5.6 Problems for Chapter 5

5.1 A random quantity has an exponential autocorrelation function $G(t) = G(0)\,e^{-\gamma t}$. What are the dimensions of γ? Calculate the correlation time of $G(t)$ using the usual definition.

Calculate the correlation time for a gaussian autocorrelation function $G(t) = G(0)e^{-\gamma^2 t^2/2}$

The dimension of γ is inverse time – as the argument of the exponential must be dimensionless.

The correlation time is the "width" of the correlation function – the area divided by the height. Thus the definition

$$\tau_c = \frac{1}{G(0)} \int_0^\infty G(t)\mathrm{d}t.$$

So for the exponential correlation function

$$\begin{aligned} \tau_c &= \int_0^\infty e^{-\gamma t}\mathrm{d}t \\ &= \left.\frac{e^{-\gamma}}{-\gamma}\right|_0^\infty = \frac{1}{\gamma}. \end{aligned}$$

The correlation time is simply $1/\gamma$, the time constant of the exponential.

For the gaussian correlation function

$$\tau_c = \int_0^\infty e^{-\gamma^2 t^2/2}\mathrm{d}t = \sqrt{\frac{\pi}{2}}\frac{1}{\gamma}.$$

So now the correlation time is $1/\gamma$ but multiplied by a constant of the order of unity (~ 1.25).

5.2 Show that the autocorrelation function of a periodically varying quantity $m = m\cos\omega t$ is given by

$$G = \frac{m^2}{2}\cos\omega t.$$

Show that the autocorrelation function is independent of the *phase* of $m(t)$. In other words, show that if $m = m\cos(\omega t + \varphi)$, then $G(t)$ is independent of φ.

The autocorrelation function is defined by

$$G(t) = \langle m(\tau)m(\tau + t)\rangle.$$

It is convenient here to regard the average as a time average. That is, we average over τ so that $G(t)$ is calculated as

$$G(t) = \frac{1}{2T}\int_{-T}^{T} m(\tau)m(\tau + t)\mathrm{d}\tau.$$

But actually we don't need to do any integration, as we shall see. We start from $m(t) = m\cos\omega t$, so that

$$\begin{aligned} G(t) &= \langle m(\tau)m(\tau + t)\rangle \\ &= \langle m\cos(\omega\tau)\, m\cos\omega(\tau + t)\rangle. \end{aligned}$$

We use the trig identity $\cos(x + y) = \cos x\cos y - \sin x\sin y$, so that

$$G(t) = \left\langle m^2\cos^2\omega\tau\cos\omega t\right\rangle + \left\langle m^2\cos\omega\tau\sin\omega\tau\sin\omega t\right\rangle.$$

The average is evaluated over τ, thus

$$G(t) = m^2\cos\omega t\left\langle\cos^2\omega\tau\right\rangle + m^2\sin\omega t\langle\cos\omega\tau\sin\omega\tau\rangle.$$

The average of $\cos^2$ is ½; the function varies smoothly between 0 and 1. The average of cos sin is zero; this function varies smoothly between -1 and $+1$. Thus we conclude that

$$G(t) = \frac{m^2}{2}\cos\omega t$$

as required.

Now consider the case $m(t) = m\cos(\omega t + \varphi)$. Then

$$\begin{aligned} G(t) &= \langle m(\tau)m(\tau + t)\rangle \\ &= \langle m\cos(\omega\tau + \varphi)\, m\cos(\omega\tau + \varphi + \omega t)\rangle \end{aligned}$$

We use the same trig identity to obtain

$$G(t) = \left\langle m^2\cos^2(\omega\tau + \varphi)\cos\omega t\right\rangle + \left\langle m^2\cos(\omega\tau + \varphi)\sin(\omega\tau + \varphi)\sin\omega t\right\rangle.$$

The average is evaluated over τ, thus

$$G(t) = m^2\cos\omega t\left\langle\cos^2(\omega\tau + \varphi)\right\rangle + m^2\sin\omega t\langle\cos(\omega\tau + \varphi)\sin(\omega\tau + \varphi)\rangle.$$

Then, once again, the average of $\cos^2$ is ½ and the average of $\cos\sin$ is zero. And so in this case also we obtain

$$G(t) = \frac{m^2}{2}\cos\omega t;$$

this shows that $G(t)$ is independent of φ as required.

