13.1.3: Examples

Define

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[B(0), B(t)]_+\rangle$$

which is just the frequency spectrum corresponding to the autocorrelation function of B. For different choices of B, $G(\omega)$ corresponds to different experimental measurements. Consider the example of a molecule with a transition dipole moment vector μ. If an electric field $\mathbf{E}(t)$ is applied, then the Hamiltonian H' becomes

$$H' = -\mu\cdot\mathbf{E}(t)$$

If we take $\mathbf{E}(t) = E(t)\hat{\mathbf{z}}$, then

$$H' = -\mu_z E(t)$$

Identifying $B = \mu_z$, the spectrum becomes

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[\mu_z(0), \mu_z(t)]_+\rangle$$

or for a general electric field, the result becomes

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}(\mu(0)\cdot\mu(t) + \mu(t)\cdot\mu(0))\rangle$$

These spectra are the *infrared* spectra.

As another example, consider a block of material placed in a magnetic field $\mathcal{H}(t)$ in the z direction. The spin S_z of each particle will couple to the magnetic field giving a Hamiltonian H'

$$H' = -\sum_{i=1}^{N} S_{i,z}\mathcal{H}(t)$$

The net magnetization created by the field m_z is given by

$$m_z = \frac{1}{N}\sum_{i=1}^{N} S_{i,z}$$

so that

$$H' = -N m_z \mathcal{H}(t)$$

Identify $B = m_z$ (the extra factor of N just expresses the fact that H' is extensive). Then the spectrum is

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[m_z(0), m_z(t)]_+\rangle$$

which is just the NMR spectrum. In general for each correlation function there is a corresponding experiment that measures its frequency spectrum.

To see what some specific lineshapes look like, consider as an ansatz a pure exponential decay for the correlation function $C_{BB}(t)$:

$$C_{BB}(t) = \langle B^2\rangle e^{-\Gamma|t|}$$

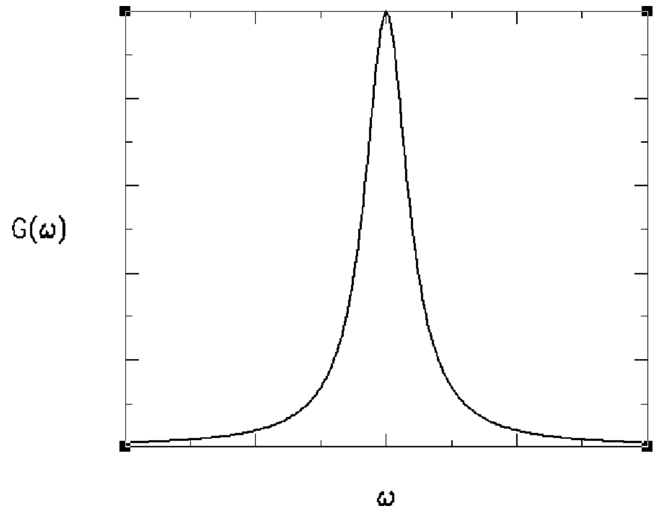
The spectrum corresponding to this time correlation function is

$$G(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t} C_{BB}(t)$$

and doing the integral gives

$$G(\omega) = \frac{\langle B^2 \rangle}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}$$

which is shown in the figure below:



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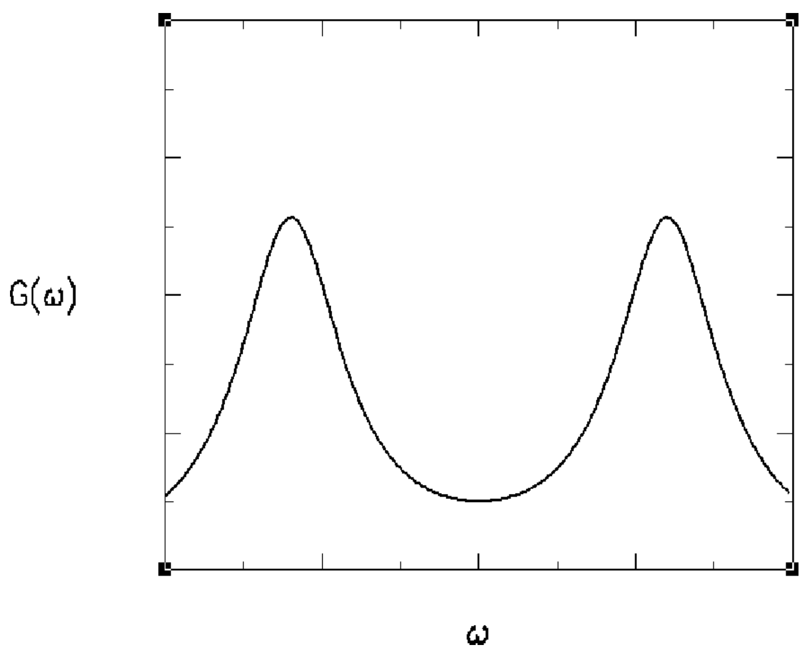
We see that the lineshape is a Lorentzian with a width Γ. As a further example, suppose $C_{BB}(t)$ is a decaying oscillatory function:

$$C_{BB}(t) = \langle B^2 \rangle e^{-\Gamma |t|} \cos \omega_0 t$$

which describes well the behavior of a harmonic diatomic coupled to a bath. The spectrum can be shown to be

$$G(\omega) = \frac{\langle B^2 \rangle \Gamma}{\pi} \left[\frac{\Gamma^2 + \omega^2 + \omega_0^2}{\left(\Gamma^2 + (\omega - \omega_0)^2\right)\left(\Gamma^2 + (\omega + \omega_0)^2\right)} \right]$$

which contains two peaks at $\omega = \pm \sqrt{\omega_0^2 - \Gamma^2}$ as shown in the figure below:



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