Lecture 10
Another important limit is the so-called "high friction" limit. Here we simply neglect the inertial term in the Langevin equation

\[ \frac{d}{dt} \mathbf{r} = -\frac{F}{m} \mathbf{r} + \mathbf{R}(t) \]

This is reasonable, provided we are only interested in phenomena on time scales longer than \( T_f = \frac{m}{F} \), which can be a very short time scale if the medium surrounding the Brownian particle is very viscous. We then write

\[ \frac{d}{dt} \mathbf{r}(t) = -\frac{F}{m} \mathbf{r}(t) \]  

high friction

Langevin eqn

It is straightforward to show that the mean-squared displacement is

\[ \langle R(t)^2 \rangle = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 6 D t \quad \text{,} \quad D = \frac{F \gamma}{m} \]

and if we construct a Fokker-Planck eqn for the distribution of particle displacements, \( f(\mathbf{r}, t) \), one finds the familiar diffusion eqn:

\[ \frac{\partial}{\partial t} f(\mathbf{r}, t) = D \nabla^2 f(\mathbf{r}, t) \]
The fundamental (Green's func) solution is

\[ f(r, t; r_0) = \left[ \frac{3}{2\pi \langle R^2(t) \rangle} \right]^{3/2} e^{-\frac{1}{2} \left( \frac{r - r_0}{\langle R^2(t) \rangle} \right)^2} \]


7. We have seen that the Brownian motion theory provides powerful tools for studying the time dependent properties of large colloidal particles dispersed in a molecular solvent. What tools are available when one returns to the original problem of a liquid of same-sized particles?

A. Projection Operators and the Generalized Langevin Eqn.

8. One of the most significant formal non-equil developments of modern SMT was the demonstration by Zwanzig (61) and Mori (65) that Langevin-type equations could be formally derived from the
Liouville equations with no approximations, regardless of the fluid density, and yielding explicit expressions for the "random force" and "drag" terms appearing in the equations. The derivation proceeds through the introduction of so-called projection operators that act on functions of the phase coordinates $\Gamma$.

Consider a set of functions of the phase coordinates $A_i = A_i(\Gamma)$, $i = 1, 2, \ldots, n$. Using these functions, we can define an $n \times n$ matrix of equilibrium correlation functions:

$$C_{ij} = \langle A_i A_j \rangle = \int d\Gamma f_0(\Gamma) A_i(\Gamma) A_j(\Gamma)$$

Consider another function $B(\Gamma)$. We define the projection operator $P_A$ by:

$$P_A B = \sum_i \sum_j (B, A_j) (C)^{-1} v_i A_i$$
Notice that $P_A$ "projects" the functions $B$ onto the subset of Liouville space spanned by linear combinations of the $\xi A_i \beta$.

Notice, e.g.

1. $P_A A_k = A_k$

2. $P_A (B + C) = P_A B + P_A C$

3. $P_A^2 B = P_A B$

We can also define a complementary projection operator $Q_A \equiv 1 - P_A$, which projects functions onto the subspace orthogonal to $\xi A_i \beta$. Thus, e.g.

1. $Q_A + P_A = 1$

2. $Q_A^2 B = Q_A B$

3. $(Q_A B, A_k) = 0$

Q. Zwanzig and Mori showed that starting with the classical EOM:
\[ \frac{d}{dt} A_i(t) = \mathbf{L} A_i \]

that one can transform the RHS into the following type of generalized Langevin equation:

\[ \frac{d}{dt} A_i(t) = \sum_j \Omega_{ij} \dot{A}_j(t) - \sum_j \int_0^t ds K_{ij}(t-s) A_j(s) + F_i(t) \]

where

\[ \Omega_{ij} = \sum_k \langle \dot{A}_i, \dot{A}_k \rangle (C^{-1})_{kj} \]

\[ F_i(t) = e^{QA_L t} \Phi_A \mathcal{L} A_i = \Phi_A F_i(t) \]

\[ K_{ij}(t) = \sum_k \langle F_i(t), F_k(0) \rangle (C^{-1})_{kj} \]

Why is the GLE useful? There are a few answers:

1. It allows us to derive linear equations that generalize the hydrodynamic laws to arbitrary times and distances – generalized hydrodynamics
2. It is a good framework for...
making approximations.

3. Unlike the hydrodyn. eqns, it is not averaged. To understand these, we defined non-equilibrium ensemble averages:

\[ \langle A(t) \rangle \equiv \int d\Gamma f(\Gamma, 0) e^{\frac{\mathcal{L}}{\hbar} t} A(\Gamma) \]

Then

\[ \langle F_i(t) \rangle = \int d\Gamma f(\Gamma, 0) e^{\frac{\mathcal{L}}{\hbar} t} \Phi_i \]

For some classes of initial distributions, e.g. a system weakly perturbed from equilibrium by conjugate fields:

\[ f(\Gamma, 0) \approx f_0(\Gamma) \left[ 1 + \sum_i \xi_i A_i(\Gamma) \right] \]

\[ \langle F_i(t) \rangle = 0 \]

Thus, Generalized hydrodynam.

\[ \frac{\partial}{\partial t} \langle A(t) \rangle = \frac{\partial}{\partial \tau} \langle A(t) \rangle - \int_0^t K(t-\tau) \langle A(\tau) \rangle d\tau \]

If we associate the various components of \( A \) with the Fourier components of a conserved density, e.g. \( \rho, e, \Phi \), or the values of these fields at discrete lattice sites, then this equation—
is evidently a generalization of the familiar hydrodynamic equations. The convective terms are associated with the matrix \( \Pi \). The dissipative (diffusion) terms are associated with \( \Xi(t) \). The latter is nonlocal in both space and time!

