

## 4. The Green Kubo Relations

### 4.1 THE LANGEVIN EQUATION

In 1828 the botanist Robert Brown observed the motion of pollen grains suspended in a fluid. Although the system was allowed to come to equilibrium, he observed that the grains seemed to undergo a kind of unending irregular motion. This motion is now known as Brownian motion. The motion of large pollen grains suspended in a fluid composed of much lighter particles can be modelled by dividing the accelerating force into two components: a slowly varying *drag* force, and a rapidly varying *random* force due to the thermal fluctuations in the velocities of the solvent molecules. The Langevin equation as it is known, is conventionally written in the form,

$$\frac{d\mathbf{v}}{dt} = -\zeta\mathbf{v} + \mathbf{F}_R \quad (4.1)$$

Using the Navier-Stokes equations to model the flow around a sphere it is known that the friction coefficient  $\zeta = 6\pi\eta d/m$ , where  $\eta$  is the shear viscosity of the fluid,  $d$  is the diameter of the sphere and  $m$  is its mass. The random force per unit mass  $\mathbf{F}_R$ , is used to model the force on the sphere due to the bombardment of solvent molecules. This force is called random because it is assumed that  $\langle \mathbf{v}(0) \cdot \mathbf{F}_R(t) \rangle = 0, \forall t$ . A more detailed investigation of the drag on a sphere which is forced to oscillate in a fluid shows that a non-Markovian generalisation (see §2.4), of the Langevin equation (Langevin, 1908) is required to describe the time dependent drag on a rapidly oscillating sphere,

$$\frac{d\mathbf{v}(t)}{dt} = -\int_0^t dt' \zeta(t-t')\mathbf{v}(t') + \mathbf{F}_R(t) \quad (4.2)$$

In this case the viscous drag on the sphere is not simply linearly proportional to the instantaneous velocity of the sphere as in (4.1). Instead it is linearly proportional to the velocity at all previous times in the past. As we will see there are many transport processes which can be described by an equation of this form. We will refer to the equation

$$\frac{dA(t)}{dt} = -\int_0^t dt' K(t-t')A(t') + F(t) \quad (4.3)$$

as the generalised Langevin equation for the phase variable  $A(\Gamma)$ .  $K(t)$  is the time dependent transport coefficient that we seek to evaluate. We assume that the equilibrium canonical ensemble average of the random force and the phase variable  $A$ , vanishes for all times .

$$\langle A(0)F(t) \rangle = \langle A(t_0)F(t_0 + t) \rangle = 0, \quad \forall t \text{ and } t_0 \quad (4.4)$$

The time displacement by  $t_0$  is allowed because the equilibrium time correlation function is independent of the time origin. Multiplying both sides of (4.3) by the complex conjugate of  $A(0)$  and taking a canonical average we see that,

$$\frac{dC(t)}{dt} = - \int_0^t dt' K(t-t')C(t') \quad (4.5)$$

where  $C(t)$  is defined to be the equilibrium autocorrelation function,

$$C(t) \equiv \langle A(t)A^*(0) \rangle \quad (4.6)$$

Another function we will find useful is the flux autocorrelation function  $f(t)$

$$\phi(t) = \langle \dot{A}(t)\dot{A}^*(0) \rangle \quad (4.7)$$

Taking a Laplace transform of (4.5) we see that there is a intimate relationship between the transport memory kernel  $K(t)$  and the equilibrium fluctuations in  $A$ . The left-hand side of (4.5) becomes

$$\int_0^\infty dt e^{-st} \frac{dC(t)}{dt} = \left[ e^{-st}C(t) \right]_0^\infty - \int_0^\infty dt (-se^{-st})C(t) = s\tilde{C}(s) - C(0)$$

and as the right-hand side is a Laplace transform convolution,

$$s\tilde{C}(s) - C(0) = -\tilde{K}(s)\tilde{C}(s) \quad (4.8)$$

So that

$$\tilde{C}(s) = \frac{C(0)}{s + \tilde{K}(s)} \quad (4.9)$$

One can convert the  $A$  autocorrelation function into a flux autocorrelation function by

realising that,

$$\begin{aligned}\frac{d^2}{dt^2} C(t) &= \frac{d}{dt} \left\langle \frac{dA(t)}{dt} A^*(0) \right\rangle = \frac{d}{dt} \langle [iLA(t)] A^*(0) \rangle \\ &= \frac{d}{dt} \langle A(t) [-iLA^*(0)] \rangle = -\langle [iLA(t)] [-iLA^*(0)] \rangle = -\phi(t)\end{aligned}$$

Then we take the Laplace transform of a second derivative to find,

$$\begin{aligned}-\tilde{\phi}(s) &= \int_0^\infty dt \ e^{-st} \frac{d^2}{dt^2} C(t) = \left[ e^{-st} \frac{d}{dt} C(t) \right]_0^\infty + s \int_0^\infty dt \ e^{-st} \frac{d}{dt} C(t) \\ &= s \left[ e^{-st} C(t) \right]_0^\infty + s^2 \int_0^\infty dt \ e^{-st} C(t) = s^2 \tilde{C}(s) - sC(0)\end{aligned}\tag{4.10}$$

