IP326. Lecture 20. Tuesday, March 12, 2019

● <u>Continued fraction representation of time correlation functions</u>

The calculations that led to the Langevin equation from the GLE were based on the existence of a small parameter, $\lambda \equiv \sqrt{m/M}$, that allowed various operators in the exact equation for a dynamical variable to be approximated by the leading order term in a series expansion. Since there may not always be such parameters in a problem (or an easy way to identify them), it's important to have other systematic and well-controlled ways of treating otherwise intractable dynamical equations. This section illustrates one such alternative, which we'll apply directly to a time-correlation function itself, rather than to its associated phase space variable.

So consider the function $C(t) \equiv \langle A | A(t) \rangle$, which is equivalent to $C(t) = \langle A | e^{iLt} | A \rangle$, where L, as usual, is the Liouville operator. We've seen that this function satisfies the so-called memory function equation, and our objective now will be to find approximations to this equation and its solution. To this end, we'll begin by re-expressing $C(t)$ in Laplace space, where it becomes

$$\hat{C}(s) = \langle A | \frac{1}{s - iL} | A \rangle \tag{1}$$

We can rewrite this equation identically as

$$\hat{C}(s) = \langle A | \frac{1}{s - iL(Q + P)} | A \rangle \tag{2}$$

where P is the projection operator $P = |A\rangle \langle A|A\rangle^{-1} \langle A|$ and $Q = 1 - P$. Let's now recall the following operator identity:

$$(M + N)^{-1} = M^{-1} - M^{-1} N (M + N)^{-1} \tag{3}$$

and identify M as $s - iLQ$ and N as $-iLP$. Introducing these definitions into Eq. (2), we see that

$$\hat{C}(s) = \langle A | \frac{1}{s - iLQ} | A \rangle + \langle A | \frac{1}{s - iLQ} iLP \frac{1}{s - iL} | A \rangle \tag{4a}$$

$$\equiv \hat{C}_1(s) + \hat{C}_2(s) \tag{4b}$$

Consider each of these functions in turn; by definition

$$\hat{C}_1(s) = \langle A | \frac{1}{s - iLQ} | A \rangle$$

$$= \frac{1}{s} \langle A \| \left(1 + \frac{1}{s} iLQ + \frac{1}{s^2} LQLQ + \cdots \right) \| A \rangle \quad (5)$$

But $Q|A\rangle = 0$ (by construction), so $\hat{C}_1(s)$ reduces to

$$\hat{C}_1(s) = \frac{1}{s} \langle A | A \rangle \quad (6)$$

Similarly,

$$\hat{C}_2(s) = \langle A | \frac{1}{s - iLQ} iLP \frac{1}{s - iL} | A \rangle$$

$$= \langle A | \frac{1}{s - iLQ} iL | A \rangle \langle A | A \rangle^{-1} \langle A | \frac{1}{s - iL} | A \rangle$$

$$= \langle A | \frac{1}{s - iLQ} iL | A \rangle \langle A | A \rangle^{-1} \hat{C}(s) \quad (7)$$

Consider the factor $\langle A | (s - iLQ)^{-1} iL | A \rangle$ in Eq. (7); it can be transformed as follows:

$$\langle A | \frac{1}{s - iLQ} iL | A \rangle = \frac{1}{s} \langle A \| \left(1 + \frac{1}{s} iLQ + \frac{1}{s^2} iLQiLQ + \cdots \right) iL | A \rangle$$

$$= \frac{1}{s} \langle A \| \left(1 + \frac{1}{s} iLQ \left\{ 1 + \frac{1}{s} iLQ + \frac{1}{s^2} iLQiLQ + \cdots \right\} \right) iL | A \rangle$$

$$= \frac{1}{s} \langle A | iLA \rangle + \frac{1}{s} \langle A | \frac{1}{s} iLQ \left(1 + \frac{1}{s} iLQ + \frac{1}{s^2} iLQiLQ + \cdots \right) iL | A \rangle$$

$$= \frac{1}{s} \langle A | iLA \rangle + \frac{1}{s} \langle A | \frac{1}{s} iLQ \left(Q + \frac{1}{s} QiLQ + \frac{1}{s^2} QiLQiLQ + \cdots \right) iL | A \rangle$$

(because $Q^2 = Q$ by idempotency)

$$= \frac{1}{s} \langle A | iLA \rangle + \frac{1}{s} \langle A | \frac{1}{s} iLQ \left(1 + \frac{1}{s} QiL + \frac{1}{s^2} QiLQiL + \cdots \right) QiL | A \rangle$$

$$= \frac{1}{s} i\Omega \langle A | A \rangle + \frac{1}{s} \langle A | iLQ \frac{1}{s - QiL} QiL | A \rangle \tag{8}$$

