

22.103 Microscopic Theory of Transport (Fall 2003)
Lecture 3 (9/12/03)

Diffusion and the Velocity Autocorrelation - Green-Kubo Relations

References --

McQuarrie, Sec. 21-8.

Boon and Yip, Sec. 2.5

Time Correlation Function Expressions for Transport Coefficients - Green-Kubo Formulas

Transport coefficients like the diffusion coefficient D , the viscosity coefficient η , and the thermal conductivity coefficient λ all can be expressed as time integrals of appropriate time correlation functions. This formulation is known as the Green-Kubo formulas, the results of linear response theory in statistical mechanics. To illustrate the main features of the Green-Kubo formalism we will treat explicitly the most straightforward case, that of diffusion.

We begin with the expression for the mean squared displacement of a typical particle in a fluid at equilibrium, $\langle \Delta^2 r(t) \rangle = \langle [R(t) - R(0)]^2 \rangle$. Using the simple relation

$$\underline{R}(t) - \underline{R}(0) = \int_0^t dt' \underline{v}(t') \quad (3.1)$$

we can write for the mean squared displacement function

$$\langle \Delta^2 r(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \underline{v}(t') \cdot \underline{v}(t'') \rangle \quad (3.2)$$

What appears in the integrand is the velocity autocorrelation function, involving the velocities of the particle at two different times, t' and t'' . For a fluid system in equilibrium one can invoke the property of time translation invariance. That is to say the correlation function depends only the time difference,

$$\langle \underline{v}(t') \cdot \underline{v}(t'') \rangle = \langle \underline{v}(t' - t'') \cdot \underline{v}(0) \rangle \quad (3.3)$$

This is essentially a statement that one can shift the time origin by any amount without affecting the correlation function. The double integral in (3.2) extends over a square region as shown in Fig. 3.1(a). To take advantage of (3.3) we transform the two integrals so that one of the variables of integration is the time difference $t' - t''$. Then the other time variable would not appear in (3.3), which is unspecified, and the integration over this

variable can be carried out without knowing the velocity autocorrelation function.. We therefore introduce a change of variable, $\tau = t' - t''$ and $d\tau = -dt''$. Eq. (3.2) becomes

$$\langle \Delta^2 r(t) \rangle = \int_0^t dt' \int_{t'-t}^{t'} d\tau \alpha(\tau) \quad (3.4)$$

with $\alpha(t) = \langle \underline{v}(t) \cdot \underline{v}(0) \rangle$ being the velocity autocorrelation function. After the coordinate transformation, the region of integration now has the shape of a parallelogram, see Fig. 3.1(b). The order of integration in (3.4) is over τ first and then t' , or covering the integration region first with a horizontal strip, extending from $t'-t$ to t' , and then moving the strip from $t' = 0$ to $t' = t$.

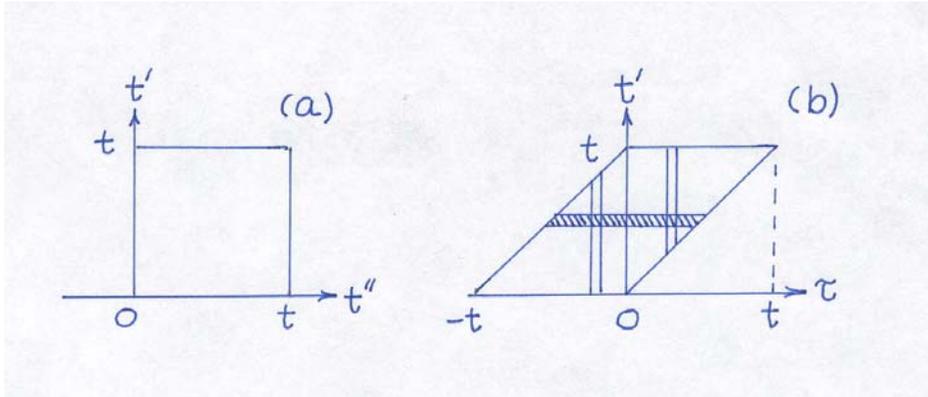


Fig. 3.1. The region of integration for the double integral in (3.2), (a), and for the double integral in (3.4), (b). Exchanging the order of integration, as (3.5), means that one integrates first over vertical strips as opposed to integrating over horizontal strips originally.

Suppose we interchange the order of integration, and use instead a vertical strip which extends from $t' = 0$ to $t' = t + \tau$ when $-t < \tau < 0$, and another strip extending from $t' = \tau$ to $t' = t$ when $0 < \tau < t$. Thus,

$$\langle \Delta^2 r(t) \rangle = \int_{-t}^0 d\tau \alpha(\tau) \int_0^{t+\tau} dt' + \int_0^t d\tau \alpha(\tau) \int_{\tau}^t dt' \quad (3.5)$$

$\downarrow \qquad \qquad \downarrow$
 $t + \tau \qquad \qquad t - \tau$

In the first integral we can change τ to $-\tau$, and make use of the fact that $\alpha(\tau) = \alpha(-\tau)$, a property of classical time correlation functions. Then the two integrals are the same, so that (3.5) becomes

$$\langle [\underline{R}(t) - \underline{R}(0)]^2 \rangle = 2 \int_0^t dt' (t - t') \langle \underline{v}(t') \cdot \underline{v}(0) \rangle$$

$$= 6v_o^2 \int_0^t dt'(t-t')\psi(t') \quad (3.6)$$

where $\psi(t) = \langle \underline{v}(t) \cdot \underline{v}(0) \rangle / \langle \underline{v}(0) \cdot \underline{v}(0) \rangle$ is the normalized velocity autocorrelation function, $\langle \underline{v}(0) \cdot \underline{v}(0) \rangle = 3v_o^2$, and $v_o^2 = k_B T / m$, v_o being the thermal speed.

