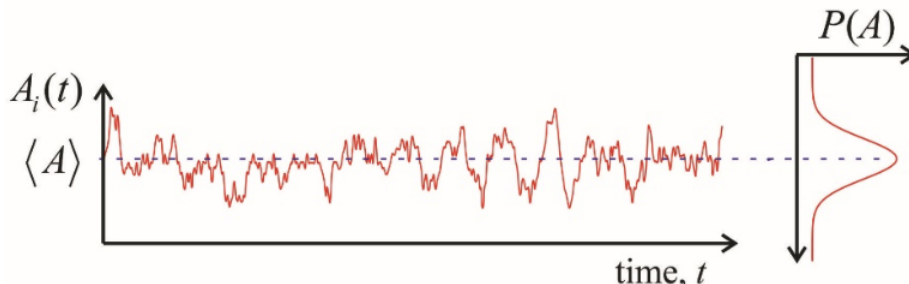


## 22.5: Time-Correlation Functions

### Time-Correlation Functions

Time-correlation functions are commonly used to characterize the dynamics of a random (or stochastic) process. If we observe the behavior of an internal variable  $A$  describing the behavior of one molecule at thermal equilibrium, it may be subject to microscopic fluctuations.



Although there may seem to be little information in this noisy trajectory, this dynamics is not entirely random, since they are a consequence of time-dependent interactions with the environment. We can provide a statistical description of the characteristic time scales and amplitudes to these changes by comparing the value of  $A$  at time  $t$  with the value of  $A$  at a later time  $t'$ . We define a time-correlation function as the product of these values averaged over an equilibrium ensemble:

$$C_{AA}(t-t') \equiv \langle A(t)A(t') \rangle \quad (22.5.1)$$

Correlation functions do not depend on the absolute point of observation ( $t$  and  $t'$ ), but rather the time interval between observations (for stationary random processes). So, we can define the time interval  $\tau \equiv t - t'$ , and express our function as  $C_{AA}(\tau)$ .

We can see that when we evaluate  $C_{AA}$  at  $\tau=0$ , we obtain the mean square value of  $A$ ,  $\langle A^2 \rangle$ . At long times, as thermal fluctuations act to randomize the system, the values of  $A$  become uncorrelated:  $\lim_{\tau \rightarrow \infty} C_{AA}(\tau) = \langle A \rangle^2$ . It is therefore common to redefine the correlation function in terms of the deviation from average

$$\delta A = A - \langle A \rangle \quad (22.5.2)$$

$$C_{\delta A \delta A}(t) = \langle \delta A(t) \delta A(0) \rangle = C_{AA}(t) - \langle A \rangle^2 \quad (22.5.3)$$

Then  $C_{\delta A \delta A}(0)$  gives the variance for the random process, and the correlation function decays to zero as  $\tau \rightarrow \infty$ . The characteristic time scale for this relaxation is the correlation time,  $\tau_c$ , which we can obtain from

$$\tau_c = \frac{1}{\langle \delta A^2 \rangle} \int_0^\infty dt \langle \delta A(t) \delta A(0) \rangle \quad (22.5.4)$$

The classical correlation function can be obtained from an equilibrium probability distribution as

$$C_{AA}(t-t') = \int dp \int dq A(p, q; t) A(p, q; t') P_{eq}(p, q) \quad (22.5.5)$$

In practice, correlation function are more commonly obtained from trajectories by calculating it as a time average

$$C_{AA}(\tau) = \overline{A(\tau)A(0)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' A_i(\tau+t') A_i(t') \quad (22.5.6)$$

If the time-average value of  $C$  is to be equal to the equilibrium ensemble average value of  $C$ , we say the system is ergodic.

Example: Velocity Autocorrelation Function for Gas

A dilute gas of molecules has a Maxwell-Boltzmann distribution of velocities, for which we will focus on the velocity component along the  $\hat{x}$  direction,  $v_x$ . We know that the average velocity is  $\langle v_x \rangle = 0$ . The velocity correlation function is

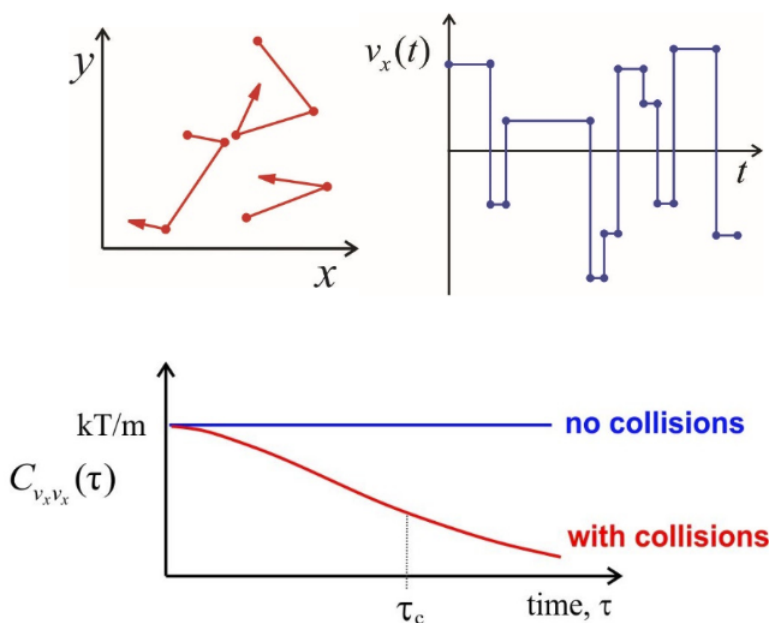
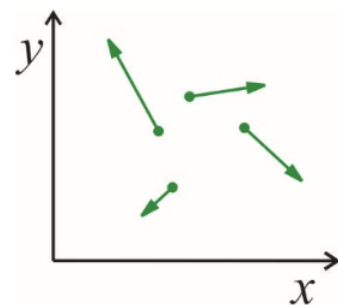
$$c_{v_x v_x}(\tau) = \langle v_x(\tau) v_x(0) \rangle$$

The average translational energy is  $\frac{1}{2}m\langle v_x^2 \rangle = k_B T/2$ , so

$$C_{v_x v_x}(0) = \langle v_x^2(0) \rangle = \frac{k_B T}{m}$$

For time scales that are short compared to the average collision time between molecules, the velocity of any given molecule remains constant and unchanged, so the correlation function for the velocity is also unchanged at  $k_B T/m$ . This non-interacting regime corresponds to the behavior of an ideal gas.