Here we have used the result that  $\dot{C}(0) = 0$ . Eliminating  $\tilde{C}(s)$  between equations (4.9) and (4.10) gives

$$\tilde{K}(s) = \frac{\tilde{\phi}(s)}{C(0) - \frac{\tilde{\phi}(s)}{s}}\tag{4.11}$$

Rather than try to give a general interpretation of this equation it may prove more useful to apply it to the Brownian motion problem.  $C(0)$  is the time zero value of an equilibrium time correlation function and can be easily evaluated as  $k_B T/m$ , and  $\dot{\mathbf{v}} = \mathbf{F}/m$  where  $\mathbf{F}$  is the total force on the Brownian particle.

$$\tilde{\zeta}(s) = \frac{\tilde{C}^F(s)}{mk_B T - \frac{\tilde{C}^F(s)}{s}}\tag{4.12}$$

where

$$\tilde{C}^F(s) = \frac{1}{3} \langle \mathbf{F}(0) \cdot \tilde{\mathbf{F}}(s) \rangle\tag{4.13}$$

is the Laplace transform of the total force autocorrelation function. In writing (4.13) we have used the fact that the equilibrium ensemble average denoted  $\langle \dots \rangle$ , must be isotropic. The average of any second rank tensor, say  $\langle \mathbf{F}(0) \mathbf{F}(t) \rangle$ , must therefore be a scalar multiple of the second rank identity tensor. That scalar must of course be  $\frac{1}{3} \text{Tr} \{ \langle \mathbf{F}(0) \mathbf{F}(t) \rangle \} = \frac{1}{3} \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle$ .

In the so-called Brownian limit where the ratio of the Brownian particle mass to the mean square of the force becomes infinite,

$$\tilde{\zeta}(s) = \frac{\beta}{3m} \int_0^\infty dt e^{-st} \langle \mathbf{F}(t) \cdot \mathbf{F}(0) \rangle \quad (4.14)$$

For any finite value of the Brownian ratio, equation (4.12) shows that the integral of the force autocorrelation function is zero. This is seen most easily by solving equation (4.12) for  $C^F$  and taking the limit as  $s \rightarrow 0$ .

Equation (4.9), which gives the relationship between the memory kernel and the phase autocorrelation function, implies that the velocity autocorrelation function  $Z(t) \equiv \frac{1}{3} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$  is related to the friction coefficient by the equation,

$$\tilde{Z}(s) = \frac{k_B T / m}{s + \tilde{\zeta}(s)} \quad (4.15)$$

This equation is valid outside the Brownian limit. The integral of the velocity autocorrelation function, is related to the growth of the mean square displacement giving yet another expression for the friction coefficient,

$$\begin{aligned} \tilde{Z}(0) &= \lim_{t \rightarrow \infty} \int_0^t dt' \frac{1}{3} \langle \mathbf{v}(0) \cdot \mathbf{v}(t') \rangle = \lim_{t \rightarrow \infty} \int_0^t dt' \frac{1}{3} \langle \mathbf{v}(t') \cdot \mathbf{v}(t') \rangle \\ &= \lim_{t \rightarrow \infty} \frac{1}{3} \langle \mathbf{v}(0) \cdot \Delta \mathbf{r}(t) \rangle = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{d}{dt} \langle \Delta \mathbf{r}(t)^2 \rangle \end{aligned} \quad (4.16)$$

Here the displacement vector  $\Delta \mathbf{r}(t)$  is defined by

$$\Delta \mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(0) = \int_0^t dt' \mathbf{v}(t') \quad (4.17)$$

Assuming that the mean square displacement is linear in time, in the long time limit, it follows from (4.15) that the friction coefficient can be calculated from

$$\frac{k_B T}{m \tilde{\zeta}(0)} \equiv D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta \mathbf{r}(t)^2 \rangle = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle \Delta \mathbf{r}(t)^2 \rangle}{t} \quad (4.18)$$

This is the Einstein (1905) relation for the diffusion coefficient  $D$ .

It should be pointed out that the transport properties we have just evaluated are properties of systems at equilibrium. The Langevin equation describes the irregular Brownian motion of particles *in an equilibrium system*. Similarly the self diffusion coefficient characterises the random walk executed by a particle in an equilibrium system. The identification of the zero frequency friction coefficient  $6\pi\eta d/m$ , with the viscous drag on a sphere which is forced to move with constant velocity through a fluid, implies that equilibrium fluctuations can be modelled by nonequilibrium transport coefficients, in this case the shear viscosity of the fluid. This hypothesis is known as the Onsager regression hypothesis (Onsager, 1931). The hypothesis can be inverted: one can calculate transport coefficients from a knowledge of the equilibrium fluctuations. We will now discuss these relations in more detail.

