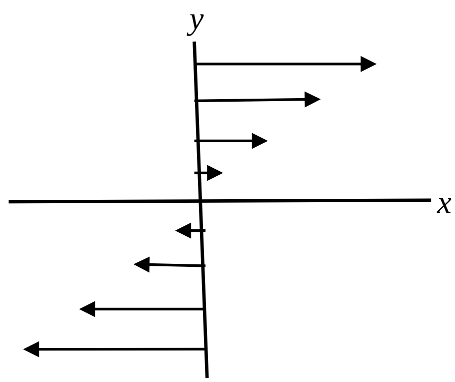
IP326. Lecture 12. Tuesday, Feb. 12, 2019

● <u>The shear viscosity</u>

One other transport coefficient that can be treated within the linear response formalism is the shear viscosity, a quantity that is a measure of the response of a system to the effects of an applied shear force. To subject a system to a shear force, one typically places the system between two plates, and then moves the plates parallel to each other in opposite directions. The rate at which the plates are pulled apart is called the shear rate, and is usually denoted $\dot{\gamma}$.

The application of a shear force in a certain direction (say, along the *x*-axis to be specific) changes the velocities of the layers of fluid lying between the two plates in the *y*-direction, the layers closest to the plates being the most affected, and those below progressively less so. These shear generated fluid flows are also chiefly directed along the *x*-axis since that is the direction the plates are moved. If arrows of different lengths are used to denote the direction and magnitude of these flows, then something like the pattern shown below will be created by the presence of shear:



If the strength of the shear force (as measured by $\dot{\gamma}$) is not too high, it's reasonable to assume – as the figure above suggests – that the fluid velocity **v** in the *x*-direction, v_x, at a height *y* above the *x*-axis is proportional to *y*, the proportionality constant being given by $\dot{\gamma}$. So we can write

$$\mathbf{v} = \dot{\gamma} y \hat{e}_x \tag{1}$$

where $\hat{e}_x$ is a unit vector along *x*. Let's also assume that at some time *t* each particle in the fluid (out of a total of *N*), when subject to the given shear force, acquires an extra velocity (in addition to whatever velocity it happens to have in the absence of the force) of the form given by Eq. (1). The momentum of the *i*th particle then becomes $\mathbf{p}_i + m\dot{\gamma} q_{iy} \hat{e}_x$, where *m* is the mass of the particle, and q_{iy} is the *y*-component of its position. The Hamiltonian of the system is therefore given by

$$H = \frac{1}{2m}\sum_{i=1}^{N}(\mathbf{p}_i + m\dot{\gamma}q_{iy}\hat{e}_x)\cdot(\mathbf{p}_i + m\dot{\gamma}q_{iy}\hat{e}_x) + U(\{\mathbf{q}_i\})$$

$$\approx \frac{1}{2m}\sum_{i=1}^{N}\mathbf{p}_i^2 + U(\{\mathbf{q}_i\}) + \dot{\gamma}\sum_{i=1}^{N}\mathbf{p}_i\cdot\hat{e}_x q_{iy} \tag{2}$$

In arriving at this expression for H, we've assumed that the contribution from the term quadratic in $\dot{\gamma}$ can be neglected, since the shear force is weak. As written, H has exactly the same structure as the general linear response Hamiltonian introduced earlier, meaning H can be written as $H(\Gamma,t) = H_0(\Gamma) - B(\Gamma)F(t)$, where

$$H_0(\Gamma) = \frac{1}{2m}\sum_{i=1}^{N}\mathbf{p}_i^2 + U(\{\mathbf{q}_i\}), \quad B(\Gamma) = -\sum_{i=1}^{N}\mathbf{p}_i\cdot\hat{e}_x q_{iy}, \quad \text{and} \quad F(t) = \dot{\gamma} \tag{3}$$

We also showed earlier that the function that appears in the time correlation function describing a transport coefficient is $\dot{B}(\Gamma)$. From (3), we see that $\dot{B}(\Gamma)$ is

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

$$= -\frac{1}{m}\sum_{i=1}^{N}p_{iy}\mathbf{p}_i\cdot\hat{e}_x - \sum_{i=1}^{N}q_{iy}\mathbf{F}_i\cdot\hat{e}_x \tag{4}$$

where $\mathbf{F}_i = \dot{\mathbf{p}}_i$ is the force on particle i.

