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12.11.2018
Due date: 19.11.2018

Advanced Statistical Physics II – Problem Sheet 4

Problem 1 – (4P) Contour Integration Warm-Up

Consider the following function in the frequency domain

$$\tilde{f}(\omega) = \frac{1}{1 - i\tau\omega} \quad . \tag{1}$$

It might look familiar to you by now. Find its time domain counterpart by doing the inverse Fourier transform $f(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \tilde{f}(\omega)$ explicitly.

Problem 2 – Spectroscopy I
As discussed in the lecture, absorption spectroscopy gives access to the imaginary part $\tilde{\chi}''(\omega)$ of the response function via

$$P \propto \omega \tilde{\chi}''(\omega) \tag{2}$$

where P denotes the absorbed power. An example is the amount of power of an infrared laser beam absorbed by a sample of water. The quantity $\sigma(\omega) = \omega\tilde{\chi}''(\omega)$ is the "absorption coefficient".

a) (2P) In the lecture, we derived the response function of a damped harmonic oscillator with non-vanishing mass m

$$\tilde{\chi}_{\text{DHO}}(\omega) = \frac{1}{k - m\omega^2 - i\gamma\omega} \quad . \tag{3}$$

Show that the absorption coefficient has a maximum at the resonance frequency $\omega_0 = \sqrt{k/m}$ of the harmonic oscillator. Calculate $\sigma(\omega_0)$.

b) (3P) Find the width of the resonance peak of $\sigma(\omega)$ defined by the "full width at half maximum" (FWHM)

$$\Delta\omega = \omega_R - \omega_L, \quad \frac{\sigma(\omega_L)}{\sigma(\omega_0)} = \frac{1}{2} = \frac{\sigma(\omega_R)}{\sigma(\omega_0)} \tag{4}$$

i.e. $\omega_{L,R}$ denotes the frequency to the left/right of the peak, at which the absorption coefficient takes on half of its maximum value. What happens in the limits $m \to 0$ and $\gamma \to 0$?
Hint: First calculate $(\omega_R - \omega_L)^2 = \omega_R^2 + \omega_L^2 - 2\omega_R\omega_L$.

c) (3P) Recall that for linear response, the relation between displacement $x(t)$ and driving force $F(t)$ reads in the frequency domain

$$\tilde{x}(\omega) = \tilde{\chi}_{\text{DHO}}(\omega)\tilde{F}(\omega) \tag{5}$$

For the response (3) of the damped harmonic oscillator (DHO), find an expression for the phase shift, i.e. the angle in the complex plane, between driving force $F(t)$ and displacement $x(t)$.

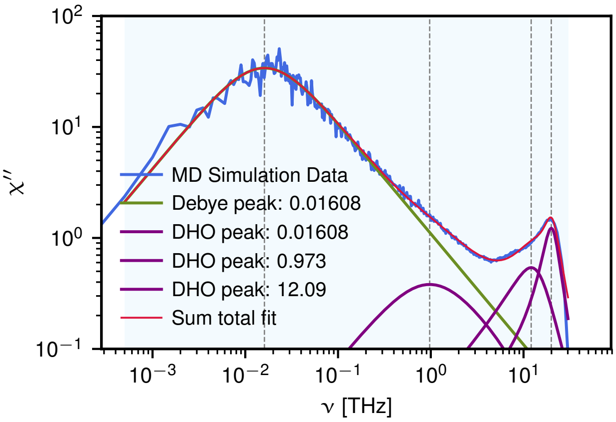

Figure 1: Imaginary part of the response function for the polarization density of water. The solid blue line shows results obtained from computer simulations. The low frequency regime is perfectly fitted by a debye function (green line), while the behaviour at higher frequencies is approximated by contributions from three massive damped harmonic oscillators (DHO) whose sum reproduces the high frequency peak. Finally, the solid red line denotes the sum of all fit functions.

Problem 3 – Spectroscopy II

For weak electric fields $E(t)$, the polarization density $p(t)$ of water obeys the linear response relation

$$\tilde{p}(\omega) = \epsilon_0 \tilde{\chi}(\omega) \tilde{E}(\omega) \tag{6}$$

where ϵ_0 is the vacuum permittivity and the response function $\tilde{\chi}(\omega)$ is now dimension-less. In spectroscopic experiments, the imaginary part $\tilde{\chi}''(\omega)$ is obtained. To obtain the full response function, the real part $\tilde{\chi}'(\omega)$ needs to be calculated as well. This for example, is important to obtain the zero frequency response, which is just the dielectric constant

$$\epsilon = \tilde{\chi}(0) = \tilde{\chi}'(0) \quad . \tag{7}$$

(Since the imaginary part of the response is odd, we have $\tilde{\chi}''(0) = 0$.)

a) (5P) Assume the absorption coefficient can be well approximated by a single Debye peak, i.e

$$\sigma(\omega) = \omega \tilde{\chi}''_{\text{Debye}}(\omega) = C_1 \frac{\tau \omega^2}{1 + \tau^2 \omega^2} \quad . \tag{8}$$

where C_1 is a yet unknown dimension-less constant. Calculate the corresponding real part of the response function by applying the appropriate Kramers-Kronig relation.

b) (3P) Now we would like to put everything we have learned so far about response functions and harmonic oscillators to some good use. Consider fig. 1. It shows the imaginary part of the response function $\tilde{\chi}(\omega)$ as obtained from all-atom computer simulations. Fitting $\tilde{\chi}''_{\text{Debye}}(\omega)$ according to eq. (8) to the low frequency peak, we obtain $C_1 = 67.93$ and $\tau = 9.9$ ps. The high frequency peak however, is better described by the contribution from three damped harmonic oscillators whose response function was discussed in problem 2. For simplicity's sake, we will just consider one of them (the rightmost one). Thus we make the following ansatz for the total response function:

$$\tilde{\chi}(\omega) \approx \tilde{\chi}_{\text{Debye}}(\omega) + C_2 \tilde{\chi}_{\text{DHO}}(\omega) \tag{9}$$

Note that we have to introduce another proportionality constant C_2 to make the response of the harmonic oscillator (3) dimension-less. Via fitting we obtain $C_2/\gamma \approx 24.64$ THz, $\omega_0/2\pi \approx 20.40$ THz and $\gamma/m \approx 8.926$ THz. Use these parameter values to estimate the total dielectric constant. How important are the contributions from the low- and high frequency peaks, respectively?