

22.103 Microscopic Theory of Transport (Fall 2003)
Lecture 2 (9/10/03)

Diffusion and the Mean Square Displacement

References --

Boon and Yip, Chap.2.

McQuarrie, Chap. 16.

Bird, Stewart, Lightfoot, Chap 16.

We begin with the simplest transport process, that of mass or particle diffusion. The basic quantity in this discussion is the self-diffusion coefficient D which is a material constant usually introduced in a phenomenological expression called the Fick's law,

$$\underline{J} = -D\underline{\nabla}n \quad (2.1)$$

where \underline{J} is the particle current, and n is the particle density (or concentration). In other words, D is the proportionality constant between a current (or flux) and a gradient of a density. A similar relation may be written between the momentum flux and the velocity gradient, in which case the constant is the viscosity η (sometimes the symbol μ is used), or between the heat current and the temperature gradient, in which case the constant is the thermal conductivity κ (sometimes denoted as λ).

Fick's law is useful because by invoking it we convert the continuity equation into a time-dependent diffusion equation. This is fine if what we want to do is solve the diffusion equation subject to an initial condition and appropriate boundary condition (we will do this later). On the other hand, (2.1) tells us nothing about what is D (how to find it), how does D depend on the motions of the molecules that are undergoing diffusion, or how does D vary with the state of the system.

Consider a simple fluid (only one type of molecule) in equilibrium at some pressure P and temperature T . One can ascribe to this system a diffusion coefficient D , which is a function of P and T . Usually, P is replaced by the fluid number density n or the mass density ρ . For now we will not be concerned about the density and temperature dependence of D ; it should be understood that later D really means $D(\rho, T)$.

For now we focus on the relation between D and the atomic motions of the particles in the fluid. If we know D , what information does that give about the motions, and vice versa? Another question is how can we calculate D , i.e., what expression can we use and what information about the fluid do we need for such a calculation? Asking such questions means that we are starting to think about *diffusion as a transport phenomenon taking place on the molecular level*. Suppose we imagine we can watch all the molecules moving around, and we have the ability, in principle, of following the trajectory of any single molecule that we pick. Since all the molecules are identical, the trajectory of any

zzmolecule, statistically, has the same importance as any other molecule. It then follows that all the molecules must contribute equally to the estimation of the self-diffusion coefficient. (In a one-component fluid the diffusion process is called *self-diffusion*, in contrast to *mutual* diffusion in a multicomponent system. In the latter one keeps of the particle species as diffusion takes place.)

There are two ways of defining the diffusion coefficient D which are more useful than (2.1) for understanding diffusion on a molecular level. The goal of this and the next lecture is to introduce them by explaining how they come about. We first define the mean square displacement function,

$$\langle \Delta^2 r(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle [\underline{R}_i(t) - \underline{R}_i(0)]^2 \rangle \quad (2.2)$$

where $\underline{R}_i(t)$ is the position of molecule i in the fluid, which we take to be a finite system of volume V containing N identical molecules, see Fig. 2.1. The angular brackets $\langle \rangle$ in

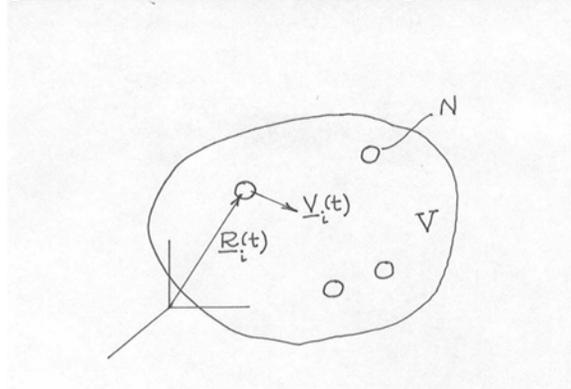


Fig. 2.1. A system of N particles and volume V . The instantaneous (at time t) position and velocity of the i th particle are denoted as $\underline{R}_i(t)$ and velocity $\underline{V}_i(t)$.

