IP326. Lecture 10. Tuesday, Feb. 5, 2019

● Time correlation functions and transport coefficients (Contd.)

We showed that a system whose response to a weak external force $F(t)$ was causal, linear and stationary generated a 'signal' $S(t)$ (a measurable property of the system) that was related to $F(t)$ in the following way

$$S(t) = \int_{-\infty}^{t} dt' \chi(t-t') F(t') \tag{1}$$

where $\chi(t)$ is referred to as a response function, which we expect to depend solely on the intrinsic properties of the *unperturbed* (force-free) system, and not on the applied force. Our objective now is to derive an expression for $\chi(t)$.

We've already argued that $S(t)$ can be identified with the ensemble average of some property A of the system that is measured a time interval t after the system – initially in equilibrium at the temperature T – has been acted on by an external force at time $t = 0$. That is,

$$S(t) \leftrightarrow \langle A(t) \rangle = \int d\Gamma A(\Gamma) f(\Gamma, t) \tag{2}$$

where

$$f(\Gamma, t) \approx f_0(\Gamma) + \Delta f(t) \tag{3}$$

We've also stated that the Hamiltonian H of the system can be approximated as

$$H(\Gamma, t) \approx H_0(\Gamma) - B(\Gamma) F(t), \tag{4}$$

the subscript 0 in Eqs. (3) and (4) referring to force-free conditions. In what follows, we'll take A and B to be real.

The time evolution of f is governed by the Liouville equation:

$$\frac{\partial f}{\partial t} = -iLf = -\sum_{i=1}^{N} \left[\dot{\mathbf{q}}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] f$$

$$= -\sum_{i=1}^{N} \left[\frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial H}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] f \,, \tag{5}$$

which, on substitution of the approximations for f and H in (3) and (4), becomes

$$\frac{\partial(f_0+\Delta f(t))}{\partial t}=-\sum_{i=1}^{N}\left[\frac{\partial(H_0-BF(t))}{\partial \mathbf{p}_i}\cdot\frac{\partial}{\partial \mathbf{q}_i}-\frac{\partial(H_0-BF(t))}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}\right](f_0+\Delta f(t))$$

$$=-\sum_{i=1}^{N}\left[\frac{\partial H_0}{\partial \mathbf{p}_i}\cdot\frac{\partial}{\partial \mathbf{q}_i}-\frac{\partial H_0}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}\right](f_0+\Delta f(t))+$$

$$+F(t)\sum_{i=1}^{N}\left[\frac{\partial B}{\partial \mathbf{p}_i}\cdot\frac{\partial}{\partial \mathbf{q}_i}-\frac{\partial B}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}\right](f_0+\Delta f(t))+ \qquad (6)$$

Therefore,

$$\frac{\partial f_0}{\partial t}+\frac{\partial \Delta f(t)}{\partial t}=-iL_0 f_0-iL_0\Delta f(t)+F(t)\sum_{i=1}^{N}\left[\frac{\partial B}{\partial \mathbf{p}_i}\cdot\frac{\partial f_0}{\partial \mathbf{q}_i}-\frac{\partial B}{\partial \mathbf{q}_i}\cdot\frac{\partial f_0}{\partial \mathbf{p}_i}\right] \qquad (7)$$

where L_0 is the Liouville operator of the unperturbed system (the Hamiltonian of which is H_0.) In arriving at Eq. (7), we've neglected the term involving $F(t)\Delta f(t)$ on the grounds that it is expected to be of higher order in the field than the terms we've retained.

