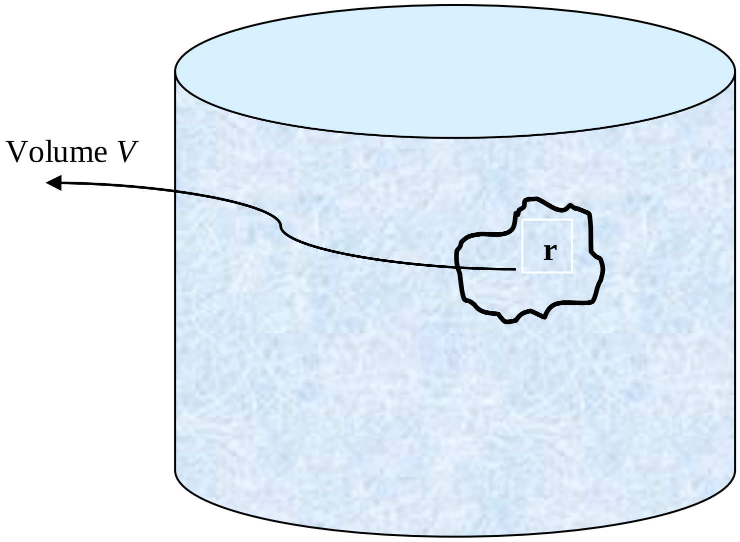
IP326. Lecture 12. Thursday, Feb. 7, 2019

● An alternative derivation of the self-diffusion coefficient

We showed earlier how an expression for the diffusion coefficient D (or the self-diffusion coefficient D_s) could be obtained as a time-correlation function using the general formalism of linear response theory. But in using this approach, we had to resort to a certain amount of hand-waving to get to the final result. In this section, we'll adopt a different, more rigorous method to derive the same result. Such methods are generally necessary when the effects of the external field that cause a response in the system are not readily incorporated into the Hamiltonian. This usually happens when the force (i.e., the perturbation) is not mechanical in origin but thermal. Thermal and other non-mechanical perturbations (such as temperature differences or concentration gradients) are what lead to transport processes like diffusion, viscous flow and heat conduction. Although we did find a way to treat diffusion within the Hamiltonian formalism (and will subsequently find a similar way to treat viscosity), the present formalism is more general.

Physically, diffusion is a process of mass (i.e., particle) redistribution, so consider what happens to some small volume of fluid V inside a much larger container of the fluid, as depicted in the figure below:



The surface enclosing V is a vector $\mathbf{S}$ centered around a point $\mathbf{r}$. The surface area is a vector because perpendicular straight lines pointing in different directions can be drawn to each point on it, giving the surface a definite *sense* or directionality.

In the vicinity of each point $\mathbf{r}$ in the volume V, and at some instant of time t, assume that there is some density of particles $\rho(\mathbf{r},t)$. In microscopic terms, what we mean by $\rho(\mathbf{r},t)$ is the following:

$$\rho(\mathbf{r},t) = \sum_{i=i}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{1}$$

where $\mathbf{r}_i(t)$ is the location at time t of the ith particle (out of a total of N), and the delta function is the continuum analogue of the Kronecker delta, and so acts like a counting device, registering a value (infinity, strictly speaking) whenever $\mathbf{r}_i(t)$ is within the volume V, and returning a value 0 when it is not. For the purposes of the present calculation, we won't need to refer to this definition again, but it's worth bearing in mind because it's the definition that will be used in talking about density correlation functions later on.

