IP326. Lecture 18. Tuesday, March 5, 2019

● The generalized Langevin equation (Cont.'d)

We've now shown that the Liouville equation for the evolution of a vector variable $\mathbf{A}(t) = (A_1, A_2, \ldots, A_n)$, viz.,

$$\frac{d\mathbf{A}(t)}{dt} = iL\mathbf{A}(t) \tag{1}$$

can be transformed exactly using the projection operators $P = \sum_{i,j} |A_i\rangle \langle A_i | A_j \rangle^{-1} \langle A_j |$ and $Q = 1 - P$ to the so-called generalized Langevin equation (or GLE), given by

$$\frac{d|A_i(t)\rangle}{dt} = i\sum_j \Omega_{ij} |A_j(t)\rangle - \sum_j \int_0^t dt' K_{ij}(t-t') |A_j(t')\rangle + |F_j(t)\rangle, \tag{2}$$

which also leads immediately to the memory function equation for the time correlation function $\mathbf{C}(t) = \langle \mathbf{A} | \mathbf{A}(t) \rangle$:

$$\frac{dC_{ij}(t)}{dt} = i\sum_k \Omega_{ik} C_{kj}(t) - \sum_k \int_0^t dt' K_{ik}(t-t') C_{kj}(t'). \tag{3}$$

In Eqs. (2) and (3), $\boldsymbol{\Omega}$ is the frequency matrix, $|\mathbf{F}(t)\rangle$ is the generalized random force, and $\mathbf{K}(t)$ is the memory function matrix, which are defined, respectively, as $\Omega_{ij} = \sum_k \langle A_i | A_k \rangle^{-1} \langle A_k | LA_j \rangle$, $|\mathbf{F}(t)\rangle = e^{QiLt} QiL |\mathbf{A}\rangle$, and $K_{ij} = \sum_k \langle A_i | A_k \rangle^{-1} \langle F_k | F_j(t) \rangle$.

● Symmetry properties (Cont.'d)

3. If the variables A_i transform under time reversal as $\gamma_i A_i$, where $\gamma_i = \pm 1$, then the random force matrix $\langle \mathbf{F} | \mathbf{F}(t) \rangle$ transforms as (i) $\langle F_i | F_j(t) \rangle \to \gamma_i \gamma_j \langle F_i | F_j(-t) \rangle$, and as (ii) $\langle F_i | F_j(-t) \rangle \to \gamma_i \gamma_j \langle F_j | F_i(t) \rangle^*$

Proofs

Under time reversal, which corresponds to the operation $\{\mathbf{q},\mathbf{p}\}\to\{\mathbf{q},-\mathbf{p}\}$, the projector P transforms as $P\to\gamma_i\gamma_i\gamma_j\gamma_j P = P$. This means that under the same operation $Q\to Q$. From the definition of the random force, the time correlation function $\langle \mathbf{F}|\mathbf{F}(t)\rangle$ is given by

$$\langle F_i|F_j(t)\rangle = \int d\Gamma f_0(\Gamma)(QiLA_i)^* e^{QiLt}QiLA_j$$

so it follows that

$$\langle F_i|F_j(t)\rangle \xrightarrow{\{\mathbf{q},\mathbf{p}\}\to\{\mathbf{q},-\mathbf{p}\}} \int d\Gamma f_0(\Gamma)[Qi(-L)\gamma_i A_i]^* e^{Qi(-L)t}Qi(-L)\gamma_j A_j$$

$$= \gamma_i\gamma_j\int d\Gamma f_0(\Gamma)(QiLA_i)^* e^{QiL(-t)}QiLA_j$$

$$= \gamma_i\gamma_j\langle F_i|F_j(-t)\rangle$$

which proves equality (i) in Property 3. To prove equality (ii), we recognize, first of all, that we can write $F_j(t)$ in the equivalent form

$$F_j(t) = e^{QiLt}QiLA_j = e^{QiLt}F_j = e^{QiLQt}F_j$$

where, in the last relation, we've used the fact that $QF_j = F_j$.

