Vibrations and Decay: Discussions on Fluctuation and Dissipation

We discuss how the thermal motion[1] which randomly shifts thermodynamic variables out of their equilibrium state is related to the properties of how these states decay under an external source. In other words, we present (one form of) the fluctuation-dissipation theorem, a theorem which appears under many guises. Our discussion mostly follows that found in [1].

1 Kubo-Green Formula for Diffusion

Before we present the formal form of the fluctuation dissipation theorem, we derive an expression for the diffusion coefficient of a stochastic position variable X. This will give us our first equation relating random thermal motion to a dissipative process.

We want a formula for the diffusion coefficient which is not dependent on any particular model of the random motion involved. For normal diffusion (i.e., diffusion which is neither sub or super diffusive) the diffusion coefficient can be defined as

$$D = \lim_{t\to\infty} \frac{1}{2t}\langle X^2(t)\rangle_{\text{eq}} \tag{1}$$

because we expect that for long times the $X^2(t)$ will eventually reach its equilibrium dispersion given by the diffusion equation. By the definition of position as the integral of velocity, we can rewrite this equation as

$$D = \lim_{t\to\infty} \frac{1}{2t}\int_0^t dt_1 \int_0^t dt_2 \,\langle v(t_1)v(t_2)\rangle_{\text{eq}}, \tag{2}$$

where the "eq" average is over all initial positions $v(0) = v_0$ (as defined by the Boltzmann distribution) and over all ensembles of the thermal noise. Also, we note that the autocorrelation function only depends on the difference in time between the two velocities, and it is an even function of this difference. To this end, for notational simplicity, we may define

$$\langle v(t_1)v(t_2)\rangle_{\text{eq}} \equiv \phi(|t_2 - t_1|), \tag{3}$$

Now, using an integration measure identity[2] we can write Eq.(2) as

$$D = \lim_{t\to\infty} \frac{1}{2t}\, 2\int_0^t dt_1 \int_0^{t_1} dt_2 \;\phi(|t_2 - t_1|). \tag{4}$$

We can justify this integration identity as follows. In Eq.(2), we split up the t_2 integral to give us the double integration

$$\int_0^t dt_1 \int_0^t dt_2\, \phi(|t_2 - t_1|) = \left[\int_0^t dt_1 \int_0^{t_1} dt_2 + \int_0^t dt_1 \int_{t_1}^t dt_2\right] \phi(|t_2 - t_1|). \tag{5}$$

Then we switch the order of integration in the second set of integrals. For such a procedure where one integration limit is an integration variable, it is useful to draw a picture of the integration region. Upon

[1] 'Vibration' is not exactly synonymous with 'fluctuation'. Vibration refers to variations which are systematic and defined by one or a set of frequencies, while fluctuations often refer to random variations.

[2] Such an identity is used to derive the Dyson series of QFT, for example

finding the new limits of integration for the reversed integral order, we find

$$\left[\int_0^t dt_1 \int_0^{t_1} dt_2 + \int_0^t dt_2 \int_0^{t_2} dt_2\right] \phi(|t_2 - t_1|), \tag{6}$$

but t_1 and t_2 are just dummy integration variables. So we can add the two integrals to obtain Eq.(4). Now, starting from Eq.(4) and changing variables from t_2 to $t' = t_1 - t_2$, we have

$$D = \lim_{t\to\infty} \frac{1}{t} \int_0^t dt_1 \int_0^{t_1} dt'\, \phi(t'). \tag{7}$$

Finally, we switch the order of integration once more (again drawing a picture if necessary) to find

$$\begin{aligned} D &= \lim_{t\to\infty} \frac{1}{t} \int_0^t dt_1 \int_0^{t_1} dt'\, \phi(t') \\ &= \lim_{t\to\infty} \frac{1}{t} \int_0^t dt' \int_{t'}^t dt_1\, \phi(t') \\ &= \lim_{t\to\infty} \frac{1}{t} \int_0^t dt'(t - t')\, \phi(t'). \end{aligned} \tag{8}$$