## 4.2 MORI-ZWANZIG THEORY

We will show that for an arbitrary phase variable  $A(\Gamma)$ , evolving under equations of motion which preserve the equilibrium distribution function, one can always write down a Langevin equation. Such an equation is an exact consequence of the equations of motion. We will use the symbol  $iL$ , to denote the Liouvillean associated with these equations of motion. These *equilibrium* equations of motion could be field-free Newtonian equations of motion or they could be field-free thermostatted equations of motion such as Gaussian isokinetic or Nosé-Hoover equations. The equilibrium distribution could be microcanonical, canonical or even isothermal-isobaric provided that if the latter is the case, suitable distribution preserving dynamics are employed. For simplicity we will compute equilibrium time correlation functions over the canonical distribution function,  $f_c$ ,

$$f_c(\Gamma) = \frac{e^{-\beta H_0(\Gamma)}}{\int d\Gamma e^{-\beta H_0(\Gamma)}} \quad (4.19)$$

We saw in the previous section that a key element of the derivation was that the correlation of the random force,  $\mathbf{F}_R(t)$  with the Langevin variable  $A$ , vanished for all time. We will now use the notation first developed in §3.5, which treats phase variables,  $A(\Gamma)$ ,  $B(\Gamma)$ , as vectors in  $6N$ -dimensional phase space with a scalar product defined by  $\int d\Gamma f_0(\Gamma) B(\Gamma) A^*(\Gamma)$ , and denoted as  $(B, A^*)$ . We will define a projection operator which will transform any phase variable  $B$ , into a vector which has no correlation with the Langevin variable,  $A$ . The component of  $B$  parallel to  $A$  is just,

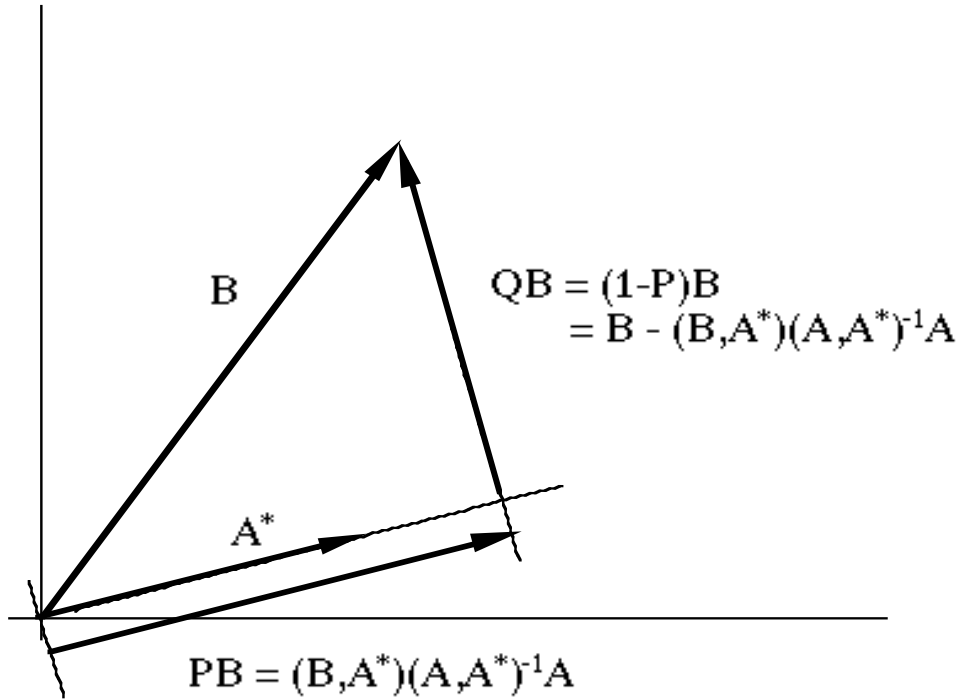
$$PB(\Gamma, t) = \frac{(B(\Gamma, t), A^*(\Gamma))}{(A(\Gamma), A^*(\Gamma))} A(\Gamma) \quad (4.20)$$

This equation defines the projection operator  $P$ .

The operator  $Q = 1 - P$ , is the complement of  $P$  and computes the component of  $B$  orthogonal to  $A$ .

$$(QB(t), A^*) = \left( B(t) - \frac{(B(t), A^*)}{(A, A^*)} A, A^* \right) = (B(t), A^*) - \frac{(B(t), A^*)}{(A, A^*)} (A, A^*) = 0 \quad (4.21)$$

In more physical terms the projection operator  $Q$  computes that part of any phase variable which is random with respect to a Langevin variable,  $A$ .



**Figure 4.1.** The projection operator  $P$ , operating on  $B$  produces a vector which is the component of  $B$  parallel to  $A$ .

Other properties of the projection operators are that,

$$PP = P, \quad QQ = Q, \quad QP = PQ = 0 \quad (4.22)$$

Secondly,  $P$  and  $Q$  are Hermitian operators (like the Liouville operator itself). To prove this we note that,

$$\begin{aligned}
(PB, C^*)^* &= \frac{((B, A^*)A, C^*)^*}{(A, A^*)^*} = \frac{(B, A^*)^*(A, C^*)^*}{(A, A^*)^*} = \frac{(B^*, A)(A^*, C)}{(A, A^*)} \\
&= \frac{(A, B^*)(C, A^*)}{(A, A^*)} = \frac{((C, A^*)A, B^*)}{(A, A^*)} = (PC, B^*)
\end{aligned} \tag{4.23}$$

Furthermore, since  $Q = 1 - P$  where 1 is the identity operator, and since both the identity operator and  $P$  are Hermitian, so is  $Q$ .

