

Chapter 3

Shear flow

3.1 Transport processes and transport coefficients

A material system composed of many particles can be either in thermodynamic equilibrium or non-equilibrium [Pry96]. The character of a system in thermodynamic equilibrium is uniform in both space and time on the macroscale. That is to say, its' properties (or phase variables), are uniform within the whole system[†]. For example, mass density, temperature, etc., are equal everywhere throughout the system and there is no net flux of mass, momentum and energy. Furthermore time averages of properties do not change with time, but can only fluctuate instantaneously around their mean values. The deviations from their mean values are so small that they cannot be observed macroscopically.

If the system is not in thermodynamic equilibrium, the properties of the system are not uniform. That is to say, some properties differ from place to place in the system, or difference of concentration of these properties exists from one region to an adjacent region. In this case, a net transport of these properties will occur. These properties will transfer or diffuse from one place to another. This kind of process is called a transfer or transport process. A transport process is one important character of non-equilibrium systems.

The most common transport processes are mass, heat (or thermal energy) and momentum transport. When the density or concentration in a system is not uniform (inhomogenous), or

[†] We note however that this definition is not strictly true for systems that are spatially inhomogeneous at the microscale, e.g., confined fluids where the pore width is of the order of nanometers.

in mathematical language, there exist density gradients, due to particle movement and interaction, diffusion and/or momentum exchange processes occur. Some mass will transfer from one place with higher density to another with lower density. This is mass transfer. Another example is thermal conduction. If the temperature in a system is not uniform, in other words, there exists a temperature gradient, some heat or thermal energy will transfer from the hotter part to the colder part. This is heat transfer. Another important transfer phenomenon is momentum transfer. For example, in a shear flow, when the velocity of one layer is different from that of an adjacent layer, there exists a velocity gradient. Viscous forces will appear and we can describe these by reference to the shear viscosity. The faster layer slows down due to the interaction with the slower layer, and the slower layer will gain velocity according to Newton's third law. In this way, momentum will transfer from faster layers to slower layers. When one part of a system is expanded or compressed, bulk viscosity can be used to describe the process. Bulk viscosity also is descriptive of momentum transfer. The difference between shear viscosity and bulk viscosity is that shear viscosity is related to the shear stress of a fluid and bulk viscosity relates to its' normal stress. Shear stress and normal stress are different components of the stress tensor, which we describe later.

Although transport processes are an important property of non-equilibrium systems, transport processes do exist in equilibrium. For example, in equilibrium, particles can transfer from one place to another. In this case, self diffusion occurs. But there is no 'net' mass transfer from one place to another. In the remainder of this work, when we describe transport processes, we mean transport under non-equilibrium conditions.

From the above discussion, we know that if there is a concentration gradient of a certain property, there will be a net flux of the property from high to low concentration. How can we describe these processes quantitatively?

When the system is not far from equilibrium, a linear relationship exists between the thermodynamic fluxes (e.g. the heat flux vector or the viscous pressure tensor) and their conjugate thermodynamic forces (such as temperature gradient or strain rate tensor) for

describing transport processes, and the four transport coefficients are defined by the following linear constitutive equations [Eva90]:

$$\text{Self diffusion:} \quad \mathbf{J}_n = -D\nabla c_n \quad (3.1)$$

$$\text{Thermal conductivity:} \quad \mathbf{J}_Q = -\lambda\nabla T \quad (3.2)$$

$$\text{Shear viscosity:} \quad \mathbf{\Pi}^S = -2\eta(\nabla\mathbf{u})^S \quad (3.3)$$