For any real gas, there will be collisions that randomize the direction and speed of the molecules, so that any molecule over a long enough time will sample the various velocities within the Maxwell-Boltzmann distribution. From the trajectory of x-velocities for a given molecule we can calculate  $C_{v_x v_x}(\tau)$  using time averaging. The correlation function will drop on with a correlation time  $\tau_c$ , which is related to mean time between collisions. After enough collisions, the correlation with the initial velocity is lost and  $C_{v_x v_x}(\tau)$  approaches  $\langle v_x^2 \rangle = 0$ . Finally, we can determine the diffusion constant for the gas, which relates the time and mean square displacement of the molecules:  $\langle x^2(t) \rangle = 2D_x t$ . From  $D_x = \int_0^\infty dt \langle v_x(t) v_x(0) \rangle$  we have  $D_x = k_B T \tau_c / m$ . In viscous fluids  $\tau_c / m$  is called the mobility.



### Calculating a Correlation Function from a Trajectory

We can evaluate eq. (22.5.6) for a discrete and finite trajectory in which we are given a series of  $N$  observations of the dynamical variable  $A$  at equally separated time points  $t_i$ . The separation between time points is  $t_{i+1} - t_i = \delta t$ , and the length of the trajectory is  $T = N \delta t$ . Then we have

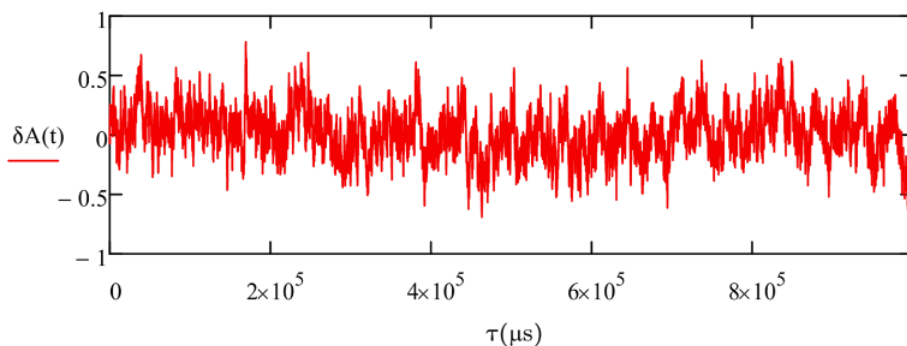
$$C_{AA} = \frac{1}{T} \sum_{i,j=1}^N \delta t A(t_i) A(t_j) = \frac{1}{N} \sum_{i,j=1}^N A_i A_j \quad (22.5.7)$$

where  $A_i = A(t_i)$ . To make this more useful we want to express it as the time interval between points  $\tau = t_j - t_i = (j - i) \delta t$ , and average over all possible pairwise products of  $A$  separated by  $\tau$ . Defining a new count integer  $n = j - i$ , we can express the delay as  $\tau = n \delta t$ . For a finite data set there are a different number of observations to average over at each time interval ( $n$ ). We have the most pairwise products— $N$  to be precise—when the time points are equal ( $t_i = t_j$ ). We only have one data pair for the maximum delay  $\tau = T$ . Therefore, the number of pairwise products for a given delay  $\tau$  is  $N - n$ . So we can write eq. (22.5.7) as

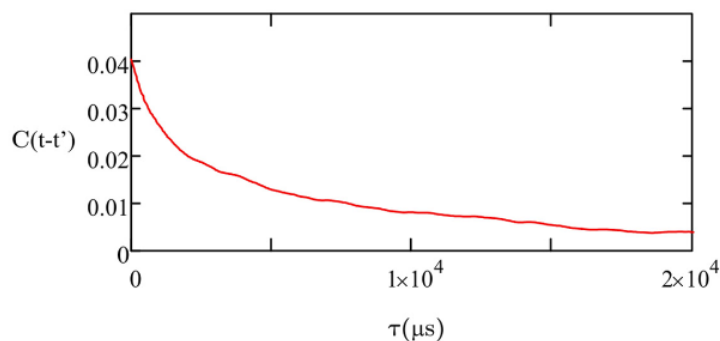
$$C_{AA}(\tau) = C(n) = \frac{1}{N - n} \sum_{i=1}^{N-n} A_{i+n} A_i \quad (22.5.8)$$

Note that this expression will only be calculated for positive values of  $n$ , for which  $t_j \geq t_i$ .

As an example consider the following calculation for fluctuations in fluorescence intensity in an FCS experiment. This trajectory consists of 32000 consecutive measurements separated by 44  $\mu\text{s}$ , and is plotted as a deviation from the mean  $\delta A(t) = A(t) - A$ .



The correlation function obtained from eq. (22.5.8) is



We can see that the decay of the correlation function is observed for sub-ms time delays. From eq. (22.5.4) we find that the correlation time is  $\tau_c = 890 \mu\text{s}$ .

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