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5.74 Introductory Quantum Mechanics II  
Spring 2009

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**5.74, Problem Set #4**  
**Spring 2009**  
**Due Date: Mar. 19, 2009**

**1. Displaced Harmonic Oscillator Model at Finite Temperature**

Based on the correlation function for the position of the harmonic oscillator that you derived in the last problem set, it should be apparent that the energy gap correlation function  $C_{eg}(t)$  for coupling to a single harmonic mode is written

$$\langle \delta\omega_{eg}(t)\delta\omega_{eg}(0) \rangle = \omega_0^2 D [(\bar{n} + 1)e^{-i\omega_0 t} + \bar{n} e^{+i\omega_0 t}]$$

Here  $\bar{n}$  is the thermally averaged occupation of the harmonic oscillator.

- a) Using  $C_{eg}(t)$ , find the real and imaginary parts of the lineshape function  $g(t) = g'(t) + ig''(t)$ .
- b) Calculate the absorption lineshape using the short time expansion  $e^{-i\omega_0 t} \approx 1 - i\omega_0 t - \omega_0^2 t^2 / 2$ .  
 What is the linewidth and how does it scale with temperature for  $kT \gg \hbar\omega_0$ ?

**2. Absorption lineshape from a frequency correlation function.**

The frequency correlation function  $\langle \delta\omega(t)\delta\omega(0) \rangle$  you calculated from a trajectory in problem set two has a roughly exponential form. From an exponential fit to this correlation function and the calculated mean frequency  $\langle \omega \rangle$ , plot the predicted absorption lineshape. Is this lineshape in the fast- or slow-modulation limit?

**3. Quantum Absorption Lineshape from Classical Correlation Function**

How would you calculate a quantum mechanical absorption lineshape if you only have a classical frequency correlation function? The classical frequency correlation function  $C_{cl}(t)$  is a real and even function in time, whereas the quantum correlation function  $C_{eg}(t) = C_{eg}^*(t)$ .

One approximation that is used is to assume that the real part of the quantum correlation function  $C'_{eg}(t)$  -also known as the symmetrized quantum mechanical correlation function- is equal to  $C_{cl}(t)$  at high temperature. Since the real and imaginary components of  $C_{eg}(t)$  are not independent, we can construct the complex correlation function from the real part. This can most effectively be done in the frequency domain:

$$\tilde{C}_{eg}(\omega) = \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}} \tilde{C}_{cl}(\omega)$$

With the frequency domain correlation function, it becomes possible to calculate spectroscopic observables even for low temperatures from

$$g(t) = \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} [\exp(-i\omega t) + i\omega t - 1]$$

Assume you have a classical correlation function of the form:

$$C_{cl}(t) = \Delta^2 [A \exp(-t/\tau_C) + (1-A) \exp(-t/\tau_B) \cos(\Omega t)]$$

with  $\Delta = 75 \text{ cm}^{-1}$ ;  $A = 0.2$ ;  $\tau_C = 100 \text{ fs}$ ;  $\tau_B = 700 \text{ fs}$ ;  $\Omega = 2\pi / 120 \text{ fs}$ . Then obtain  $\tilde{C}_{eg}(\omega)$  with this method. Calculate and plot:

- $\text{Re}[\tilde{C}_{eg}(\omega)]$  (a semilog plot is useful),
- the real and imaginary components of the dephasing function  $F(t)$ , and
- the absorption lineshape.

for two temperatures, 300K and 30K. Interpret what you see. Of course other things will change with temperature in real systems, for instance the correlation times are expected to lengthen. What effect would this have?

Note: You can in principle do this problem mostly analytically, however, it is probably easier to do it numerically. In that case, a significant part of obtaining a nice lineshape will be to perform proper numerical Fourier transforms. Be sure that your correlation functions reach baseline, and that for nice integrations you want the amplitude of your data to asymptotically reach zero at high time or frequency. Also, to make life easier, you might consider defining a detuning

$$\xi = \omega - \omega_{eg} \text{ and a Fourier transform } F(\xi) = \int_{-\infty}^{\infty} e^{i\xi t} F(t) dt.$$