We will wish to compute the random and direct components of the propagator  $e^{iLt}$ . The random and direct parts of the Liouvillean  $iL$  are  $iQL$  and  $iPL$  respectively. These Liouvilleans define the corresponding random and direct propagators,  $e^{iQLt}$  and  $e^{iPLt}$ . We can use the Dyson equation to relate these two propagators. If we take  $e^{iQLt}$  as the reference propagator in (3.100) and  $e^{iLt}$  as the test propagator then,

$$e^{iLt} = e^{iQLt} + \int_0^t d\tau e^{iL(t-\tau)} iPL e^{iQL\tau} \tag{4.24}$$

The rate of change of  $A(t)$ , the Langevin variable at time  $t$  is,

$$\frac{dA(t)}{dt} = e^{iLt} iLA = e^{iLt} i(Q + P)LA \tag{4.25}$$

But,

$$e^{iLt} iPLA = e^{iLt} \frac{(iLA, A^*)}{(A, A^*)} A = \frac{(iLA, A^*)}{(A, A^*)} e^{iLt} A \equiv i\Omega A(t) \tag{4.26}$$

This defines the frequency  $i\Omega$  which is an equilibrium property of the system. It only involves equal time averages. Substituting this equation into (4.25) gives,

$$\frac{dA(t)}{dt} = i\Omega A(t) + e^{iLt} iQLA \tag{4.27}$$

Using the Dyson decomposition of the propagator given in equation (4.24), this leads to,

$$\frac{dA(t)}{dt} = i\Omega A(t) + \int_0^t d\tau e^{iL(t-\tau)} iPL e^{iQL\tau} iQLA + e^{iQLt} iQLA \tag{4.28}$$

We identify  $e^{iQLt} iQLA$  as the random force  $F(t)$  because,

$$(F(t), A^*) = (e^{iQLt} iQLA, A^*) = (QF(t), A^*) = 0 \quad (4.29)$$

where we have used (4.22). It is very important to remember that the propagator which generates  $F(t)$  from  $F(0)$  is not the propagator  $e^{iLt}$ , rather it is the random propagator  $e^{iQLt}$ . The integral in (4.28) involves the term,

$$iPL e^{iQLt} iQLA = iPLF(t) = iPLQF(t) = \frac{(iLQF(t), A^*)}{(A, A^*)} A = -\frac{(QF(t), (iLA)^*)}{(A, A^*)} A$$

as  $L$  is Hermitian and  $i$  is anti-Hermitian,  $(iL)^* = (d/dt)^* = (\dot{\Gamma} \cdot \partial / \partial \Gamma)^* = d/dt = iL$ , (since the equations of motion are real). Since  $Q$  is Hermitian,

$$iPL e^{iQLt} iQLA = -\frac{(F(t), (iQLA)^*)}{(A, A^*)} A = -\frac{(F(t), F(0)^*)}{(A, A^*)} A \equiv -K(t)A \quad (4.30)$$

where we have defined a memory kernel  $K(t)$ . It is basically the autocorrelation function of the random force. Substituting this definition into (4.28) gives

$$\begin{aligned} \frac{dA(t)}{dt} &= i\Omega A(t) - \int_0^t d\tau e^{iL(t-\tau)} K(\tau) A + F(t) \\ &= i\Omega A(t) - \int_0^t d\tau K(\tau) A(t-\tau) + F(t) \end{aligned} \quad (4.31)$$

This shows that the *Generalised Langevin Equation* is an exact consequence of the equations of motion for the system (Mori, 1965a, b; Zwanzig, 1961). Since the random force is random with respect to  $A$ , multiplying both sides of (4.31) by  $A^*(0)$  and taking a canonical average gives the memory function equation,

$$\frac{dC(t)}{dt} = i\Omega C(t) - \int_0^t d\tau K(\tau) C(t-\tau) \quad (4.32)$$

This is essentially the same as equation (4.5).

As we mentioned in the introduction to this section the generalised Langevin equation and the memory function equation are exact consequences of any dynamics which preserves the equilibrium distribution function. As such the equations therefore describe equilibrium fluctuations in the phase variable  $A$ , and the equilibrium autocorrelation function for  $A$ , namely  $C(t)$ .

However the generalised Langevin equation bears a striking resemblance to a



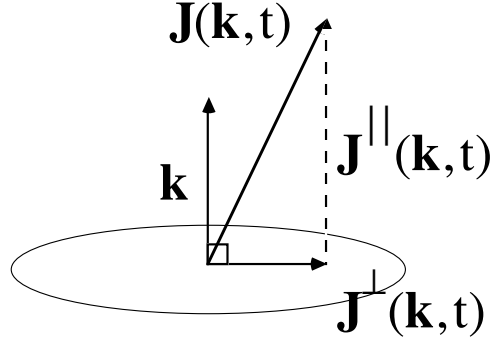
nonequilibrium constitutive relation. The memory kernel  $K(t)$  plays the role of a transport coefficient. Onsager's regression hypothesis (1931) states that the equilibrium fluctuations in a phase variable are governed by the same transport coefficients as is the relaxation of that same phase variable to equilibrium. This hypothesis implies that the generalised Langevin equation can be interpreted as a linear, **nonequilibrium** constitutive relation with the memory function  $K(t)$ , given by the **equilibrium** autocorrelation function of the random force.

