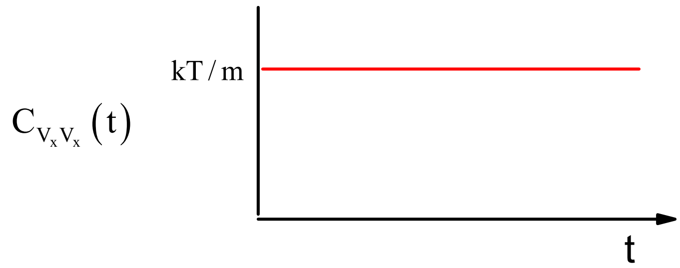
$$\tau_c = \frac{1}{\langle \delta A^2\rangle}\int_0^\infty dt\,\langle \delta A(t)\delta A(0)\rangle$$

<u>EXAMPLE 1</u>: Velocity autocorrelation function for gas.

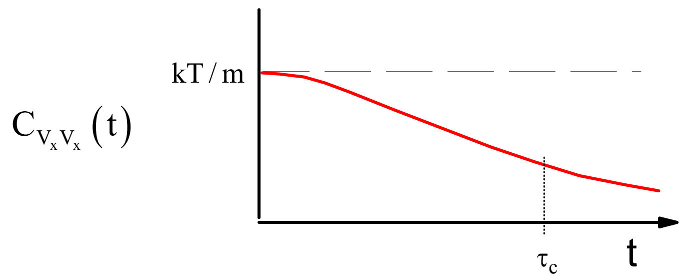
V_x: $\hat{x}$ Component of molecular velocity $\qquad \langle V_x \rangle = 0$

$$C_{V_xV_x}(t) = \langle V_x(t) V_x(0) \rangle \qquad C_{V_xV_x}(0) = \langle V_x^2(0) \rangle = \frac{kT}{m}$$

Ideal gas: no collisions



Dilute gas: infrequent collisions



$$V_x(t) = V_x(0) \quad \text{for} \quad t < \tau_c$$
$$V_x(t) = V_x(0) \pm \delta \quad \text{for} \quad t \gtrsim \tau_c$$

τ_c is related to the mean time between collisions.

<u>EXAMPLE 2</u>: $\overline{\mu}_i$: dipole moment for diatomic molecule in dilute gas.

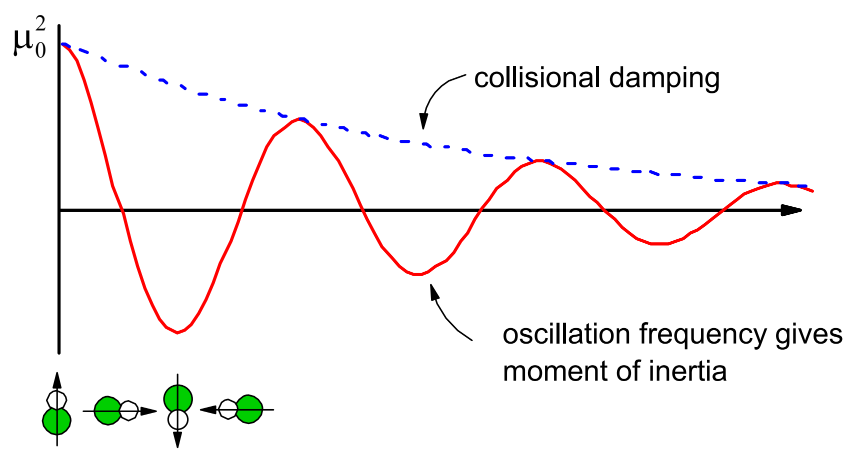
$\langle \overline{\mu}_i \rangle = 0$ (all angles are equally likely: isotropic system)

$\overline{\mu}_i = \mu_0 \cdot \hat{u}$

unit vector along dipole

$$C_{\mu\mu}(t) = \langle \overline{\mu}(t) \overline{\mu}(0) \rangle$$
$$= \mu_0^2 \langle \hat{u}(t) \cdot \hat{u}(0) \rangle$$

Project time-dependent orientation onto initial orientation

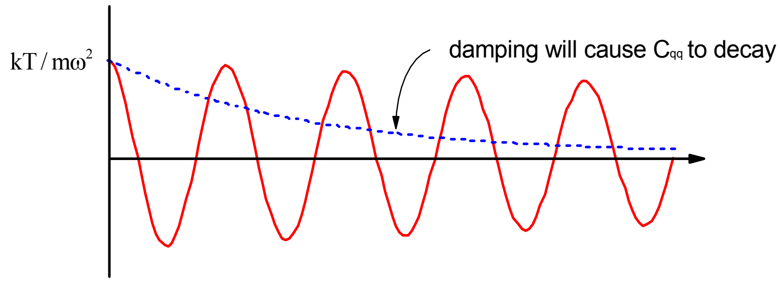


EXAMPLE 3: Displacement of harmonic oscillator.