B. Linear Laws of Irreversible Thermodynamics

Obviously, the memory function matrix is very difficult to evaluate. However, it becomes a simpler object if the \( \Xi_{ij}(t) \) encompasses all the slowly relaxing variables in a fluid. Besides the small \( \xi \) Fourier components of the conserved densities, this set might also include "order parameters" which are field variables that relax very slowly in systems near critical points or phase boundaries. Thus,

\[
A(t) \leftrightarrow \text{slowly relaxing},
\]

\[
E(t) \leftrightarrow \text{faster relaxing}
\]

Since \( E \) is orthogonal to \( A \),
Also,

\[ K(t) \approx \langle E(t) E(0) \rangle \quad \text{fast relaxing} \]

With this selection, we then have a similar situation as in the theory of Brownian motion: \( E(t) \) has a short correlation time and can be approximated by a white noise source:

\[ K(t) \approx 2 \sum S(t) \quad \text{or}\quad \text{Markov approx} \]

Normally, one decomposes the relaxation rate matrix \( \Gamma \) as

\[ \Gamma = \Lambda \cdot \Sigma^{-1} \]

where \( \Lambda \) is the \( \text{Onsager\ kinetic\ coefficient} \) matrix. Obviously

\[ \Lambda = \int_0^\infty \, dt \, \langle E(t) E(0) \rangle \]

which is a Green-Kubo formula. Elements of \( \Lambda \) would include \( \text{viscosity coefficients, thermal diffusivities, and diffusion constants} \). The resulting linear equations...
\[
\frac{d}{dt} \langle A(t) \rangle = \frac{D}{2} \langle A(t) \rangle - \frac{D}{2} \langle \mathcal{A}^{-1}(t) \rangle
\]

are simply linear hydrodynamic signs, which are often known as the linear laws of irreversible thermodynamics.

C. Tracer - Diffusion Example

\(Q\) To make the above concrete, consider a tracer atom in a fluid. Choose the Fourier components of its density as the \(A\) variables:

\[
A_k(t) = e^{i \mathbf{k} \cdot \mathbf{r}(t)}
\]

\[k = \frac{w_k}{L}, \quad \mathbf{r}_i = 0, \quad i = 1, \ldots, N\]

It is easy to show that \(Q_{k, k'} = 0\).

Moreover

\[
C_{k, k'} = (e^{i \mathbf{k} \cdot \mathbf{r}(t)}, e^{i \mathbf{k'} \cdot \mathbf{r}(t)}) = \delta_{k, k'}
\]

\[
F_{k}(t) = e^{Q_{A} \mathbf{r}(t)} e^{i \mathbf{k} \cdot \mathbf{r}}
\]

\[
= e^{Q_{A} \mathbf{r}(t)} [e^{i \mathbf{k} \cdot \mathbf{r}}, u] , \quad u = \frac{i \mathbf{k}}{m}
\]

\[
= e^{Q_{A} \mathbf{r}(t)} i \mathbf{k} \cdot \mathbf{u}
\]

\[
= e^{Q_{A} \mathbf{r}(t)} i \mathbf{k} \cdot \mathbf{u}
\]
\[ \phi_{k,k'}(t) = \delta_{k,k'} \frac{k}{k'} \langle \psi \psi^{*} e^{-i k \cdot x} e^{-i k' \cdot x} \rangle \]

\[ = \delta_{k,k'} k^2 D(k,t) \]

where

\[ D(k,t) = \langle \psi \varphi_{k,t}^{1/2} \varphi_{k,t}^{1/2} \rangle \]

The GLE is

\[ \frac{2}{\beta} A_{\psi} (t) = -k^2 \int_{0}^{t} ds \ D(k, t-s) A_{\psi} (s) + F_{\psi} (t) \]

and describes tracer transport at all length and timescales. If the smallest \( k = 1 \) modes are the slowest to relax, then we can make the Markov approx for these:

\[ D(t) = D(0, t) = \frac{1}{2} \langle \psi \varphi_{k,t}^{1/2} \varphi_{k,t}^{1/2} \rangle \]

\[ = \frac{1}{2} \langle \psi \varphi_{k,t}^{1/2} \varphi_{k,t}^{1/2} \rangle \]

\[ = \frac{1}{2} \langle \psi \varphi_{k,t}^{1/2} \varphi_{k,t}^{1/2} \rangle = \frac{1}{2} \langle \psi(t), \psi(0) \rangle \]

\[ \propto 2 D_{\psi}(t) \]

\[ \Rightarrow \ D = \frac{1}{3} \int_{0}^{\infty} dt \langle \psi(t), \psi(0) \rangle \]
and the GLE becomes

$$\frac{\partial}{\partial t} A_{\xi}(t) = -k^2 D A_{\xi}(t) + F_{\xi}(t)$$

where \( \langle F_{\xi} \rangle = 0 \)

$$\langle F_{\xi}(t) F_{\xi}(t') \rangle = 2 k^2 D \delta_{\xi, \xi'} \delta(t-t')$$

The second eqn is a type of 2nd FDT relationship.

Finally, if we invert the Fourier transforms:

\[ \begin{cases} \frac{\partial}{\partial t} A(\xi, t) = D \nabla^2 A(\xi, t) + F(\xi, t) \\ \langle F(\xi, t) \rangle \\ \langle F(\xi, t) F(\xi', t') \rangle = -2 D \nabla^2 \delta(\xi - \xi') \delta(t-t') \end{cases} \]

Comments:

1. Eqns (8) are a stochastic version of the diffusion eqn \( \rightarrow \) "fluctuating hydrodynamics"

2. These are useful for building models of kinetic processes where the hydrodynamic description is appropriate, e.g. light scattering.

3. The noise statistics are not arbitrary.

4. Computations are as in Brownian motion then...