The nature of the response of a system experiencing the effects of $\dot{\gamma}$ is contained in the function $\left\langle A(t)\middle|\dot{B}\right\rangle$, but the variable $A(t)$ is still to be identified. We can identify it by noting that a shearing force creates an asymmetry in the internal pressure of the system, and that to describe this asymmetry, it becomes necessary to generalize the notion of pressure to allow for differences in its value in different directions. This generalized pressure is the pressure tensor, and its definition is based on the following definition of the conventional isotropic pressure P:

$$P = \frac{1}{3V}\left\langle\sum_{i=1}^{N}\left(\frac{\mathbf{p}_i^2}{m} + \mathbf{q}_i\cdot\mathbf{F}_i\right)\right\rangle \tag{5}$$

where as usual, the angular brackets denote an equilibrium ensemble average. Before proceeding from here to the pressure tensor, we need to understand where Eq. (5) itself comes from. To this end, consider the expression for P that one obtains from statistical thermodynamics in the canonical ensemble:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T\left(\frac{\partial}{\partial V}\ln Q(T,V,N)\right)_{T,N} \tag{6}$$

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

$$Q = \frac{1}{h^{3N}N!}\int d\Gamma \exp(-\beta H_0(\Gamma)) \tag{7}$$

The volume dependence of Q is contained both in the Hamiltonian as well as in the limits of integration of the components of the coordinate variables; although often simply set to $\pm\infty$, these limits, strictly speaking, only extend up to some linear dimension $V^{1/3}$ of the container holding the system. The volume arising out of these integrations can be explicitly extracted by introducing the change of variables $q_{i\alpha} = V^{1/3} r_{i\alpha}$, $\alpha = x, y, z$. This change of variables will, of course, alter $d\Gamma$, but it should not, because as we'll now prove, $d\Gamma$ is a constant, a result that Gibbs described as the conservation of extension in phase space. What this means is that even though the phase space variables $\{\mathbf{p}^N, \mathbf{q}^N\}$ may change (as they inevitably would when they evolve in time or when they are the subjects of a variable transformation), the phase space volume elements of the original and transformed variables still stay the same. That is,

$$d\Gamma = d\Gamma'$$

This is equivalent to the statement that the Jacobian J of the transformation from old to new variables is unity. This is an important and non-obvious result, so it's worth showing how it comes about.

• Proof of the conservation of phase space extension

By definition, the Jacobian J is given by

$$J = \frac{\partial(p'_{1x}, p'_{1y}, p'_{1z}, \ldots, q'_{Nx}, q'_{Ny}, q'_{Nz})}{\partial(p_{1x}, p_{1y}, p_{1z}, \ldots, q_{Nx}, q_{Ny}, q_{Nz})}$$

$$= \begin{vmatrix} \frac{\partial p'_{1x}}{\partial p_{1x}} & \frac{\partial p'_{1x}}{\partial p_{1y}} & \cdots & \frac{\partial p'_{1x}}{\partial q_{Ny}} & \frac{\partial p'_{1x}}{\partial q_{Nz}} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial q'_{Nz}}{\partial p_{1x}} & \frac{\partial q'_{Nz}}{\partial p_{1y}} & \cdots & \frac{\partial q'_{Nz}}{\partial q_{Ny}} & \frac{\partial q'_{Nz}}{\partial q_{Nz}} \end{vmatrix} \tag{8}$$

Let's now rename the variables as follows:

$$p_{1x}, q_{1x}, p_{1y}, q_{1y}, \ldots, p_{Ny}, q_{Ny}, p_{Nz}, q_{Nz} = y_1, y_2, y_3, y_4, \ldots, y_{6N-3}, y_{6N-2}, y_{6N-1}, y_{6N} \tag{9}$$

with the primed variables renamed the same way. So in this new system of nomenclature, y's with even subscripts refer to position variables, and y's with odd subscripts refer to momentum variables. (Thus, for instance, $y_1 = p_{1x}$, $y_2 = q_{1x}$, $y_3 = p_{1y}$, $y_4 = q_{1y}$, etc.) In general, then, if $y_j = q_{jx}$, then $y_{j+1} = p_{jx}$, and likewise for the primed variables. The elements of the Jacobian are therefore the derivatives $J_{ij} \equiv \frac{\partial y'_i}{\partial y_j}$, and J can be considered a function of the J_{ij}. Which means that when the J_{ij} are varied, the change, dJ, in J itself is given by

$$dJ = \frac{\partial J}{\partial J_{11}} dJ_{11} + \frac{\partial J}{\partial J_{12}} dJ_{12} + \cdots + \frac{\partial J}{\partial J_{6N,6N}} dJ_{6N,6N}$$

$$= \sum_{i=1}^{6N} \sum_{j=1}^{6N} \frac{\partial J}{\partial J_{ij}} dJ_{ij} \tag{10}$$

We can now see what happens to J as time evolves and the phase space variables acquire new values. First of all, at the initial time, $J = 1$, because the old and new variables are the same. But at later times, the change in J is determined by

$$\frac{dJ}{dt} = \sum_{i=1}^{6N} \sum_{j=1}^{6N} \frac{\partial J}{\partial J_{ij}} \frac{dJ_{ij}}{dt} \tag{11}$$