$$\text{Bulk viscosity:} \quad \Pi = -\eta_v\nabla\cdot\mathbf{u} \quad (3.4)$$

In the above expressions, equation (3.1) is Fick's law for mass diffusion. \mathbf{J}_n is the mass flux vector. It represents the quantity of mass transferred per second per unit area; c_n is the concentration of species n and D is the self diffusion coefficient. Equation (3.2) is known as Fourier's law of heat conduction. \mathbf{J}_Q is the heat flux vector, which gives the thermal energy transferred across a unit area per unit time. T is temperature, and λ is the thermal conductivity[†]. Equation (3.3) is known as Newton's law of viscosity. It provides a definition of the shear viscosity coefficient η . $\mathbf{\Pi}$ is the viscous or non-equilibrium pressure tensor. \mathbf{u} is the streaming velocity of the fluid. The superscript 'S' means the symmetric traceless part, $\mathbf{\Pi}^S = \frac{1}{2}(\mathbf{\Pi} + \mathbf{\Pi}^T) - \frac{1}{3}\text{tr}(\mathbf{\Pi})\mathbf{I}$, and the superscript T denotes the transpose. The pressure tensor is a second rank tensor, and we will discuss it in more detail later. Equation (3.4) defines the bulk viscosity coefficient η_v .

3.2 Navier-Stokes equations

In hydrodynamics, the basic equations describing the transport of mass, momentum and energy are the Navier-Stokes equations. If we substitute the linear constitutive equations

[†] It has recently been proposed and verified by numerical simulation that an additional term couples the gradient of the square of the strain rate tensor with the heat flux vector even in the linear weak-field regime. Little is known about this new transport coefficient [Bar92, Tod97a, Ayt99].

into the mass, momentum and energy conservation equations, we obtain the following Navier-Stokes equations [Eva90]:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}) \quad (3.5)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p + \eta \nabla^2 \mathbf{u} + \left(\frac{\eta}{3} + \eta_v \right) \nabla (\nabla \cdot \mathbf{u}) \quad (3.6)$$

$$\rho \frac{dU}{dt} = \lambda \nabla^2 T - p (\nabla \cdot \mathbf{u}) + \eta_v (\nabla \cdot \mathbf{u})^2 + 2\eta (\nabla \mathbf{u})^S : (\nabla \mathbf{u})^S \quad (3.7)$$

For incompressible, planar shear flow, the above Navier-Stokes equations reduce to the following form:

$$\nabla \cdot \mathbf{u} = 0 \quad (3.8)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p + \eta \nabla^2 \mathbf{u} \quad (3.9)$$

$$\rho \frac{dU}{dt} = \lambda \nabla^2 T + 2\eta (\nabla \mathbf{u})^S : (\nabla \mathbf{u})^S \quad (3.10)$$

If we know all the transport coefficients, with suitable boundary conditions, the Navier-Stokes equations can completely describe a non-equilibrium flow. So the study of transport coefficients of materials has a clear technological importance.

3.3 Stress tensor and pressure tensor

The basic meaning of the concept of stress is force per unit area exerted on a material body [Fer91a]. Consider an arbitrary point P in a fluid. We can choose a surface S containing the point P. This surface can be considered a vector. Its magnitude is the area S . Its direction is determined by its normal vector \mathbf{n} . Now assume a certain force \mathbf{F} acts on this surface. The force \mathbf{F} is also a vector. We can use F to express its magnitude, \mathbf{m} to express its direction. The directions of \mathbf{n} and \mathbf{m} can be different. Now let us define a stress vector.

$$\mathbf{T}_{mn} = \lim_{S \rightarrow 0} \frac{F}{S} \mathbf{m} \quad (3.11)$$

If the above limit exists, and the limit is independent of the manner in which the area S approaches zero, \mathbf{T}_{mn} is called a stress vector. Here we use two subscripts m and n to reflect that there are two directions associated with the stress. The first one (m) shows the direction of the force, and the second one (n) shows the direction of the surface. This vector depends on the choice of P and the direction of \mathbf{n} .

In a Cartesian coordinate system x_i ($i = 1, 2, 3$), the stress vector \mathbf{T}_{mn} can be expressed as its components T_{in} ($i = 1, 2, 3$). In another Cartesian coordinate system x'_i ($i = 1, 2, 3$), the same vector can be expressed as T'_{in} ($i = 1, 2, 3$). Since the stress vector is a vector, its components should satisfy the transformation formula for a vector between two Cartesian coordinate systems:

$$T'_{jn} = a_{ji} T_{in} \quad (3.12)$$

Where a_{ji} is the cosine of the angles between the axis j of the coordinate system x_i and the axis i of the coordinate system x'_i .