Onsager's hypothesis can be justified by the fact that in observing an *equilibrium* system for a time which is of the order of the relaxation time for the memory kernel, it is impossible to tell whether the system is at equilibrium or not. We could be observing the final stages of a relaxation towards equilibrium or, we could be simply observing the small time dependent fluctuations in an equilibrium system. On a short time scale there is simply no way of telling the difference between these two possibilities. When we interpret the generalised Langevin equation as a nonequilibrium constitutive relation, it is clear that it can only be expected to be valid close to equilibrium. This is because it is a linear constitutive equation.

### 4.3 SHEAR VISCOSITY

It is relatively straightforward to apply the Mori-Zwanzig formalism to the calculation of fluctuation expressions for linear transport coefficients. Our first application of the method will be the calculation of shear viscosity. Before we do this we will say a little more about constitutive relations for shear viscosity. The Mori-Zwanzig formalism leads naturally to a non-Markovian expression for the viscosity. Equation (4.31) refers to a memory function rather than a simple Markovian transport coefficient such as the Newtonian shear viscosity. We will thus be lead to a discussion of viscoelasticity (see §2.4).

We choose our test variable  $A$ , to be the  $x$ -component of the wavevector dependent transverse momentum current  $\mathbf{J}^\perp(\mathbf{k}, t)$ .



$$\mathbf{J}(\mathbf{k}, t) = \mathbf{J}^{\perp}(\mathbf{k}, t) + \mathbf{J}^{\parallel}(\mathbf{k}, t)$$

**Figure 4.2.** We can resolve the wavevector dependent momentum density into components which are parallel and orthogonal to the wavevector,  $\mathbf{k}$ .

For simplicity, we define the coordinate system so that  $\mathbf{k}$  is in the  $y$  direction and  $\mathbf{J}^{\perp}$  is in the  $x$  direction.

$$J_x(k_y, t) = \sum_i m v_{xi}(t) \exp(ik_y y_i(t)) \quad (4.33)$$

In §3.8 we saw that

$$\dot{J} = ik P_{yx}(k, t) \quad (4.34)$$

where for simplicity we have dropped the Cartesian indices for  $J$  and  $k$ . We note that at zero wavevector the transverse momentum current is a constant of the motion,  $\dot{J} = 0$ . The quantities we need in order to apply the Mori-Zwanzig formalism are easily computed.

The frequency matrix  $i\Omega$ , defined in (4.26), is identically zero. This is always so in the single variable case as  $\langle A^* \dot{A} \rangle = 0$ , for any phase variable  $A$ . The norm of the transverse current is calculated

$$\begin{aligned} \langle J(k) J^*(k) \rangle &= \left\langle \sum_{i=1}^N p_{xi} e^{iky_i} \sum_{j=1}^N p_{xj} e^{-iky_j} \right\rangle \\ &= N \langle p_{x1}^2 \rangle + N(N-1) \langle p_{x1} p_{x2} e^{ik(y_1 - y_2)} \rangle = N m k_B T \end{aligned} \quad (4.35)$$

At equilibrium  $p_{x1}$  is independent of  $p_{x2}$  and  $(y_1 - y_2)$  so the correlation function factors into the product of three equilibrium averages. The values of  $\langle p_{x1} \rangle$  and  $\langle p_{x2} \rangle$  are

identically zero. The random force,  $F$ , can also easily be calculated since, if we use (4.34)

$$PP_{yx}(k) = \frac{(P_{yx}(k), J(-k))}{\langle |J(k)|^2 \rangle} J = 0 \quad (4.36)$$

we can write,

$$F(0) = iQLJ = (1 - P)ikP_{yx}(k) = ikP_{yx}(k) \quad (4.37)$$

The time dependent random force (see (4.29)), is

$$F(t) = e^{iQLt} ikP_{yx}(k) \quad (4.38)$$

A Dyson decomposition of  $e^{iQLt}$  in terms of  $e^{iLt}$  shows that,

$$e^{iLt} = e^{iQLt} + \int_0^t ds e^{iL(t-s)} iPL e^{iQLs} \quad (4.39)$$

Now for any phase variable  $B$ ,

$$iPLB = \langle J^* iLB \rangle \frac{J}{Nmk_B T} = -\langle B(iLJ)^* \rangle \frac{J}{Nmk_B T} = -ik \langle BP_{yx}(-k) \rangle \frac{J}{Nmk_B T} \quad (4.40)$$

Substituting this observation into (4.39) shows that the difference between the propagators  $e^{iQLt}$  and  $e^{iLt}$  is of order  $k$ , and can therefore be ignored in the zero wavevector limit.

From equation (4.30) the memory kernel  $K(t)$  is  $\langle F(t)F^*(0) \rangle / \langle AA^* \rangle$ . Using equation (4.38), the small wavevector form for  $K(t)$  becomes,

$$K(t) = k^2 \frac{\langle P_{yx}(k, t) P_{yx}(-k, 0) \rangle}{Nmk_B T} \quad (4.41)$$