(2.2) indicate an average over initial (at time $t = 0$) positions and velocities of the molecules. Notice that the quantity inside the angular brackets is the square of the displacement that molecule has undergone during a time interval t . Summing over all the molecules and dividing by the number of molecules gives the mean value, so (2.2) is the mean square displacement of the molecules in the fluid over a period of time t . The angular brackets in (2.2) denotes what is known as a *thermal or ensemble* average. It means that if we were doing an actual measurement of the mean square displacement by starting the molecules off in an initial distribution of positions of the molecules, with each having some initial velocity (according to the temperature of the fluid), we should repeat the measurement, each time choosing for initial positions and velocities of the particles a distribution drawn from an ensemble of distributions. After repeating a number of these measurements we then average the results. In each measurement, the time interval over which we let molecule i wander around in the fluid is the same, and what we record is the square of the vector displacement of molecule i from its initial position $\underline{R}_i(0)$ (when we start over again with a different initial distribution, $\underline{R}_i(0)$ will be different from the preceding run).

To make clear what is involved in the thermal average, we take any dynamical variable $A(t)$, which is a function of the particle positions at time t , and define

$$\langle A(t) \rangle = \int d^3R^N(0) d^3V^N(0) f_{eq}(\underline{R}^N(0), \underline{V}^N(0)) A(\underline{R}^N(t)) \quad (2.3)$$

In (2.3) $\underline{R}^N(t)$ stands for a collection of positions, $\underline{R}_1(t), \underline{R}_2(t), \dots, \underline{R}_N(t)$, all at time t . The integral, however, is taken over the initial positions and velocities, $\underline{R}^N(0)$ and $\underline{V}^N(0)$, with f_{eq} being an appropriate ensemble distribution. Typically we will take f_{eq} to be the canonical distribution in thermodynamics, then

$$f_{eq}(\underline{R}^N, \underline{V}^N) = \frac{e^{-U(\underline{R}^N)/k_B T}}{Z} f_M(\underline{V}^N) \quad (2.4)$$

where U is the system potential energy, k_B the Boltzmann's constant, T the system temperature, and Z is the partition function,

$$Z = \int d^3R^N e^{-U(\underline{R}^N)/k_B T} \quad (2.5)$$

Moreover, in (2.4) f_M is the normalized Maxwell distribution of velocities. Except for the velocity distribution we will manipulate f_{eq} only formally.

Since the thermal average is involved in the mean square displacement function, the quantity of our interest in this lecture, it is instructive to see how one can perform the indicated integration. To do the integral in (2.3) means we need to know what is the relation between the particle positions and velocities at the initial time $t = 0$ and their positions at time t later. This relation can be very simple, as in the case of an ideal gas where all particles move in straight lines,

$$\underline{R}_i(t) = \underline{R}_i(0) + \underline{V}_i(0)t \quad (2.4)$$

Or it can be very complicated, as in the case of a liquid where one can only write it down formally (which is not that useful for seeing what is going on). Let us now work out the mean square displacement function for the ideal gas. Inserting (2.4) into (2.2) we get

$$\begin{aligned} \langle \Delta^2 r(t) \rangle &= \langle \underline{V}(0) \cdot \underline{V}(0) \rangle t^2 \\ &= 3v_o^2 t^2 \end{aligned} \quad (2.5)$$

with $v_o^2 = k_B T / M$, v_o is known as the thermal speed. This is a simple and exact result which says that the mean square displacement of a gas in which there are no collisions grows quadratically in time. Since any collision will have the effect of slowing down the

molecules, we can expect that when collision effects are taken into account $\langle \Delta^2 r(t) \rangle$ will not grow as quickly at t^2 .

It is instructive to compare the behavior of $\langle \Delta^2 r(t) \rangle$ for three idealized systems, one of them being the ideal gas we have just discussed. The other two are a simple liquid and a solid. These three systems represent the three states of matter that we usually encounter, so it is important to see how $\langle \Delta^2 r(t) \rangle$ varies in each of these idealized systems.

Knowing the behavior in these models can help us understand what kinds of atomic motions take place in a particular physical situation. We will defer the derivation of $\langle \Delta^2 r(t) \rangle$ for a liquid and a solid to a later occasion. For now, we show in Fig.2.2 the characteristic behavior of the three systems.