Therefore,

$$\langle F_i|F_j(t)\rangle = \int d\Gamma f_0(\Gamma)F_i^*(\Gamma)e^{QiLQt}F_j(\Gamma)$$

$$= \sum_{n=0}^{\infty}\frac{t^n}{n!}\int d\Gamma f_0 F_i^*(QiLQ)(QiLQ)^{n-1}F_j$$

$$= \sum_{n=0}^{\infty}\frac{t^n}{n!}\int d\Gamma f_0(QiLQF_i^*)(QiLQ)^{n-1}F_j \quad \text{(because } Q \text{ and } L \text{ are Hermitian)}$$

$$= \sum_{n=0}^{\infty}\frac{t^n}{n!}\int d\Gamma f_0[(QiLQ)^n F_i^*]F_j \qquad \text{(after } n \text{ iterations of the above step)}$$

$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} \left(\int d\Gamma f_0 F_j^* [(QiLQ)^n F_i] \right)^* \qquad \text{(because } (iL)^* = iL, \ iL \text{ being real)}$$

$$= \left(\int d\Gamma f_0 F_j^* e^{QiLQt} F_i \right)^*$$

$$= \left\langle F_j \middle| F_i(t) \right\rangle^*$$

But since $\left\langle F_i \middle| F_j(t) \right\rangle \xrightarrow{\{\mathbf{q},\mathbf{p}\}\to\{\mathbf{q},-\mathbf{p}\}} \gamma_i \gamma_j \left\langle F_i \middle| F_j(-t) \right\rangle$, this means that $\left\langle F_i \middle| F_j(-t) \right\rangle \xrightarrow{\{\mathbf{q},\mathbf{p}\}\to\{\mathbf{q},-\mathbf{p}\}} \gamma_i \gamma_j \left\langle F_j \middle| F_i(t) \right\rangle^*$.

4. Parity. Under an inversion of parity, the signs of both positions and momenta are reversed, i.e., $\{\mathbf{q},\mathbf{p}\} \to \{-\mathbf{q},-\mathbf{p}\}$. If the variables A_i have a definite signature under parity inversion, we've already shown that the time correlation function $C_{ij}(t) = \left\langle A_i \middle| A_j(t) \right\rangle$ will vanish unless A_i and A_j have the same parity. The elements of the memory function matrix, on the other hand, will transform as

$$\left\langle F_i \middle| F_j(t) \right\rangle \xrightarrow{\{\mathbf{q},\mathbf{p}\}\to\{-\mathbf{q},-\mathbf{p}\}} \gamma_i \gamma_j \left\langle F_i \middle| F_j(t) \right\rangle$$

Proof. Under parity inversion, the projectors P and Q are unchanged. Also, since $F_j(t) = e^{QiLt} QiLA_j$, we have $F_j(t) \to \gamma_j F_j(t)$ (because $iL \to iL$.) Hence, $\left\langle F_i \middle| F_j(t) \right\rangle \to \gamma_i \gamma_j \left\langle F_i \middle| F_j(t) \right\rangle$. This also means that the memory function is non-vanishing only when A_i and A_j have the same signature under parity inversion.

The following results can be proved similarly.

5. If A_i transforms as $\alpha_i A_i$ (where $\alpha_i = \pm 1$) under reflection, then $C_{ij}(t)$ vanishes unless A_i and A_j have the same reflection symmetry. The symmetry matrix Ω_{ij} is also 0 if A_i and A_j have different reflection symmetries. And so also is the random force matrix (because under reflection $\left\langle F_i \middle| F_j(t) \right\rangle \to \alpha_i \alpha_j \left\langle F_i \middle| F_j(t) \right\rangle$.)

● Revisiting Self-Diffusion with the GLE

The fact that the GLE represents an alternative exact expression for the equation of motion of a dynamical variable suggests that expressions we've derived earlier for various transport coefficients – which were based on linearized versions of the Liouville equation – may themselves have more general forms. We'll now consider this possibility by investigating what the GLE has to say about the self-diffusion coefficient.