The generalised Langevin equation (the analogue of equation 4.31) is

$$\lim_{k \rightarrow 0} \frac{dJ_x(k_y, t)}{dt} = -\frac{k^2}{Nmk_B T} \int_0^t ds \langle P_{yx}(k_y, s) P_{yx}(-k_y, 0) \rangle_0 J_x(k_y, t-s) + ik_y P_{yx}(k_y, t) \quad (4.42)$$

where we have taken explicit note of the Cartesian components of the relevant functions. Now we know that the rate of change of the transverse current is  $ikP_{yx}(k, t)$ . This means

that the left hand side of (4.42) is related to equilibrium fluctuations in the shear stress. We also know that  $J(k) = \int dk' \rho(k' - k)u(k')$ , so, close to equilibrium, the transverse momentum current (our Langevin variable  $A$ ), is closely related to the wavevector dependent strain rate  $\gamma(k)$ . In fact the wavevector dependent strain rate  $\gamma(k)$  is  $-ikJ(k)/\rho(k=0)$ . Putting these two observations together we see that the generalised Langevin equation for the transverse momentum current is essentially a relation between fluctuations in the shear stress and the strain rate - a constitutive relation. Ignoring the random force (constitutive relations are deterministic), we find that equation (4.42) can be written in the form of the constitutive relation (2.76),

$$\lim_{k \rightarrow 0} P_{yx}(t) = -\int_0^t ds \eta(k=0, t-s) \gamma(k=0, s) \quad (4.43)$$

If we use the fact that,  $P_{yx}V = \lim_{k \rightarrow 0} P_{yx}(k)$ ,  $\eta(t)$  is easily seen to be

$$\eta(t) = \beta V \langle P_{yx}(t) P_{yx}(0) \rangle \quad (4.44)$$

Equation (4.43) is identical to the viscoelastic generalisation of Newton's law of viscosity equation (2.76).

The Mori-Zwanzig procedure has derived a viscoelastic constitutive relation. No mention has been made of the shearing boundary conditions required for shear flow. Neither is there any mention of viscous heating or possible non linearities in the viscosity coefficient. Equation (4.42) is a description of equilibrium fluctuations. However unlike the case for the Brownian friction coefficient or the self diffusion coefficient, the viscosity coefficient refers to nonequilibrium rather than equilibrium systems.

The zero wavevector limit is subtle. We can imagine longer and longer wavelength fluctuations in the strain rate  $\gamma(k)$ . For an equilibrium system however  $\gamma(k=0) \equiv 0$  and  $\langle \gamma(k=0) \gamma^*(k=0) \rangle \equiv 0$ . There are **no** equilibrium fluctuations in the strain rate at  $k=0$ . The zero wavevector strain rate is completely specified by the boundary conditions.

If we invoke Onsager's regression hypothesis we can obviously identify the memory kernel  $\eta(t)$  as the memory function for planar (ie.  $k=0$ ) Couette flow. We might observe that there is no fundamental way of knowing whether we are watching small equilibrium fluctuations at small but non-zero wavevector, or the *last* stages of relaxation toward equilibrium of a finite  $k$ , nonequilibrium disturbance. Provided the nonequilibrium system is sufficiently close to equilibrium, the Langevin memory function will be the nonequilibrium memory kernel. However the Onsager regression hypothesis is additional

to, and not part of, the Mori-Zwanzig theory. In §6.3 we prove that the nonequilibrium linear viscosity coefficient is given exactly by the infinite time integral of the stress fluctuations. In §6.3 we will not use the Onsager regression hypothesis.

At this stage one might legitimately ask the question: what happens to these equations if we do **not** take the zero wavevector limit? After all we have already defined a wavevector dependent shear viscosity in (2.77). It is not a simple matter to apply the Mori-Zwanzig formalism to the finite wavevector case. We will instead use a method which makes a direct appeal to the Onsager regression hypothesis.

Provided the time and spatially dependent strain rate is of sufficiently small amplitude, the generalised viscosity can be defined as (2.77),

$$P_{yx}(k, t) = - \int_0^t ds \eta(k, t-s) \gamma(k, s) \quad (4.45)$$

Using the fact that  $\gamma(k, t) = -iku_x(k, t) = -ikJ(k, t)/\rho$ , and equation (4.34), we can rewrite (4.45) as,

$$\dot{J}(k, t) = - \frac{k^2}{\rho} \int_0^t ds \eta(k, t-s) J(k, s) \quad (4.46)$$

If we Fourier-Laplace transform both sides of this equation in time, and using Onsager's hypothesis, multiply both sides by  $J(-k, 0)$  and average with respect to the equilibrium canonical ensemble we obtain,

$$\tilde{C}(k, \omega) = \frac{C(k, 0)}{i\omega + \frac{k^2 \tilde{\eta}(k, \omega)}{\rho}} \quad (4.47)$$

where  $C(k, t)$  is the equilibrium transverse current autocorrelation function  $\langle J(k, t) J(-k, 0) \rangle$  and the tilde notation denotes a Fourier-Laplace transform in time,

$$\tilde{C}(\omega) = \int_0^\infty dt C(t) e^{-i\omega t} \quad (4.48)$$

We call the autocorrelation function of the wavevector dependent shear stress,

$$N(k, t) \equiv \frac{1}{Vk_B T} \langle P_{yx}(k, t) P_{yx}(-k, 0) \rangle \quad (4.49)$$

We can use the equation (4.34), to transform from the transverse current autocorrelation function  $C(k, t)$  to the stress autocorrelation function  $N(k, t)$  since,

$$\frac{d^2}{dt^2} \langle J(k, t) J(-k, 0) \rangle = - \langle \dot{J}(k, t) \dot{J}(-k, 0) \rangle = -k^2 \langle P_{yx}(k, t) P_{yx}(-k, 0) \rangle \quad (4.50)$$

