

G25.2651: Statistical Mechanics

Notes for Lecture 21

I. CLASSICAL LINEAR RESPONSE THEORY

Consider Hamilton's equations in the form

$$\begin{aligned}\dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}\end{aligned}$$

We noted early in the course that an ensemble of systems evolving according to these equations of motion would generate an equilibrium ensemble (in this case, microcanonical). Recall that the phase space distribution function $f(\mathbf{\Gamma}, t)$ satisfied a Liouville equation:

$$\frac{\partial f}{\partial t} + iL f = 0$$

where $iL = \{\dots, H\}$. We noted that if $\partial f/\partial t = 0$, then $f = f(H)$ is a pure function of the Hamiltonian which defined the general class of distribution functions valid for equilibrium ensembles.

What does it mean, however, if $\partial f/\partial t \neq 0$? To answer this, consider the problem of a simple harmonic oscillator. In an equilibrium ensemble of simple harmonic oscillators at temperature T , the members of the ensemble will undergo oscillatory motion about the potential minimum, with the amplitude of this motion determined by the temperature. Now, however, consider driving each oscillator with a time-dependent driving force $F(t)$. Depending on how complicated the forcing function $F(t)$ is, the motion of each member of the ensemble will, no longer, be simple oscillatory motion about the potential minimum, but could be a very complex kind of motion that explores large regions of the potential energy surface. In other words, the ensemble of harmonic oscillators has been driven away from equilibrium by the time-dependent force $F(t)$. Because of this nonequilibrium behavior of the ensemble, averages over the ensemble could become time-dependent quantities rather than static quantities. Indeed, the distribution function $f(\mathbf{\Gamma}, t)$, itself, could be time-dependent. This can most easily be seen by considering the equation of motion for a forced oscillator

$$m\ddot{x} = -m\omega^2 x + F(t)$$

The solution now depends on the entire history of the forcing function $F(t)$, which can introduce explicit time-dependence into the ensemble distribution function.

A. Generalized equations of motion

The most general way a system can be driven away from equilibrium by a forcing function $F_e(t)$ is according to the equations of motion:

$$\begin{aligned}\dot{q}_i &= \frac{\partial H}{\partial p_i} + C_i(\mathbf{\Gamma})F_e(t) \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} + D_i(\mathbf{\Gamma})F_e(t)\end{aligned}$$

where the $3N$ functions C_i and D_i are required to satisfy the incompressibility condition

$$\sum_{i=1}^{3N} \left[\frac{\partial C_i}{\partial q_i} + \frac{\partial D_i}{\partial p_i} \right] = 0$$

in order to insure that the Liouville equation for $f(\mathbf{\Gamma}, t)$ is still valid. These equations of motion will give rise to a distribution function $f(\mathbf{\Gamma}, t)$ satisfying

$$\frac{\partial f}{\partial t} + iL f = 0$$

with $\partial f/\partial t \neq 0$. (We assume that f is normalized so that $\int d\mathbf{\Gamma} f(\mathbf{\Gamma}, t) = 1$.)

What does the Liouville equation say about the nature of $f(\mathbf{\Gamma}, t)$ in the limit that C_i and D_i are small, so that the displacement away from equilibrium is, itself, small? To examine this question, we propose to solve the Liouville equation perturbatively. Thus, let us assume a solution of the form

$$f(\mathbf{\Gamma}, t) = f_0(H(\mathbf{\Gamma})) + \Delta f(\mathbf{\Gamma}, t)$$

Note, also, that the equations of motion $\dot{\mathbf{\Gamma}}$ take a perturbative form

$$\dot{\mathbf{\Gamma}}(t) = \dot{\mathbf{\Gamma}}_0 + \Delta \dot{\mathbf{\Gamma}}(t)$$

and as a result, the Liouville operator contains two pieces:

$$iL = \dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} = \dot{\mathbf{\Gamma}}_0 \cdot \nabla_{\mathbf{\Gamma}} + \Delta \dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} = iL_0 + i\Delta L$$

where $iL_0 = \{\dots, H\}$ and $f_0(H)$ is assumed to satisfy

$$iL_0 f_0(H(\mathbf{\Gamma})) = 0$$

$\dot{\mathbf{\Gamma}}_0$ means the Hamiltonian part of the equations of motion

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned}$$

For an observable $A(\mathbf{\Gamma})$, the ensemble average of A is a time-dependent quantity:

$$\langle A(t) \rangle = \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) f(\mathbf{\Gamma}, t)$$

which, when the assumed form for $f(\mathbf{\Gamma}, t)$ is substituted in, gives

$$\langle A(t) \rangle = \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) f_0(\mathbf{\Gamma}) + \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) \Delta f(\mathbf{\Gamma}, t) = \langle A \rangle_0 + \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) \Delta f(\mathbf{\Gamma}, t)$$

where $\langle \cdot \rangle_0$ means average with respect to $f_0(\mathbf{\Gamma})$.

B. Perturbative solution of the Liouville equation

Substituting the perturbative form for $f(\mathbf{\Gamma}, t)$ into the Liouville equation, one obtains

$$\frac{\partial}{\partial t} (f_0(\mathbf{\Gamma}) + \Delta f(\mathbf{\Gamma}, t)) + (iL_0 + i\Delta L(t))(f_0(\mathbf{\Gamma}) + \Delta f(\mathbf{\Gamma}, t)) = 0$$

Recall $\partial f_0/\partial t = 0$. Thus, working to linear order in small quantities, one obtains the following equation for $\Delta f(\mathbf{\Gamma}, t)$:

$$\left(\frac{\partial}{\partial t} + iL_0 \right) \Delta f(\mathbf{\Gamma}, t) = -i\Delta L f_0(\mathbf{\Gamma})$$

which is just a first-order inhomogeneous differential equation. This can easily be solved using an integrating factor, and one obtains the result

$$\Delta f(\mathbf{\Gamma}, t) = - \int_0^t ds e^{-iL_0(t-s)} i\Delta L(s) f_0(\mathbf{\Gamma})$$

Note that

$$i\Delta L f_0(\mathbf{\Gamma}) = iL f_0(\mathbf{\Gamma}) - iL_0 f_0(\mathbf{\Gamma}) = iL f_0(\mathbf{\Gamma}) = \dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} f_0(\mathbf{\Gamma})$$

But, using the chain rule, we have

$$\begin{aligned} \dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} f_0(\mathbf{\Gamma}) &= \dot{\mathbf{\Gamma}} \cdot \frac{\partial f_0}{\partial H} \frac{\partial H}{\partial \mathbf{\Gamma}} \\ &= \frac{\partial f_0}{\partial H} \sum_{i=1}^N \left[\dot{\mathbf{p}}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} + \dot{\mathbf{q}}_i \frac{\partial H}{\partial \mathbf{q}_i} \right] \\ &= \frac{\partial f_0}{\partial H} \sum_{i=1}^N \left[\frac{\mathbf{p}_i}{m_i} \cdot (\mathbf{F}_i + \mathbf{D}_i F_e(t)) - \mathbf{F}_i \cdot \left(\frac{\mathbf{p}_i}{m_i} + \mathbf{C}_i F_e(t) \right) \right] \\ &= \frac{\partial f_0}{\partial H} \sum_{i=1}^N \left[\mathbf{D}_i(\mathbf{\Gamma}) \cdot \frac{\mathbf{p}_i}{m_i} - \mathbf{C}_i(\mathbf{\Gamma}) \cdot \mathbf{F}_i \right] F_e(t) \end{aligned}$$

where $\mathbf{F}_i(\mathbf{q}_1, \dots, \mathbf{q}_N)$ is the force on the i th particle. Define

$$j(\mathbf{\Gamma}) = \sum_{i=1}^N \left[\mathbf{C}_i(\mathbf{\Gamma}) \cdot \mathbf{F}_i - \mathbf{D}_i(\mathbf{\Gamma}) \cdot \frac{\mathbf{p}_i}{m_i} \right]$$

called the *dissipative flux*. Then

$$\dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} f_0(\mathbf{\Gamma}) = -\frac{\partial f_0}{\partial H} j(\mathbf{\Gamma}) F_e(t)$$