Now we'd shown earlier that the equilibrium density distribution f_0 is time-independent, and so $\partial f_0/\partial t=0=-iL_0 f_0$. Further, if we assume that f_0 corresponds to the canonical ensemble, then

$$\frac{\partial f_0}{\partial \mathbf{q}_i}=-\beta f_0\frac{\partial H_0}{\partial \mathbf{q}_i} \qquad \text{and} \qquad \frac{\partial f_0}{\partial \mathbf{p}_i}=-\beta f_0\frac{\partial H_0}{\partial \mathbf{p}_i}$$

and so

$$\sum_{i=1}^{N}\left[\frac{\partial B}{\partial \mathbf{p}_i}\cdot\frac{\partial f_0}{\partial \mathbf{q}_i}-\frac{\partial B}{\partial \mathbf{q}_i}\cdot\frac{\partial f_0}{\partial \mathbf{p}_i}\right]=-\beta f_0\sum_{i=1}^{N}\left[\frac{\partial H_0}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}-\frac{\partial H_0}{\partial \mathbf{p}_i}\frac{\partial}{\partial \mathbf{q}_i}\right]B$$

$$=\beta f_0 iL_0 B$$

Note also that $iL_0B(\Gamma)=\dot{B}(\Gamma)$. Putting all these results back into Eq. (7), we see that it reduces to

$$\frac{\partial \Delta f(t)}{\partial t}=-iL_0\Delta f(t)+\beta f_0 F(t)\dot{B}(\Gamma) \qquad (8)$$

Equation (8) is a first order linear differential equation in $\Delta f(t)$, which we can solve by the method of integrating factors. This involves first multiplying both sides of the equation by an as yet undetermined function of *t*, *g*(*t*). This leads to

$$g(t)\frac{\partial \Delta f(t)}{\partial t} = -ig(t)L_0\Delta f(t) + \beta f_0 g(t)F(t)\dot{B}(\Gamma)$$

which we then rewrite identically as

$$\frac{\partial \Delta f(t)g(t)}{\partial t} - \left[\frac{\partial g(t)}{\partial t} - ig(t)L_0\right]\Delta f(t) = \beta f_0 g(t)F(t)\dot{B}(\Gamma) \qquad (9)$$

Since *g*(*t*) is arbitrary, we can choose it to eliminate the second term on the left-hand side of Eq. (9). This choice leads to a simple differential equation for *g*(*t*) that we'll solve *formally* as

$$g(t) = g(0)\exp(itL_0)$$

This is a formal solution in the sense that L_0 is being treated essentially as a constant, and not as an operator, but the approach gives the correct final answers, so we'll ignore its lack of rigor. With this solution for *g*(*t*) in hand, we can immediately integrate Eq. (9) to

$$\Delta f(t)g(0)e^{iL_0 t} - \Delta f(0)g(0) = \beta f_0 g(0)\int_0^t dt' e^{it'L_0}F(t')\dot{B}(\Gamma) \qquad (10)$$

At the initial time $t = 0$, the system is in equilibrium in the absence of the force, so $\Delta f(0) = 0$, and Eq. (10), after rearranging terms, simplifies to

$$\Delta f(t) = \beta f_0 \int_0^t dt' e^{-i(t-t')L_0}F(t')\dot{B}(\Gamma) \qquad (11)$$

Substituting Eq. (11) into Eq. (2), we find that

$$\langle A(t)\rangle = \int d\Gamma A(\Gamma)\left[f_0(\Gamma) + \beta\int_0^t dt' F(t') f_0(\Gamma)e^{-i(t-t')L_0}\dot{B}(\Gamma)\right]$$

$$= \int d\Gamma A(\Gamma) f_0(\Gamma) + \beta\int_0^t dt' F(t')\int d\Gamma f_0(\Gamma)A(\Gamma)e^{-i(t-t')L_0}\dot{B}(\Gamma) \qquad (12)$$

From one of the operator identities derived earlier, Eq. (12) can be written as

$$\left\langle A(t)\right\rangle - \left\langle A\right\rangle_0 = \beta\int_0^t dt' F(t')\, f_0(\Gamma)\left[e^{i(t-t')L_0} A(\Gamma)\right]\dot{B}(\Gamma)$$

$$= \frac{1}{k_B T}\int_0^t dt' \left\langle A(t-t')\middle|\dot{B}\right\rangle_0 F(t') \qquad (13)$$

Comparing Eq. (13) with Eq. (1), and identifying $\left\langle A(t)\right\rangle - \left\langle A\right\rangle_0$ with $S(t)$, we can immediately see that

$$\chi(t) = \frac{1}{k_B T}\left\langle A(t)\middle|\dot{B}\right\rangle_0, \qquad (14)$$

which can also be rewritten identically as

$$\chi(t) = -\frac{1}{k_B T}\frac{d}{dt}\left\langle B\middle|A(t)\right\rangle_0, \qquad \text{(show)} \qquad (15)$$

so as advertised, the response of a system to a weak external force is determined by a time correlation function of the system's intrinsic, force-free properties.