Therefore, we are left with the result

$$D = \lim_{t\to\infty} \int_0^t dt' \left(1 - \frac{t'}{t}\right) \langle v(0)v(t')\rangle_{\text{eq}}, \tag{9}$$

where we used the fact that the autocorrelation function only depends on the time difference between the dynamical variables. Now, assuming $\langle v(0)v(t)\rangle_{\text{eq}} \sim 1/t^k$ for $k > 1$ as $t \to \infty$, the limit produces a finite integral and we have our main result

$$D = \int_0^\infty dt\, \langle v(0)v(t)\rangle_{\text{eq}}. \tag{10}$$

However, for a slow power law decay (i.e., for $0 < k \leq< 1$), we have to employ an analytic continuation. We first define

$$\widetilde{\phi}(s) = \int_0^\infty dt\, e^{-st}\, \phi(t) = \int_0^\infty dt\, e^{-st} \langle v(0)v(t)\rangle_{\text{eq}}, \tag{11}$$

which is finite for $\text{Re}(s) > 0$. Then we analytically continue $\widetilde{\phi}(s)$ in the complex plane to $s = 0$ to find the diffusion coefficient:

$$D = \lim_{s\to 0} \widetilde{\phi}(s) \tag{12}$$

2 First Fluctuation Dissipation Theorem

Here, we derive what is termed in [1] the first fluctuation dissipation theorem. We start with the un-forced Langevin equation at an instant of time $t_0 + t$[3][4]:

$$\dot{v}(t_0 + t) + \gamma v(t_0 + t) = \frac{1}{m}\eta(t_0 + t) \tag{13}$$

[3] I'm not exactly sure why we take the equation at $t + t_0$. The text says we're trying to distinguish a time t_0 from a time $t = 0$ at which the initial condition is imposed. I don't fully understand this explanation.

[4] I think I understand it now. At $t_0 > 0$ we can assume that the velocities are Boltzmann distributed, but at $t = 0$ they are not because we impose an initial condition on them. Thus the $t_0 + t$ is necessary

Multiplying the equation by $v(t_0)$ and averaging over all the realizations of the random noise $\eta(t)$ and all the initial conditions $v(0) = v_0$ (distributed according to the Boltzmann distribution) gives us

$$\langle v(t_0)\dot{v}(t_0+t)\rangle_{\text{eq}} + \gamma\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} = \frac{1}{m}\langle v(t_0)\eta(t_0+t)\rangle_{\text{eq}}. \tag{14}$$

By causality, however, the last term must be zero. It represents the correlation between a dynamical response and a later source. An effect cannot be correlated with a source which occurs *after* the effect itself, and hence the correlation is zero. Thus we have

$$\frac{d}{dt}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} + \gamma\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} = 0 \tag{15}$$

Multiplying this equation by $e^{i\omega t}$ and integrating from 0 to ∞, we obtain

$$\begin{aligned}
0 &= \int_0^\infty dt\, e^{i\omega t}\frac{d}{dt}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} + \gamma\int_0^\infty dt\, e^{i\omega t}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} \\
&= e^{i\omega t}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}}\Big|_{t=0}^{t=\infty} - i\omega\int_0^\infty dt\, e^{i\omega t}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} \qquad (16)\\
&\quad + \gamma\int_0^\infty dt\, e^{i\omega t}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} \\
&= -\frac{k_BT}{m} + (\gamma - i\omega)\int_0^\infty dt\, e^{i\omega t}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}}. \qquad (17)
\end{aligned}$$

In the third line we used the results

$$\lim_{t\to\infty}\langle v(t_0)v(t_0+t)\rangle_{\text{eq}} = 0 \quad \text{and} \quad \langle v^2(t_0)\rangle_{\text{eq}} = k_BT/m, \tag{18}$$

the first result coming from the fact that velocities greatly spaced in time are uncorrelated and the second result coming from the Boltzmann properties of the velocity distribution.