$$m\ddot{q} = -\kappa q \quad \rightarrow \quad \ddot{q} = -\omega^2 q \qquad\qquad q(t) = q(0)\cos\omega t$$

Since $\left\langle q^2(0)\right\rangle = \dfrac{kT}{m\omega^2}$

$$C_{qq}(t) = \left\langle q(t)q(0)\right\rangle = \left\langle q^2(0)\right\rangle \cos\omega t$$
$$= \left(\frac{kT}{m\omega^2}\right)\cos\omega t$$



QUANTUM CORRELATION FUNCTIONS

Equilibrium (thermal) ensemble average over product of Hermetian operators evaluated two times.

→ Heisenberg Representation

$$C_{AA}(t,t') = \left\langle\left\langle A(t)A(t')\right\rangle\right\rangle$$

Here I'm temporarily using a double bracket to remind you that this is the equilibrium ensemble average over the expectation value of the product of operators. It is also sometimes written $\left\langle A(t)A(0)\right\rangle_{eq}$

Referring back to our notation for mixed states, we can represent the state of the system through

$$\left|\psi_k\right\rangle = \sum_n a_n^k \left|n\right\rangle$$

$$C_{AA}(t,t') = \sum_k \left\langle\psi_k\right| A(t)A(t') \left|\psi_k\right\rangle p_k$$

$$= \sum_{k,n,m} p_k \left(a_n^k\right)^* a_m^k \left\langle n\right| A(t)A(t') \left|m\right\rangle$$

$$= \sum_{n,m} \left\langle a_n^* a_m\right\rangle \left\langle n\right| A(t)A(t') \left|m\right\rangle$$

The equilibrium ensemble average of the expansion coefficients is equivalent to phase averaging over the expansion coefficients, since at equilibrium all phases are equally probable:

$$\left\langle a_n^* \, a_m \right\rangle = \frac{1}{2\pi}\int_0^{2\pi} a_n^* a_m \, d\phi = \frac{1}{2\pi}\left|a_n\right|\left|a_m\right| \int_0^{2\pi} e^{-i\overbrace{(\phi_n - \phi_m)}^{\phi nm}} d\phi_{nm} \qquad \text{where } a_n = \left|a_n\right| e^{i\phi_n}$$

The integral is quite clearly zero unless $\phi_n = \phi_m$, giving

$$\left\langle a_n^* \, a_m \right\rangle = p_n \, \delta_{n,m} = \frac{e^{-\beta E_m}}{Z} \, \delta_{m,n}$$

So

$$C_{AA}(t,t') = \sum_n p_n \left\langle n \middle| A(t) A(t') \middle| n \right\rangle \qquad \textit{Heisenberg representation}$$

More commonly, we will be writing correlation functions in the interaction picture operators.

We can also write this in the Schrödinger picture:

$$U = \exp(-iH\,t/\hbar)$$

$$C_{AA}(t,t') = \sum_n p_n \left\langle \underleftarrow{n \middle| U^\dagger(t)} A \, U(t) U^\dagger(t') A \, \underrightarrow{U(t') A \middle| n} \right\rangle$$

$$= \sum_n p_n \left\langle n \middle| A \, U(t-t') A \middle| n \right\rangle e^{+i\omega_n (t-t')}$$

insert $\sum_j |j\rangle\langle j|$

$$= \sum_{n,j} p_n \left\langle n \middle| A \middle| j \right\rangle \left\langle j \middle| A \middle| n \right\rangle e^{-i\omega_{jn}(t-t')}$$

$$= \sum_{n,j} p_n \left|A_{jn}\right|^2 e^{-i\omega_{jn}(t-t')}$$

Notice that $C_{AA}(t,t') = C_{AA}(t-t') \quad \Rightarrow \quad C_{AA}(t)$

$$C_{AA}(-t) = C_{AA}^*(t)$$

Properties of Quantum Correlation Functions

There are various properties of quantum correlation functions that can be obtained using the properties of the time-evolution operator.

