IP326. Lecture 15. Thursday, Feb. 21, 2019

● <u>Hydrodynamic approach to the shear viscosity</u> (Cont.'d)

The Navier-Stokes equation, shown below in all its lurid detail, is the starting point for deriving an expression for the shear viscosity η:

$$m\rho\left(\frac{\partial}{\partial t}+\mathbf{u}\cdot\nabla\right)\mathbf{u} = -\nabla P + \eta\nabla^2\mathbf{u} + \left(\frac{1}{3}\eta+\kappa\right)\nabla\nabla\cdot\mathbf{u} \tag{1}$$

Because it is a nonlinear equation, however (the nonlinearity arising from the term in $\mathbf{u}\cdot\nabla\mathbf{u}$, which is quadratic in the velocity), it is difficult to treat mathematically, and approximations are usually needed to extract something from it. An approximation we shall use is to assume that the dynamical variables $\rho(\mathbf{r},t)$ and $\mathbf{u}(\mathbf{r},t)$ are not very different from the values they have in equilibrium. In other words,

$$\rho(\mathbf{r},t) = \overline{\rho} + \delta\rho(\mathbf{r},t) + O((\delta\rho)^2) \tag{2a}$$

$$\mathbf{u}(\mathbf{r},t) = \delta\mathbf{u}(\mathbf{r},t) + O((\delta\mathbf{u})^2) \tag{2b}$$

In (2a), $\overline{\rho}$ is the mean number density (a time and space independent quantity), and $\delta\rho(\mathbf{r},t)$ is a small deviation from it. In a fluid that's quiescent, there is no net flow, so the mean velocity is 0, and $\delta\mathbf{u}(\mathbf{r},t)$, the fluctuation around this value, is just the local velocity itself, but regarded as small. When (2a) and (2b) are substituted into (1) and only the terms linear in the density and velocity fluctuations retained, the result is the so-called *linearized* Navier-Stokes equation, given by

$$m\overline{\rho}\frac{\partial\delta\mathbf{u}}{\partial t} = -\nabla P + \eta\nabla^2\delta\mathbf{u} + \left(\frac{1}{3}\eta+\kappa\right)\nabla\nabla\cdot\delta\mathbf{u} \tag{3}$$

This equation, being linear in $\delta\mathbf{u}(\mathbf{r},t)$, is amenable to treatment, in this case by the method of Fourier transforms. Defining the Fourier transform of a function $f(\mathbf{r})$ through the relation

$$\hat{f}(\mathbf{k}) = \int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})f(\mathbf{r})$$

and applying this definition to both sides of Eq. (3), we arrive at

$$m\overline{\rho}\frac{\partial\delta\hat{\mathbf{u}}}{\partial t} = i\mathbf{k}\hat{P} - \eta k^2\delta\hat{\mathbf{u}} - \left(\frac{1}{3}\eta+\kappa\right)\mathbf{k}\mathbf{k}\cdot\delta\hat{\mathbf{u}} \tag{4}$$

which makes use of the relations $\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla f(\mathbf{r}) = -i\mathbf{k}\hat{f}(\mathbf{k})$ and $\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla^2 f(\mathbf{r}) = -k^2 \hat{f}(\mathbf{k})$ to deal with the Fourier transforms of derivatives (under the assumption that $f(\mathbf{r})$ vanishes at $x, y, z \to \pm\infty$.)

Eq. (4) can be simplified by selecting a specific Cartesian axis along which to align the vector $\mathbf{k}$ and then separating $\delta\hat{\mathbf{u}}$ into two components, one lying along this selected axis and the other along the axes perpendicular to it. If the unit vector in the direction of the selected axis (which we will later identify with the *z* axis) is denoted $\hat{e}_{\|}$, we can write $\mathbf{k}$ and $\delta\hat{\mathbf{u}}$ as

$$\mathbf{k} = \hat{e}_{\|} k \qquad \text{and} \qquad \delta\hat{\mathbf{u}} = \hat{e}_{\|}\delta\hat{u}_{\|} + \delta\hat{\mathbf{u}}_{\perp} \tag{5}$$