Now, suppose $f_0(\mathbf{\Gamma})$ is a canonical distribution function

$$f_0(H(\mathbf{\Gamma})) = \frac{1}{Q(N, V, T)} e^{-\beta H(\mathbf{\Gamma})}$$

then

$$\frac{\partial f_0}{\partial H} = -\beta f_0(H)$$

so that

$$\dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} f_0(\mathbf{\Gamma}) = \beta f_0(\mathbf{\Gamma}) j(\mathbf{\Gamma}) F_e(t)$$

Thus, the solution for $\Delta f(\mathbf{\Gamma}, t)$ is

$$\Delta f(\mathbf{\Gamma}, t) = -\beta \int_0^t ds e^{-iL_0(t-s)} f_0(\mathbf{\Gamma}) j(\mathbf{\Gamma}) F_e(s)$$

The ensemble average of the observable $A(\mathbf{\Gamma})$ now becomes

$$\begin{aligned} \langle A(t) \rangle &= \langle A \rangle_0 - \beta \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) \int_0^t ds e^{-iL_0(t-s)} f_0(\mathbf{\Gamma}) j(\mathbf{\Gamma}) F_e(s) \\ &= \langle A \rangle_0 - \beta \int_0^t ds \int d\mathbf{\Gamma} A(\mathbf{\Gamma}) e^{-iL_0(t-s)} f_0(\mathbf{\Gamma}) j(\mathbf{\Gamma}) F_e(s) \\ &= \langle A \rangle_0 - \beta \int_0^t ds \int d\mathbf{\Gamma} f_0(\mathbf{\Gamma}) A(\mathbf{\Gamma}) e^{-iL_0(t-s)} j(\mathbf{\Gamma}) F_e(s) \end{aligned}$$

Recall that the classical propagator is $\exp(iLt)$. Thus the operator appearing in the above expression is a classical propagator of the unperturbed system for propagating backwards in time to $-(t-s)$. An observable $A(\mathbf{\Gamma})$ evolves in time according to

$$\begin{aligned}\frac{dA}{dt} &= iLA \\ A(t) &= e^{iLt}A(0) \\ A(-t) &= e^{-iLt}A(0)\end{aligned}$$

Now, if we take the complex conjugate of both sides, we find

$$A^*(t) = A^*(0)e^{-iLt}$$

where now the operator acts to the left on $A^*(0)$. However, since observables are real, we have

$$A(t) = A(0)e^{-iLt}$$

which implies that forward evolution in time can be achieved by acting to the left on an observable with the time reversed classical propagator. Thus, the ensemble average of A becomes

$$\begin{aligned}\langle A(t) \rangle &= \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \int d\mathbf{\Gamma}_0 f_0(\mathbf{\Gamma}_0) A(\mathbf{\Gamma}_{t-s}(\mathbf{\Gamma}_0)) j(\mathbf{\Gamma}_0) \\ &= \langle A \rangle_0 - \beta \int_0^t ds F_e(s) \langle j(0) A(t-s) \rangle_0\end{aligned}$$

where the quantity on the last line is an object we have not encountered yet before. It is known as an *equilibrium time correlation function*. An equilibrium time correlation function is an ensemble average over the unperturbed (canonical) ensemble of the product of the dissipative flux at $t = 0$ with an observable A evolved to a time $t - s$. Several things are worth noting:

1. The nonequilibrium average $\langle A(t) \rangle$, in the linear response regime, can be expressed solely in terms of equilibrium averages.
2. The propagator used to evolve $A(\mathbf{\Gamma})$ to $A(\mathbf{\Gamma}, t - s)$ is the operator $\exp(iL_0(t - s))$, which is the propagator for the unperturbed, Hamiltonian dynamics with $C_i = D_i = 0$. That is, it is just the dynamics determined by H .
3. Since $A(\mathbf{\Gamma}, t - s) = A(\mathbf{\Gamma}(t - s))$ is a function of the phase space variables evolved to a time $t - s$, we must now specify over which set of phase space variables the integration $\int d\mathbf{\Gamma}$ is taken. The choice is actually arbitrary, and for convenience, we choose the initial conditions. Since $\mathbf{\Gamma}(t)$ is a function of the initial conditions $\mathbf{\Gamma}(0)$, we can write the time correlation function as

$$\langle j(0) A(t-s) \rangle_0 = \frac{1}{Q} \int d\mathbf{\Gamma}_0 e^{-\beta H(\mathbf{\Gamma}_0)} j(\mathbf{\Gamma}_0) A(\mathbf{\Gamma}_{t-s}(\mathbf{\Gamma}_0))$$