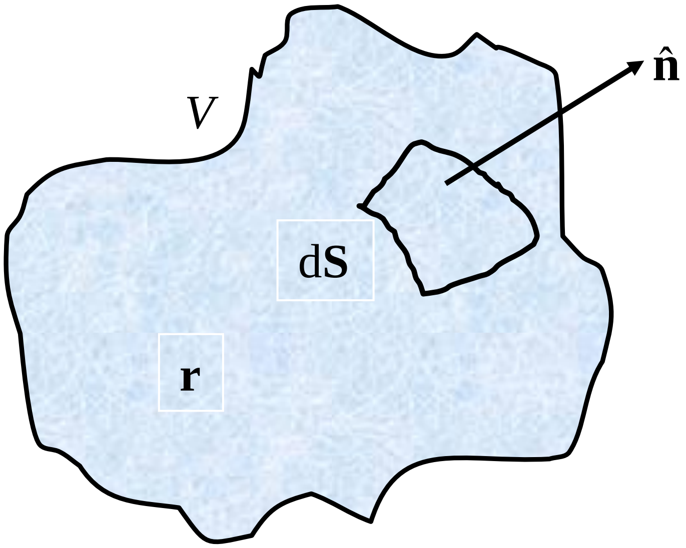
Knowing the density of particles at $\mathbf{r}$, we can determine the total mass M of particles in V at time t from the formula

$$M(t) = m\int_V d\mathbf{r}\rho(\mathbf{r},t) \tag{2}$$

where m is the mass of each particle, and the subscript V on the integral denotes the restriction of the integration variable $d\mathbf{r}$ to the confines of the given volume. The change of $M(t)$ with time is therefore given by

$$\frac{dM(t)}{dt} = m\int_V d\mathbf{r}\,\frac{\partial\rho(\mathbf{r},t)}{\partial t} \tag{3}$$

This change in mass is the result of the flow of particles into and out of V through the surface $\mathbf{S}$, an infinitesimal element of which is shown below, along with the unit normal $\hat{\mathbf{n}}$ that indicates its orientation.



The mass of fluid around **r** in the volume V can be imagined to move with a velocity $\mathbf{u}(\mathbf{r},t)$ at time t, such that the rate of flow of mass density is $m\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$. This flow is in the direction of the vector **u**. We'd like to know how much of this flow lies along the normal at $d\mathbf{S}$; the answer is $-md\mathbf{S}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$. The negative sign is introduced to indicate that the flow *exits* V when $\hat{\mathbf{n}}\cdot\mathbf{u}>0$ (thereby *decreasing* the number of particles in *V*) and that it *enters* V when $\hat{\mathbf{n}}\cdot\mathbf{u}<0$ (thereby *increasing* the number of particles in *V*.) The integral of $-md\mathbf{S}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$ over the entire surface area is the change in the total mass with time. That is,

$$\frac{dM(t)}{dt}=-m\int_{\mathrm{S}}d\mathbf{S}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{4}$$

Equating (3) and (4), we get

$$\int_V d\mathbf{r}\,\frac{\partial\rho(\mathbf{r},t)}{\partial t}=-\int_{\mathrm{S}}d\mathbf{S}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{5}$$

The integral on the RHS can be converted into an integral over **r** using Gauss's divergence theorem, which leads to

$$\int_V d\mathbf{r}\left[\frac{\partial\rho(\mathbf{r},t)}{\partial t}+\nabla_{\mathbf{r}}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\right]=0$$

Since this relation must hold for integrals over any arbitrary volume, it follows that

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=-\nabla_{\mathbf{r}}\cdot\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{6}$$

Equation (6) is simply the mathematical statement of the conservation of mass: any change in time of the mass of material in *V* is the result of the flow of material into or out of *V*. This relation is exact.

It's possible to derive a more useful, but approximate, relation for the change in mass density with time if we invoke Fick's law, which states that mass flows result from concentration gradients, and are directly proportional to them when the gradients are not too steep. According to Fick's law then,

$$\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)=-D\nabla_{\mathbf{r}}\cdot\rho(\mathbf{r},t) \tag{7}$$

where *D* is the diffusion coefficient, the negative sign indicating that the flow proceeds from high to low concentrations. Substitution of (7) into (6) produces the diffusion equation, given by

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = D\nabla_{\mathbf{r}}^2 \rho(\mathbf{r},t) \tag{8}$$

Equation (8), although referring to the time evolution of the number density $\rho(\mathbf{r},t)$, can also be re-interpreted as an equation for the probability $G(\mathbf{r},t)d\mathbf{r}$ that a particle starting out from the point $\mathbf{r}=0$ at time 0 is located between $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$ at time *t*. Writing this equation out explicitly, we have

$$\frac{\partial G(\mathbf{r},t)}{\partial t} = D_s \nabla_{\mathbf{r}}^2 G(\mathbf{r},t) \tag{9}$$

the constant D_s now being identified with the *self*-diffusion coefficient.