5.3 The mean square displacement of a Brownian particle at long times was given by Eq. (5.2.12)

$$\langle x^2\rangle = 2t\int_0^\infty G_v(\tau)\mathrm{d}\tau - 2\int_0^\infty \tau G_v(\tau)\mathrm{d}\tau\,.$$

It was stated in the text that the second term was negligible, compared with the first, and so could be ignored.

(a) In that case, show that the mean square displacement may be expressed

$$\langle x^2\rangle = 2G_v(0)\tau_v\,t\,,$$

where τ_v is the correlation time associated with $G_v(\tau)$.

(b) Show that the second integral above may be expressed, approximately, as

$$\int_0^\infty \tau G_v(\tau)\mathrm{d}\tau \approx G_v(0)\tau_v^2\,.$$

There is a choice of ways for demonstrating this. You might approximate $G_v(\tau)$ by a decaying exponential $G_v(0)e^{-\tau/\tau_v}$ before doing the integral.

(c) Using this approximate expression, show that without neglecting the second term, the expression for $\langle x^2\rangle$ becomes

$$\langle x^2\rangle = 2G_v(0)\tau_v\,(t-\tau_v)\,.$$

Hence justify the neglect of the second term.

(a) When the second term is neglected

$$\langle x^2\rangle = 2t\int_0^\infty G_v(\tau)\mathrm{d}\tau\,.$$

The velocity autocorrelation time is defined as

$$\tau_v = \frac{1}{G_v(0)}\int_0^\infty G_v(\tau)\mathrm{d}\tau\,.$$

So

$$\langle x^2 \rangle = 2G_v(0)\tau_v\, t\,,$$

as required.

(b) We must consider the integral

$$\int_0^\infty \tau G_v(\tau)\mathrm{d}\tau\,.$$

If $G_v(\tau)$ has an exponential form, $G_v(\tau) = G_v(0)e^{-\tau/\tau_v}$, then the integral is simply τ_v^2. (We note that if $G_v(\tau)$ has a Gaussian form, $G_v(\tau) = G_v(0)e^{-\tau^2/2\tau_v^2}$, then again the integral is τ_v^2).

(c) Using this result in the (full) expression for $\langle x^2 \rangle$ is

$$\begin{aligned}\langle x^2 \rangle &= 2G_v(0)\tau_v\, t - 2G_v(0)\tau_v^2 \\ &= 2G_v(0)\tau_v\,(t-\tau_v)\end{aligned}$$

as required.

Neglect of the second term is equivalent to neglecting the τ_v in the bracket $(t-\tau_v)$. Recall that the original expression, Eq. (5.2.12), is a *long time* result. Here we see that, similarly, at long times $t \gg \tau_v$, the τ_v in the bracket $(t-\tau_v)$ may be ignored. So the approximation is consistent with the long time limit.

(Extra) More general treatment of the integral of part (b). We note that $G_v(\tau)$ must be a function of τ/τ_v. So we may write

$$G_v(\tau) = G_v(0)g(\tau/\tau_v).$$

Then by a change of variables to $x = \tau/\tau_v$ we have

$$\int_0^\infty \tau G_v(\tau)\mathrm{d}\tau = G_v(0)\tau_v^2 \int_0^\infty x g(x)\mathrm{d}x\,.$$

The integral on the right hand side is a pure number, of order unity. So in general

$$\int_0^\infty \tau G_v(\tau)\mathrm{d}\tau \approx G_v(0)\tau_v^2$$

for reasonably shaped $G_v(\tau)$.
(This is another example of the Physics coming outside the integral through a change of variables.)