C. General properties of time correlation functions

Define a time correlation function between two quantities $A(\mathbf{\Gamma})$ and $B(\mathbf{\Gamma})$ by

$$\begin{aligned}C_{AB}(t) &= \langle A(0)B(t) \rangle \\ &= \int d\mathbf{\Gamma} f(\mathbf{\Gamma}) A(\mathbf{\Gamma}) e^{iLt} B(\mathbf{\Gamma})\end{aligned}$$

The following properties follow immediately from the above definition:

$$\langle A(0)B(t) \rangle = \langle A(-t)B(0) \rangle$$

- 1.

$$C_{AB}(0) = \langle A(\mathbf{\Gamma})B(\mathbf{\Gamma}) \rangle$$

2. Thus, if $A = B$, then

$$C_{AA}(t) = \langle A(0)A(t) \rangle$$

known as the *autocorrelation function* of A , and

$$C_{AA}(0) = \langle A^2 \rangle$$

If we define $\delta A = A - \langle A \rangle$, then

$$C_{\delta A \delta A}(0) = \langle (\delta A)^2 \rangle = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$$

which just measures the fluctuations in the quantity A .

3. A time correlation function may be evaluated as a time average, assuming the system is ergodic. In this case, the phase space average may be equated to a time average, and we have

$$C_{AB}(t) = \lim_{T \rightarrow \infty} \frac{1}{T-t} \int_0^{T-t} ds A(\mathbf{\Gamma}(s)) B(\mathbf{\Gamma}(t+s))$$

which is valid for $t \ll T$. In molecular dynamics simulations, where the phase space trajectory is determined at discrete time steps, the integral is expressed as a sum

$$C_{AB}(k\Delta t) = \frac{1}{N-k} \sum_{j=1}^{N-k} A(\mathbf{\Gamma}_k) B(\mathbf{\Gamma}_{k+j}) \quad k = 0, 1, 2, \dots, N_c$$

where N is the total number of time steps, Δt is the time step and $N_c \ll N$.

4. *Onsager regression hypothesis*: In the long time limit, A and B eventually become uncorrelated from each other so that the time correlation function becomes

$$C_{AB}(t) = \langle A(0)B(t) \rangle \rightarrow \langle A \rangle \langle B \rangle$$

For the autocorrelation function of A , this becomes

$$C_{AA}(t) \rightarrow \langle A \rangle^2$$

Thus, $C_{AA}(t)$ decays from $\langle A^2 \rangle$ at $t = 0$ to $\langle A \rangle^2$ as $t \rightarrow \infty$.

An example of a signal and its time correlation function appears in the figure below. In this case, the signal is the magnitude of the velocity along the bond of a diatomic molecule interacting with a Lennard-Jones bath. Its time correlation function is shown beneath the signal:

