

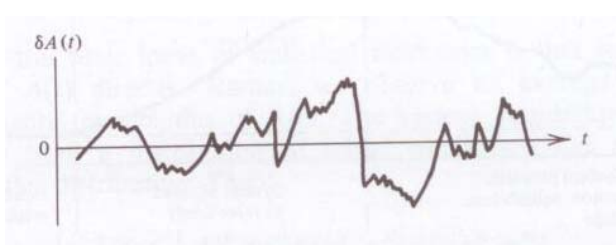
$$\delta A(t) = A(t) - \langle A \rangle$$

instantaneous fluctuation of A  
from its average (at equilibrium)

$$\delta A(t) = \delta A[r^N(t), p^N(t)]$$

assuming a classical  
description

$$\langle \delta A \rangle = 0$$



$A(t)$  looks chaotic

(from Chandler)

Let's examine correlations between fluctuations

$$C(t) = \langle \delta A(0) \delta A(t) \rangle$$

$$= \langle A(0) A(t) \rangle - \langle A \rangle^2$$

$$C(t) = \int dr^N dp^N f(r^N, p^N) \delta A(0) \delta A(t)$$

equil. phase-space  
distrib. function

In general,

$$C(t) = \langle \delta A(t') \delta A(t'') \rangle \quad \text{where } t = t'' - t'$$

$$C(t) = \langle \delta A(0) \delta A(t) \rangle = \langle \delta A(-t) \delta A(0) \rangle$$

$$\Rightarrow C(t) = C(-t)$$

At small  $t$

$$C(0) = \langle (\delta A)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$$

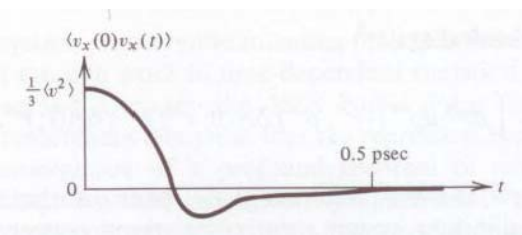
At long  $t$

$$C(t) \rightarrow \langle \delta A(0) \rangle \langle \delta A(t) \rangle$$

correlations are lost

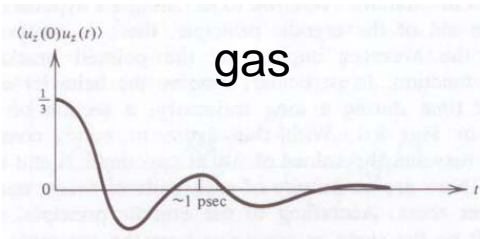
but  $\langle \delta A \rangle = 0 \Rightarrow$

$$C \rightarrow 0 \text{ as } t \rightarrow \infty$$



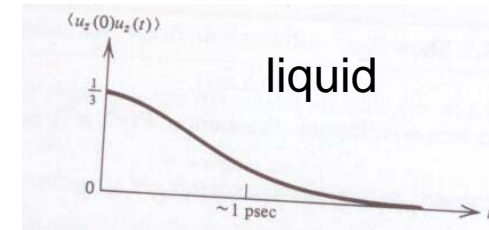
(from Chandler)

velocity correlation  
function for simple fluid



(from Chandler)

orientational correlation function



(from Chandler)

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

along principal axis of tagged molecule

### Onsager's hypothesis

$$\frac{\Delta \bar{A}(t)}{\Delta \bar{A}(0)} = \frac{C(t)}{C(0)}$$

$$\Delta \bar{A}(t) = \bar{A}(t) - \langle A \rangle = \delta \bar{A}(t)$$

$$C(t) = \langle \delta A(0) \delta A(t) \rangle$$

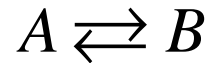


non-equil. from perturbation



monitors decay of fluctuations  
in equil. system

Illustrate with a simple problem from chemical kinetics



$$\frac{dc_A}{dt} = -k_{BA}c_A + k_{AB}c_B$$

$$\frac{dc_B}{dt} = k_{BA}c_A - k_{AB}c_B$$

$$c_A(t), c_B(t)$$

concentrations

at equil.

$$-k_{BA}\langle c_A \rangle + k_{AB}\langle c_B \rangle = 0$$

$$k_{eq} = \frac{\langle c_B \rangle}{\langle c_A \rangle} = \frac{k_{BA}}{k_{AB}}$$

