IP326. Lecture 13. Thursday, Feb. 14, 2019

● <u>The shear viscosity</u> (Cont.'d)

It was argued earlier that the application of a shear force to a system in equilibrium creates an asymmetry in its internal pressure. So it is this *anisotropic* pressure that is the manifestation of the system's response to the external perturbation, and that is, therefore, the quantity analogous to the dynamical variable *A* in the relation $\chi(t) \propto \left\langle A(t)\dot{B} \right\rangle$ for the response function $\chi(t)$. (We've already determined the structure of the variable *B*.) To find a suitable structure for *A*, recall that we had asserted that the usual *isotropic* pressure *P* that appears in thermodynamics could be expressed as the following equilibrium ensemble average:

$$P = \frac{1}{3V}\left\langle \sum_{i=1}^{N}\left(\frac{\mathbf{p}_i^2}{m} + \mathbf{q}_i \cdot \mathbf{F}_i \right) \right\rangle \tag{1}$$

Before writing down the generalization of this result for anisotropic systems, we'll first show how Eq. (1) is derived.

Under constant temperature conditions, *P* can be found from the relations

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T\left(\frac{\partial}{\partial V}\ln Q(T,V,N)\right)_{T,N}$$

$$= \frac{k_B T}{Q}\left(\frac{\partial Q}{\partial V}\right)_{T,N} \tag{2}$$

Here *F* is the Helmholtz free energy, *V* is the volume and *Q* is the canonical partition function, which is given by

$$Q = C_N \int d\Gamma \exp(-\beta H_0(\Gamma)) \tag{3}$$

where $C_N = 1/h^{3N}N!$ In order to differentiate *Q* with respect to *V*, we introduced the change of variable $q_{i\alpha} = V^{1/3} r_{i\alpha}$, $\alpha = x, y, z$ in (3), which caused the transformed phase space volume element to be multiplied by a factor of V^N. But we also proved that phase space extension is conserved, and the only way that can happen after the change from **q** to **r** variables is if this V^N factor is cancelled by a compensating factor of V^{-N}. This is easily accomplished if we now introduce another change of variable: $p_{i\alpha} = V^{-1/3}\pi_{i\alpha}$, $\alpha = x, y, z$. Once we do this, the partition function *Q* becomes

$$Q = C_N \left(\prod_{i=1}^{N} \int d\boldsymbol{\pi}_i \int d\mathbf{r}_i \right) \exp\left[-\beta \left\{ \frac{V^{-2/3}}{2m} \sum_{i=1}^{N} \boldsymbol{\pi}_i^2 + U(V^{1/3}\mathbf{r}_1, \ldots, V^{1/3}\mathbf{r}_N) \right\} \right] \tag{4}$$

Therefore, after differentiating (4) with respect to *V*, we find that

$$P = \frac{k_B T}{Q} C_N \left(\prod_{i=1}^{N} \int d\boldsymbol{\pi}_i \int d\mathbf{r}_i \right) \exp\left[-\beta \left\{ \frac{V^{-2/3}}{2m} \sum_{i=1}^{N} \boldsymbol{\pi}_i^2 + U(V^{1/3}\mathbf{r}_1, \ldots, V^{1/3}\mathbf{r}_N) \right\} \right] \times$$

$$\times \left[\frac{2\beta}{3} \frac{V^{-5/3}}{2m} \sum_{i=1}^{N} \boldsymbol{\pi}_i^2 - \beta \left\{ \frac{\partial U}{\partial V^{1/3}\mathbf{r}_1} \cdot \frac{1}{3} V^{-2/3}\mathbf{r}_1 + \cdots + \frac{\partial U}{\partial V^{1/3}\mathbf{r}_N} \cdot \frac{1}{3} V^{-2/3}\mathbf{r}_N \right\} \right] \tag{5}$$