One can see that at short times $\langle \Delta^2 r(t) \rangle$ increases like t^2 for all three systems. This can be seen by the following argument. For any system we can make a Taylor series expansion of the displacement of a particle by writing

$$\underline{R}(t) = \underline{R}(0) + \underline{\dot{R}}(0)t + \frac{1}{2}\underline{\ddot{R}}(0)t^2 + O(t^3) \quad (2.6)$$

Inserting this into (2.2) we get a time expansion of $\langle \Delta^2 r(t) \rangle$,

$$\langle \Delta^2 r(t) \rangle = 3v_0^2 t^2 + O(t^3) \quad (2.7)$$

This says that for any system, $\langle \Delta^2 r(t) \rangle$ behaves initially like an ideal gas up to the second order term in t . We can understand this as just the inertial part of the motion of any physical system. We see in Fig. 2 that the curves for the liquid and the solid rather quickly deviate from the t^2 behavior once the dynamics of the system set in. One way to think about the dynamics is through particle collisions with their neighbors, this is quite intuitive for a liquid environment. For the solid, one can think about restoring forces on each atom provided by the crystal binding. This is what holds each atom in its equilibrium position in the crystal lattice. In a simplified way we can say that atomic motions in a liquid is like Brownian motion, a particle undergoes continuous collisions with its neighbors as it diffuses through the liquid. On the other hand, a particle in the solid cannot diffuse very far from its lattice site, its motions are vibratory rather than diffusive. This difference is seen in Fig. 2. At long times, the diffusive behavior in the liquid gives rise to a linear time dependence in $\langle \Delta^2 r(t) \rangle$. In contrast, $\langle \Delta^2 r(t) \rangle$ reaches a plateau value because it cannot grow indefinitely, no matter how long one waits.

The connection between $\langle \Delta^2 r(t) \rangle$ and the conventional picture of diffusion lies in the behavior of $\langle \Delta^2 r(t) \rangle$ at long times. Fig. 2.2 shows that for times long compared to some typical collision or correlation time t_c (we will come back to make this more precisely later), $\langle \Delta^2 r(t) \rangle$ increases linearly with time for a liquid. *This linear time*

dependence is what is characteristic of diffusive motion. In this case the slope of $\langle \Delta^2 r(t) \rangle$ is proportional to the diffusion coefficient D ,

$$\langle \Delta^2 r(t) \rangle \sim 6Dt \quad t \gg t_c \quad (2.8)$$

Since $\langle \Delta^2 r(t) \rangle$ goes to a plateau value at long times in a solid, D is effectively zero for a solid according to the definition,

$$D = \left[\frac{1}{6t} \langle \Delta^2 r(t) \rangle \right]_{t \gg t_c} \quad (2.9)$$

Eq.(2.9) also shows that for an ideal gas D would have infinite diffusion coefficient. In reality, we know that there is diffusion in the solid, although $D(\text{solid})$ is smaller than $D(\text{liquid})$ typically by several orders of magnitude, and $D(\text{gas})$ is large but finite at any nonzero pressure.

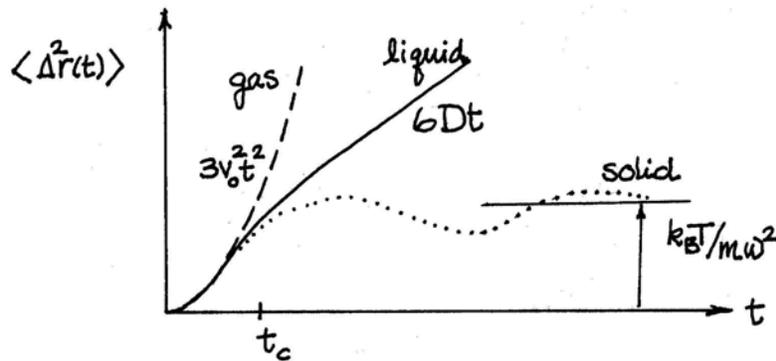


Fig.2.2. Mean squared displacement of three idealized systems, an ideal gas (no intermolecular collisions), a liquid, and a solid. The characteristic features of $\langle \Delta^2 r(t) \rangle$ are a quadratic time dependence for all times for the gas, with $v_o^2 = k_B T / m$, where T is the temperature and m the particle mass, a long-time linear behavior with a slope given by $6D$, where D is diffusion coefficient, for the liquid, and a long-time plateau value of $k_B T / m \omega^2$, where ω the characteristic vibrational frequency, for the solid.

In the next lecture we will show that $\langle \Delta^2 r(t) \rangle$ can be expressed in terms of the velocity autocorrelation function of the system. Combining this with (2.8) we then obtain a relation between the diffusion coefficient D and the velocity autocorrelation function. This relation turns out to be quite a general result of statistical mechanics and is known as the Green-Kubo expression for the diffusion coefficient. Unlike the Fick's law (2.1), the Green-Kubo relation, or (2.8), can be used to directly calculate the diffusion coefficient.