Now consider the deviation of  $c_A$  from equilibrium

$$\Delta c_A(t) = c_A(t) - \langle c_A \rangle$$

$$= \Delta c_A(0) e^{-t/\tau}, \quad \frac{1}{\tau} = k_{AB} + k_{BA}$$

suppose  $n_A$  is a dynamical variable such that

$$\overline{n_A(t)} \propto c_A(t)$$

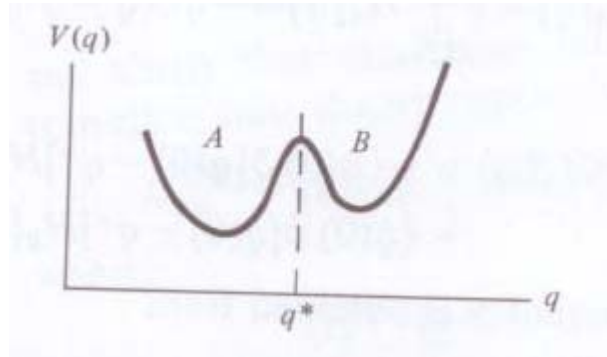
$$\frac{\Delta c_A(t)}{\Delta c_A(0)} = \frac{\langle \delta n_A(0) \delta n_A(t) \rangle}{\langle \delta n_A^2 \rangle} = e^{-t/\tau}$$

microscopic

involves rate constant  
for macroscopic reaction

But how do we find  $n_A$ ?

Simple, if there is a single reaction coordinate  $q$



(from Chandler)

$$\begin{aligned} \text{let } n_A(t) &= H_A[q(t)] \\ &= 1, \quad q < q^* \\ &= 0, \quad q > q^* \end{aligned}$$

$$\langle H_A \rangle = X_A = \frac{\langle c_A \rangle}{\langle c_A \rangle + \langle c_B \rangle}$$

$$\langle H_A^2 \rangle = \langle H_A \rangle = X_A$$

$$\langle (\delta H_A)^2 \rangle = \langle H_A^2 \rangle - \langle H_A \rangle^2 = X_A(1 - X_A) = X_A X_B$$

from the fluctuation-dissipation theorem

$$e^{-t/\tau} = \frac{\langle H_A(0) H_A(t) \rangle - X_A^2}{X_A X_B}$$

## Self Diffusion

solute present at low concentration:  $n(\vec{r}, t)$

$$\frac{\partial}{\partial t} n(\vec{r}, t) = -\nabla \cdot \vec{j}(\vec{r}, t) \quad \text{continuity eq.}$$

$\vec{j}$  = non-equil. avg. flux of solute molecules

$$\left. \begin{aligned} \vec{j}(\vec{r}, t) &= -D \nabla n(\vec{r}, t) \\ \frac{\partial}{\partial t} n(\vec{r}, t) &= D \nabla^2 n(\vec{r}, t) \end{aligned} \right\} \text{ Ficks Law} \quad \left| \begin{array}{l} \text{mass flow requires} \\ \text{a concentration} \\ \text{gradient} \end{array} \right.$$

$D$  = self-diffusion constant

how concentration gradients relax

$$C(\vec{r}, t) = \langle \delta\rho(\vec{r}, t) \delta\rho(\vec{r}, 0) \rangle$$

From Onsager's regression hypothesis:

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

$$\langle \rho(\vec{r}, t) \rho(\vec{0}, 0) \rangle \propto P(\vec{r}, t)$$

prob. that a solute particle is at  $\vec{r}, t$   
given that it was *at the origin* at  $t=0$

$$\Rightarrow \frac{\partial P}{\partial t} = D\nabla^2 P$$

$$\begin{aligned} \Delta R^2(t) &= \langle |\vec{r}_1(t) - \vec{r}_1(0)|^2 \rangle \\ &= \int d\vec{r} r^2 P(\vec{r}, t) \end{aligned}$$



$$\begin{aligned} \frac{d}{dt} \Delta R^2(t) &= \int d\vec{r} D \nabla^2 P(\vec{r}, t) \\ &= 6 \int d\vec{r} D P(\vec{r}, t) \end{aligned} \quad \int \text{ by parts}$$

$$\frac{d}{dt} \Delta R^2(t) = 6D$$

or  $\Delta R^2(t) = 6Dt$  the Einstein expression

valid only after an initial  
transient time

diffusional motion  $\Delta R^2(t) \propto t$  "long" time diffusive

inertial motion  $\Delta R(t) \propto t$  short time inertial

---

$$\vec{r}_1(t) - \vec{r}_1(0) = \int_0^t dt' \vec{v}(t')$$

$$\Delta R^2(t) = \int_0^t dt' \int_0^t dt'' \langle \vec{v}(t') \cdot \vec{v}(t'') \rangle$$

$$\frac{d}{dt} \Delta R^2 = 2 \langle \vec{v}(t) \cdot [\vec{r}_1(t) - \vec{r}_1(0)] \rangle$$

$$= 2 \int_0^t \langle \vec{v}(0) \cdot \vec{v}(t') \rangle dt'$$

$$= 2 \int_0^t \langle \vec{v}(0) \vec{v}(t) \rangle dt$$

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

$$\tau_{relax} = \int_0^\infty dt \frac{\langle \vec{v}(0) \cdot \vec{v}(t) \rangle}{\langle v^2 \rangle}$$

$$\tau_{relax} = \frac{mD}{kT}$$

$$\langle \vec{v}(0) \cdot \vec{v}(t') \rangle \approx \langle v^2 \rangle e^{-t'/\tau}$$

Time for diffusive motion to set in  
= time for velocity perturbation to  
decay back to equilibrium