where *k* is the magnitude of $\mathbf{k}$, and $\delta\hat{\mathbf{u}}_{\perp}$ is a vector lying in the plane of the axes normal to $\hat{e}_{\|}$. The substitution of (5) into (4) leads to

$$m\overline{\rho}\frac{\partial}{\partial t}(\hat{e}_{\|}\delta u_{\|} + \delta\hat{\mathbf{u}}_{\perp}) = i\hat{e}_{\|}k\hat{P} - \eta k^2(\hat{e}_{\|}\delta u_{\|} + \delta\hat{\mathbf{u}}_{\perp}) - \left(\frac{1}{3}\eta + \kappa\right)\hat{e}_{\|}k^2\delta u_{\|} \tag{6}$$

from which it follows that the terms on either side of the equality sign that involve the vectors parallel and perpendicular to the direction of $\mathbf{k}$ must be equal to each other. That is,

$$m\overline{\rho}\frac{\partial \delta u_{\|}}{\partial t} = ik\hat{P} - \eta k^2\delta u_{\|} - \left(\frac{1}{3}\eta + \kappa\right)k^2\delta u_{\|} \tag{7a}$$

$$m\overline{\rho}\frac{\partial \delta\hat{\mathbf{u}}_{\perp}}{\partial t} = -\eta k^2\delta\hat{\mathbf{u}}_{\perp} \tag{7b}$$

For the present purposes, only the second of these equations – viz., (7b) – needs to be considered further, since that is the equation that contains η in isolation. Equation (7b) is easily solved; the solution is

$$\delta\hat{u}_{\perp\alpha}(t) = \delta\hat{u}_{\perp}(0)\exp\left(-\eta k^2 t / m\overline{\rho}\right), \qquad \alpha = x, y \tag{8}$$

which, for a specific choice of α, can be used in constructing a time correlation function. Since neither direction, *x* or *y*, is special, either may be used for this purpose, so we'll choose to work with $\delta\hat{u}_{\perp x}(t)$. From (8), the normalized time correlation function of this dynamical variable is

$$\overline{C}(t) = \frac{\left\langle \hat{u}^*_{\perp x}(t)\hat{u}_{\perp x}(0)\right\rangle}{\left\langle \hat{u}^*_{\perp x}(0)\hat{u}_{\perp x}(0)\right\rangle} = \exp\left(-\eta k^2 t / m\overline{\rho}\right) \tag{9}$$

The shear viscosity can be obtained from this expression by differentiating $\overline{C}(t)$ twice with respect to *k*, and then setting *k* to 0 in the result. This yields

$$\eta = -\frac{m\overline{\rho}}{2t}\frac{\partial^2 \overline{C}(t)}{\partial t^2}\bigg|_{k=0} \tag{10}$$

To use this equation to obtain η, we need to derive an expression for the time-correlation function $\overline{C}(t)$ in terms of an appropriate set of microscopic variables. For this purpose, we'll note that the velocity $\mathbf{u}(\mathbf{r},t)$ [or equivalently $\delta\mathbf{u}(\mathbf{r},t)$] has the following definition:

$$\delta\mathbf{u}(\mathbf{r},t) = \sum_{i=1}^{N}\mathbf{u}_i(t)\delta(\mathbf{r}-\mathbf{r}_i(t)) \tag{11}$$

(which means that $\mathbf{u}(\mathbf{r},t)$ is really to be identified with the net velocity of all the particles located in the immediate neighbourhood of the point **r** at time *t*.)