To obtain the full characterization of the stress at one point P , knowing the stress at only one surface is not enough. We need to know the stress at any surface with an arbitrary direction \mathbf{n} . At first glance this seems to be not easy, because an infinite number of surfaces surround one point P . However, one can prove that if we know three stress vectors on three mutually perpendicular surfaces, then we can compute the stress on any surface.

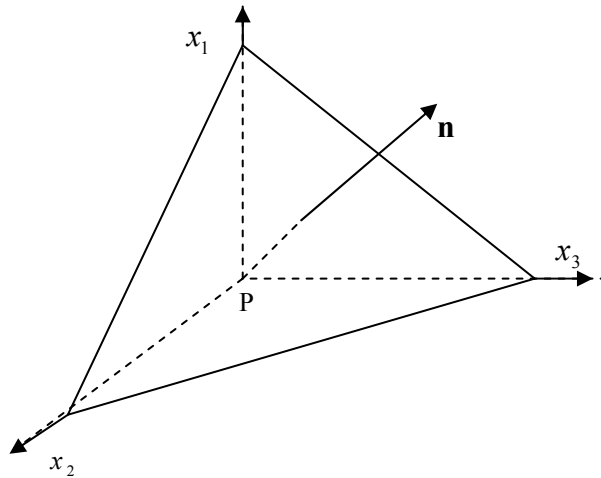


Figure. 3.1 An elementary tetrahedron with three of its faces parallel to the coordinate planes through point P and the fourth with normal \mathbf{n} .

Consider Figure 3.1, where we use the point P as the origin to construct a Cartesian coordinate system. Then we construct a tetrahedron with its three surfaces perpendicular to the three axes. According to the conventional rule, normals of surfaces point outside the tetrahedron. Because we can adjust the intersect point on the three axis, the normal of the fourth surface \mathbf{n} can have any arbitrary direction.

Assume that we know the three stress vectors which are acted on three mutually perpendicular surfaces: \mathbf{A} , \mathbf{B} , \mathbf{C} .

Their components are:

$$\text{vector } \mathbf{A} : T_{11}, T_{21}, T_{31}$$

$$\text{vector } \mathbf{B} : T_{12}, T_{22}, T_{32}$$

$$\text{vector } \mathbf{C} : T_{13}, T_{23}, T_{33}$$

These components are denoted by two subscripts. The first signifies the direction of force and second the surface normal. These three stress vectors are on three surfaces perpendicular to the axes. But they themselves are not necessary perpendicular to each other.

We denote the stress vector on the fourth surface as \mathbf{D} : T_{1n}, T_{2n}, T_{3n} .

Noticing that the body force will limit to zero when the volume approaches zero and in the limit the tetrahedron is locally balanced, we know the sum of all the forces acting on the four surfaces is zero. From here we can find:

$$T_{in} = T_{ij} a_{jn} \quad (3.13)$$

Where a_{jn} is the cosine of the angle between the direction of the axis x_j and the direction of vector \mathbf{n} . This formula proves that stress in any direction can be expressed by the stresses on three mutually perpendicular surfaces.

Now we want to express this stress vector in another coordinate system. From the vector transformation formula Eqn. (3.12), we know:

$$T'_{kn} = a_{ki} T_{in} \quad (3.14)$$

Substituting Eqn. (3.13) into Eqn. (3.14), we get:

$$T'_{kn} = a_{ki} T_{ij} a_{jn} \quad (3.15)$$

This relation is called the transformation formula for the components of tensor \mathbf{T} . Any set of nine numbers which transform according to this formula is defined as a second-rank tensor. The nine components of stress T_{ij} are in fact those of a second-rank tensor. We can express it as a matrix:

$$\mathbf{T} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \quad (3.16)$$

At every point, given the nine components of the stress tensor, we can know the stress on every surface. In the above matrix, the components in one column denote different components of the same stress, whereas the components in one row denote the components of different stresses in the same direction. The diagonal components, which have the identical subscript T_{ii} , are called normal stress components. They relate to the compression or extension of a material body. Other components T_{ij} ($i \neq j$) are called tangential stress or shear stress. They characterize shearing.