To proceed from here, we need to recall some facts about matrices and determinants, in particular the fact that the determinant D of an $n \times n$ matrix **A** whose elements are a_{ij} is given by

$$D = \sum_{j=1}^{n} a_{ij} C_{ij}, \qquad i = 1 \text{ or } 2 \text{ or } 3 \text{ or} \cdots \text{or } n \tag{12}$$

where C_{ij} is the cofactor of the element a_{ij}, a cofactor being defined as the *signed* minor of a_{ij}, i.e.,

$$C_{ij} = (-1)^{i+j} M_{ij} \tag{13}$$

with M_{ij}, the minor of a_{ij} , defined as the determinant of a sub-matrix of **A** obtained by eliminating the elements of **A**'s ith row and jth column. From (12), we have the relation

$$\frac{\partial D}{\partial a_{ik}} = \sum_{j=1}^{n} \frac{\partial a_{ij}}{\partial a_{ik}} C_{ij}, \qquad i = 1 \text{ or } 2 \text{ or } 3 \text{ or} \cdots \text{or } n$$

$$= \sum_{j=1}^{n} \delta_{jk} C_{ij} = C_{ik}, \qquad i = 1 \text{ or } 2 \text{ or } 3 \text{ or} \cdots \text{or } n \tag{14}$$

Returning now to our expression for the time derivative of the Jacobian (Eq. (11)), we can use the above result (Eq. (14)), to write Eq. (11) as

$$\frac{dJ}{dt} = \sum_{i=1}^{6N} \sum_{j=1}^{6N} J^{ij} \frac{dJ_{ij}}{dt} \tag{15}$$

where the symbol J^{ij} stands for the cofactor of the i,j th element.

Let's recall our naming convention for the elements of the Jacobian; within that convention

$$\frac{dJ_{ij}}{dt} = \frac{d}{dt} \frac{\partial y_i'}{\partial y_j} \tag{16}$$

the y's and y''s being either positions or momenta. If we now interchange the order of differentiations in (16) , the right hand side becomes $\partial \dot{y}_i' / \partial y_j$. The variable $\dot{y}_i'$ is the time evolution of the position or momentum of the ith particle, which is determined by Hamilton's equations, which means that $\dot{y}_i' = (-1)^i \dfrac{\partial H}{\partial y_{i\pm1}'}$, where the plus sign holds when i is odd, and the minus sign when it is even (convince yourself of this!) So (16) now becomes

$$\frac{dJ_{ij}}{dt} = \frac{\partial}{\partial y_j} (-1)^i \frac{\partial H}{\partial y_{i\pm1}'} = (-1)^i \frac{\partial^2 H}{\partial y_j \partial y_{i\pm1}'} \tag{17}$$

which we can rewrite using the chain rule as

$$\frac{dJ_{ij}}{dt} = \sum_{k=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y_k' \partial y_{i\pm1}'} \frac{\partial y_k'}{\partial y_j}$$

$$= \sum_{k=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y_k' \partial y_{i\pm1}'} J_{kj} \tag{18}$$

If (18) is substituted into (15), the result is

$$\frac{dJ}{dt} = \sum_{i=1}^{6N} \sum_{j=1}^{6N} J^{ij} \sum_{k=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y'_k \partial y'_{i\pm 1}} J_{kj}$$

which, after interchanging the order of summations, becomes

$$\frac{dJ}{dt} = \sum_{i=1}^{6N} \sum_{k=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y'_k \partial y'_{i\pm 1}} \sum_{j=1}^{6N} J^{ij} J_{kj} \qquad (19)$$

In the last sum in (19) (over *j*), when the index *i* equals *k*, the sum works out to be the determinant *J* (cf. Eq. (12)). But when the two are not equal, one can show – although we won't do it here – that sum works out to be 0. This means that $\sum_{j=1}^{6N} J^{ij} J_{kj} = J\delta_{ik}$. Putting this result back into (19), we find that

$$\frac{dJ}{dt} = \sum_{i=1}^{6N} \sum_{k=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y'_k \partial y'_{i\pm 1}} J\delta_{ik}$$

$$= J \sum_{i=1}^{6N} (-1)^i \frac{\partial^2 H}{\partial y'_i \partial y'_{i\pm 1}} \qquad (20)$$

When (20) is re-expressed in terms of the original variables (positions and momenta), one sees that the terms in the sum occur in pairs of the following kind:

$$\frac{\partial^2 H}{\partial q_{ix} \partial p_{ix}} - \frac{\partial^2 H}{\partial p_{ix} \partial q_{ix}}$$

which is, of course, 0, so the entire sum in (20) vanishes, which means that $dJ/dt = 0$, and that *J* is independent of time. Since *J* started out at the value 1, it continues to remain unity thereafter. In other words, changes to the phase space variables leave the phase space volume element unchanged.