Eq.(3.6) is the desired relation between the mean squared displacement and the velocity autocorrelation function. We know that the self-diffusion coefficient D is related to the mean squared displacement according to

$$D = \frac{1}{6} \left[\frac{\langle [R(t) - R(0)]^2 \rangle}{t} \right]_{t \rightarrow \infty} \quad (3.7)$$

Then combining this with (3.6) we obtain

$$D = v_o^2 \int_0^{\infty} dt \psi(t) \quad (3.8)$$

Eq.(3.8) is one of the Green-Kubo formulas for the transport coefficient of a fluid. It relates a transport coefficient to a time integral of a time correlation function, in this the relation is between the self-diffusion coefficient and the velocity autocorrelation function. Analogous relations exist for the shear viscosity η and the thermal conductivity λ , and the corresponding time correlation functions, the transverse component of the stress-stress correlation and the heat flux correlation function, respectively.

The significance of the Green-Kubo formulas is that one can use them to calculate the transport coefficients which describe the relaxation or dissipation response of a fluid (to an external perturbation) in terms of time correlation functions which describe the thermal fluctuations in the fluid at equilibrium. This connection between the dissipation in the fluid out of equilibrium and the fluctuations in the fluid at equilibrium is a general feature of linear response theory in statistical mechanics; it is expressed by the so-called fluctuation-dissipation theorem. One should keep in mind that this equivalence holds only in the linear response regime, meaning that the perturbation to the fluid is sufficiently small that one need only to consider the first term in the deviation from equilibrium, the linear response.

Just as it was instructive in Lec 2 to examine how the mean squared displacement function $\langle \Delta^2 r(t) \rangle$ varies from one idealized system to another, it is also helpful to our understanding of atomic motions in physical systems to see the behavior of $\psi(t)$ for idealized systems. Fig. 3.2 shows the typical behavior for an ideal gas, a dense gas, a liquid and a solid. Since all collisions are neglected in the ideal gas model, the velocity autocorrelation function does not change from its initial value. As we increase the gas pressure or density, collisional effects become important, so $\psi(t)$ starts to decrease with

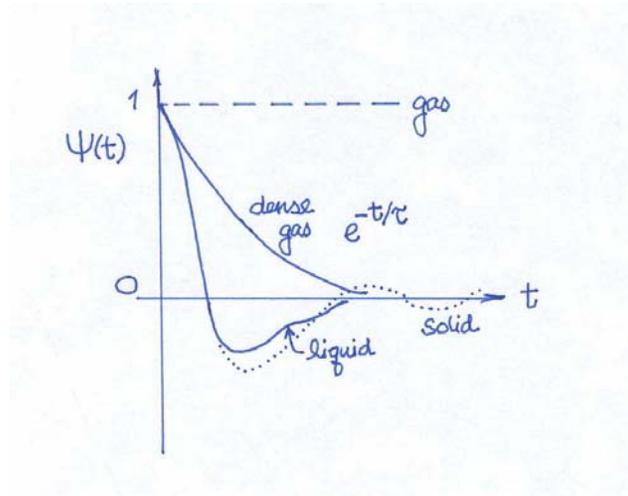


Fig. 3.2. The velocity autocorrelation function for an ideal gas, a dense gas, a liquid, and a solid. Compare these behavior with those of the mean squared displacement shown in Fig. 2.2.

time. For a dense gas there will be many collisions during the time interval shown in the sketch, the decay is then expected to be an exponential with a characteristic relaxation time τ . This is what is expected for the Brownian motion model. As we approach liquid density, the molecules are very tightly packed, the density of a liquid is only a few percent larger than that of the corresponding solid. This means that a molecule in a liquid environment will be in continuous interaction with its near neighbors, the forces exerted by these neighbors are sufficiently strong to keep the molecule rattling around in a local region - as if the neighbors are forming a cage. Because of the large fluctuations in a liquid, such cages have a rather short life time, so after a while the trapped molecule is able to diffuse away. In terms of $\psi(t)$ the cage effect is revealed by $\psi(t)$ becoming negative during a certain interval, typically picoseconds for a simple liquid. As can be seen in Fig. 3.2, the effect is also present in the solid.

A comparison of Fig. 3.2 with the mean squared displacement behavior given in Fig. 2.2 should reinforce our physical intuition of the dynamics of molecules in the three states of matter. Since the diffusion coefficient is given by the time integral (3.8), or the area under the curve of $\psi(t)$, we see that the infinite diffusion coefficient previously noted for the ideal gas based on (2.9), or Fig. 2.2, now shows up as a diverging integral in (3.8), or a non-decaying $\psi(t)$. As the system becomes more dense, $\psi(t)$ decreases faster in time because of more frequent collisions. This has the effect of giving a smaller D . In the case of a solid, the greatly reduced D means that the cancellation between the positive and negative regions of $\psi(t)$ is nearly complete. All these features are simple and rather intuitive. The student should keep them in mind as we proceed to consider other ways of describing dynamical systems, from the point of view of fundamental concepts as well as methods of quantitative calculations.