Consider now an elementary cube as a case study. Noticing that the resultant moment of force about any axis is zero, we can find an important property of the stress tensor, namely symmetry

$$T_{ij} = T_{ji} \quad (3.17)$$

This is Cauchy's law of the symmetry of tangential forces. Because of symmetry, to completely characterize the stress at a point, one has to know not nine but six stress components: three normal stress components and three shear stress components.

The sum $T_{ii} = T_{11} + T_{22} + T_{33}$ is called the trace of the tensor:

$$\text{tr}\mathbf{T} = T_{ii} \quad (3.18)$$

Using the following property of transformation matrix a_{ij}

$$a_{ik}a_{il} = a_{ki}a_{li} = \begin{cases} 1 & \text{when } k = l \\ 0 & \text{when } k \neq l \end{cases} \quad (3.19)$$

we can prove that the trace of the stress tensor has the same value in different coordinate systems. In other words, the trace of the stress tensor does not depend on the choice of coordinate system. It is an invariant. Note that the trace is the sum of diagonal components. These components are normal stresses. Therefore one-third of this trace is the average normal stress and is regarded as identical to the isotropic pressure p .

Very often in molecular simulations, the pressure tensor is used instead of the stress tensor. The pressure tensor is simply the negative of the stress tensor.

$$\mathbf{P} = -\mathbf{T} \quad (3.20)$$

For a homogeneous fluid, the pressure tensor is calculated as [Irv50]

$$\mathbf{P}V = \sum_{i=1}^N \frac{\mathbf{p}_i \mathbf{p}_i}{m_i} - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \mathbf{r}_{ij} \mathbf{F}_{ij} \quad (3.21)$$

For stress, forces acting on the surface inside (opposite the normal) are considered as positive. For pressure, on the contrary, outside forces are considered as positive. Since the pressure tensor and stress tensor only differ in a minus symbol, we can choose any of them for our use.

To calculate the force $d\mathbf{F}$ exerted on an elementary area $d\mathbf{S}$ by the fluid, we can use following formula:

$$d\mathbf{F} = -d\mathbf{S} \cdot \mathbf{P} \quad (3.22)$$

We can define the viscous pressure tensor as the nonequilibrium part of the pressure tensor

$$\boldsymbol{\Pi} = \mathbf{P} - p\mathbf{I} \quad (3.23)$$

Here p is the isotropic pressure, and \mathbf{I} is the second-rank unit tensor. For a more comprehensive discussion of the pressure tensor and its definitions, see ref [Tod95] and references therein, as well as recent work by Hafskjold and Ikeshoji [Haf02].

3.4 Shear flow and strain rate tensor

In this section, we will use planar Couette flow as a typical and simple example to introduce some basic knowledge about shear flow [Mar01b, Pry96, Sea76].

Figure 3.2 illustrates a planar Couette flow. There are two parallel plates a distance L apart. Each plate has an area S . A fluid is confined between the two plates. The bottom plate is stationary. The upper plate moves to the right with a constant velocity v . From experiments, we know the velocity distribution in the fluid. Solution of the Navier-Stokes equations also gives the velocity distribution. The layer of fluid which contacts the plate has the same velocity as the plate. So the top layer of the fluid has velocity v and the bottom layer is at rest. The velocities of intermediate layers of fluid increase linearly from the bottom to the top.

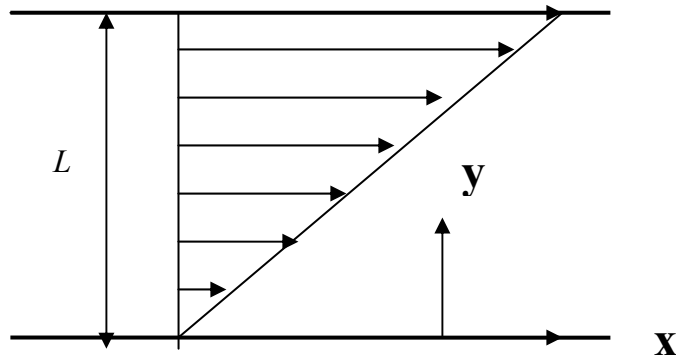


Figure 3.2 Planar Couette flow of a viscous fluid between a moving upper plate and a stationary lower plate.