5.4 A small mirror is suspended from a quartz fibre whose torsion constant is κ. When the mirror is rotated an angle θ the torque exerted by the fibre is $\Gamma = -\kappa\theta$. The moment of inertia of the mirror about the suspension axis is I. The mirror reflects a beam of light so that the angular fluctuations caused by the impact of surrounding molecules can be read on a suitable scale. The position of the equilibrium is $\langle\theta\rangle = 0$. The average value $\langle\theta^2\rangle$ is observed. From this the goal is to find the Avogadro constant (or, what is the same thing since the gas constant R is known, to determine the Boltzmann constant).

The following are the data: At $T = 287\,\mathrm{K}$, for a fibre with $\kappa = 9.43 \times 10^{-16}\,\mathrm{Nm}$ it was found that $\langle\theta^2\rangle = 4.20 \times 10^{-6}$.

Calculate the Avogadro constant.

The potential energy of the fibre is $\frac{1}{2}\kappa\theta^2$. The mean potential energy has its equipartition value

$$\frac{1}{2}kT = \frac{1}{2}\kappa\left\langle\theta^2\right\rangle$$

so that

$$k = \frac{\kappa\left\langle\theta^2\right\rangle}{T} = \frac{9.43 \times 10^{-16} \times 4.20 \times 10^{-6}}{287} = 1.38 \times 10^{-23}.$$

Thus we obtain $k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ (a respectable value). since $R = N_\mathrm{A}k$, and using the accepted gas constant value $R = 8.31\,\mathrm{J\,mol^{-1}\,K^{-1}}$, this gives $N_\mathrm{A} = 6.02 \times 10^{23}$.

5.5 The assembly of the previous question is placed in a chamber from which the air may be evacuated. Can the amplitude of these fluctuations be reduced by reducing air density? Describe the change in the behaviour of the fluctuations as the air pressure is lowered. In particular, discuss the behaviour as the pressure goes to zero.

The amplitude of the fluctuations cannot be reduced by reducing the temperature; so long as the system remains in thermal equilibrium at temperature T, it will have the corresponding equipartition energy.

The spectrum of the fluctuations is spread over a bandwidth $\Delta f \approx f_0/Q$, where f_0 is the oscillation frequency of the fibre-mirror assembly and Q is the Q-factor of the oscillations. Lowering the pressure will reduce the dissipation and so increase the Q. Then the equipartition fluctuations will be contained in a smaller bandwidth.

Even when the pressure is zero, so long as the system is still in thermal equilibrium at temperature T, the mean square fluctuations will still be given by $\langle\theta^2\rangle = kT/\kappa$. At zero pressure thermal equilibrium will not be established by impacts from the air molecules; it will be established by conduction along the quartz fibre.

5.6 In Section 5.3.9 we considered an electrical analogue of the Langevin Equation based on a circuit comprising an inductor and a resistor in series. In this problem we shall examine a different analogue: a circuit of a capacitor and a resistor in parallel. Show that the equation analogous to the Langevin equation, in this case, is

$$C\frac{\mathrm{d}V}{\mathrm{d}t} + \frac{1}{R}V = I.$$

Hence show that the fluctuation-dissipation result relates the resistance to the current fluctuations through

$$\frac{1}{R} = \frac{1}{2kT}\int_{-\infty}^{\infty} \langle I\,(0)\,I\rangle\,\mathrm{d}t.$$

The current in the capacitor is $C\mathrm{d}V/\mathrm{d}t$ and the current in the resistor is V/R. These add to give the total current, thus

$$C\frac{\mathrm{d}V(t)}{\mathrm{d}t} + \frac{1}{R}V(t) = I(t)$$

as required.

Comparing with the Langevin equation

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \frac{1}{\mu}v(t) = f(t)$$

we see that the equipartition expression $\langle v^2\rangle = kT/M$ translates to $\langle V^2\rangle = kT/C$ and the fluctuation-dissipation expression

$$\frac{1}{\mu} = \frac{1}{2kT}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\mathrm{d}t$$

translates to

$$\frac{1}{R} = \frac{1}{2kT}\int_{-\infty}^{\infty}\langle I(0)I(t)\rangle\mathrm{d}t$$

as required.

