IP326. Lecture 9. Thursday, Jan. 31, 2019

In the model of 1-d coupled harmonic oscillators introduced earlier, we derived the following expression for the normalized velocity autocorrelation function of the central heavy particle:

$$\overline{C}_{vv}(t) \equiv \frac{\langle v_0(0)v_0(t)\rangle}{\langle v_0^2(0)\rangle} = \frac{M}{m}\mathcal{L}^{-1}\frac{s\hat{\phi}(s)}{1+Qs^2\hat{\phi}(s)} \tag{1}$$

The time dependence of $\overline{C}_{vv}(t)$ in this expression is still only implicit; to determine how it depends on time explicitly, the Laplace inverse of the function $\hat{G}(s) \equiv s\hat{\phi}(s)/[1+Qs^2\hat{\phi}(s)]$ must be calculated. To carry out this calculation, we need an expression for the function $\hat{\phi}(s)$, which at the moment is known only through its definition in terms of the following integral:

$$\hat{\phi}(s) = \frac{1}{2N}\int_{-N}^{N} dl \frac{1}{s^2 + (2b/m)[1-\cos(\pi l/N)]}, \tag{2}$$

As it turns out, an exact evaluation of this integral is possible. The evaluation begins with the change of variable $\pi l/N = x$, producing

$$\hat{\phi}(s) = \frac{1}{\pi}\int_0^{\pi} dx \frac{1}{s^2 + \frac{2b}{m} - \frac{2b}{m}\cos x} \tag{3}$$

An indefinite integral of this form is known, and is given by

$$\int dx \frac{1}{p+q\cos x} = \frac{2}{\sqrt{p^2-q^2}}\tan^{-1}\left(\frac{(p-q)\tan(x/2)}{\sqrt{p^2-q^2}}\right) \tag{4}$$

That this result is indeed correct can be verified by differentiating the right hand side, and showing that the original integrand is exactly recovered. The demonstration proceeds as follows:

$$\frac{d}{dx}\frac{2}{\sqrt{p^2-q^2}}\tan^{-1}\left(\frac{(p-q)\tan\frac{x}{2}}{\sqrt{p^2-q^2}}\right) = \frac{2}{\sqrt{p^2-q^2}}\frac{1}{1+\frac{(p-q)^2\tan^2\frac{x}{2}}{p^2-q^2}}\frac{(p-q)}{\sqrt{p^2-q^2}}\frac{1}{2}\sec^2\frac{x}{2}$$

$$= \frac{1}{\sqrt{p^2 - q^2}} \frac{p^2 - q^2}{p^2 - q^2 + (p-q)^2 \dfrac{\sin^2(x/2)}{\cos^2(x/2)}} \frac{(p-q)}{\sqrt{p^2 - q^2}} \frac{1}{\cos^2(x/2)}$$

$$= \frac{\cos^2(x/2)}{(p^2 - q^2)\cos^2(x/2) + (p-q)^2 \sin^2(x/2)} \frac{(p-q)}{\cos^2(x/2)}$$

$$= \frac{(p-q)}{(p^2 - q^2)\cos^2(x/2) + (p-q)^2 \sin^2(x/2)}$$

$$= \frac{(p-q)}{(p^2 - q^2)\cos^2(x/2) + (p-q)^2 [1 - \cos^2(x/2)]}$$

$$= \frac{(p-q)}{2q(p-q)\cos^2(x/2) + (p-q)^2}$$

$$= \frac{1}{2q\cos^2(x/2) + p - q} = \frac{1}{q[2\cos^2(x/2) - 1] + p} = \frac{1}{p + q\cos x}$$

If Eq. (4) is now used in Eq. (3), along with the formulas $\tan^{-1}(0) = 0$ and $\tan^{-1}(\infty) = \pi/2$, we find that

$$\hat{\phi}(s) = \frac{1}{\sqrt{\left(s^2 + \dfrac{2b}{m}\right)^2 - \left(\dfrac{2b}{m}\right)^2}}$$

$$= \frac{1}{s\sqrt{s^2 + 4b/m}} \qquad (5)$$

Substitution of the above expression into Eq. (1) leads to

$$\overline{C}_{vv}(t) = \frac{M}{m} \mathcal{L}^{-1} \frac{1}{sQ + \sqrt{s^2 + 4b/m}} \qquad (6)$$