Because of viscosity, the internal friction of a fluid, a force F_x must be applied to the top surface of the fluid so that it can keep a constant velocity. The direction of this force is to the right. At the same time a force F_x to the left should exert to the bottom surface to keep it at rest. So there is a stress F_x/S exerted on the fluid surface. This stress will induce deformation of the fluid. Usually we use strain to describe deformation. The term strain is defined as the relative change in dimensions or shape of a body which is subjected to stress.

If a solid is confined between the plates, after a certain time Δt , the system will reach a balanced state. The top part has a certain displacement, d , so the strain is d/L . Within the elastic limit the shearing stress is proportional to the shearing strain. But for a fluid, the deformation, or strain, will continue to increase due to the movability of the fluid. In this case, stress does not depend on strain, but on the strain rate, the rate of change in strain with time. In our situation, the strain rate is $d/L/\Delta t = v/L$. This is just the velocity gradient.

The coefficient of viscosity η is defined by the constitutive relation (Eqn. 3.3) as:

$$\frac{F_x}{S} = \eta \frac{v}{L} \quad (3.24)$$

To get a certain strain rate, a different material needs a stress of a different magnitude. For example, molasses and glycerine need greater shearing stress than water and kerosene to get the same rate of shearing strain. So the former materials have greater viscosities than the latter. Viscosity therefore reflects a property of a material.

In the general situation, noticing that the pressure tensor differs only by a minus sign with stress tensor, and the velocity gradient may not be uniform, equation (3.24) may be generalized to

$$P_{xy} = -\eta \frac{\partial v_x}{\partial y} \quad (3.25)$$

where P_{xy} is the x - y component of the pressure tensor and v_x is the x component of velocity.

Consider now the shearing strain rate $\frac{\partial v_x}{\partial y}$. It represents the gradient of the x component of the fluid velocity in the y direction. Noticing that every one of three velocity components can change in every one of three directions, we can generalize a strain rate tensor as:

$$\nabla \mathbf{v} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_y}{\partial x} & \frac{\partial v_z}{\partial x} \\ \frac{\partial v_x}{\partial y} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial y} \\ \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} & \frac{\partial v_z}{\partial z} \end{bmatrix} \quad (3.26)$$

Here we defined the velocity gradient tensor as the strain rate tensor. We should note that many workers define the strain rate tensor as $\nabla \mathbf{u} + (\nabla \mathbf{u})^T$.

For our planar Couette flow, because only the x component velocity is non-zero and a gradient exists only in the y direction, the only non-zero element of the tensor in Eqn. (3.26) is $(\nabla \mathbf{v})_{xy} = \frac{\partial v_x}{\partial y}$. This element is usually called the strain rate and expressed as the symbol $\dot{\gamma}$.

$$\nabla \mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.27)$$

In the linear regime, we can express the relation between pressure tensor and strain rate tensor by the constitutive equation (3.3).

In Eqn. (3.25), viscosity is defined as shear stress divided by shear rate. For many materials, viscosity is a constant that depends only on temperature and density. This kind of fluid is called a Newtonian fluid. However, not all materials satisfy this condition. For them, the viscosity may change with shear rate, and they are called non-Newtonian fluids (for more detailed definitions of Newtonian fluids, please refer to [Fer91a, Bar89]). Examples of non-Newtonian fluids include polymer melts and solutions. In fact, all fluids are non-Newtonian in the limit of $\dot{\gamma} \rightarrow \infty$.

3.5 Mode-coupling theory

One of the most important issues in rheology is the stress-strain (or strain rate) relationship. It is assumed that in the region of sufficiently small strain, a linear relationship between the pressure tensor and strain rate tensor is always possible. But when the strain rate is large, the relation is more complicated.

Transport coefficients are connected with both stress and rate of strain. In classical hydrodynamics, the Navier-Stokes transport coefficients defined in Eqn. (3.1) to (3.4) are supposed to be constants. They are dependent of thermodynamic variables only, such as density and temperature. They are assumed not to depend on the driving thermodynamic forces (or thermodynamic gradients), no matter how large they are [Tra99]. But much experimental evidence has shown that this assumption is not true, or is only approximately true in the linear regime. For example, for shear flow, many substances display a shear thinning phenomena, that is, when the shear rate (gradient of streaming velocity) increases, the shear viscosity decreases. In contrast, some other substances appear to shear thicken, that is, the shear viscosity increases as shear rate increases.