5.7 The dynamical response function $X(t)$ must vanish at zero times, as shown in Fig. 5.13. What is the physical explanation of this? What is the consequence for the step response function $\Phi(t)$? Is this compatible with an exponentially decaying $\Phi(t)$?

The step response function $\Phi(t)$ is proportional to the autocorrelation function of the response variable

$$\Phi(t) \propto \langle M(0)M(t)\rangle,$$

from the Onsager hypothesis or the linear response derivation. Since, certainly in the classical case, $M(0)$ and $M(t)$ commute, we may swap these around so that

$$\Phi(t) = \Phi(-t).$$

Thus $\Phi(t)$ is an even function and its odd derivatives must vanish at $t = 0$. And then since $X(t)$ is the first derivative of $\Phi(t)$, it follows that $X(0) = 0$ as required.

If the odd derivatives of $\Phi(t)$ vanish at the origin, this is clearly incompatible with an exponential decay. More precisely $\Phi(t)$ cannot decay exponentially *in the vicinity of* $t = 0$; it can elsewhere.

5.8 We saw in Section 5.4.2 that $\chi'(\omega)$ and $\chi''(\omega)$ may be regarded as the cosine and sine transforms of the dynamical susceptibility $X(t)$. Now these real Fourier transforms may be inverted; $X(t)$ may be found equivalently from either $\chi'(\omega)$ or $\chi''(\omega)$. The point about this is that $\chi'(\omega)$ and $\chi''(\omega)$ are not independent; they both come (invertibly) from $X(t)$. So, in particular, $\chi'(\omega)$ may be found from $\chi''(\omega)$ or *vice versa* (the Kramers-Kronig relations).

(a) In this way derive the following expressions

$$\chi'(\omega) = -\frac{2}{\pi}\int_0^\infty \frac{\omega'\chi''(\omega')}{\omega'^2-\omega^2}\,\mathrm{d}\omega'$$

$$\chi''(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega\chi'(\omega')}{\omega'^2-\omega^2}\,\mathrm{d}\omega'.$$

(b) These are not *quite* the same as those in Eq. (5.4.61). Why is this?

(c) Where, exactly, does the requirement of causality enter into this derivation?

(a) We have $\chi'(\omega)$ and $\chi''(\omega)$ in Eqs. (5.4.14) and (5.4.15):

$$\chi'(\omega) = \int_0^\infty X(t)\cos(\omega t)\,\mathrm{d}t \tag{5.4.14}$$

$$\chi''(\omega) = \int_0^\infty X(t)\sin(\omega t)\,\mathrm{d}t. \tag{5.4.15}$$

These real Fourier transforms may be inverted, so $X(t)$ may be found equivalently from either $\chi'(\omega)$ or $\chi''(\omega)$:

$$X(t) = \frac{2}{\pi}\int_0^\infty \chi'(\omega)\cos(\omega t)\,\mathrm{d}\omega \tag{5.6.1}$$

$$X(t) = \frac{2}{\pi}\int_0^\infty \chi''(\omega)\sin(\omega t)\,\mathrm{d}\omega. \tag{5.6.2}$$

We may substitute $X(t)$ from Eq. (5.6.2) into Eq. (5.4.14); this gives $\chi'(\omega)$ in terms of $\chi''(\omega)$

$$\chi'(\omega) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega' \left[\int_0^\infty \mathrm{d}t\cos\omega t\sin\omega' t\right]\chi''(\omega') \tag{5.6.3}$$

or we may substitute $X(t)$ from Eq. (5.6.1) into Eq. (5.4.15); this gives $\chi''(\omega)$ in terms of $\chi'(\omega)$

$$\chi''(\omega) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega' \left[\int_0^\infty \mathrm{d}t\sin\omega t\cos\omega' t\right]\chi'(\omega'). \tag{5.6.4}$$

In evaluating the integrals in the square brackets we must take the upper limit to infinity carefully. Let's put the upper limit as T to start with.