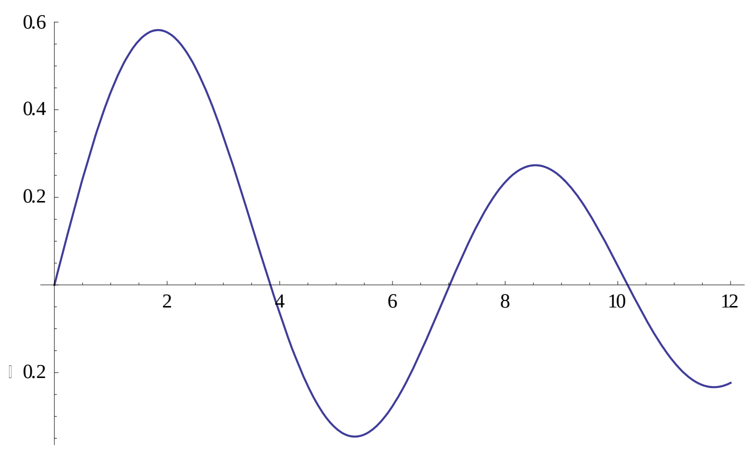
Unfortunately, for arbitrary values of the parameter Q, it doesn't seem possible to find an analytical expression for the Laplace inverse in Eq. (6). But there are two special cases for which such an expression is known: one is $Q = 0$, corresponding to $M = m$, and the other is $Q = 1$, corresponding to $M = 2m$. We'll consider only the second case for now; for this case it can shown that

$$\overline{C}_{vv}(t) = 2\frac{1}{2t}\sqrt{\frac{m}{b}}J_1(2t\sqrt{b/m}) \tag{7}$$

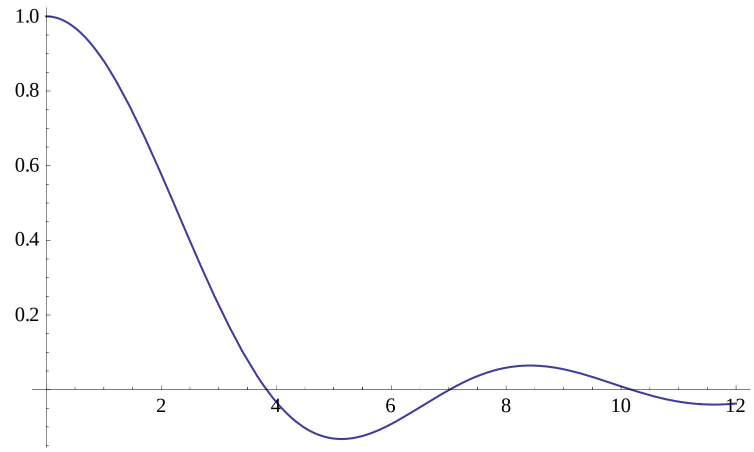
where $J_1(z)$ is a special function called the *Bessel function* of order 1; it is a solution to the following differential equation

$$\frac{d^2J_1}{dz^2} + \frac{1}{z}\frac{dJ_1}{dz} + \left(1 - \frac{1}{z^2}\right)J_1 = 0$$

For our purposes, it's enough to know how J_1 varies as a function of its argument, which is as shown below.



This means that as a function of the reduced time $t/\sqrt{m/4b} \equiv \bar{t}$, $\overline{C}_{vv}(t)$ itself varies as



This time-dependence shares many similarities with the decay profile of the corresponding velocity autocorrelation function of realistically simulated liquids, as the figure below, taken from a paper by Levesque and Verlet [Phys. Rev. A **2**, 2514 (1970)], illustrates.