This derivation closely parallels that for equation (4.10) and (4.11) in §4.1. The reader should refer to that section for more details. Using the fact that,  $\rho = Nm/V$ , we see that,

$$k^2 V k_B T \tilde{N}(k, \omega) = \omega^2 \tilde{C}(k, \omega) + i\omega C(k, 0) \quad (4.51)$$

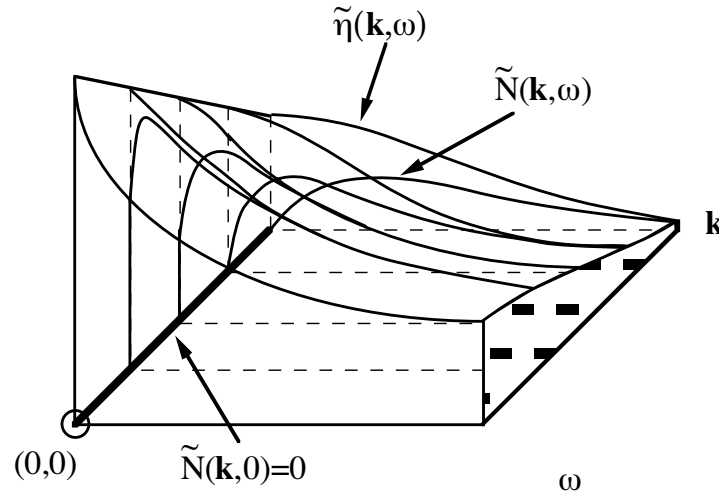
The equilibrium average  $C(k, 0)$  is given by equation (4.35). Substituting this equation into equation (4.47) gives us an equation for the frequency and wavevector dependent shear viscosity in terms of the stress autocorrelation function,

$$\tilde{\eta}(k, \omega) = \frac{\tilde{N}(k, \omega)}{1 - \frac{k^2 \tilde{N}(k, \omega)}{i\omega\rho}} \quad (4.52)$$

This equation is **not** of the Green-Kubo form. Green-Kubo relations are exceptional being only valid for infinitely slow processes. Momentum relaxation is only infinitely slow at **zero** wavevector. At finite wavevectors momentum relaxation is a *fast* process. We can obtain the usual Green-Kubo form by taking the zero  $k$  limit of equation (4.52). In that case

$$\tilde{\eta}(0, \omega) = \lim_{k \rightarrow 0} \tilde{N}(k, \omega) \quad (4.53)$$

Schematic Diagram of the frequency and wavevector dependent viscosity and stress autocorrelation function.



**Figure 4.3.** The relationship between the viscosity,  $\tilde{\eta}(k, \omega)$ , and the stress autocorrelation function,  $\tilde{N}(k, \omega)$ . At  $k = 0$  both functions are identical. At  $\omega = 0$  but  $k \neq 0$ , the stress autocorrelation function is identically zero. The stress autocorrelation function is discontinuous at the origin. The viscosity is continuous everywhere but non-analytic at the origin (see Evans, (1981)).

Because there are no fluctuations in the zero wavevector strain rate the function  $\tilde{N}(k, \omega)$  is discontinuous at the origin. For all nonzero values of  $k$ ,  $\tilde{N}(k, 0) = 0$ ! Over the years many errors have been made as a result of this fact. Figure 4.3 above illustrates these points schematically. The results for shear viscosity precisely parallel those for the friction constant of a Brownian particle. Only in the Brownian limit is the friction constant given by the autocorrelation function of the Brownian force.

An immediate conclusion from the theory we have outlined is that **all** fluids are viscoelastic. Viscoelasticity is a direct result of the Generalised Langevin equation which is in turn an exact consequence of the microscopic equations of motion.

#### 4.4 GREEN-KUBO RELATIONS FOR NAVIER-STOKES TRANSPORT COEFFICIENTS

It is relatively straightforward to derive Green-Kubo relations for the other Navier-Stokes transport coefficients, namely bulk viscosity and thermal conductivity. In §6.3 when we

describe the SLLOD equations of motion for viscous flow we will find a simpler way of deriving Green-Kubo relations for both viscosity coefficients. For now we simply state the Green-Kubo relation for bulk viscosity as (Zwanzig, 1965),

$$\eta_v = \frac{1}{Vk_B T} \int_0^\infty dt \langle (p(t)V(t) - \langle pV \rangle)(p(0)V(0) - \langle pV \rangle) \rangle \quad (4.54)$$