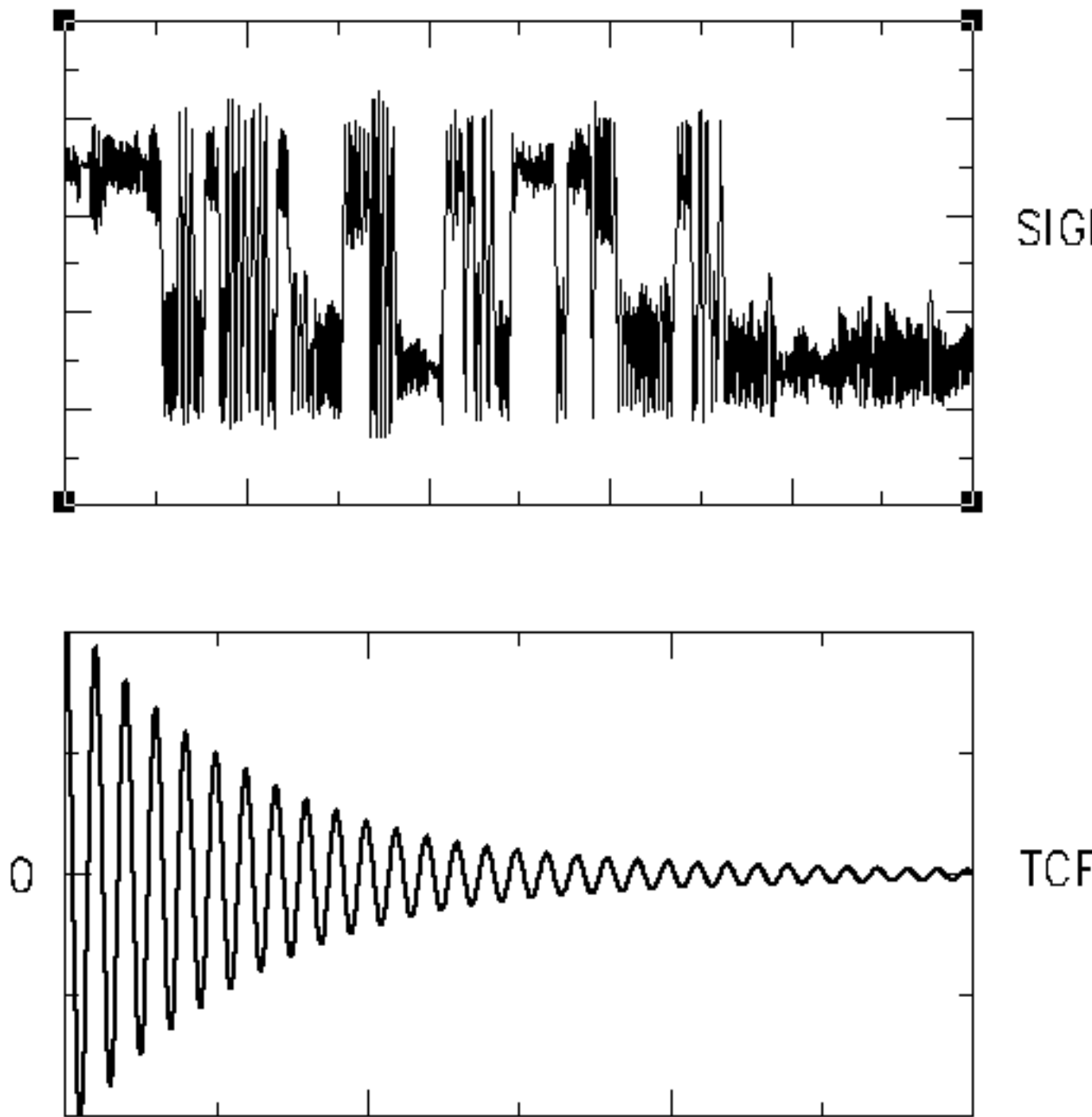


FIG. 1.

Over time, it can be seen that the property being autocorrelated eventually becomes uncorrelated with itself.

II. TIME CORRELATION FUNCTIONS AND TRANSPORT COEFFICIENTS

A. The shear viscosity

The shear viscosity of a system measures its resistance to flow. A simple flow field can be established in a system by placing it between two plates and then pulling the plates apart in opposite directions. Such a force is called a *shear force*, and the rate at which the plates are pulled apart is the shear rate. A set of microscopic equations of motion for generating shear flow is

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} + \gamma y_i \hat{\mathbf{x}} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \gamma p_{y_i} \hat{\mathbf{x}}\end{aligned}$$

where γ is a parameter known as the shear rate. These equations have the conserved quantity

$$H' = \sum_{i=1}^N (\mathbf{p}_i + m_i \gamma y_i \hat{\mathbf{x}})^2 + U(\mathbf{q}_1, \dots, \mathbf{q}_N)$$

The physical picture of this dynamical system corresponds to the presence of a velocity flow field $\mathbf{v}(y) = \gamma y \hat{\mathbf{x}}$ shown in the figure.