For shear flow, such as planar Couette flow, a typical and simple shear case, the linear regime is usually referred to as the first Newtonian region. For many substances, after the first Newtonian region, a region of shear thinning follows. When the shear rate reaches or

exceeds a certain value, the shear viscosity becomes constant again and this region is referred to as the second Newtonian region.

In the linear region, the isotropic pressure is a function of only the thermodynamic variables (temperature and density). But in the nonlinear region (large $\dot{\gamma}$ region), besides the usual thermodynamic variables, the isotropic pressure is a function of the strain rate as well. This phenomenon is called shear dilatancy. And under high strain rate, differences in the normal stresses will occur [Eva81].

For a fluid in shear flow, when the deviation from equilibrium is not small, then the viscosity is not independent of shear rate, but is a strong function of it. Other quantities like pressure and energy are also functions of shear rate. In our work we are interested in the forms these functions take. In the weak field limit, we can expand the function in shear rate, assuming it is analytic, in a Taylor series expansion:

$$A = a + b\dot{\gamma} + c\dot{\gamma}^2 + d\dot{\gamma}^3 + \dots \quad (3.28)$$

A is a physical quantity, like viscosity, pressure, energy, and so on, and a, b, c, \dots are constants.

To understand the relation between physical variables and shear rate, a group of associated theories sometimes called “long-time tail theories,” try to predict the leading terms of non-Newtonian behavior from knowledge of the equilibrium and linear Newtonian properties of the system. One significant implication of these predictions is that the pressure tensor is a nonanalytic function of both frequency and strain rate [Eva81]. We will consider this in greater detail in Chapter 5.

The mode coupling theory of Kawasaki and Gunton [Kaw73] is one of the most well-known theoretical treatments of molecular hydrodynamics. In their paper, they first derived formally exact equations of motion with the aid of a projection operator in nonequilibrium statistical mechanics. These equations are satisfied by the gross variables of a macroscopic

system and they are valid far from thermal equilibrium. These equations were then used to study nonlinear shear viscosity and normal stress of an incompressible fluid in the presence of a shear flow. They found that the mode-coupling mechanism responsible for the long-time tails in time-correlation functions became very important and that a simple power-series expansion in the strain rate $\dot{\gamma}$ failed. The shear viscosity and normal stresses were found to vary as $|\dot{\gamma}|^{1/2}$ and $|\dot{\gamma}|^{3/2}$, respectively (by implication, the pressure and energy are also predicted to vary as $\dot{\gamma}^{3/2}$). The mode coupling theory predicts a square root dependence of shear viscosity upon strain rate in 3-dimensional fluids and a logarithmic dependence in 2-dimensional fluids. In both cases, the shear viscosity is predicted to be a non-analytical function of the strain rate, as indeed are the pressure and energy.

$$\eta = a + b\dot{\gamma}^{1/2} \quad (3.29)$$

$$p = a + b\dot{\gamma}^{3/2} \quad (3.30)$$

$$\varepsilon = a + b\dot{\gamma}^{3/2} \quad (3.31)$$

Quentrec's local order theory [Que82, Tro84, Tra99] is another theory which attempt to describe the breakdown of Newton's law of viscosity and of the local equilibrium hypothesis for increasing applied perturbation. In contrast to the mode coupling theory, Quentrec's theory predicts an analytical shear viscosity function, which behaves as $\dot{\gamma}^2$ in the limit of vanishing strain rate.

Various molecular simulation results have been reported. Some of them, like Ref [Eva81, Eva80a], confirm the predictions of the mode coupling theory. Travis *et al*, [Tra99, Tra98] found that the strain rate dependence of viscosity could not be fitted by a single square root function, but instead, two square root functions at different regions were required. Travis *et al.*'s results were found to be consistent with the predictions of mode coupling theory. In contrast, other workers [Mar01b, Pom75] found evidence of non-mode coupling theory behaviour. For example, Marcelli *et al*, [Mar01b] found a quadratic dependence of the pressure and energy with strain rate instead of the $\dot{\gamma}^{3/2}$ behaviour. The work reported in this thesis follows on from this.