Then we find

$$\begin{aligned}\int_0^T \cos\omega t \sin\omega' t \,\mathrm{d}t &= \int_0^T \frac{1}{2}\Big\{\sin(\omega+\omega')t - \sin(\omega-\omega')t\Big\}\mathrm{d}t \\ &= -\frac{1}{2}\left\{\frac{\cos(\omega+\omega')t}{\omega+\omega'} - \frac{\cos(\omega-\omega')t}{\omega-\omega'}\right\}\Bigg|_0^T \\ &= \frac{1}{2}\left\{\frac{1-\cos(\omega+\omega')T}{\omega+\omega'} - \frac{1-\cos(\omega-\omega')T}{\omega-\omega'}\right\}.\end{aligned} \tag{5.6.5}$$

Now we argue that as $T\to\infty$ the cosines vary very fast: so rapidly that they average to zero. This means that effectively, when the limit of the integral goes to zero, we have

$$\begin{aligned}\int_0^\infty \cos\omega t \sin\omega' t \,\mathrm{d}t &= \frac{1}{2}\left\{\frac{1}{\omega+\omega'} - \frac{1}{\omega-\omega'}\right\} \\ &= \frac{\omega'}{\omega'^2-\omega^2}.\end{aligned} \tag{5.6.6}$$

Using this result in Eqs. (5.6.3) and (5.6.4) then gives

$$\begin{aligned}\chi'(\omega) &= \frac{2}{\pi}\int_0^\infty \frac{\omega'\chi''(\omega')}{\omega'^2-\omega^2}\mathrm{d}\omega' \\ \chi''(\omega) &= -\frac{2}{\pi}\int_0^\infty \frac{\omega\chi'(\omega')}{\omega'^2-\omega^2}\mathrm{d}\omega'\end{aligned} \tag{5.6.7}$$

as required.

(b) These expressions are not the same as Eq. (5.4.61); in those expressions the integrals ranged over positive and negative frequencies whereas here the integrals cover just positive frequencies. But using the relations from Eq. (5.4.51)

$$\begin{aligned}\chi'(\omega) &= \chi'(-\omega) \\ \chi''(\omega) &= -\chi''(-\omega)\end{aligned}$$

we see thy are equivalent.

(c) The requirement of causality is expressed in Eq. (5.4.8): that $X(t)$ be zero for negative times. We see this is reflected directly in the domains of the time integrations. *That* makes $\chi'(\omega)$ and $\chi''(\omega)$ the cosine and sine integral of the same $X(t)$.

5.9 Show that for the Debye susceptibility, the relation

$$\chi_0 = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)}{\omega}\mathrm{d}\omega$$

holds. Demonstrate that χ'' vanishes sufficiently fast at $\omega = 0$ so there is no pole in the integral and there is thus no need to take the principal part of the integral in the Kramers-Kronig relations.

In the Debye case

$$\chi''(\omega) = \chi_0\frac{\omega\tau}{1+\omega^2\tau^2}$$

so that the integrand is

$$\frac{\chi''(\omega)}{\omega} = \chi_0\frac{\tau}{1+\omega^2\tau^2}.$$

The ω in the denominator has been cancelled by the ω in the numerator. Thus there is no pole in the integral.

We wish to evaluate the integral

$$I = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)}{\omega}\mathrm{d}\omega = \chi_0\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\tau}{1+\omega^2\tau^2}\mathrm{d}\omega.$$

We can remove the τ by changing variables to $x = \omega\tau$, so that $\mathrm{d}\omega = \mathrm{d}x/\tau$, and

$$I = \chi_0\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{d}x}{1+x^2}.$$

The integral is standard; its value is π. Thus we have shown that $I = \chi_0$; we have demonstrated that the Kramers-Kronig sum rule holds in the Debye case.