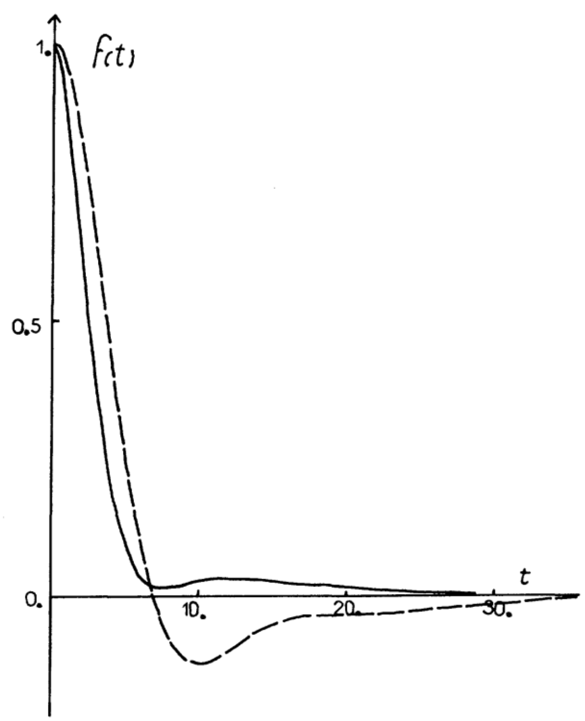


FIG. 2. Normalized velocity autocorrelation function $f(t)$ for density $\rho = 0.85$. Solid line: $T = 4.70$; dashed line: $T = 0.76$. The time units are equal to 0.128 reduced units, i.e., 4.10^{-14} sec for argon.

The shapes of these curves in different regions of the graph can be plausibly explained as follows: at times less than or on the order of the characteristic collision time (which corresponds roughly to when the correlation function first vanishes) a particle's velocity at time t retains some memory of its velocity at time 0, causing the product of initial and final velocities to be positive on average. At later times, when particles have begun to experience the effects of collisions, the chances are greater that a significant number of the collisions reverse a particle's trajectory, causing its initial and final velocities to be of opposite sign, and their product to be negative on average. Repeated inter-particle collisions at still later times lead eventually to complete decorrelation of these velocities, and the velocity correlation function then vanishes. But these effects depend on the state of the liquid; at high temperatures, for instance (see the figure above), or low density, the correlation function can remain positive at all times. Indeed, this is the case for gases at ambient conditions. So the local environment around a particle and the strength of their mutual interactions plays a key role in how the particle's velocities are correlated from instant to instant.

● Time correlation functions, transport coefficients and linear response

As indicated at the outset of these lectures, the importance of time correlation functions lies in the fact that they are related to a set of physical quantities called *transport coefficients*. Broadly speaking, transport coefficients measure the response of a system in equilibrium to the effects of an external force. As a specific example, consider a system consisting of a length of metallic wire. If a voltage difference is applied to the ends of the wire, electrons from the metal are transported from one end to the other, generating an electric current. The strength of this current is controlled by the wire's *electrical conductivity,* which is one type of transport coefficient; its value is unique to the kind of material carrying the current. Another type of transport coefficient – also system-specific – is associated with the response of a fluid, initially in thermal equilibrium, to a temperature gradient. The response in this case is a flow of heat, the extent of which is controlled by a transport coefficient called the *thermal conductivity*. In the same way, all absorption spectroscopy measurements are essentially probes of the response of a system to weak electromagnetic fields, the nature of the response (manifested as an attenuation of the transmitted light intensity) again being dictated by a parameter – the extinction coefficient in this instance – intrinsic to the perturbed system.

The general framework in which we'll relate these kinds of coefficients to time correlation functions is called linear response theory, the qualifying adjective 'linear' referring to a regime in which the applied forces are sufficiently weak that their effects are only manifested at linear order in the force. Before we apply this formalism to the calculation of specific transport coefficients, we'll set down a set of general criteria that we believe a system should satisfy to fall within the ambit of the linear response framework.

