Lecture 5 : Thursday 20 Feb 2003

1 Dynamical variables, correlation functions

Our probability space is the 2ν-dimensional phase space Ω. The coordinates of its elements ω are the ν momentum coordinates $p_1(\omega) \ldots p_\nu(\omega)$ and the ν position coordinates $q_1(\omega) \ldots q_\nu(\omega)$.

If $X : \Omega \to R$ is a dynamical variable, its value varies with time, i.e. it is a stochastic process (a randomly chosen function of time) $X_t = X_t(\omega) := X(\omega_t)$ where ω_t satisfies the Hamiltonian eqns of motion

$$\begin{aligned} dp_i(\omega_t)/dt &= -\partial H(\omega_t)/\partial q_i(\omega_t) \\ dq_i(\omega_t)/dt &= \partial H(\omega_t)/\partial p_i(\omega_t) \quad (i = 1 \ldots \nu) \end{aligned} \tag{1}$$

with initial condition $\omega_0 = \omega$.

If X and Y are two dynamical variables, their equilibrium correlation function is defined as

$$\langle X_s Y_t \rangle := \int_\Omega X(\omega_s) Y(\omega_t) \rho(\omega) d\omega \tag{2}$$

where ρ is the equilibrium phase-space density, for which I'll use the canonical ensemble $\rho \propto \exp(-H(\omega)/kT)$. Since the Hamiltonian for a system in equilibrium is independent of time, the equilibrium correlation function is time-shift invariant, i.e. it is a function of $t - s$ only.

Provided that the expectations of X_s and Y_t are zero, the correlation function gives a measure of the amount of correlation between these two random variables. If these expecations are not zero, it is better to use the truncated correlation function, defined as

$$\langle X_s Y_t \rangle - \langle X_s \rangle \langle Y_t \rangle \tag{3}$$

In statistical language this is the covariance of X_s and Y_t.

2 The Liouville operator

A formal expression for the time dependence of X_t can be obtained by writing

$$\begin{aligned} (\partial/\partial t) X_t(\omega) &= (\partial/\partial t) X(\omega_t) \\ &= L X(\omega_t) \quad \text{by (1) and the rules of calculus} \\ &= L X_t(\omega) \end{aligned} \tag{4}$$

where L is the Liouville operator (acting in some space of functions $\Omega \to R$) defined by

$$L = \sum_{i=1}^{\nu} \left\{ \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right\} \tag{5}$$

Eqn (4) can be written as a differential equation in some space of functions over Ω

$$dX_t/dt = LX_t \tag{6}$$

If L is independent of t this has the formal solution

$$X_t = \exp(Lt)X \tag{7}$$

which will come in useful later.

The Liouville operator is an antisymmetric operator, i.e.

$$\langle X(LY)\rangle = -\langle (LY)X\rangle \tag{8}$$

In terms of it, Liouville's theorem can be written

$$\partial\rho/\partial t = -L\rho \tag{9}$$

3 Linear response theory

Suppose that we apply to the system a small time-dependent external force $\xi(t) \in R$ conjugate to the dynamical variable $X : \Omega \to R^{2\nu}$. This means changing the Hamiltonian to

$$H = H^0 + H^1(t) = H^0 - X\xi(t) \tag{10}$$

where H^0 is the unperturbed Hamiltonian. For example, X could be the x-coordinate of the position of an ion and $\xi(t)$ the force exerted on it by an external (i.e. controlled by the experimenter) electric field in the x direction. Suppose that $\xi(t)$ is switched on at time 0, i.e. $\xi(t) = 0$ if $t < 0$, and, for simplicity, that the equilibrium expectation of X is zero. Hence $\langle X_t\rangle = 0$ for $t < 0$. The purpose of the calculation is to find how the expectation of X_t varies with time for $t > 0$.

Write $\rho = \rho^0 + \rho^1$ where ρ^0 is the canonical prob. distribution, satisfying $L^0\rho^0 = 0$ where L^0 is the unperturbed Liouville operator. Liouville's eqn gives

$$d\rho^1/dt = -L^0\rho^1 - L^1(t)\rho^0 + O(\xi^2) \tag{11}$$

where L^0 and L^1 are the contributions to L, as defined in (5), from the two terms in the Hamiltonian (10); in particular

$$L^1(t) := -\xi(t)\sum_{i=1}^{\nu}\left\{\frac{\partial X}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial X}{\partial q_i}\frac{\partial}{\partial p_i}\right\} \tag{12}$$

Since L^0 is independent of t the differential eqn (11) can be solved (using the condition $\rho^1_0 = 0$) as

$$\begin{aligned}\exp(tL^0)\rho^1_t &= -\int_0^t ds\,\exp(sL^0)L^1(s)\rho^0 \\ i.e.\quad \rho^1_t &= -\int_0^t ds\,\exp((s-t)L^0)L^1(s)\rho^0 \qquad (13)\end{aligned}$$

