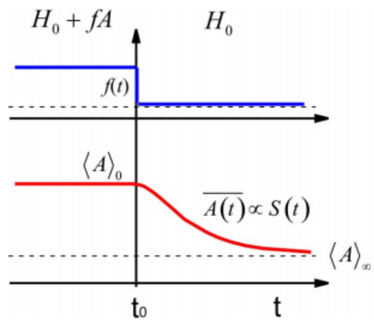
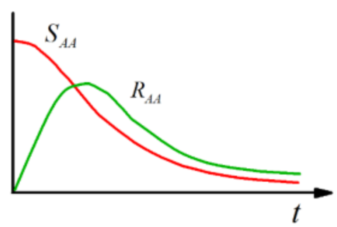
11.4: Relaxation of a Prepared State

The impulse response function $R(t)$ describes the behavior of a system initially at equilibrium that is driven by an external field. Alternatively, we may need to describe the relaxation of a prepared state, in which we follow the return to equilibrium of a system initially held in a nonequilibrium state. This behavior is described by step response function $S(t)$. The step response comes from holding the system with a constant field $H = H_0 - fA$ until a time t_0 when the system is released, and it relaxes to the equilibrium state governed by $H = H_o$.



We can anticipate that the forms of these two functions are related. Just as we expect that the impulse response to rise from zero and be expressed as an odd function in time, the step response should decay from a fixed value and look even in time. In fact, we might expect to describe the impulse response by differentiating the step response, as seen in the classical case.

$$R(t) = \frac{1}{kT} \frac{d}{dt} S(t) \tag{11.4.1}$$



An empirical derivation of the step response begins with a few observations. First, response functions must be real since they are proportional to observables, however quantum correlation functions are complex and follow

$$C(-t) = C^*(t). \tag{11.4.2}$$

Classical correlation functions are real and even,

$$C(t) = C(-t) \tag{11.4.3}$$

and have the properties of a step response. To obtain the relaxation of a real observable that is even in time, we can construct a symmetrized function, which is just the real part of the correlation function:

$$S_{AA}(t) = \frac{1}{2}\{\langle A_I(t) A_I(0)\rangle + \langle A_I(0) A_I(t)\rangle\} \tag{11.4.4}$$

$$= \frac{1}{2}\{C_{AA}(t) + C_{AA}(-t)\} \tag{11.4.5}$$

$$= C'_{AA}(t) \tag{11.4.6}$$

The step response function S defined as follows for $t \geq 0$.

$$S(\tau) \equiv \frac{1}{\hbar} \Theta(\tau) \langle [A_I(\tau), A_I(0)] \rangle_+ \tag{11.4.7}$$

From the eigenstate representation of the correlation function,

$$C(t) = \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn} t} \tag{11.4.8}$$

we see that the step response function can be expressed as an expansion in cosines

$$S(t)=\frac{2}{\hbar}\Theta(t)\sum_{n,m}p_n\left|A_{mn}\right|^2\cos\omega_{mn}t \tag{11.4.9}$$

Further, one can readily show that the real and imaginary parts are related by

$$\omega\frac{dC'}{dt}=C'' \tag{11.4.10}$$

$$\omega\frac{dC''}{dt}=C' \tag{11.4.11}$$

Which shows how the impulse response is related to the time-derivative of the step response.

In the frequency domain, the spectral representation of the step response is obtained from the Fourier–Laplace transform

$$S_{AA}(\omega)=\int_0^\infty dt S_{AA}(t)e^{i\omega t} \tag{11.4.12}$$

$$S_{AA}(\omega)=\frac{1}{2}[C_{AA}(\omega)+C_{AA}(-\omega)] \tag{11.4.13}$$

$$=\frac{1}{2}\left(1+e^{-\beta\hbar\omega}\right)C_{AA}(\omega) \tag{11.4.14}$$

Now, with the expression for the imaginary part of the susceptibility,

$$\chi''(\omega)=\frac{1}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right)C_{AA}(\omega) \tag{11.4.15}$$

we obtain the relationship

$$\chi''(\omega)=\frac{1}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)S_{AA}(\omega) \tag{11.4.16}$$

Equation 11.4.16 is the formal expression for the *fluctuation-dissipation theorem*, proven in 1951 by Callen and Welton. It followed an observation made many years earlier (1930) by Lars Onsager for which he was awarded the 1968 Nobel Prize in Chemistry: “The relaxation of macroscopic nonequilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium state.”