If we now transform Eq. (5) back to the original variables, we get

$$P = \frac{k_B T}{Q} C_N \left(\prod_{i=1}^{N} \int d\mathbf{p}_i \int d\mathbf{q}_i \right) e^{-\beta H_0(\{\mathbf{p}_i\},\{\mathbf{q}_i\})} \left[\frac{\beta}{3V} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m} - \frac{\beta}{3V} \sum_{i=1}^{N} \mathbf{q}_i \cdot \frac{\partial U}{\partial \mathbf{q}_i} \right]$$

$$= \frac{1}{3V} \left\langle \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{m} + \mathbf{q}_i \cdot \mathbf{F}_i \right) \right\rangle, \tag{6}$$

which is the microscopic form of the isotropic pressure. The structure of this function suggests that a quantity analogous to pressure and applicable to anisotropic systems can be defined as follows:

$$P_{\alpha\beta} = \frac{1}{V} \left\langle \sum_{i=1}^{N} \left(\frac{1}{m} (\mathbf{p}_i \cdot \hat{e}_\alpha)(\mathbf{p}_i \cdot \hat{e}_\beta) + (\mathbf{q}_i \cdot \hat{e}_\alpha)(\mathbf{F}_i \cdot \hat{e}_\beta) \right) \right\rangle, \quad \alpha, \beta = x, y, z \tag{7}$$

This is actually just one element of a 3×3 matrix, so in fact this anisotropic pressure is a tensor, which from now on we'll refer to as the pressure tensor, and denote **P**. The ordinary pressure *P* is just the isotropic part of **P**, specifically

$$P = \frac{1}{3} \sum_{\alpha = x,y,z} P_{\alpha\alpha} \tag{8}$$

In the specific case of a shear force, where the shear is applied along the *x* direction, the induced flow is along the *y* direction, and the *xy* component of **P** thus becomes non-zero. It is this component that is observed to be proportional to the velocity gradient, the proportionality constant being the shear viscosity. That is,

$$P_{xy} = -\eta \frac{\partial v_x}{\partial y} = -\eta\dot{\gamma}$$

So the shear viscosity can now be *defined* as

$$\eta = -\frac{1}{\dot{\gamma}} \lim_{t\to\infty} P_{xy} = -\frac{1}{\dot{\gamma}} \lim_{t\to\infty} \left\langle p_{xy}(t) \right\rangle \tag{9}$$

where $p_{\alpha\beta}(t) \equiv p_{\alpha\beta}(\Gamma, t)$ is the analogue of the variable *A*(*t*), and the $t \to \infty$ limit is introduced to ensure that the system has had enough time to eliminate transient behavior and to settle into a steady state condition.

Now we had shown earlier that

$$\dot{B}(\Gamma) = -\frac{1}{m} \sum_{i=1}^{N} p_{iy} \mathbf{p}_i \cdot \hat{e}_x - \sum_{i=1}^{N} q_{iy} \mathbf{F}_i \cdot \hat{e}_x$$

which can also be written as

$$\dot{B}(\Gamma) = -\sum_{i=1}^{N} \left[\frac{1}{m} (\mathbf{p}_i \cdot \hat{e}_y)(\mathbf{p}_i \cdot \hat{e}_x) + (\mathbf{q}_i \cdot \hat{e}_y)(\mathbf{F}_i \cdot \hat{e}_x) \right] \tag{10}$$

This quantity is therefore also related to the pressure tensor; specifically

$$\dot{B}(\Gamma) = -V p_{xy}(\Gamma)$$

So on the basis of our linear response formalism, we can write

$$\left\langle p_{xy}(t) \right\rangle = \left\langle p_{xy} \right\rangle_0 - \beta\dot{\gamma}V \int_0^t dt' \left\langle p_{xy}(t-t') p_{xy}(0) \right\rangle \tag{11}$$

But $\left\langle p_{xy} \right\rangle_0$ is 0 (show this!). Using these results in (9), along with the stationarity property of time correlation functions, we finally arrive at the following expression for the shear viscosity

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \left\langle p_{xy}(t) p_{xy} \right\rangle, \tag{12}$$

Formulas like (12) (and the analogous one for the self-diffusion coefficient *D*) are referred to as Green-Kubo relations.

● <u>Alternative derivation of the Green-Kubo relation for shear viscosity</u>

Equation (12) can also be derived along the lines of our derivation of the self-diffusion coefficient, which was based on an exact equation for the conservation of mass and an empirical relation for the density dependence of the mass current. In that particular case, it was a concentration gradient that caused the flow of mass. When a shear force is the external perturbation, the result is a *velocity* gradient, and this leads to a flow of momentum. What we'll do now is derive an expression for the rate of flow of this momentum. The approach we'll take is to again focus on an element of volume in the fluid of interest, account for all the ways momentum can pass into and out of it, and eventually end up with an equation for the conservation of momentum. We'll then simplify this equation using empirical information on the relation between the flux of momentum and a gradient in the velocity.