From (11), the *x* component of the Fourier transform of $\mathbf{u}(\mathbf{r},t)$ with respect to the Fourier variable $\mathbf{k} = \hat{e}_{\|}k$ is seen to be

$$\delta\hat{u}_{\perp x}(k,t) = \sum_{i=1}^{N}\dot{x}_i(t)\exp[ikz_i(t)] \tag{12}$$

where we've replaced the velocity of the *i*th particle along *x* by its definition in terms of the time derivative of $x_i(t)$, and where the parallel axis has now explicitly been identified with the *z* axis. With this expression for the velocity, we see that the associated normalized time correlation function becomes

$$\overline{C}(t) = \frac{\sum_{i,j=1}^{N}\left\langle \dot{x}_i(t)\dot{x}_j(0)\exp[-ik(z_i(t)-z_j(0))]\right\rangle}{\sum_{i,j=1}^{N}\left\langle \dot{x}_i(0)\dot{x}_j(0)\exp[-ik(z_i(0)-z_j(0))]\right\rangle} \tag{13}$$

The denominator of (13) is readily evaluated, since it is just an equilibrium average with respect to the distribution of a canonical ensemble. This means that

$$\left\langle \dot{x}_i(0)\dot{x}_j(0)\exp[-ik(z_i(0)-z_j(0))]\right\rangle = \left\langle \dot{x}_i(0)\dot{x}_j(0)\right\rangle\left\langle \exp[-ik(z_i(0)-z_j(0))]\right\rangle$$

$$= \frac{2}{m}\left\langle \frac{1}{2} m u_{ix}^2 \right\rangle \delta_{ij} \left\langle \exp[-ik(z_i(0) - z_j(0))] \right\rangle$$

$$= \frac{2}{m}\frac{k_B T}{2}\delta_{ij} \left\langle \exp[-ik(z_i(0) - z_j(0))] \right\rangle \tag{14}$$

the middle equation following from the independence of particle velocities, and the last from the equipartition of energies. If we use (14) in the denominator of (13), we find that

$$\sum_{i,j=1}^{N} \left\langle \dot{x}_i(0)\dot{x}_j(0)\exp[-ik(z_i(0) - z_j(0))] \right\rangle = \frac{k_B T}{m}\sum_{i,j=1}^{N}\delta_{ij}\left\langle \exp[-ik(z_i(0) - z_j(0))] \right\rangle$$

$$= \frac{N k_B T}{m} \tag{15}$$

Substituting (15) into (13), then taking two derivatives with respect to *k*, next setting **k** to 0, and finally substituting the result into (10), we find that

$$\eta = \frac{m^2 \bar{\rho}}{2 N k_B T t}\sum_{i,j=1}^{N} \left\langle \dot{x}_i(t)\dot{x}_j(0)[z_i(t) - z_j(0)]^2 \right\rangle$$

$$= \frac{1}{2 V k_B T t}\sum_{i,j=1}^{N} \left\langle p_{ix}(t) p_{jx}(0)[z_i^2(t) + z_j^2(0) - 2 z_i(t) z_j(0)] \right\rangle \tag{16}$$

Consider the first term on the right hand side of (16); because of momentum conservation (which implies that the total momentum of the particles at some initial time $t = 0$ equals their momentum at a later time *t*), the sum $\sum_{j=1}^{N} p_{jx}(0)$ can also be written $\sum_{j=1}^{N} p_{jx}(t)$. And likewise, in the second term on the right hand side of (16), the sum $\sum_{i=1}^{N} p_{ix}(t)$ can be written $\sum_{i=1}^{N} p_{ix}(0)$. When these transformations are introduced into (16), the equation can be expressed as a complete square:

$$\eta = \frac{1}{2 V k_B T t}\left\langle \left(\sum_{i=1}^{N} [p_{ix}(t) z_i(t) - p_{ix}(0) z_i(0)] \right)^2 \right\rangle. \tag{17}$$

The summand in (17) also happens to admit of the following integral representation

$$p_{ix}(t) z_i(t) - p_{ix}(0) z_i(0) = \int_0^t dt_1 \left[\frac{1}{m} p_{ix}(t_1) p_{iz}(t_1) + F_{ix}(t_1) z_i(t_1) \right], \tag{18}$$

which can be proved by differentiating both sides of (18) with respect to t, and using the general result

$$\frac{\partial}{\partial t}\int_{a(t)}^{b(t)} dt' f(t',t) = f(b(t),t)\frac{\partial b(t)}{\partial t} - f(a(t),t)\frac{\partial a(t)}{\partial t} + \int_{a(t)}^{b(t)} dt' \frac{\partial f(t',t)}{\partial t}$$

to treat the right hand side of (18).