- Expressing the self-diffusion coefficient as a time correlation function

Starting from (9), we can relate D_s to measurable properties of the system. We proceed by first rewriting (9) in terms of Fourier transforms, the Fourier transform $\tilde{f}(\mathbf{k})$ of a function $f(\mathbf{r})$ being defined as $\tilde{f}(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})$. When we apply this transform to (9), the result is

$$\frac{\partial \tilde{G}(\mathbf{k},t)}{\partial t} = D_s \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla_{\mathbf{r}}^2 G(\mathbf{r},t)$$

which, after integration by parts twice becomes

$$\frac{\partial \tilde{G}(\mathbf{k},t)}{\partial t} = -D_s k^2 \tilde{G}(\mathbf{k},t) \tag{10}$$

In arriving at this expression we've thrown away the surface terms, which involve the function $G(\mathbf{r},t)$ or its first derivative with respect to $\mathbf{r}$ evaluated at points infinitely far away from $\mathbf{r}=0$; since these terms are probabilities, their neglect is justified because we can assume that particles are unlikely to be found infinitely far away from their starting location in a finite period of time. Furthermore, given our initial condition on the particle position, which mathematically can be expressed as $G(\mathbf{r},0)=\delta(\mathbf{r})$, it's easy to show that the corresponding Fourier space initial condition is $\tilde{G}(\mathbf{k},0)=1$. The solution of Eq. (10) is then immediately seen to be

$$\tilde{G}(\mathbf{k},t) = \exp(-k^2 D_s t) \tag{11}$$

from which we have the identity

$$-2D_s t = \frac{\partial^2}{\partial k^2}\tilde{G}(\mathbf{k},t)\Big|_{k=0} \tag{12}$$

The definition of $\tilde{G}(\mathbf{k},t)$ as the integral $\int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}G(\mathbf{r},t)$ means that the right-hand side of Eq. (12) is given by

$$\frac{\partial^2}{\partial k^2}\tilde{G}(\mathbf{k},t)\Big|_{k=0} = \int d\mathbf{r}(ir\cos\theta)^2 G(\mathbf{r},t) \tag{13}$$

where θ is the angle between **k** and **r**. A transformation of the variables in the above integral to spherical polar coordinates, with the *z*-axis in the Cartesian frame taken to lie along the direction of **k**, leads to the relation

$$\frac{\partial^2}{\partial k^2}\tilde{G}(\mathbf{k},t)\Big|_{k=0} = -\int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, r^2 \cos^2\theta G(\mathbf{r},t) \tag{14}$$

The integral over ϕ in Eq. (14) produces a factor of 2π, while the integral over θ , which is evaluated using the result (show this) $\int dx \sin x \cos^2 x = -(1/3)\cos^3 x$, produces a factor of 2/3. So (14) becomes

$$\frac{\partial^2}{\partial k^2}\tilde{G}(\mathbf{k},t)\Big|_{k=0} = -\frac{4\pi}{3}\int_0^\infty dr r^4 G(\mathbf{r},t) \tag{15}$$

If $G(\mathbf{r},t)$ is assumed to be isotropic (meaning there's no directional preference for the location of the particle, which is reasonable), Eq. (15) can be rewritten as

$$\frac{\partial^2}{\partial k^2}\tilde{G}(\mathbf{k},t)\Big|_{k=0} = -\frac{1}{3}\int d\mathbf{r}\, r^2 G(r,t) \tag{16}$$

The integral on the right hand side is nothing but the definition of the average of the particle's square displacement, and this result, along with Eq. (12), implies that

$$\left\langle \mathbf{r}^2(t)\right\rangle = 6D_s t \tag{17}$$

One of the ways self-diffusion constants are estimated is through Eq. (17), which can be rearranged to $D_s = \left\langle \mathbf{r}^2(t)\right\rangle / 6t$. Reasonable estimates of D_s can be obtained from experiments or simulations of particle motion by taking the long-time limit of the ratio of the square of the distance travelled by the particle to the duration of its travel time. (The long time limit ensures that transient behavior has died out, and that the system is in steady, time-independent conditions.)

