Time Correlation Functions

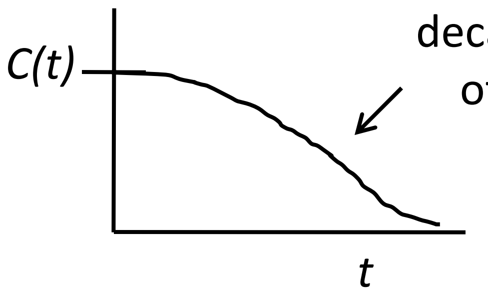
$$C(t) = \langle A(0) A(t) \rangle = \int \cdots \int dp\,dq\, A(p,q,0) A(p,q,t) f(p,q)$$

f = equil. phase space distribution function

example velocity

$$C(t) = \langle \vec{\mathrm{v}}(0) \cdot \vec{\mathrm{v}}(t) \rangle \rightarrow \frac{3kT}{m} \text{ at } t = 0$$

can calculate using molecular dynamics



decays to 0
often exponentially

Fourier-Laplace transform of *C(t)* $\rightarrow$ power spectrum

Can show diffusion constant $D = \frac{1}{3}\int_0^{\infty}\langle \vec{v}(0)\cdot\vec{v}(t)\rangle dt$

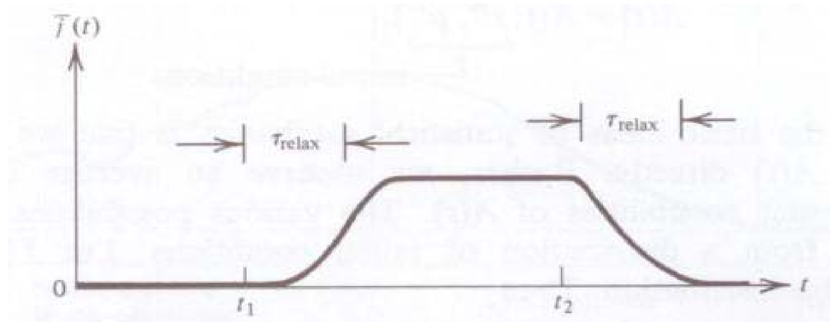
time correl. function is the fundamental quantity
in nonequil. systems

Why these are so useful experimentally

- Apply perturbation

- Follow response in t

  assume perturbation *A* gives a
  response that is linear



from Chandler

Most importantly, the information on how the system decays back to equilibrium is closely related to the fluctuations that occur in the equilibrium system. (fluctuation-dissipation theorem)

Another example

time dependent electric field across conductor

$\rightarrow$ current to flow

$$\sigma(\omega) = \frac{1}{kT}\int_0^\infty dt\ e^{-i\omega t}\left\langle J(0)\,J(t)\right\rangle$$

$$J(t) = \sum_j q_j u_j$$

The diffusion coefficient that we examined earlier is the $\omega \rightarrow 0$ limit of such an expression.

Absorption

$$I(\omega) = \frac{3}{2\pi}\int_{-\infty}^{\infty} dte^{-i\omega t}\left\langle \vec{\varepsilon}\cdot\vec{M}(0)\,\vec{\varepsilon}\cdot\vec{M}(t)\right\rangle$$

where $\vec{\mathcal{E}}$ is the electric field direction

For an isotropic fluid

$$\underline{I(\omega)} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dte^{-i\omega t}\left\langle \underline{\vec{M}(0)\cdot\vec{M}(t)}\right\rangle$$

line shape

time correlation function of dipole moment operator in absence of field

$$\vec{M}(0)\cdot\vec{M}(t) = \left(\sum_{j=1}^{N}\vec{u}_j(0)\right)\left(\sum_{i=1}^{N}\vec{u}_i(t)\right)$$

μ_j is a molecular dipole

if dipolar molecules are at low concentration, can ignore cross terms

$$\left\langle \vec{M}(0)\cdot\vec{M}(t)\right\rangle = \left\langle \sum_{j}^{N} \vec{u}_j(0)\vec{u}_j(t)\right\rangle = N\left\langle \vec{u}(0)\cdot\vec{u}(t)\right\rangle$$

Onsager (1930)
Regression hypothesis:

relaxation of macroscopic nonequil. perturbations governed by same laws as regression of spontaneous microscopic fluctuations in the equil. system.