Equation (14), or its equivalent (15), can be thought as an example of a fluctuation-dissipation relation, an equation between the response of a system, as contained in the fluctuations of some of its dynamical variables, and the force responsible for it. The reason the relation makes reference to 'fluctuations' is that time correlations of the above kind actually do involve correlations between fluctuating quantities, as we can show.

What we mean by a fluctuation is the deviation of some property from its mean value. If the properties in question are *A* and *B*, then their fluctuations at time *t*, $\delta A(t)$ and $\delta B(t)$, respectively, are given by

$$\delta A(t) = A(t) - \left\langle A\right\rangle_0 \qquad \text{and} \qquad \delta B(t) = B(t) - \left\langle B\right\rangle_0$$

From these definitions it follows that

$$\left\langle B\middle|A(t)\right\rangle_0 = \left\langle \delta B\middle|\delta A(t)\right\rangle_0 + \left\langle \delta B\right\rangle_0\left\langle A\right\rangle_0 + \left\langle B\right\rangle_0\left\langle \delta A(t)\right\rangle_0 + \left\langle B\right\rangle_0\left\langle A\right\rangle_0$$

Since equilibrium ensemble averages are time-independent, both $\left\langle \delta B\right\rangle_0$ and $\left\langle \delta A(t)\right\rangle_0$ vanish, and since $\left\langle B\right\rangle_0\left\langle A\right\rangle_0$ is time-independent too,

$$\frac{d}{dt}\left\langle B\middle|A(t)\right\rangle_0 = \frac{d}{dt}\left\langle \delta B\middle|\delta A(t)\right\rangle_0$$

So the response function really is associated with fluctuations, and it's these fluctuations that ultimately *dissipate* the effects introduced by the external force; hence the name 'fluctuation-dissipation'.

• <u>The diffusion coefficient</u>

We'll now illustrate how linear response theory allows us to relate transport coefficients to one or more of a system's dynamical variables. The transport coefficient we'll consider first is the diffusion coefficient, which is a measure of how quickly the particles in a particular system are transported across space when their distribution is not uniform, i.e., when there are concentration gradients in the system. These concentration gradients are akin to an external force, and they cause mass to flow from regions of high to low concentration. It's been found empirically that the resulting 'current' is directly proportional to the magnitude of the concentration gradient, a relation referred to as Fick's law, and usually written as

$$\mathbf{J} = -D\nabla_{\mathbf{r}} c(\mathbf{r}, t) \tag{16}$$

where $c(\mathbf{r}, t)$ is the particle concentration at $\mathbf{r}$ at time t, $\mathbf{J}$ is the current (a vectorial quantity to account for the flow's directionality), D is the diffusion coefficient, the quantity we're interested in deriving an expression for in terms of the intrinsic properties of the system, and the negative sign is introduced to indicate that the flow is from high to low concentration. (The units of $\mathbf{J}$, D and c are, respectively, $\text{mol.m}^{-2}.\text{s}^{-1}$, $\text{m}^2.\text{s}^{-1}$ and mol.m^{-3}.) We'll derive this expression in two ways: one very heuristically, ignoring mathematical niceties, but highlighting the connection to linear response theory, and the other more rigorously.

In the heuristic approach, we interpret Fick's law (Eq. (16)) as a relation between a cause (the concentration gradient) and an effect (the particle current), so that $\mathbf{J}$ effectively becomes the 'signal' we measure after we've applied the weak external field $\nabla_{\mathbf{r}} c$, which we'll now denote $\mathbf{F}(t)$ to indicate that it acts like a force. In this interpretation D is proportional to the response function $\chi(t)$ of the system. Since $\mathbf{J}$ is a current, we'll identify it with the *steady* average net velocity of a collection of particles, and we'll also assume, for specificity, that it is directed along the x-axis. This means that

$$J_x(t) = \lim_{t \to \infty} \sum_{i=1}^{N} \langle \dot{q}_{ix}(t) \rangle \tag{17}$$

where $\mathbf{q}_i(t)$ is the position of the ith particle at time t. The $t \to \infty$ limit is introduced to ensure that the system has had a long enough time to settle into regular reproducible behavior.