$$\begin{aligned}\left\langle A(0)A(t)\right\rangle &= \left\langle A(0)U^{\dagger} A U\right\rangle \\ &= \left\langle U A U^{\dagger} A\right\rangle \\ &= \left\langle A(-t)A(0)\right\rangle\end{aligned}$$

$$\begin{aligned}\left\langle A(t)A(0)\right\rangle^{*} &= \left\langle U^{\dagger} A U A\right\rangle^{*} \\ &= \left\langle U A U^{\dagger} A\right\rangle \\ &= \left\langle A(0)A(t)\right\rangle\end{aligned}$$

$$\therefore \quad \left\langle A(-t)A(0)\right\rangle = \left\langle A(t)A(0)\right\rangle^{*} = \left\langle A(0)A(t)\right\rangle \qquad\qquad C_{AA}{}^{*}(t) = C_{AA}(-t)$$

$$\begin{aligned}\left\langle A(t)A(t')\right\rangle &= \left\langle U^{\dagger}(t)A(0)U(t)U^{\dagger}(t')A(0)U(t')\right\rangle \\ &= \left\langle U(t')U^{\dagger}(t)A\,U(t)U^{\dagger}(t')A\right\rangle \\ &= \left\langle U^{\dagger}(t-t')A\,U(t-t')A\right\rangle \\ &= \left\langle A(t-t')A(0)\right\rangle\end{aligned}$$

Note that $C_{AA}(t)$ is complex. You cannot directly measure a quantum correlation function, but observables are often related to the real or imaginary part of correlation functions, or other combinations of correlation functions.

$$C_{AA}(t) = C'_{AA}(t) + i\,C''_{AA}(t)$$

$$C'_{AA}(t) = \frac{1}{2}\left[C_{AA}(t) + C^{*}_{AA}(t)\right] = \frac{1}{2}\left[\left\langle A(t)A(0)\right\rangle + \left\langle A(0)A(t)\right\rangle\right] = \frac{1}{2}\left\langle\left[A(t),A(0)\right]\right\rangle_{+}$$

$$C''_{AA}(t) = \frac{1}{2i}\left[C_{AA}(t) - C^{*}_{AA}(t)\right] = \frac{1}{2i}\left[\left\langle A(t)A(0)\right\rangle + \left\langle A(0)A(t)\right\rangle\right] = \frac{1}{2i}\left\langle\left[A(t),A(0)\right]\right\rangle$$

Density Matrix

Earlier we showed that:

$$\langle A(t)\rangle = \sum_{n,m} a_n^*(t)\,a_m(t)\langle n|A|m\rangle = \mathrm{Tr}\left[A\,\rho(t)\right]$$

We also showed that

$$\rho(t) = U\rho(0)U^{\dagger}$$

$$\langle A(t)\rangle = Tr[A(t)\rho(0)].$$

ρ_0 (or $\rho(0)$ or $\rho(-\infty)$ or ρ_{eq}) is the equilibrium canonical density matrix.

$$\rho_0 = \frac{e^{-\beta H}}{Z} \qquad\qquad Z = \mathrm{Tr}\left(e^{-\beta H}\right)$$

for $H|n\rangle = E_n|n\rangle$

$$Z = \sum_n \langle n|e^{-\beta H}|n\rangle = \sum_n e^{-\beta E_n}$$

$$(\rho_0)_{nm} = \tfrac{1}{Z}\langle n|e^{-\beta H}|m\rangle = \tfrac{1}{Z}e^{-\beta E_n}\,\delta_{n,m}$$

$$= p_n\,\delta_{n,m}$$

So, the ensemble averaged expectation value (at equilibrium) is

$$\langle A(t)\rangle = Tr[A(t)\rho_0]$$

or for correlation functions:

$$C_{AA} = \sum_n p_n\langle n|A(t)A(0)|n\rangle \qquad\qquad p_n = \langle n|\rho_0|n\rangle$$

$$= \mathrm{Tr}\left(\rho_0\,A(t)A(0)\right)$$

$$= \mathrm{Tr}\left(A(t)A(0)\rho_0\right)$$

More on Stationary Processes[1]

We stated that correlation functions are stationary: they do not depend on the absolute point of observation, but rather the time-interval between observations.

Let's look at this a bit more: the ensemble average value of A can be expressed as a time-average or an ensemble average. For an equilibrium system:

$$\overline{A} = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} dt\, A_i(t) \qquad \overline{\ldots} = \text{ time} - \text{average}$$

$$\langle A \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A | n \rangle \qquad \langle \ldots \rangle = \text{equil. ensemble average}$$

These quantities are equal for an ergodic system $\langle A \rangle = \overline{A}$. We assume this property for our correlation functions.

So, the correlation of fluctuations can be written:

$$\overline{A(t)A(0)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T d\tau\, A_i(t+\tau) A_i(\tau)$$

$$\langle A(t)A(0) \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A(t)A(0) | n \rangle$$

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[1] See McQuarrie, p. 553