Substituting Eq. (8) into Eq. (7), we see that

$$\hat{C}_2(s) = \left[\frac{1}{s} i\Omega \langle A | A \rangle + \frac{1}{s} \langle A | iLQ \frac{1}{s - QiL} QiL | A \rangle \right] \langle A | A \rangle^{-1} \hat{C}(s) \tag{9}$$

The function $QiL|A\rangle = |QiLA\rangle$ in Eq. (9) will be recognized as the definition of the generalized random force $|F\rangle$. So $\langle A|iLQB\rangle$, where B stands for $(s - QiL)^{-1} QiLA$, can be written as $i\langle QLA|B\rangle = -\langle QiLA|B\rangle = -\langle F|B\rangle$. Hence, the function $\hat{C}_2(s)$ simplifies to

$$\hat{C}_2(s) = \left[\frac{1}{s} i\Omega - \frac{1}{s} \langle A | A \rangle^{-1} \langle F | \frac{1}{s - QiL} | F \rangle \right] \hat{C}(s) \tag{10}$$

Recall that the memory function $K(t)$ in the GLE was defined as

$$K(t) = \langle A | A \rangle^{-1} \langle F | F(t) \rangle = \langle A | A \rangle^{-1} \langle F | e^{QiLt} F \rangle$$

so, formally, its Laplace transform is given by

$$\hat{K}(s) = \langle A | A \rangle^{-1} \langle F | \frac{1}{s - QiL} | F \rangle \tag{11}$$

which means that $\hat{C}_2(s)$ in Eq. (10) can be written as

$$\hat{C}_2(s) = \frac{1}{s} \left[i\Omega - \hat{K}(s) \right] \hat{C}(s) \tag{12}$$

After putting Eqs. (12) and (6) back into Eq. (4b), and solving for $\hat{C}(s)$, the result is

$$\hat{C}(s) = \frac{C(0)}{s - i\Omega + \hat{K}(s)} \tag{13}$$

where we've replaced the autocorrelation function $\langle A|A\rangle$ by its definition in terms of the $t = 0$ value of $C(t)$.

This expression for $\hat{C}(s)$ could actually have been obtained directly and much more simply from the memory function equation itself:

$$\frac{\partial C(t)}{\partial t} = i\Omega C(t) - \int_0^t dt' K(t-t')C(t') \quad (14)$$

All one needs to do is take the Laplace transform of both sides of the equation (using the convolution theorem to treat the term in $K(t)$); this leads to

$$-C(0) + s\hat{C}(s) = i\Omega\hat{C}(s) - \hat{K}(s)\hat{C}(s)$$

which when rearranged recovers Eq. (13). The reason for following the elaborate procedure we did is that we'll need to use exactly this procedure again to manipulate $\hat{C}(s)$ into another exact form.

But our starting point this time will be the memory function $\hat{K}(s)$, which is also a time correlation function, but one involving the generalized random force $|F\rangle$. So let's now introduce a set of two new projection operators, P_1 and Q_1, that project an arbitrary vector (i.e., dynamical variable) onto the parallel and perpendicular directions of $|F\rangle$, respectively. From our discussions, P_1 will be given by

$$P_1 = |F\rangle\langle F|F\rangle^{-1}\langle F| \quad (15)$$

and Q_1 by $Q_1 = 1 - P_1$. We can now rewrite the expression for $\hat{K}(s)$ in Eq. (11) first as

$$\hat{K}(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQ}|F\rangle$$

(because $Q|F\rangle = |F\rangle$), and then as

$$\hat{K}(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQ(Q_1 + P_1)}|F\rangle$$

$$= \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1 - QiLQP_1)}|F\rangle \quad (16)$$

Making use once more of the identity $(M+N)^{-1} = M^{-1} - M^{-1}N(M+N)^{-1}$, but with M chosen to be $s - QiLQQ_1$ and N chosen to be $-QiLQP_1$, we transform Eq. (16) to

$$\hat{K}(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1}|F\rangle + \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1}QiLQP_1\frac{1}{s - QiLQ}|F\rangle \quad (17a)$$

$$\equiv \hat{C}_3(s) + \hat{C}_4(s) \tag{17b}$$

Consider $\hat{C}_3(s)$, which from the above equations has the definition

$$\hat{C}_3(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1}|F\rangle \tag{18}$$

This can be rewritten as a series expansion:

$$\hat{C}_3(s) = \langle A|A\rangle^{-1}\frac{1}{s}\langle F|\left(1 + \frac{1}{s}QiLQQ_1 + \frac{1}{s^2}QiLQQ_1QiLQQ_1 + \cdots\right)|F\rangle \tag{19}$$

