Lecture 11: Mori-Zwanzig equation

1 Introduction

In earlier lectures we mentioned that often a stochastic model is used for non-equilibrium systems. In this case the deterministic variables represent slow system degrees of freedom while the noise represents the fast degrees of freedom. In general the noise and the slow variables in such models are uncorrelated while different slow variables exhibit a temporal decorrelation timescale. Such behaviour is what is typically seen to a very good approximation in systems in which there is a sharp separation of timescales. The Mori-Zwanzig equation provides a justification for this approach. As we shall see however the approach is really only valid for systems that are near equilibrium.

2 Mathematical preliminaries

Central to the approach adopted is the notion of slow variables for the system. Clearly in a closed system invariants belong to such a category however there are usually other non-invariants which have a timescale comparable with that which we are interested in when studying the coarse grained relaxation of a system to equilibrium. Note that in general this selection of variables requires emprical observation of the system of interest. For the sake of pedagogical clarity we confine our attention to just one such slow variable. The generalization to a finite number is straightforward which we leave as an exercise and comment on as we proceed through the derivation. Let us denote the variable of interest by $A(\boldsymbol{p}.\boldsymbol{q})$.

It will be useful to project a general system variable B onto these slow variables. We do this by introducing a suitable inner product for such variables using the equilibrium density for the system p_{eq}:

$$(X,Y) \equiv \int p_{eq} X(\boldsymbol{p},\boldsymbol{q}) Y(\boldsymbol{p},\boldsymbol{q}) d^N \boldsymbol{p} d^N \boldsymbol{q}$$

Assuming that the variables involved have zero means[1] for the equilibrium state of the system, we see that this inner product is the covariance of such variables for the equilibrium system. We now define a projection operator P in the direction of A by

$$PB \equiv \frac{(A,B)}{(A,A)} A$$

which is the usual definition of a one dimensional projection operator for a given inner product. A projection onto an orthogonal subspace is given by

[1] We make such an assumption henceforth. It is, of course always possible to obtain such a variable by subtraction of the equilibrium mean and no generality is lost.

$Q = I - P$. The generalization to several slow variables A_i is straightforward. The following facts about these operators are easily checked

$$
\begin{aligned}
P^2 &= P \\
Q^2 &= Q \\
PQ &= QP = 0 \\
(PX, Y) &= (X, PY) \\
(QX, Y) &= (X, QY)
\end{aligned}
$$

The final two relations assert that P and Q are self adjoint with respect to the scalar product introduced. The projection operators have a clear intuitive interpretation. P projects any particular variable onto the slow variable(s) of the system while Q projects the variable onto the fast variables of the system and because $QP = 0$ it follows from the self adjointness of the projection operators that the result of the Q projection is orthogonal to that of the P projection with respect to the inner product i.e. these two vectors are uncorrelated for the equilibrium density. The fast part of the system being defined as that which is uncorrelated with the slow variable at least as far as the equilibrium distribution is concerned. Now we shall be interested in the time evolution of the slow variable A and as was noted in Lecture 4 for Hamiltonian dynamical systems we have

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$$

We shall assume that our slow variable does not depend explicitly on time which allows us to write

$$
\begin{aligned}
\frac{dA}{dt} &= LA \qquad (1) \\
LX &\equiv \{X, H\}
\end{aligned}
$$

The operator L known sometimes as the Liouvillean operator. It may be shown, using the Hamiltonian nature of the system, to be anti self-adjoint i.e. with respect to our inner product we have

$$
\begin{aligned}
L^T &= -L \\
(LX, Y) &= -(X, LY)
\end{aligned}
$$

Using a Taylor series we can use equation (1) to show that

$$A(t) = \exp(Lt)\, A(0)$$

The operator $\exp(Lt)$ is known as the propagator and is widely seen in quantum mechanical applications.

2.1 Dyson Identity

We make use of this much used[2] identity for operators: Consider the Laplace transform of the exponential of an operator $-Rt$:

$$\begin{aligned}
\int_0^\infty dte^{-st}e^{-Rt} &= \int_0^\infty dte^{-st}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}R^n t^n \\
&= \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}R^n\int_0^\infty e^{-st}t^n dt \\
&= \sum_{n=0}^{\infty}(-1)^n\frac{R^n}{s^{n+1}} \\
&= \frac{1}{s}\left(I+\frac{R}{s}\right)^{-1} = (s+R)^{-1} \qquad (2)
\end{aligned}$$

Now the following operator identity is easily verfied by algebraic manipulation:

$$(U+V)^{-1} = U^{-1} - U^{-1}V(U+V)^{-1}$$

from which it follows[3] that

$$(s+R+S)^{-1} = (s+R)^{-1} - (s+R)^{-1}S(s+R+S)^{-1}$$

Using equation (2) we can take the inverse Laplace transform of this equation obtaining after the use of the convolution theorem for Laplace transform products:

$$e^{-(R+S)t} = e^{-Rt} - \int_0^t dt_1 e^{-Rt_1}Se^{-(R+S)(t-t_1)}$$

which is the important Dyson operator identity. Now if we make the substitutions

$$\begin{aligned}
R &= LQ \\
S &= LP
\end{aligned}$$

and take the adjoint of both sides of the Dyson identity we obtain using the anti self-adjointness of L and the self-adjointness of the projection operators that

$$e^{Lt} = e^{QLt} + \int_0^t dt_1 e^{L(t-t_1)}PLe^{QLt_1} \qquad (3)$$

[2] In mathematical physics that is.