The Green-Kubo relation for thermal conductivity can be derived by similar arguments to those used in the viscosity derivation. Firstly we note from (2.26), that in the absence of a velocity gradient, the internal energy per unit volume  $\rho U$  obeys a continuity equation,  $\rho dU/dt = -\nabla \cdot \mathbf{J}_Q$ . Secondly, we note that Fourier's definition of the thermal conductivity coefficient  $\lambda$ , from equation (2.56a), is  $\mathbf{J}_Q = -\lambda \nabla T$ . Combining these two results we obtain

$$\rho \frac{dU}{dt} = \lambda \nabla^2 T \quad (4.55)$$

Unlike the previous examples, both  $U$  and  $T$  have nonzero equilibrium values; namely,  $\langle U \rangle$  and  $\langle T \rangle$ . A small change in the left-hand side of equation (4.55) can be written as  $(\rho + \Delta\rho)d(\langle U \rangle + \Delta U)/dt$ . By definition  $d\langle U \rangle/dt = 0$ , so to first order in  $\Delta$ , we have  $\rho d\Delta U/dt$ . Similarly, the spatial gradient of  $\langle T \rangle$  does not contribute, so we can write

$$\rho \frac{d\Delta U}{dt} = \lambda \nabla^2 \Delta T \quad (4.56)$$

The next step is to relate the variation in temperature  $\Delta T$  to the variation in energy per unit volume  $\Delta(\rho U)$ . To do this we use the thermodynamic definition,

$$\left. \frac{1}{V} \frac{\partial E}{\partial T} \right|_V = \left. \frac{\partial(\rho U)}{\partial T} \right|_V = \rho c_v \quad (4.57)$$

where  $c_v$  is the specific heat per unit mass. We see from the second equality, that a small variation in the temperature  $\Delta T$  is equal to  $\Delta(\rho U)/\rho c_v$ . Therefore,

$$\rho \Delta \dot{U} = \frac{\lambda}{\rho c_v} \nabla^2 \rho \Delta U \quad (4.58)$$

If  $D_T \equiv \lambda/\rho c_v$  is the thermal diffusivity, then in terms of the wavevector dependent internal energy density equation (4.58) becomes,



$$\rho \Delta \dot{U}(\mathbf{k}, t) = -k^2 \tilde{D}_T \rho \Delta U(\mathbf{k}, t) \quad (4.59)$$

If  $C(k, t)$  is the wavevector dependent internal energy density autocorrelation function,

$$C(k, t) \equiv \langle \rho \Delta U(\mathbf{k}, t) \rho \Delta U(-\mathbf{k}, 0) \rangle \quad (4.60)$$

then the frequency and wavevector dependent diffusivity is the memory function of energy density autocorrelation function,

$$\tilde{C}(k, \omega) = \frac{C(k, 0)}{i\omega + k^2 \tilde{D}_T(k, \omega)} \quad (4.61)$$

Using exactly the same procedures as in §4.1 we can convert (4.61) to an expression for the diffusivity in terms of a current correlation function. From (4.7 & 10) if  $\phi = -\ddot{C}$  then,

$$\phi(k, t) = k^2 \langle J_{Qx}(k, t) J_{Qx}(-k, 0) \rangle \quad (4.62)$$

Using equation (4.10), we obtain the analogue of (4.11),

$$k^2 \tilde{D}_T(k, \omega) = \frac{C(k, 0) - i\omega \tilde{C}(k, \omega)}{\tilde{C}(k, \omega)} = \frac{\tilde{\phi}(k, \omega)}{C(k, 0) - \frac{\tilde{\phi}(k, \omega)}{i\omega}} \quad (4.63)$$

If we define the analogue of equation (4.49), that is  $\phi(k, t) = k^2 N_Q(k, t)$ , then equation (4.63) for the thermal diffusivity can be written in the same form as the wavevector dependent shear viscosity equation (4.52). That is

$$\tilde{D}_T(k, \omega) = \frac{\tilde{N}_Q(k, \omega)}{C(k, 0) - \frac{k^2}{i\omega} \tilde{N}_Q(k, \omega)} \quad (4.64)$$

Again we see that we must take the zero wavevector limit **before** we take the zero frequency limit, and using the canonical ensemble fluctuation formula for the specific heat,

$$\rho c_V = \frac{V}{k_B T^2} C(0, 0) \quad (4.65)$$

we obtain the Green-Kubo expression for the thermal conductivity

$$\lambda = \frac{V}{k_B T^2} \int_0^\infty dt \langle J_{Qx}(t) J_{Qx}(0) \rangle \quad (4.66)$$

This completes the derivation of Green-Kubo formula for thermal transport coefficients. These formulae relate thermal transport coefficients to equilibrium properties. In the next chapter we will develop nonequilibrium routes to the thermal transport coefficients.

## REFERENCES

- Zwanzig, R., (1965). *Ann. Rev. Phys. Chem.*, **16**, 67.  
 Mori, H., (1965a). *Prog. Theo. Phys.*, **33**, 423.  
 Mori, H., (1965b). *Prog. Theo. Phys.*, **34**, 399.  
 Zwanzig, R., (1961). "Lectures in Theoretical Physics (Boulder)", Vol III, p.135, Wiley, New York.  
 Kubo, R., (1957). *J. Phys. Soc. Japan*, **12**, 570.  
 Green, M. S., (1954). *J. Chem. Phys.*, **22**, 398.  
 Einstein, A., (1905). *Ann. d. Phys.*, **17**, 549.  
 Onsager, L., (1931). *Phys. Rev.*, **37**, 405; **38**, 2265.  
 Brown, R., (1828). *Phil. Mag.*, **4**, 161.  
 Brown, R., (1828). *Ann. d. Phys. u. Chem.*, **14**, 294.  
 Langevin, P., (1908). *C.R. Acad. Sci. (Paris)*, **146**, 530.  
 Evans, D.J., (1981). *Phys. Rev.*, **A23**, 2622.