5.10 In Section 5.4.11 we examined the form of the dynamical susceptibility $\chi(\omega)$ that followed from the assumption that the step response function $\Phi(t)$ decayed exponentially. In this question consider a step response function that decays with a gaussian profile: $\Phi = \chi_0 e^{-t^2/2\tau^2}$. Evaluate the real and imaginary parts of the dynamical susceptibility and plot them as a function of frequency. The real part of the susceptibility is difficult to evaluate without a symbolic mathematics system such as *Mathematica*. Compare and discuss the differences and similarities between this susceptibility and that deduced from the exponential step response function (Debye susceptibility).

The response function $X(t)$ is given by minus the derivative of $\Phi(t)$, thus

$$\begin{aligned} X(t) &= -\frac{\mathrm{d}}{\mathrm{d}t}\chi_0 e^{-t^2/2\tau^2} \\ &= \chi_0 \frac{t}{\tau^2} e^{-t^2/2\tau^2}. \end{aligned}$$

The dynamical susceptibility is the Fourier transform of this

$$\chi(\omega) = \int_{-\infty}^{\infty} X(t) e^{\mathrm{i}\omega t}\mathrm{d}t$$

so that

$$\chi(\omega) = \frac{\chi_0}{\tau^2}\int_{-\infty}^{\infty} t e^{-t^2/2\tau^2} e^{\mathrm{i}\omega t}\mathrm{d}t.$$

Upon integration we obtain the real and imaginary parts as

$$\begin{aligned} \chi'(\omega) &= \chi_0 \left\{1 - \sqrt{\frac{\pi}{2}}\,\omega\tau e^{-\omega^2\tau^2/2}\,\mathrm{erfi}\,\frac{\omega\tau}{\sqrt{2}}\right\} \\ \chi''(\omega) &= \chi_0 \sqrt{\frac{\pi}{2}}\,\omega\tau e^{-\omega^2\tau^2/2}. \end{aligned}$$

These are plotted in the figure.

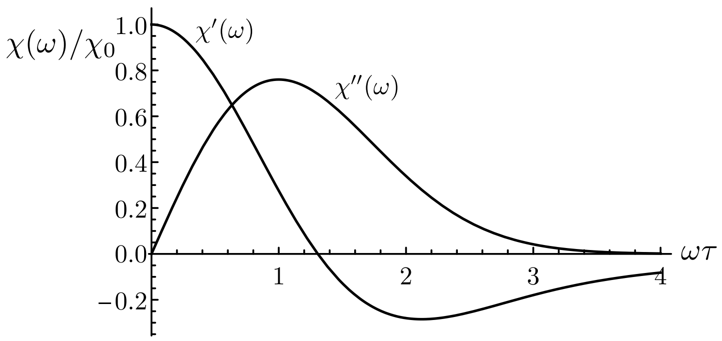

Figure 5.17: Dynamical susceptibility for a Gaussian response function

The imaginary part of the susceptibility is always positive, as required by energy considerations. In this case the real part of the susceptibility goes negative. This is in contrast to that of the Debye susceptibility, that remains positive at all frequencies.

5.11 The Debye form for the dynamical susceptibility, Eq. (5.4.84), is

$$\chi'(\omega) = \chi_0 \frac{1}{1+\omega^2\tau^2}$$
$$\chi''(\omega) = \chi_0 \frac{\omega\tau}{1+\omega^2\tau^2}$$

Plot the imaginary part against the real part and show that the figure corresponds to a semicircle. This pictorial representation is known as a Cole-Cole plot.

The Cole-Cole plot of the Debye susceptibility is shown below.