[3] We are of course assuming invertibility of the relevant operators here.

3 Mori-Zwanzig equation

The time rate of change for the slow variable A at time t follows easily from equation (1):

$$\frac{dA}{dt}(t) = e^{Lt}LA = e^{Lt}(Q+P)LA$$

Now we have

$$e^{Lt}PLA = e^{Lt}\frac{(LA,A)}{(A,A)}A = \frac{(LA,A)}{(A,A)}e^{Lt}A \equiv \Omega A(t)$$

Note that Ω becomes a matrix when several slow variables are considered. Note also that the form of Ω may be deduced from the form of A and the equilibrium density for the system. We have therefore now the equation

$$\frac{dA}{dt}(t) = \Omega A(t) + e^{Lt}QLA$$

The first term on the right here is a slow variable tendency but we still require an interpretation for the second term. We use the Dyson identity to obtain

$$\frac{dA}{dt}(t) = \Omega A(t) + \int_0^t dt_1 e^{L(t-t_1)}PLe^{QLt_1}QLA + e^{QLt}QLA \tag{4}$$

Defining

$$F(t) \equiv e^{QLt}QLA$$

we can show using the projective nature of the operator Q that

$$(F(t),A) = \left(e^{QLt}QLA, A\right) = (QF(t),A) = 0$$

Thus at least for the near equilibrium case the random variable F is uncorrelated with the slow variable it may therefore be interpreted as a noise. It is very important to note here that this interpretation of F relies for veracity on the system density being close to equilibrium which indicates the limitation of Mori-Zwanzig theory. Note also that this argument generalises easily to the multiple slow variable case (exercise). We still need to interpret the second term on the RHS of equation (4). We have using the adjointness properties of L and Q

$$\begin{aligned} PLe^{QLt}QLA &= PLF(t) = PLQF(t) = \frac{(LQF(t),A)}{(A,A)}A = -\frac{(QF(t),LA)}{(A,A)}A \\ &= -\frac{(F(t),QLA)}{(A,A)}A = -\frac{(F(t),F(0))}{(A,A)}A \equiv -K(t)A \end{aligned}$$

where $K(t)$ is like Ω calculatable from the properties of A, L and the equilibrium density. Note that it is proportional to the time lagged correlation function of the "noise" F which in general is not white. Substituting the above equation and the noise definition into (4) we obtain

$$\begin{aligned} \frac{dA}{dt}(t) &= \Omega A(t) - \int_0^t dt_1 e^{L(t-t_1)} K(t_1) A + F(t) \\ &= \Omega A(t) - \int_0^t dt_1 K(t_1) A(t-t_1) + F(t) \end{aligned} \tag{5}$$

which is referred generally to as the Mori-Zwanzig equation. Note that it differs from a normal stochastic differential equation (SDE) in that the time tendency for the slow variable involves a lag backwards in time with a so-called "memory kernel" $K(t)$ (the second term) and also that the stochastic forcing is not white. These facts imply that the theory is not Markovian since the temporal tendency depends on the macrostate at past times whereas an ordinary SDE is Markovian since only the present time macrostate is required for all future evolution. Notice also that the memory kernel here depends on the temporal decorrelation of the noise identified i.e. on the temporal decorrelation of certain fast modes for the system.

If we take the inner product of this equation with respect to $A(0)$ and use the fact that F is uncorrelated with A we obtain the following slow variable temporal lag correlation equation which can be useful

$$\begin{aligned} \frac{dC(t)}{dt} &= \Omega C(t) - \int_0^t dt_1 K(t_1) C(t-t_1) \\ C(t) &\equiv (A(t), A(0)) \end{aligned}$$

There is an extensive literature on the Mori-Zwanzig equation which was developed in the 1960s and early 1970s. Two good starting points for further exploration may be found in the books [1] Chapter 4 and [2] Chapter 5. The lecture notes here were prepared from the first reference.

References

[1] D. J. Evans and G. Morriss. *Statistical mechanics of nonequilibrium liquids.* Cambridge University Press, 2008.

[2] G. F. Mazenko. *Nonequilibrium Statistical Mechanics.* Wiley-Vch, 2006.