● General aspects of linear response

Consider a system that when perturbed by an external time-dependent force $F(t)$ responds by producing a time-dependent signal $S(t)$. Let's require that $F(t)$ be such that $S(t)$ has these characteristic features:

(i) $S(t) = 0,\ \forall t$ when $F(t) = 0$ (meaning, the system produces no signal if it's left alone.)
(ii) $S(t)$ is produced only after $F(t)$ is applied (meaning, the response of the system is *causal*.)
(iii) (a) The magnitude of $S(t)$ is changed by λ when $F(t)$ is changed by λ (meaning, a system's response is proportional to the applied force.)
(b) If two separate forces, $F_1(t)$ and $F_2(t)$, produce separate signals $S_1(t)$ and $S_2(t)$, then $F_1(t)+F_2(t)$ produces $S_1(t)+S_2(t)$ (meaning, the system's response is *linear*.)
(iv) The magnitude of the signal is independent of the time at which the force is applied (meaning, if $F(t)$ produces $S(t)$, then $F(t-t')$ produces $S(t-t')$; i.e., the response of the system is *stationary*.)

For a system whose response to an external force has the above characteristics, i.e., it is linear, causal and stationary, the relation between $S(t)$ and $F(t)$ is given, very generally by

$$S(t) = \int_{-\infty}^{t} dt' \chi(t-t') F(t') \tag{8}$$

where $\chi(t)$ is called a *response* function. It is systems with these general features that we'll henceforth restrict our attention to.

It's immediately obvious that Eq. (8) satisfies properties (i) – (iii); to show that it also satisfies property (iv), imagine changing $F(t)$ to $F'(t)$, where $F'(t) = F(t-t_1)$. Let $S'(t)$ be the new signal that's produced. From Eq. (8), we have

$$S'(t) = \int_{-\infty}^{t} dt' \chi(t-t') F(t'-t_1) \tag{9}$$

Change variables from t' to $x = t' - t_1$. Eq. (9) then becomes

$$S'(t) = \int_{-\infty}^{t-t_1} dx \chi(t-t_1-x) F(x)$$

The right hand side of this expression is the definition of $S(t-t_1)$, so the new signal is "time advanced" by exactly the same amount as the applied for is, and (8) therefore fulfills the stationarity condition of the system's response.

● Determination of the response function $\chi(t)$

The foregoing considerations tell us nothing about the structure of the function $\chi(t)$, but if $F(t)$ is weak, as we'll assume, it can only depend on properties that are intrinsic to the system alone, properties the system has, in other words, when it is unperturbed by the force. We would now like to obtain an expression for $\chi(t)$ in terms of these properties.

For this purpose, consider a system initially in thermal equilibrium at temperature *T*. At some arbitrary time $t=0$, imagine applying a weak time-dependent field to it, and then measuring the value of some property *A* of the system at a later time *t*. *A* can be identified with the signal *S* of the previous section. Repeat this process many times and average the measured values of *A*; the result is the value $\overline{A}_{\exp}$, which we'll assume can be obtained from statistical mechanics by calculating the ensemble average of *A* according to the prescription

$$\langle A(t)\rangle = \int d\Gamma A(\Gamma)\, f(\Gamma,t) \tag{10}$$

where $f(\Gamma,t)$ is the density of microstates at time *t* that have evolved from the microstate Γ at time $t=0$; it is *not* the equilibrium density distribution $f_0(\Gamma)$. However, because the field is weak we expect that the two will not be all that different from each other. Accordingly, it should be reasonable to write

$$f(\Gamma,t) \approx f_0(\Gamma) + \Delta f(t) \tag{11}$$

where $\Delta f(t)$ is some as yet unknown time-dependent correction factor. Now the evolution of $f(\Gamma,t)$ – its time-dependence, that is – is governed by the system's Hamiltonian H, which we'll also assume is not very different from its field-free value H_0, and can therefore be approximated as

$$H(\Gamma,t) \approx H_0(\Gamma) - B(\Gamma)F(t) \tag{12}$$

where $B(\Gamma)$ is some other property of the *unperturbed* system that $F(t)$ couples to when it interacts with the system. What we'll now do is use Eqs. (11) and (12) in the Liouville equation, solve for $\Delta f(t)$, use the result to determine $f(\Gamma,t)$, and then use $f(\Gamma,t)$ to calculate $\langle A(t)\rangle$, and thereby, hopefully, identify the structure of $\chi(t)$.