Recall that in our hydrodynamic approach to the calculation of this coefficient, the starting point was essentially the following diffusion equation:

$$\frac{\partial G(\mathbf{r},t)}{\partial t} = D\nabla_{\mathbf{r}}^2 G(\mathbf{r},t) \tag{4}$$

where we interpreted $G(\mathbf{r},t)$ as the probability density that a particle initially located at some point at time $t=0$ would be found at the point $\mathbf{r}$ at time t. What this interpretation really means is that $G(\mathbf{r},t)$ should be understood as being defined by the relation

$$G(\mathbf{r},t) = \left\langle \delta[\mathbf{r} - (\mathbf{r}(t) - \mathbf{r}(0))] \right\rangle \tag{5}$$

where $\mathbf{r}(0)$ and $\mathbf{r}(t)$ are the coordinates of the particle at the initial and final times, respectively. The delta function in this definition acts to select just those particles that have travelled a distance $\mathbf{r}$ in this time interval, while the angular brackets perform an average over the equilibrium distribution of these particles.

We found it convenient earlier to work in Fourier space, and if we now Fourier transform Eq. (5), we get

$$\begin{aligned} \tilde{G}(\mathbf{k},t) &= \left\langle \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \delta[\mathbf{r} - (\mathbf{r}(t) - \mathbf{r}(0))] \right\rangle \\ &= \left\langle e^{i\mathbf{k}\cdot(\mathbf{r}(t)-\mathbf{r}(0))} \right\rangle \end{aligned} \tag{6}$$

which suggests that $\tilde{G}(\mathbf{k},t)$ can actually be represented as a time correlation function of the form $\langle A | A(t)\rangle$ in which $|A(t)\rangle$ can be identified with $e^{i\mathbf{k}\cdot\mathbf{r}(t)}$ and $|A\rangle$ with $e^{i\mathbf{k}\cdot\mathbf{r}(0)}$, such that $\langle A| = e^{-i\mathbf{k}\cdot\mathbf{r}(0)}$.

Once we recognize that $\tilde{G}(\mathbf{k},t)$ can be expressed as a time correlation function, we know that it will satisfy a memory function equation, in this case the equation

$$\frac{\partial \tilde{G}(\mathbf{k},t)}{\partial t} = i\Omega\tilde{G}(\mathbf{k},t) - \int_0^t dt' \tilde{K}(\mathbf{k},t-t')\tilde{G}(\mathbf{k},t') \tag{7}$$

Now for a single variable, $\Omega \propto \langle A | LA\rangle \propto \langle A | \dot{A}\rangle$, where $\dot{A}$ is the time derivative of A evaluated at $t=0$. We've seen that time correlation functions with this structure are 0 by time reversal symmetry, so $\Omega = 0$, and Eq. (7) reduces to

$$\frac{\partial \tilde{G}(\mathbf{k},t)}{\partial t} = -\int_0^t dt' \tilde{K}(\mathbf{k},t-t')\tilde{G}(\mathbf{k},t') \tag{8}$$

The memory function in this expression is given by

$$\tilde{K}(\mathbf{k},t) = \langle A|A\rangle^{-1}\langle F|F(t)\rangle \tag{9}$$

With $|A\rangle$ given by $|A\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$, the generalized random force becomes

$$|F(t)\rangle = e^{QiLt}QiL|A\rangle = e^{QiLt}Qi|\dot{A}\rangle$$

$$= e^{QiLt}Qi\mathbf{k}\cdot\mathbf{v}(0)e^{i\mathbf{k}\cdot\mathbf{r}(0)} \tag{10}$$

where $\mathbf{v}(0)$ is the initial velocity of the particle. In the same way

$$|F\rangle = Qi\mathbf{k}\cdot\mathbf{v}(0)e^{i\mathbf{k}\cdot\mathbf{r}(0)} \tag{11}$$