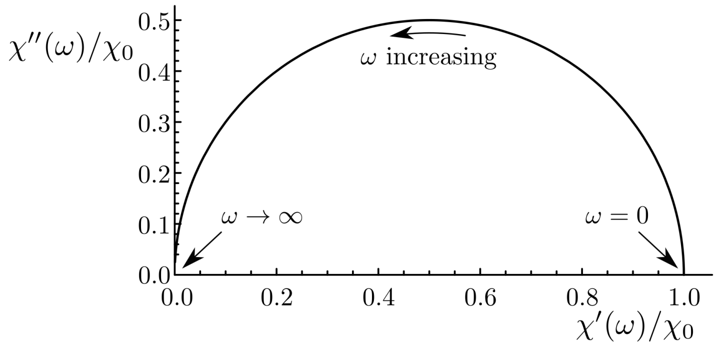

Figure 5.18: Cole-Cole plot for a Debye susceptibility

The real and imaginary parts of the Debye susceptibility are seen to satisfy the equation

$$\left(\frac{\chi''}{\chi_0}\right)^2 + \left(\frac{\chi'}{\chi_0} - \frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^2$$

This is corresponds to a circle of radius ½ centred on $\chi'/\chi_0 = 1/2$

5.12 Plot the Cole-Cole plot (Problem 5.11) for the dynamical susceptibility considered in Problem 5.10. How does it differ from that of the Debye susceptibility?

In Problem 5.10 we obtained the expressions for the real and the imaginary parts of the dynamical susceptibility

$$\chi'(\omega) = \chi_0 \left\{ 1 - \sqrt{\frac{\pi}{2}}\,\omega\tau e^{-\omega^2\tau^2/2}\,\mathrm{erfi}\,\frac{\omega\tau}{\sqrt{2}} \right\}$$
$$\chi''(\omega) = \chi_0 \sqrt{\frac{\pi}{2}}\,\omega\tau e^{-\omega^2\tau^2/2}.$$

From these we can make the Cole-Cole plot:

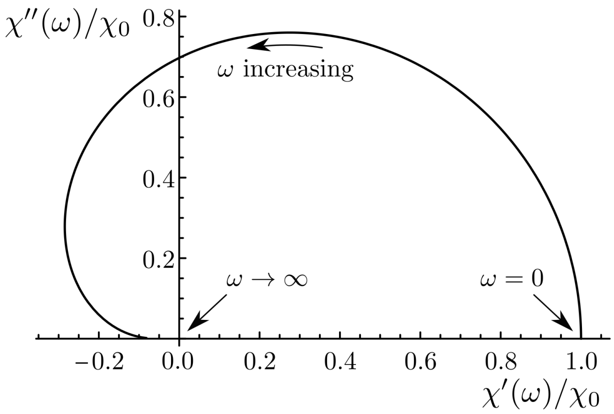

Figure 5.19: Cole-Cole plot corresponding to a gaussian response function

The main difference from the Debye form is that this curve passes to the left of the y axis (high frequencies), where the real part of the susceptibility becomes negative. Since in the high frequency limit the real and imaginary parts of the susceptibility must both vanish, this gives the cardioid shape to the plot.

5.13 The full quantum-mechanical calculation of the Johnson noise of a resistor gives

$$\left\langle v^2 \right\rangle_{\Delta f} = 4R\frac{hf}{e^{hf/kT} - 1}\Delta f.$$

Show that this reduces to the classical Nyquist expression at low frequencies. At what frequency will there start to be serious deviations from the Nyquist value? Estimate the value of this frequency.

At low frequencies such that $hf \ll kT$ we can expand the exponential so that

$$\begin{aligned}\left\langle v^2\right\rangle_{\Delta f} &= 4R\frac{hf}{1+hf/kT+\cdots-1}\Delta f\\ &= 4R\frac{hf}{hf/kT+\ldots}\Delta f\end{aligned}$$

and in the low frequency limit the hf cancels, giving

$$\left\langle v^2\right\rangle_{\Delta f} = 4kTR\,\Delta f,$$

the classical Nyquist expression.

For the Nyquist expression to be valid we require the frequency to satisfy $f \ll kT/h$ so at room temperature ($T \sim 300\text{K}$) this means

$$f \ll \frac{1.4\times10^{-23}\times300}{6.6\times10^{-34}} = 6.4\times10^{12}\,\text{Hz}.$$