Equation (17) also provides a way of expressing D_s as a time correlation function. To make the connection, one recognizes that a particle's displacement **r**(t) in the interval t is related to its velocity **v** as

$$\mathbf{r}(t) = \int_0^t dt'\mathbf{v}(t')$$

Therefore,

$$\left\langle \mathbf{r}^2(t) \right\rangle = \int_0^t dt_1 \int_0^t dt_2 \left\langle \mathbf{v}(t_1) \cdot \mathbf{v}(t_2) \right\rangle$$

$$= \int_0^t dt_1 \int_0^t dt_2 \left\langle \mathbf{v}(t_1 - t_2) \cdot \mathbf{v}(0) \right\rangle \qquad \text{(by the stationarity of TCFs)}$$

$$= \int_0^t dt_1 \int_0^{t_1} dt_2 \left\langle \mathbf{v}(t_1 - t_2) \cdot \mathbf{v}(0) \right\rangle + \int_0^t dt_1 \int_{t_1}^t dt_2 \left\langle \mathbf{v}(t_1 - t_2) \cdot \mathbf{v}(0) \right\rangle$$

$$\equiv I_1 + I_2 \tag{18}$$

Consider the evaluation of I_1. It is first simplified by changing variables from t_2 to τ, where $\tau = -t_2 + t_1$; this leads to

$$I_1 = \int_0^t dt_1 \int_0^{t_1} d\tau \left\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \right\rangle$$

Then by introducing a step function into the integrand (a step function $\theta(z)$ being a function with the property that $\theta(z) = 1$ if $z > 0$ and $\theta(z) = 0$ if $z < 0$), it is rewritten as

$$I_1 = \int_0^t dt_1 \int_0^t d\tau\, \theta(t_1 - \tau) \left\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \right\rangle$$

$$= \int_0^t d\tau \int_0^t dt_1 \theta(t_1 - \tau) \left\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \right\rangle$$

$$= \int_0^t d\tau \int_\tau^t dt_1 \left\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \right\rangle = \int_0^t d\tau\, (t - \tau) \left\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \right\rangle$$

$$= t\int_0^t d\tau (1-\tau/t)\langle \mathbf{v}(\tau)\cdot\mathbf{v}(0)\rangle \tag{19}$$

I_2 is treated similarly. Using the time reversal symmetry of time auto-correlation functions, it is first written as

$$I_2 = \int_0^t dt_1 \int_0^t dt_2 \theta(t_2 - t_1)\langle \mathbf{v}(t_2 - t_1)\cdot\mathbf{v}(0)\rangle$$

$$= \int_0^t dt_2 \int_0^t dt_1 \theta(t_2 - t_1)\langle \mathbf{v}(t_2 - t_1)\cdot\mathbf{v}(0)\rangle$$

$$= \int_0^t dt_2 \int_0^{t_2} dt_1 \langle \mathbf{v}(t_2 - t_1)\cdot\mathbf{v}(0)\rangle$$

which, by relabeling t_1 as t_2 and t_2 as t_1, is seen to be identical to I_1. Thus, from (18), $\langle \mathbf{r}^2(t)\rangle = 2I_1$, and from (17) and (19),

$$D_s = \frac{1}{3}\int_0^t d\tau (1-\tau/t)\langle \mathbf{v}(\tau)\cdot\mathbf{v}(0)\rangle$$

$$\approx \frac{1}{3}\int_0^\infty d\tau \langle \mathbf{v}(\tau)\cdot\mathbf{v}(0)\rangle \tag{20}$$

The last line follows from the assumption that the velocity auto-correlation decays quickly enough (in fact, in experiments and simulations it typically does so on the picosecond timescale) that no error is introduced by extending the upper limit *t* in the first integral to ∞ and neglecting the factor of τ/t.

Equation (20) is identical to the expression we'd derived for D_s from linear response theory.