So consider an arbitrary element of volume V centered at the point $\mathbf{r}$. Let the mass density there be $m\rho(\mathbf{r},t)$. Assume that this mass has the velocity $\mathbf{u}(\mathbf{r},t)$; its momentum density, $\mathbf{g}(\mathbf{r},t)$, is then given by

$$\mathbf{g}(\mathbf{r},t) = m\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{13}$$

so the total momentum $\mathbf{G}(t)$ of the fluid in V is

$$\mathbf{G}(t) = m\int_V d\mathbf{r}\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) \tag{14}$$

The rate of change of this momentum is therefore

$$\frac{d\mathbf{G}(t)}{dt} = m\int_V d\mathbf{r}\frac{\partial}{\partial t}\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) = \int_V d\mathbf{r}\frac{\partial \mathbf{g}(\mathbf{r},t)}{\partial t} \tag{15}$$

There are two contributions to this momentum change: (i) a so-called *convective* contribution originating in the direct transport of $\mathbf{g}$ through the surface of V, and (ii) a contribution that comes from the forces exerted on the surface of V by the fluid lying outside it.

Turning first to the convective flow of momentum, consider an infinitesimal element of area $d\mathbf{S}$ on the surface of V. Since the fluid at $\mathbf{r}$ moves with the velocity $\mathbf{u}(\mathbf{r},t)$, the component of this velocity that flows *out* of V along the outward pointing normal at $d\mathbf{S}$ is $-d\mathbf{S}\cdot\mathbf{u}(\mathbf{r},t)$, so the rate of change of momentum density at $\mathbf{r}$ caused by fluid moving through $d\mathbf{S}$ with the velocity $\mathbf{u}(\mathbf{r},t)$ is $-[d\mathbf{S}\cdot\mathbf{u}(\mathbf{r},t)]\mathbf{g}(\mathbf{r},t)$. So the total rate of change of momentum originating in convection is

$$\left.\frac{d\mathbf{G}(t)}{dt}\right|_{conv} = -m\int_S [d\mathbf{S}\cdot\mathbf{u}(\mathbf{r},t)]\mathbf{u}(\mathbf{r},t)\rho(\mathbf{r},t)$$

$$= -m\int_S d\mathbf{S}\cdot[\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]\rho(\mathbf{r},t) \tag{16}$$

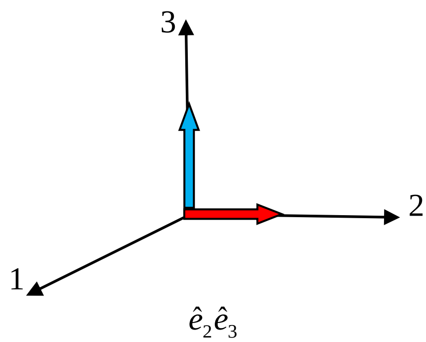
In arriving at the second equality in (16), we used the fact that there is a third way of multiplying vectors together called the direct product. To illustrate this operation, consider two vectors **A** and **B** in three-space; *by definition*, their direct (or dyadic) product is

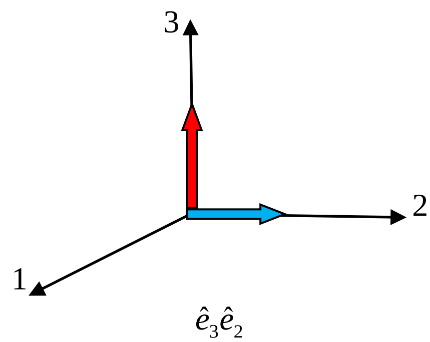
$$\mathbf{AB} = \begin{pmatrix} A_1B_1 & A_1B_2 & A_1B_3 \\ A_2B_1 & A_2B_2 & A_2B_3 \\ A_3B_1 & A_3B_2 & A_3B_3 \end{pmatrix} \tag{17}$$

where A_i and B_i, $i = 1, 2, 3$, are the components of **A** and **B** along the Cartesian axes labeled 1, 2 and 3. This definition of the direct product makes **AB** a tensor. Tensors, like vectors, can be expanded in terms of their components. So, for example, a tensor **T** with components T_{ij} can be written as

$$\mathbf{T} = \sum_{i,j=1}^{3} \hat{e}_i\hat{e}_j T_{ij}$$

where $\hat{e}_i\hat{e}_j$ is the tensor known as the unit dyad. Unit dyads are *ordered* pairs of unit vectors that lie along specific Cartesian axes, as illustrated below for the unit dyads $\hat{e}_2\hat{e}_3$ and $\hat{e}_3\hat{e}_2$.