The flow field points in the $\hat{\mathbf{x}}$ direction and increases with increasing y -value. Thus, layers of a fluid, for example, will slow past each other, creating an anisotropy in the system. From the conserved quantity, one can see that the momentum of a particle is the value of \mathbf{p}_i plus the contribution from the field evaluated at the position of the particle

$$\mathbf{p}_i \rightarrow \mathbf{p}_i + m_i \mathbf{v}(y_i)$$

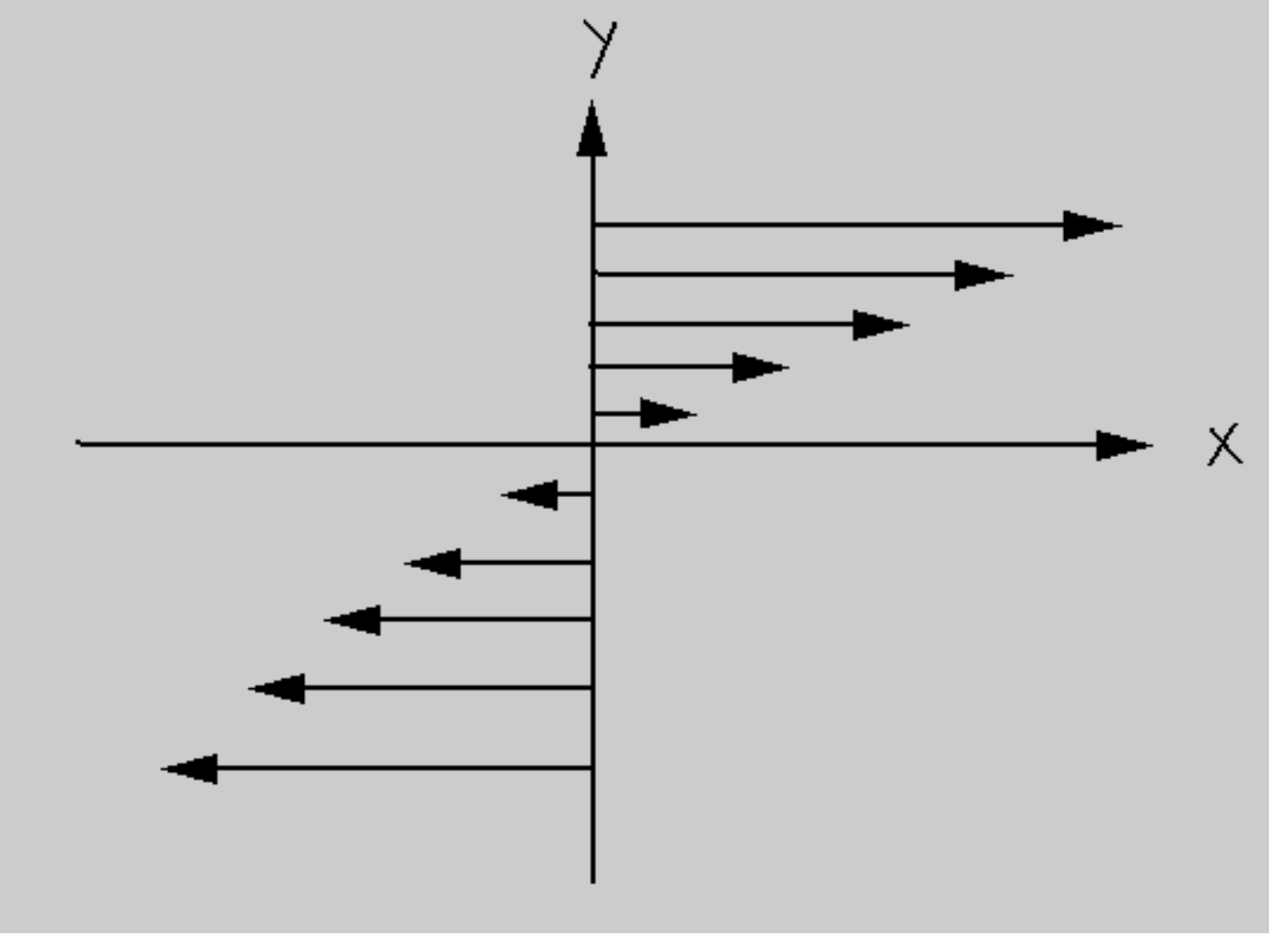


FIG. 2.