Now, we momentarily turn to the Langevin equation:

$$m\frac{dv}{dt} + m\gamma v = F_{\text{ext}}(t) + \eta(t) \tag{19}$$

We set our initial condition to be at $t = -\infty$, so that for positive t the effect of the initial condition has been washed away. Now, we average over all initial conditions and all realizations of the noise $\eta(t)$ except because of the presence of $F_{\text{ext}}(t)$ we cannot take an equilibrium average, but must instead perform a sort of 'non-equilibrium average'.[5]. Taking such complete averages on both sides of the Langevin equation, we find

$$m\frac{d}{dt}\langle v(t)\rangle + m\gamma\langle v(t)\rangle = F_{\text{ext}}(t). \tag{20}$$

Now, multiplying by $e^{i\omega t}$ and integrating from $t = -\infty$ to $t = \infty$, we find

$$\langle\widetilde{v}(\omega)\rangle\,(-im\omega + m\gamma) = \widetilde{F}_{\text{ext}}(\omega), \tag{21}$$

or

$$\langle\widetilde{v}(\omega)\rangle = \mu(\omega)\widetilde{F}_{\text{ext}}(\omega) \tag{22}$$

[5] This is stated in quotation marks within the text as well. What does it mean?

where $\mu(\omega) \equiv 1/\left[m(\gamma - i\omega)\right]$ is defined as the dynamic mobility. More theoretically, the the dynamic mobility is defined as

$$\mu(\omega) = \frac{\langle \widetilde{v}(\omega) \rangle}{\widetilde{F}_{\text{ext}}(\omega)}. \tag{23}$$

[6] We may then rewrite as

$$\mu(\omega) = \frac{1}{k_B T} \int_0^\infty dt \, e^{i\omega t} \, \langle v(t_0) v(t_0 + t) \rangle_{\text{eq}} \tag{25}$$

Further assuming that we take the initial condition for the Langevin solution to be defined at $t \to -\infty$, we can take $t_0 = 0$ above so that the result reduces to

$$\mu(\omega) = \frac{1}{k_B T} \int_0^\infty dt \, e^{i\omega t} \, \langle v(0) v(t) \rangle_{\text{eq}} = \frac{\pi}{k_B T} S_v(\omega), \tag{26}$$

which is the first fluctuation dissipation theorem.

Remark:
It is worth mentioning that this isn't the only representation of the fluctuation dissipation theorem. Indeed in the same section where this formula is discussed, Balakrishnan presents another formula he terms the second fluctuation-dissipation theorem. This formula concerns the fluctuations in the noise function as opposed to the dynamical variable which responds to it. Using the result (derived from an analysis of the correlation functions of the Langevin equation)

$$\Gamma = 2 k_B T \gamma / m \tag{27}$$

where γ is defined according to $F_{\text{drag}} = -\gamma v$, and using the definition of white noise as $\langle \eta(0) \eta(t) \rangle = \Gamma \delta(t)$, he finds

$$m\gamma = \frac{1}{k_B t} \int_0^\infty dt \, \langle \eta(0) \eta(t) \rangle \tag{28}$$

which he terms the second fluctuation dissipation theorem. What's more, in [2] a result derived from quantum principles is presented and takes the form

$$\chi''_{AB}(\omega) = \frac{\omega}{2 k_B T} S_{AB}(\omega) \tag{29}$$

where $S_{AB}(\omega)$ is the power spectrum associated with $\langle A(0) B(t) \rangle$, and $\chi_{AB}(\omega)$ is defined by the response function.

3 Extension

- **Gas and Kubo-Green:** Could we derive the diffusion coefficient of a particle diffusing through an ideal gas of identical particles using the Kubo-Green formula?
- **Kubo, Green, and Kinetic Ising:** Could we use the Kubo-Green formula to compute the relaxation properties of the kinetic ising model? How would we compute the autocorrelation function?
- **Examples of Analytic Continuation:** Posit some example "slow" power laws for the velocity autocor-

[6] I can imagine an even more general stochastic situation unconcerned with the motile properties of particles. In such a situation, the dynamic mobility may be defined as

$$\mu(\omega) = \frac{\langle \widetilde{\varphi}(\omega) \rangle}{\widetilde{J}(\omega)} \tag{24}$$

where $\varphi(t)$ is the dynamical variable and $J(t)$ is the external source.

relation function, and attempt to derive an explicit form of the diffusion coefficient.

References

[1] V. Balakrishnan, *Elements of Nonequilibrium Statistical Mechanics*. Ane Books, 2008.

[2] R. Pathria and P. Beale, "Statistical mechanics. butterworh," 2009.