It's important to note that the order of the vectors matters; in general, $\hat{e}_2\hat{e}_3 \neq \hat{e}_3\hat{e}_2$. This is certainly the case for physical problems involving flow caused by the application of an external force; the flow along a given direction will often depend on which direction the force is applied from.

There are different ways of multiplying tensors with vectors and other tensors, but for now we'll only be concerned with what's referred to as the dot product of a tensor and vector. To define this operation, we note the following relations between unit vectors:

$$\hat{e}_i\hat{e}_j \cdot \hat{e}_k = \hat{e}_i(\hat{e}_j \cdot \hat{e}_k) = \hat{e}_i\delta_{jk}$$

and

$$\hat{e}_i \cdot \hat{e}_j\hat{e}_k = (\hat{e}_i \cdot \hat{e}_j)\cdot \hat{e}_k = \delta_{ij}\hat{e}_k$$

These relations make use of familiar identities involving the dot product of two vectors. Now if **T** is a tensor and **v** a vector, their dot product is defined as

$$\mathbf{T}\cdot\mathbf{v} = \sum_{i,j=1}^{3}\hat{e}_i\hat{e}_jT_{ij}\cdot\sum_{k=1}^{3}\hat{e}_kv_k$$

$$= \sum_{i,j,k=1}^{3}\hat{e}_i\hat{e}_j\cdot\hat{e}_kT_{ij}v_k$$

$$= \sum_{i,j,k=1}^{3}\hat{e}_i\delta_{jk}T_{ij}v_k$$

$$= \sum_{i=1}^{3}\hat{e}_i\left(\sum_{j=1}^{3}T_{ij}v_j\right) \tag{18}$$

so the dot product of a tensor and a vector is another vector whose *i*th component (from the above relation) is the sum $\sum_{j=1}^{3}T_{ij}v_j$. We'll eventually use this result to treat the expression for the rate of convective momentum flow in Eq. (16).

In the meantime, we'll turn to the other contribution to $d\mathbf{G}(t)/dt$, which comes from the force acting on the surface of *V*. Assume that over the area *d***S**, the force is *d***F**. In some sense, the "ratio" of this force to the area is a pressure, except that since both *d***S** and *d***F** are vectors, the only way they can be related to each other is if *d***S** is dotted into a tensor. In other words, it must be the case that

$$d\mathbf{F} = d\mathbf{S}\cdot\boldsymbol{\sigma} \tag{19}$$

We'll refer to the tensor $\boldsymbol{\sigma}$ in this relation as the <u>stress tensor</u>. If the force and area had been scalars, then $\boldsymbol{\sigma}$ would simply have been the usual isotropic pressure *P*.

From (19), we see that the total force **F** acting over **S** is given by

$$\mathbf{F} = \int_{\mathrm{S}} d\mathbf{S}\cdot\boldsymbol{\sigma} \equiv \left.\frac{d\mathbf{G}(t)}{dt}\right|_{force} \tag{20}$$

Combining Eqs. (15), (16) and (20), we obtain

$$\int_V d\mathbf{r}\,\frac{\partial \mathbf{g}(\mathbf{r},t)}{\partial t} = -m\int_S d\mathbf{S}\cdot[\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]\rho(\mathbf{r},t) + \int_S d\mathbf{S}\cdot\boldsymbol{\sigma}$$

$$= \int_V d\mathbf{r}\nabla_{\mathbf{r}}\cdot[\boldsymbol{\sigma} - m\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]$$

From this relation it follows that

$$\frac{\partial \mathbf{g}(\mathbf{r},t)}{\partial t} = \nabla_{\mathbf{r}}\cdot[\boldsymbol{\sigma} - m\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] \tag{21}$$

which is the equation for the conservation of momentum. Like the equation for the conservation of mass, Eq. (21) is also exact. We'll later find an approximation to it that can be used to derive an expression for the shear viscosity.