Such an applied external shearing force will create an asymmetry in the internal pressure. In order to describe this asymmetry, we need an analog of the internal pressure that contains a dependence on specific spatial directions. Such a quantity is known as the *pressure tensor* and can be defined analogously to the isotropic pressure P that we encountered earlier in the course. Recall that an estimator for the pressure was

$$p = \frac{1}{3V} \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{m_i} + \mathbf{q}_i \cdot \mathbf{F}_i \right]$$

and $P = \langle p \rangle$ in equilibrium. Here, V is the volume of the system. By analogy, one can write down an estimator for the pressure tensor $p_{\alpha\beta}$:

$$p_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^N \left[\frac{(\mathbf{p}_i \cdot \hat{\mathbf{e}}_\alpha)(\mathbf{p}_i \cdot \hat{\mathbf{e}}_\beta)}{m_i} + (\mathbf{q}_i \cdot \hat{\mathbf{e}}_\alpha)(\mathbf{F}_i \cdot \hat{\mathbf{e}}_\beta) \right]$$

and

$$P_{\alpha\beta} = \langle p_{\alpha\beta} \rangle$$

where $\hat{\mathbf{e}}_\alpha$ is a unit vector in the α direction, $\alpha = x, y, z$. This (nine-component) pressure tensor gives information about spatial anisotropies in the system that give rise to off-diagonal pressure tensor components. The isotropic pressure can be recovered from

$$P = \frac{1}{3} \sum_{\alpha} P_{\alpha\alpha}$$

which is just 1/3 of the trace of the pressure tensor. While most systems have diagonal pressure tensors due to spatial isotropy, the application of a shear force according to the above scheme gives rise to a nonzero value for the xy component of the pressure tensor P_{xy} . In fact, P_{xy} is related to the velocity flow field by a relation of the form

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

where the coefficient η is known as the *shear viscosity* and is an example of a *transport coefficient*. Solving for η we find

$$\eta = -\frac{P_{xy}}{\gamma} = -\lim_{t \rightarrow \infty} \frac{\langle p_{xy}(t) \rangle}{\gamma}$$

where $\langle p_{xy}(t) \rangle$ is the nonequilibrium average of the pressure tensor estimator using the above dynamical equations of motion.

Let us apply the linear response formula to the calculation of the nonequilibrium average of the xy component of the pressure tensor. We make the following identifications:

$$F_e(t) = 1 \quad \mathbf{C}_i(\mathbf{\Gamma}) = \gamma y_i \hat{\mathbf{x}} \quad \mathbf{D}_i(\mathbf{\Gamma}) = -\gamma p_{y_i} \hat{\mathbf{x}}$$

Thus, the dissipative flux $j(\mathbf{\Gamma})$ becomes

$$\begin{aligned} j(\mathbf{\Gamma}) &= \sum_{i=1}^N \left[\mathbf{C}_i \cdot \mathbf{F}_i - \mathbf{D}_i \cdot \frac{\mathbf{p}_i}{m_i} \right] \\ &= \sum_{i=1}^N \left[\gamma y_i (\mathbf{F}_i \cdot \hat{\mathbf{x}}) + \gamma p_{y_i} \frac{\mathbf{p}_i \cdot \hat{\mathbf{x}}}{m_i} \right] \\ &= \gamma \sum_{i=1}^N \left[\frac{(\mathbf{p}_i \cdot \hat{\mathbf{y}})(\mathbf{p}_i \cdot \hat{\mathbf{x}})}{m_i} + (\mathbf{q}_i \cdot \hat{\mathbf{y}})(\mathbf{F}_i \cdot \hat{\mathbf{x}}) \right] \\ &= \gamma V p_{xy} \end{aligned}$$

According to the linear response formula,

$$\langle p_{xy}(t) \rangle = \langle p_{xy} \rangle_0 - \beta \gamma V \int_0^t ds \langle p_{xy}(0) p_{xy}(t-s) \rangle_0$$

so that the shear viscosity becomes

$$\eta = \lim_{t \rightarrow \infty} \left[-\frac{\langle p_{xy} \rangle_0}{\gamma} + \beta V \int_0^t ds \langle p_{xy}(0) p_{xy}(t) \rangle_0 \right]$$

Recall that $\langle \dots \rangle_0$ means average of a canonical distribution with $\gamma = 0$. It is straightforward to show that $\langle p_{xy} \rangle_0 = 0$ for an equilibrium canonical distribution function. Finally, taking the limit that $t \rightarrow \infty$ in the above expression gives the result

$$\eta = \frac{V}{kT} \int_0^{\infty} dt \langle p_{xy}(0) p_{xy}(t) \rangle_0$$

which is a relation between a transport coefficient, in this case, the shear viscosity coefficient, and the integral of an equilibrium time correlation function. Relations of this type are known as *Green-Kubo* relations. Thus, we have expressed a new kind of thermodynamic quantity to an equilibrium time correlation function, which, in this case, is an autocorrelation function of the xy component of the pressure tensor.