From the definition of the (unperturbed) canonical distribution we have

$$
\begin{aligned}
L^1(s)\rho^0 &= -(1/kT)(L^1(s)H^0)\rho^0 \\
&= (1/kT)\xi(s)\sum_{i=1}^{\nu}\left\{\frac{\partial X}{\partial p_i}\frac{\partial H^0}{\partial q_i} - \frac{\partial X}{\partial q_i}\frac{\partial H^0}{\partial p_i}\right\}\rho^0 \quad \text{by} \;\; (12) \\
&= -(1/kT)\xi(s)(L^0X)\rho^0 \quad \text{by} \;\; (5) \\
&= -(1/kT)\xi(s)\dot{X}\rho^0 \quad \text{by} \;\; (6) \qquad (14)
\end{aligned}
$$

where $\dot{X}$ is the time derivative dX/dt calculated in accordance with (6) using the unperturbed Hamiltonian H^0. Hence we may write (13) as

$$
\rho_t^1 \;\; = \;\; (1/kT)\int_0^t ds \exp((s-t)L^0)\xi(s)\dot{X}\rho^0 \qquad (15)
$$

Soppose we observe a dynamical variable Y (which may or not be the same as X) at time t; as a result of the perturbation, its expectation changes by

$$
\begin{aligned}
\langle Y_t\rangle - \langle Y_0\rangle &= \int_\Omega Y(\omega)\rho_t^1(\omega)\, d\omega \\
&= (1/kT)\int_\Omega Y(\omega)\int_0^t ds \exp((s-t)L^0)\dot{X}\rho^0 \, d\omega\xi(t) \quad by (15) \\
&= \int_0^t \phi_{YX}(t-s)\xi(s)ds \qquad (16)
\end{aligned}
$$

where

$$
\begin{aligned}
\phi_{YX}(t-s) &:= (1/kT)\int_\Omega Y(\omega)[\exp((s-t)L^0)\dot{X}\rho^0](\omega)\, d\omega \\
&= (1/kT)\langle Y[(\exp((s-t)L^0)\dot{X})]\rangle \\
&= (1/kT)\langle Y[(\exp((s-t)L^0)\dot{X})](\omega)\rangle_{eq} \\
&= (1/kT)\langle[\exp((t-s)L^0 Y]\dot{X})\rangle_{eq} \qquad (17)
\end{aligned}
$$

by the antisymmetry of L^0, eqn (8). Using (7) with L the unperturbed Liouville operator, this last formula can be written

$$
\phi_{YX}(t-s) = (1/kT)\langle Y_{t-s}\dot{X}\rangle_{eq} \qquad (18)
$$

where the formula is evaluated at equilibrium, using the unperturbed Hamiltonian. This is Kubo's (or Green-Kubo) formula, or the fluctuation-dissipation theorem.

4 Transport coefficients

Often we are interested in the long-time response to a force that is held constant over a long time, e.g a constant electric field applied to an ion. Differentiation of (16) gives

$$\begin{aligned} (d/dt)\langle Y_t \rangle &= (1/kT) \int_0^t \langle \dot{Y}_{t-s} \dot{X} \rangle_{eq} ds \xi \\ &\approx \Lambda_{YX} \xi \end{aligned} \tag{19}$$

where

$$\Lambda_{YX} := (1/kT) \int_0^\infty \langle \dot{Y}_t \dot{X} \rangle_{eq} dt \tag{20}$$

which is assumed to converge (this is a form of "mixing", a concept in ergodic theory).

For example, if X is the x-coordinate of an ion and ξ is the electric force on it, then Λ_{XX} is the mobility of the ion, the velocity per unit applied force. There are analogous 'Kubo' formulas for a variety of transport coefficients : viscosity, heat conductivity and so on.

5 Onsager's reciprocal relations

Let $\mathbf{T}$ be the velocity reversal operator i.e. $\mathbf{T}(p,q) = (-p,q)$. Suppose that H is invariant under velocity reversal (not the case in an external magnetic field), and suppose that X and Y are also velocity reversal invariant. Then the matrix Λ_{XY} is symmetric, i.e.

$$\Lambda_{XY} = \Lambda_{YX} \tag{21}$$

Proof: the eqns of motion give

$$\mathbf{T}\omega_t = (\mathbf{T}\omega)_{-t} \tag{22}$$

Then the equilibrium correlation function satisfy

$$\begin{aligned} \langle X_t Y_s \rangle &= \langle X_{-t} Y_{-s} \rangle \quad \text{using } \mathbf{T} \\ &= \langle X_s Y_t \rangle \end{aligned} \tag{23}$$

by time-shift invariance (shifing by $t+s$). Apply this to $\dot{X}$ and $\dot{Y}$, set $s=0$ and integrate w.r.t from 0 to ∞ and we have Onsager's reciprocal relation (21).

In using this one has to be careful to use the right pairs (X,ξ) in (19) (a point sometimes overlooked, even by authors of books on irreversible thermodynamics). They can be identified using the thermodynamic formula

$$\begin{aligned} -(1/kT)\partial F/\partial \xi &= (\partial/\partial \xi) \log \int_\Omega \exp(-H^0 + X\xi)/kT \\ &= (1/kT)\langle X \rangle \end{aligned} \tag{24}$$

i.e.

$$\langle X \rangle = -\partial F/\partial \xi \tag{25}$$

where F is the thermodynamic free energy. To use Onsager's formula there must be more than one externally applied force ξ, say $\xi_1, \xi_2, \ldots$; then the partial derivative in (25) is taken with respect to ξ_i with all the other ξ_j parameters held fixed.

6 References

To be supplied