Noting that

$$\tanh(x)=\frac{e^x-e^{-x}}{e^x+e^{-x}} \tag{11.4.17}$$

and

$$\tanh(x)\to x \tag{11.4.18}$$

for $x\gg 1$, we see that in the high temperature (classical) limit

$$\chi''(\omega)\Rightarrow\frac{1}{2kT}\omega S_{AA}(\omega) \tag{11.4.19}$$

Appendix: Derivation of step response function

We can show more directly how the impulse and step response are related. To begin, let’s consider the step response experiment,

$$H=\begin{cases}H_0-fA & t<0\\ H_0 & t\geq 0\end{cases} \tag{11.4.20}$$

and write the expectation values of the internal variable A for the system equilibrated under H at time $t=0$ and $t=\infty$.

$$\langle A\rangle_0=\left\langle\frac{e^{-\beta(H_0-fA)}}{Z_0}A\right\rangle \tag{11.4.21}$$

with

$$Z_0 = \left\langle e^{-\beta(H_0 - fA)} \right\rangle \tag{11.4.22}$$

and

$$\langle A \rangle_\infty = \left\langle \frac{e^{-\beta H_0}}{Z_\infty} A \right\rangle \tag{11.4.23}$$

with

$$Z_\infty = \langle e^{-\beta H_0} \rangle \tag{11.4.24}$$

If we make the classical linear response approximation, which states that when the applied potential fA is very small relative to 0_o, then

$$e^{-\beta(H_0 - fA)} \approx e^{-\beta H_0}(1 + \beta f A) \tag{11.4.25}$$

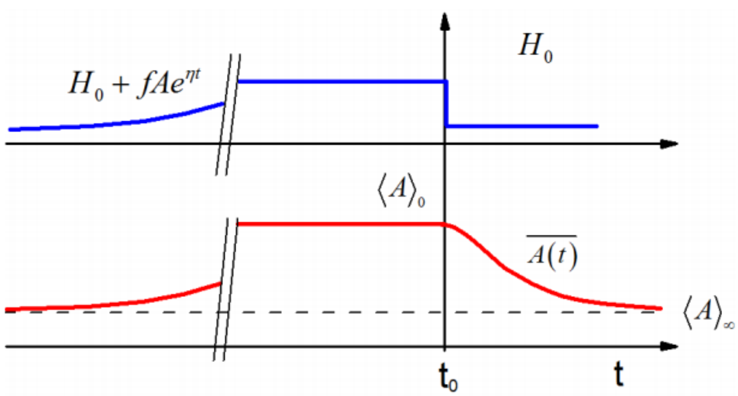
and $Z_0 \approx Z_\infty$, that

$$\delta A = \langle A \rangle_0 - \langle A \rangle_\infty \approx \beta f \left\langle A^2 \right\rangle \tag{11.4.26}$$

and the time dependent relaxation is given by the classical correlation function

$$\delta A(t) = \beta f \langle A(0) A(t) \rangle \tag{11.4.27}$$

For a description that works for the quantum case, let's start with the system under H_o at $t = -\infty$, ramp up the external potential at a slow rate η until $t = 0$, and then abruptly shut off the external potential and watch the system. We will describe the behavior in the limit $\eta \to 0$.



$$H = \begin{cases} H_0 + fAe^{\eta t} & t < 0 \\ H_0 & t \geq 0 \end{cases} \tag{11.4.28}$$

Writing the time-dependence in terms of a convolution over the impulse response function R, we have

$$\overline{\delta A(t)} = \lim_{\eta \to 0} \int_{-\infty}^{0} dt' \Theta(t - t') R(t - t') e^{\eta t'} f \tag{11.4.29}$$

Although the integral over the applied force (t') is over times t<0, the step response factor ensures that t≥0. Now, expressing R as a Fourier transform over the imaginary part of the susceptibility, we obtain

$$\begin{aligned}
\overline{\delta A(t)} &= \lim_{\eta\to 0} \frac{f}{2\pi} \int_{-\infty}^{0} dt' \int_{-\infty}^{\infty} d\omega e^{(\eta - i\omega)t'} e^{i\omega t} \chi''(\omega) \\
&= \frac{f}{2\pi} \int_{-\infty}^{\infty} d\omega PP \left(\frac{1}{-i\omega} \right) \chi''(\omega) e^{i\omega t} \\
&= \frac{f}{2\pi i} \int_{-\infty}^{\infty} d\omega \chi'(\omega) e^{i\omega t} \\
&= f C'(t)
\end{aligned}$$

A more careful derivation of this result that treats the quantum mechanical operators properly is found in the references.

Readings

1. Mazenko, G., Nonequilibrium Statistical Mechanics. Wiley-VCH: Weinheim, 2006.
2. Zwanzig, R., Nonequilibrium Statistical Mechanics. Oxford University Press: New York, 2001.

Contributors and Attributions

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