B. The diffusion constant

The diffusive flow of particles can be studied by applying a constant force f to a system using the microscopic equations of motion

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{P}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}_1, \dots, \mathbf{q}_N) + f\hat{\mathbf{x}}\end{aligned}$$

which have the conserved energy

$$H' = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2m_i} + U(\mathbf{q}_1, \dots, \mathbf{q}_N) - f \sum_{i=1}^N x_i$$

Since the force is applied in the $\hat{\mathbf{x}}$ direction, there will be a net flow of particles in this direction, i.e., a current J_x . Since this current is a thermodynamic quantity, there is an estimator for it:

$$u_x = - \sum_{i=1}^N \dot{x}_i$$

and $J_x = \langle u_x \rangle$. The constant force can be considered as arising from a potential field

$$\phi(x) = -xf$$

The potential gradient $\partial\phi/\partial x$ will give rise to a concentration gradient $\partial c/\partial x$ which is opposite to the potential gradient and related to it by

$$\frac{\partial c}{\partial x} = -\frac{1}{kT} \frac{\partial \phi}{\partial x}$$

However, Fick's law tells how to relate the particle current J_x to the concentration gradient

$$J_x = -D \frac{\partial c}{\partial x} = \frac{D}{kT} \frac{\partial \phi}{\partial x} = -\frac{D}{kT} f$$

where D is the *diffusion constant*. Solving for D gives

$$D = -kT \frac{J_x}{f} = -kT \lim_{t \rightarrow \infty} \frac{\langle u_x(t) \rangle}{f}$$

Let us apply the linear response formula again to the above nonequilibrium average. Again, we make the identification:

$$F_e(t) = 1 \quad \mathbf{D}_i = f\hat{\mathbf{x}} \quad \mathbf{C}_i = 0$$

Thus,

$$\begin{aligned}\langle u_x(t) \rangle &= \langle u_x \rangle_0 - \beta \int_0^t ds f \left\langle \left(\sum_{i=1}^N \dot{x}_i(0) \right) \left(\sum_{i=1}^N \dot{x}_i(t-s) \right) \right\rangle_0 \\ &= \langle u_x \rangle_0 - \beta f \int_0^t ds \sum_{i,j} \langle \dot{x}_i(0) \dot{x}_j(t-s) \rangle_0\end{aligned}$$

In equilibrium, it can be shown that there are no cross correlations between different particles. Consider the initial value of the correlation function. From the virial theorem, we have

$$\langle \dot{x}_i \dot{x}_j \rangle_0 = \delta_{ij} \langle \dot{x}_i^2 \rangle_0$$

which vanishes for $i \neq j$. In general,

$$\langle \dot{x}_i(0) \dot{x}_j(t) \rangle_0 = \delta_{ij} \langle \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

Thus,

$$\langle u_x(t) \rangle = \langle u_x \rangle_0 - \beta f \int_0^t ds \sum_{i=1}^N \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

In equilibrium, $\langle u_x \rangle_0 = 0$ being linear in the velocities (hence momenta). Thus, the diffusion constant is given by, when the limit $t \rightarrow \infty$ is taken,

$$D = \int_0^\infty \sum_{i=1}^N \langle \dot{x}_i(0) \dot{x}_i(t) \rangle_0 dt$$

However, since no spatial direction is preferred, we could also choose to apply the external force in the y or z directions and average the result over the these three. This would give a diffusion constant

$$D = \frac{1}{3} \int_0^\infty dt \sum_{i=1}^N \langle \dot{\mathbf{q}}_i(0) \cdot \dot{\mathbf{q}}_i(t) \rangle_0$$

The quantity

$$\sum_{i=1}^N \langle \dot{\mathbf{q}}_i(0) \cdot \dot{\mathbf{q}}_i(t) \rangle_0$$

is known as the *velocity autocorrelation function*, a quantity we will encounter again in other contexts.