But since $Q_1|F\rangle = 0$, by construction, Eq. (19) immediately simplifies to

$$\hat{C}_3(s) = \frac{1}{s}\langle A|A\rangle^{-1}\langle F|F\rangle \tag{20}$$

Turning now to $\hat{C}_4(s)$, which has the definition

$$\hat{C}_4(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1}QiLQP_1\frac{1}{s - QiLQ}|F\rangle\ , \tag{21}$$

we introduce the expression P_1, and arrive at

$$\hat{C}_4(s) = \langle A|A\rangle^{-1}\langle F|\frac{1}{s - QiLQQ_1}QiLQ|F\rangle\langle F|F\rangle^{-1}\langle F|\frac{1}{s - QiLQ}|F\rangle$$

$$\equiv \langle F|F\rangle^{-1}\hat{C}_5(s)\hat{K}(s) \tag{22}$$

where

$$\hat{C}_5(s) \equiv \langle F|\frac{1}{s - QiLQQ_1}QiLQ|F\rangle \tag{23}$$

The function $\hat{C}(s)$ can be transformed as follows:

$$\hat{C}_5(s) = \frac{1}{s}\langle F|\left(1 + \frac{1}{s}QiLQQ_1 + \frac{1}{s^2}QiLQQ_1QiLQQ_1 + \cdots\right)QiLQ|F\rangle$$

$$= \frac{1}{s}\langle F | QiLQF \rangle + \frac{1}{s}\langle F | \frac{1}{s} QiLQQ_1 \left(1 + \frac{1}{s} QiLQQ_1 + \frac{1}{s^2} QiLQQ_1 QiLQQ_1 + \cdots \right) QiLQ | F \rangle$$

$$= \frac{i}{s}\langle F | F \rangle \Omega_1 + \frac{1}{s}\langle F | \frac{1}{s} QiLQQ_1 \left(Q_1 + \frac{Q_1}{s} QiLQQ_1 + \frac{Q_1}{s^2} QiLQQ_1 QiLQQ_1 + \cdots \right) QiLQ | F \rangle \tag{24}$$

where $\Omega_1 = \langle F | F \rangle^{-1} \langle F | LF \rangle$. In arriving at this expression for Ω_1, we used the fact that $\langle F | QLQF \rangle = \langle F | QLF \rangle = \langle QF | LF \rangle = \langle F | LF \rangle$, which itself made use of the idempotent and Hermitian properties of Q. Similarly, the second term in Eq. (24) used the fact that $Q_1^2 = Q_1$. Equation (24) can be further transformed to

$$\hat{C}_5(s) = \frac{i}{s}\langle F | F \rangle \Omega_1 + \frac{1}{s}\langle F | \frac{1}{s} QiLQQ_1 \left(1 + \frac{1}{s} Q_1 QiLQ + \frac{1}{s^2} Q_1 QiLQQ_1 QiLQ + \cdots \right) Q_1 QiLQ | F \rangle$$

$$= \frac{i}{s}\langle F | F \rangle \Omega_1 + \frac{1}{s}\langle F | \frac{1}{s} QiLQQ_1 \frac{1}{1 - Q_1 QiLQ / s} Q_1 QiLQ | F \rangle$$

$$= \frac{i}{s}\langle F | F \rangle \Omega_1 + \frac{1}{s}\langle F | QiLQQ_1 \frac{1}{s - Q_1 QiLQ} Q_1 QiLQ | F \rangle \tag{25}$$

The structure of the second term in Eq. (25) suggests that we can identify a new generalized random force $| f \rangle$ as

$$| f \rangle = Q_1 QiLQ | F \rangle \tag{26}$$

This means that $\langle F | QiLQQ_1 B' \rangle$, where B' stands for $(s - Q_1 QiLQ)^{-1} f$, can be written as $i\langle Q_1 QLQF | B' \rangle = -\langle Q_1 QiLQF | B' \rangle = -\langle f | B' \rangle$. So the function $\hat{C}_5(s)$ in Eq. (25) becomes

$$\hat{C}_5(s) = \frac{i}{s}\langle F | F \rangle \Omega_1 - \frac{1}{s}\langle f | \frac{1}{s - Q_1 QiLQ} | f \rangle$$

$$= \frac{i}{s}\langle F | F \rangle \Omega_1 - \frac{1}{s}\langle F | F \rangle \hat{K}_1(s) \tag{27}$$

where $\hat{K}_1(s) \equiv \langle F | F \rangle^{-1} \langle f | (s - Q_1 QiLQ)^{-1} | f \rangle$.

Putting all the pieces together, we find that

$$\hat{K}(s) = \frac{K(0)/C(0)}{s - i\Omega_1 + \hat{K}_1(s)} \tag{28}$$

And substituting this expression into the expression for $\hat{C}(s)$, we finally arrive at

$$\hat{C}(s) = \frac{C(0)}{s - i\Omega + \dfrac{K(0)/C(0)}{s - i\Omega_1 + \hat{K}_1(s)}} \tag{29}$$

The above sequence of steps can be repeated ad infinitum with each new memory function that's generated by the procedure. The result is a continued fraction representation of $\hat{C}(s)$. Truncation of the continued fraction at some particular order leads to an approximation for $\hat{C}(s)$.