In the language of the previous section, the current corresponds to the dynamical variable A, and so

$$A(t) = \sum_{i=1}^{N} \dot{q}_{ix}(t) \tag{18}$$

The other dynamical variable B is linked to the force, which in the x direction we'll assume is given by $F\hat{e}_x$, where F is a constant and $\hat{e}_x$ is a unit vector along x. The precise connection between B and the phase space variables of the system can be determined by considering the equations of motion of these phase space variables; they are

$$\dot{\mathbf{q}}_i(t) = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_i(t) = -\frac{\partial H_0}{\partial \mathbf{q}_i} + F\hat{e}_x$$

The structure of the second of these two equations suggests that the Hamiltonian of the system is given by

$$H = H_0 - F\sum_{j=1}^{N} \mathbf{q}_j$$

This implies that the variable B is given by

$$B = \sum_{i=1}^{N} \mathbf{q}_i \tag{19}$$

Now in the unperturbed system, the flow of current is 0 (meaning, $\langle A \rangle_0 = 0$), so from Eqs. (13), (18) and (19), it follows that

$$\sum_{i=1}^{N} \langle \dot{q}_{ix}(t) \rangle = \beta F \int_0^t dt' \left\langle \sum_{i=1}^{N} \dot{q}_{ix}(t-t') \sum_{j=1}^{N} \dot{q}_{jx} \right\rangle_0$$

$$= \beta F \int_0^t dt' \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \dot{q}_{ix}(t-t') \dot{q}_{jx} \rangle_0 \tag{20}$$

The Boltzmann distribution over which the average in (20) is carried out factors into contributions from individual particles, so $\langle \dot{q}_{ix}(t-t') \dot{q}_{jx} \rangle_0 = \delta_{i,j} \langle \dot{q}_{ix}(t-t') \dot{q}_{jx} \rangle_0$. After using this result in (20), along with the change of variable $t' = t - \tau$, we get

$$\sum_{i=1}^{N} \left\langle \dot{q}_{ix}(t) \right\rangle = \beta F \int_0^t dt' \sum_{i=1}^{N} \left\langle \dot{q}_{ix}(t') \dot{q}_{ix} \right\rangle_0 \tag{21}$$

Had the current been directed along the *y* or *z* directions, the result would have been the same except for a change of label, so we can write quite generally that

$$\sum_{i=1}^{N} \left\langle \dot{q}_{ix}(t) \right\rangle = \frac{1}{3} \beta F \int_0^t dt' \sum_{i=1}^{N} \left\langle \dot{\mathbf{q}}_i(t') \cdot \dot{\mathbf{q}}_i \right\rangle_0 \tag{22}$$

Finally, from Fick's law and Eqs. (17) and (22), we make the identification

$$D \equiv \frac{J_x}{\beta F} = \lim_{t\to\infty} \frac{1}{3} \int_0^t dt' \sum_{i=1}^{N} \left\langle \mathbf{v}_i(t') \cdot \mathbf{v}_i \right\rangle_0 \tag{23}$$

Since there's no reason why, under equilibrium conditions, different particles should have different velocity correlation functions, we can write Eq. (23) as

$$D = N \lim_{t\to\infty} \frac{1}{3} \int_0^t dt' \left\langle \mathbf{v}(t') \cdot \mathbf{v} \right\rangle_0$$

where **v** now refers to the velocity of any one particle. Given this expression, it's possible to define a so-called self-diffusion coefficient D_s as the value of *D* per particle. So D_s is given by

$$D_s = \frac{1}{3} \int_0^\infty dt' \left\langle \mathbf{v}(t') \cdot \mathbf{v} \right\rangle_0 \tag{24}$$

It is this expression for D_s that we will now rederive by a more rigorous approach.