In general,

$$Q|\dot{A}\rangle = (1-|A\rangle\langle A|A\rangle^{-1}\langle A|)|\dot{A}\rangle$$

$$= |\dot{A}\rangle \tag{12}$$

Therefore,

$$|F(t)\rangle = e^{QiLt}i\mathbf{k}\cdot\mathbf{v}(0)e^{i\mathbf{k}\cdot\mathbf{r}(0)} \tag{13}$$

and

$$|F\rangle = i\mathbf{k}\cdot\mathbf{v}(0)e^{i\mathbf{k}\cdot\mathbf{r}(0)} \tag{14}$$

which means that $\langle F| = -i\mathbf{k}\cdot\mathbf{v}(0)e^{-i\mathbf{k}\cdot\mathbf{r}(0)}$, and so

$$\langle F|F(t)\rangle = \mathbf{k}\cdot\left\langle e^{-i\mathbf{k}\cdot\mathbf{r}(0)}\mathbf{v}(0)e^{QiLt}\mathbf{v}(0)e^{\mathbf{k}\cdot\mathbf{r}(0)}\right\rangle\cdot\mathbf{k} \tag{15}$$

From the definition of the memory function, we therefore have

$$\tilde{K}(\mathbf{k},t) = \langle A|A\rangle^{-1}\mathbf{k}\cdot\left\langle e^{-i\mathbf{k}\cdot\mathbf{r}(0)}\mathbf{v}(0)e^{QiLt}\mathbf{v}(0)e^{\mathbf{k}\cdot\mathbf{r}(0)}\right\rangle\cdot\mathbf{k}$$

$$\equiv \left\langle A \middle| A \right\rangle^{-1} \mathbf{k} \cdot \tilde{\mathbf{D}}(\mathbf{k},t) \cdot \mathbf{k} = \mathbf{k} \cdot \tilde{\mathbf{D}}(\mathbf{k},t) \cdot \mathbf{k} \tag{16}$$

the last equality following from the fact that with $\left| A \right\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$, $\left\langle A \middle| A \right\rangle = 1$.

Let's return now to Eq. (8); because it has the structure of a convolution in time, it's natural to consider treating it using Laplace transforms. So if both sides of the equation are Laplace transformed, the result is

$$-\tilde{G}(\mathbf{k},0) + s\hat{\tilde{G}}(\mathbf{k},s) = -\hat{\tilde{K}}(\mathbf{k},s)\hat{\tilde{G}}(\mathbf{k},s) \tag{17}$$

where the tilde-circumflex notation refers to a Fourier transform with respect to a spatial variable and a Laplace transform with respect to a time variable. After solving Eq. (17) for $\hat{\tilde{G}}(\mathbf{k},s)$, we get

$$\hat{\tilde{G}}(\mathbf{k},s) = \frac{\tilde{G}(\mathbf{k},0)}{s + \hat{\tilde{K}}(\mathbf{k},s)}$$

$$= \frac{\tilde{G}(\mathbf{k},0)}{s + \mathbf{k} \cdot \hat{\tilde{D}}(\mathbf{k},s) \cdot \mathbf{k}} \tag{18}$$

where $\hat{\tilde{D}}(\mathbf{k},s)$ is the Laplace transform of $\tilde{D}(\mathbf{k},t)$. If we had Fourier-Laplace transformed Eq. (4) (the equation for the density distribution of $\mathbf{r}$ obtained from hydrodynamics), the result would have been

$$\hat{\tilde{G}}(\mathbf{k},s) = \frac{\tilde{G}(\mathbf{k},0)}{s + k^2 D} \tag{19}$$

A comparison of these last two equations suggests that the self-diffusion coefficient is really a limiting form of a much more complicated object that depends both on a wavevector (that is, on a quantity that is inversely related to a length) and a frequency (a quantity inversely related to time.) In fact, it can be shown (though we won't show it here) that

$$D = \lim_{k \to 0} \lim_{s \to 0} \frac{\mathbf{k} \cdot \hat{\tilde{\mathbf{D}}}(\mathbf{k},s) \cdot \mathbf{k}}{k^2} \tag{20}$$

The above limit corresponds to what we refer to as the hydrodynamic limit, i.e., the limit of large distances and long times. Other transport coefficients (like the shear viscosity, for instance) can also be shown using the GLE to correspond to limiting forms of wavevector and frequency dependent quantities.