12.4: General Properties of Time Correlation Functions

Define a time correlation function between two quantities $A(x)$ and $B(x)$ by

$$\begin{aligned} C_{AB}(t) &= \langle A(0)B(t)\rangle \\ &= \int d\mathrm{x} f(\mathrm{x}) A(\mathrm{x}) e^{iLt} B(\mathrm{x}) \end{aligned}$$

The following properties follow immediately from the above definition:

Property 1

$$\langle A(0)B(t)\rangle = \langle A(-t)B(0)\rangle$$

Property 2

$$C_{AB}(0) = \langle A(\mathrm{x})B(\mathrm{x})\rangle$$

Thus, if $A = B$, then

$$C_{AA}(t) = \langle A(0)A(t)\rangle$$

known as the autocorrelation function of A, and

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

If we define $\delta A = A - \langle A\rangle$, then

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

which just measures the fluctuations in the quantity A.

Property 3

A time correlation function may be evaluated as a time average, assuming the system is ergodic. In this case, the phase space average may be equated to a time average, and we have

$$C_{AB}(t) = \lim_{T\to\infty} \frac{1}{T-t} \int_0^{T-t} ds A(\mathrm{x}(s)) B(\mathrm{x}(t+s))$$

which is valid for $t << T$. In molecular dynamics simulations, where the phase space trajectory is determined at discrete time steps, the integral is expressed as a sum

$$C_{AB}(k\Delta t) = \frac{1}{N-k} \sum_{j=1}^{N-k} A(\mathrm{x}_k) B(\mathrm{x}_{k+j}) \qquad k = 0, 1, 2, \ldots, N_c$$

where N is the total number of time steps, Δt is the time step and $N_c << N$.

Property 4: Onsager regression hypothesis

In the long time limit, A and B eventually become uncorrelated from each other so that the time correlation function becomes

$$C_{AB}(t) = \langle A(0)B(t)\rangle \to \langle A\rangle\langle B\rangle$$

For the autocorrelation function of A, this becomes

$$C_{AA}(t) \to \langle A\rangle^2$$

Thus, $C_{AA}(t)$ decays from $\langle A^2\rangle$ at $t = 0$ to $\langle A^2\rangle$ as $t \to \infty$.

An example of a signal and its time correlation function appears in Figure $12.4.1$. In this case, the signal is the magnitude of the velocity along the bond of a diatomic molecule interacting with a Lennard-Jones bath. Its time correlation function is shown beneath the signal:

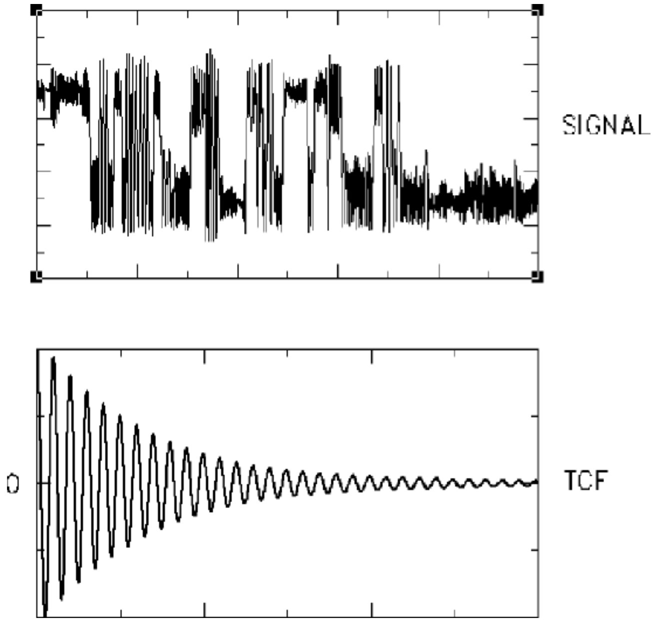

Figure 12.4.1

Over time, it can be seen that the property being autocorrelated eventually becomes uncorrelated with itself.