Lecture 4

Jeff's AT:

\[ e^{-it} f(c, \omega) \rightarrow f_0(\Omega) \rightarrow e^{-i\Omega t} \]

But any \( f(\mathcal{H}_M) \) analytic in \( \mathcal{H} \) is a solution!

Need ergodic (not chaotic) system. \( f_0(\Omega) \) is one that maximizes f.e.; in entropy.

\[ C_{A(\mathcal{H})} = \langle A(\mathcal{H}) B(\mathcal{L}) \rangle = \lim_{S \rightarrow \infty} \frac{1}{S} \int_0^S dt \langle A(\mathcal{H}) B(\mathcal{L}) \rangle \]

\[ = \langle A(\mathcal{H}) B(\mathcal{L}) \rangle \]

\[ = \langle A(\mathcal{H}) B(\mathcal{L}) \rangle \]

\[ = -\langle A(\mathcal{H}) B(\mathcal{L}) \rangle \]
Often it is convenient to define such time correlation functions in a way that emphasizes the degree of correlation between $A$ and $B$:

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

$$SB(t) = B(t) - \langle B \rangle$$

$$D_{AB}(t) = \langle SA(t) SB(t) \rangle$$

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

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

Hence, the time CF $D_{AB}(t)$ is non-zero only for the range of times $0 < t < T$ for which $A$ and $B$ are correlated. The timescale $T$ is known as the correlation time.

If the functions $C_{AA}(t)$ or $D_{AB}(t)$ are known as autocorrelation functions since $B = A$. If we monitor $SA(t)$ in a simulation for some typical property, e.g.
the deviation in the number of particles in some region of the volume, it might look like:

\[ S_A \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad t \]

The correlation time \( \tau \) could be identified as the typical time for \( S_A \) to switch sign. More quantitatively, we could compute the TCF \( D_{AA}(t) \). Two types of decay of \( D_{AA}(t) \) are usual:

- **Overdamped** (typical in dense fluids) "high friction"

\[ D_{AA} \]

\[ 0 \quad t \quad t \]

- **Underdamped** (typical in gases and dilute phases) "high inertia"

\[ D_{AA} \]

\[ 0 \quad t \quad t \]
Note that in both cases, the intercept (static limit) is

\[ D_{AA}(0) = \langle A^2 \rangle - \langle A \rangle^2 \]

which only involves the evaluation of equilibrium averages.

Indeed, one can formally develop a TCF like \( D_{AA}(t) \) in a short time expansion, where the expansion coeffs to all orders only require the evaluation of equilibrium averages. In particular,

\[
D_{AA}(t) = D_{AA}(0) + t \frac{\delta}{\delta t} \bigg|_{t=0} D_{AA}(t) + \frac{t^2}{2!} \frac{\delta^2}{\delta t^2} \bigg|_{t=0} D_{AA}(t) + \ldots
\]

\[
= \langle A^2 \rangle - \langle A \rangle^2 + t \langle \dot{A}(0) \dot{A}(0) \rangle + \frac{1}{2} t^2 \langle \ddot{A}(0) \dot{A}(0) \rangle + O(t^4)
\]

where obviously the odd coeffs vanish because \( D_{AA}(t) = D_{AA}(-t) \). Hence,

\[
D_{AA}(t) = \langle A^2 \rangle - \langle A \rangle^2 - \frac{1}{2} t^2 \langle \dot{A}(0) \dot{A}(0) \rangle + O(t^4)
\]

The \( t^2 \) coefficient can be calculated as:
\[ \langle A^* A \rangle = \int d\Gamma \, f_0(\Gamma) \, A(\Gamma) \, A(\Gamma) = \langle A A \rangle \]

While formally one can carry out the evaluation of such series to very high order, using only equil. SM, such short-time expansions tend to have a very small radius of convergence and are not too practically useful.

E. Green-Kubo Formulae

8. Obviously time correlation functions give us quantitative informations about the spontaneous dynamical fluctuations of an equilibrium system. Perhaps not so obvious is that time correlation functions can be directly linked with linear transport coefficients, i.e. the familiar viscosity \( \eta \), diffusion coeff. \( D \), and thermal conductivity of a fluid.

8. Let's illustrate for the self-diffusion coefficient \( D \). Consider one atom in an equil. fluid. Its displacement over some interval \( (0, t) \) is
\[ R(t) \equiv \overline{\mathbf{r}(t) - \mathbf{r}(0)} = \int_0^t dt' \mathbf{v}(t') = \frac{1}{m} \int_0^t dt' \mathbf{p}(t') \]

so

\[ \langle R(t) \cdot R(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle \]

is the average squared displacement. Now,

\[ \langle R^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t'-t'') \cdot \mathbf{v}(0) \rangle \]

\[ = 2 \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t'-t'') \cdot \mathbf{v}(0) \rangle \]

\[ = 2 \int_0^t dt' \int_0^t ds \langle \mathbf{v}(s) \cdot \mathbf{v}(0) \rangle \]

\[ \frac{d}{dt} \langle R^2(t) \rangle = 2 \int_0^t ds \langle \mathbf{v}(s) \cdot \mathbf{v}(0) \rangle \]