The substitution of (18) into (17) now leads to

$$\eta = \frac{1}{2Vk_BTt}\left\langle \sum_{i,j=1}^{N}\int_0^t dt_1 \int_0^t dt_2 \left[\frac{1}{m^2} p_{ix}(t_1)p_{iz}(t_1)p_{jx}(t_2)p_{jz}(t_2) + F_{ix}(t_1)z_i(t_1)F_{jx}(t_2)z_j(t_2) + \right.\right.$$
$$\left.\left. + \frac{2}{m} p_{ix}(t_1)p_{iz}(t_1)F_{jx}(t_2)z_j(t_2) \right]\right\rangle \tag{19}$$

This expression is now further treated by first separating the integrals over t_1 and t_2 into the following two integrals

$$\int_0^t dt_1 \int_0^t dt_2 = \int_0^t dt_1 \int_0^{t_1} dt_2 + \int_0^t dt_1 \int_{t_1}^t dt_2$$

and then by switching the order of integration in the second, using step functions to effect this step; the result is

$$\int_0^t dt_1 \int_0^t dt_2 = \int_0^t dt_1 \int_0^{t_1} dt_2 + \int_0^t dt_2 \int_0^{t_2} dt_1$$

When this is put back into (19), one sees (by simple relabeling) that the contributions from the two integrals are identical, and that the equation can therefore be reduced to

$$\eta = \frac{1}{Vk_BTt}\left\langle \sum_{i,j=1}^{N}\int_0^t dt_1 \int_0^{t_1} dt_2 \left[\frac{1}{m^2} p_{ix}(t_1)p_{iz}(t_1)p_{jx}(t_2)p_{jz}(t_2) + F_{ix}(t_1)z_i(t_1)F_{jx}(t_2)z_j(t_2) + \right.\right.$$
$$\left.\left. + \frac{2}{m} p_{ix}(t_1)p_{iz}(t_1)F_{jx}(t_2)z_j(t_2) \right]\right\rangle \tag{20}$$

The ensemble averages in this expression are of the general form $\langle A(t_1)B(t_2)\rangle$, and so, because of stationarity, can also be written as $\langle A(t_1 - t_2)B(0)\rangle$. This means that the integral $\int_0^t dt_1 \int_0^{t_1} dt_2 \langle A(t_1 - t_2)B \rangle$, after the change of variable $t' = -t_2 + t_1$, followed by an interchange of the order of integration (again effected by the introduction of a suitable step function), can be written as $\int_0^t dt' \int_{t'}^t dt_1 \langle A(t')B \rangle$, which can be immediately evaluated to $\int_0^t dt'(t - t')\langle A(t')B \rangle$. Using these results, we see that Eq. (20) can be expressed as

$$\eta = \frac{1}{Vk_B Tt} \int_0^t dt'(t - t') \left\langle \left(\sum_{i=1}^N \left[\frac{1}{m} p_{ix}(t') p_{iz}(t') + F_{ix}(t') z_i(t') \right] \right) \times \right.$$

$$\left. \times \left(\sum_{j=1}^N \left[\frac{1}{m} p_{jx}(0) p_{jz}(0) + F_{jx}(0) z_j(0) \right] \right) \right\rangle \qquad (21)$$

The term $\sum_{i=1}^N [p_{ix}(t) p_{iz}(t)/m + F_{ix}(t) z_i(t)]$ in (21) will be recognized as $Vp_{xz}(t)$, where $p_{xz}(t)$ is the *xz* element of the pressure tensor at time *t*. Thus, by passing to the limit $t \to \infty$ in this equation, setting t'/t to 0 in the process, one sees that Eq. (21) finally reduces to the Green-Kubo relation for the shear viscosity derived earlier:

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle p_{xz}(t) p_{xz} \rangle$$