If the transport becomes diffusive at long times, we have Einstein's formula:

\[ \langle R^2(t) \rangle = 6 D t \]

or

\[ \frac{d}{dt} \langle R^2(t) \rangle = 6 D \quad t \to \infty \]
Thus,

\[ D = \frac{1}{3} \int_{0}^{\infty} ds \left( \langle \vec{v}(s) \cdot \vec{v}(0) \rangle \right) \]

This is our first example of a Green-Kubo formula, which expresses a transport coeff. in terms of an integral over an equil. TCF. Similarly, it can be shown that the shear viscosity is given by

\[ \eta = \frac{V}{k_B T} \int_{0}^{\infty} ds \left( \langle P_{xy}(s) P_{xy}(0) \rangle \right) \]

where \( P_{\alpha\beta}(t) \) is the microscopic pressure tensor.

\[ P_{\alpha\beta} = \frac{1}{V} \left( \sum_{i} \delta_{\alpha\beta} P_{i\beta} \delta_{\text{mu}} + \sum_{i} \delta_{\alpha\mu} P_{i\beta} \right) \]

With formulae like these, we already have two different routes to computing linear transport coefficients in a computer simulation:

1. Via an Einstein formula
- Equilibrate

- Compute \( \langle R^2(t) \rangle = \frac{1}{N} \sum_i \langle (\bar{\theta}_i(t) - \bar{\theta}_i(0))^2 \rangle \)

\[ \langle E^2(t) \rangle \]

\[ \text{slope} = 6D \]

2. Via a Green-Kubo formulae

- Equilibrate

- Compute \( C_{uu}(t) = \frac{1}{N} \sum_i \langle \dot{\theta}_i(t) \dot{\theta}_i(0) \rangle \)

\[ C_{uu}(t) \]

- Numerically integrate

\[ D = \frac{1}{3} \int_0^\infty dt C_{uu}(t) \]

F: Space - Time Correlation Functions

Another important type of correlation function also proves important in studying the fluctuation dynamics of equilibrium.
fluids. We define the space-time CF of two variables $A(\zeta, t)$, $B(\zeta', t)$ by

$$C_{AB}(\zeta, \zeta', t) = \langle A(\zeta, t) B(\zeta', 0) \rangle$$

where the average is that appropriate for an equilibrium system. If we have a homogeneous fluid (not xtal solid), far from any surfaces or interfaces, then $C_{AB}$ has translational invariance

$$C_{AB}(\zeta, \zeta', t) = C_{AB}(\zeta - \zeta', t)$$

Moreover, if the fluid is isotropic (i.e., not a liquid crystal),

$$C_{AB}(\zeta, \zeta'; t) = C_{AB}(1\zeta - \zeta', t)$$

The most important space-time CF relates to density-density correlations. Recall
8. Space-time CFs have a number of important properties. Most important for us are:

1. Decoherence / Statistical independence

\[ \langle A(\xi, t) B(\xi', 0) \rangle \quad \longrightarrow \quad \langle A \rangle \langle B \rangle \]

as \( \xi - \xi' \to \infty \) or \( t \to \infty \) equil. ave.

2. Static limit

\[ \langle A(\xi, t) B(\xi', 0) \rangle \quad \longrightarrow \quad \langle A(\xi) B(\xi') \rangle \]

as \( t \to 0 \) equil. ave.

3. TCF limit

\[ \langle A(\xi, t) B(\xi', 0) \rangle \quad \longrightarrow \quad \langle A(\xi, t) B(\xi', 0) \rangle \]

as \( \xi' \to \xi \) indep. TCF

4. The most important space-time CF relates to density-density correlations. Recall that the microscopic number density of atoms is given by
\[ \hat{\rho}(\xi, t) = \sum_i S[\xi - \xi_i(t)] \]

\[ \langle \hat{\rho} \rangle = \rho = N/V \]

The so-called Van Hove pair correlation function is defined by

\[ G(\xi, t) = \rho^{-1} \langle \hat{\rho}(\xi + \xi', t) \hat{\rho}(\xi', 0) \rangle \]

\[ = \rho^{-1} \sum_i \sum_j \langle S[\xi + \xi' - \xi_i(0)] S[\xi' - \xi_j(0)] \rangle \]

\[ \text{(note } \xi' \text{)} = \frac{1}{N} \sum_i \sum_j \langle S[\xi + \xi' - \xi_i(0) - \xi_j(0)] \rangle \]

In the static limit,

\[ G(\xi, 0) = \delta(\xi) + \rho \varrho(\xi) \]

\[ \text{radial distribution function} \]

Two related forms are

\[ I(k, t) = \int_{d\xi} \rho \left[ G(\xi, t) - \rho \right] \]

\[ S(k, \omega) = \int_0^\infty \exp(-i\omega t) I(k, t) \]

which as we shall discuss are related to