1   Introduction

Mechanics provides a complete microscopic description of the state of a system. When the equations of motion are combined with initial conditions and boundary conditions, the subsequent time evolution of a classical system can be predicted. In systems with more than just a few degrees of freedom such an exercise is impossible. There is simply no practical way of measuring the initial microscopic state of for example, a glass of water, at some instant in time. In any case, even if this was possible we could not then solve the equations of motion for a coupled system of 10^{23} molecules.

In spite of our inability to fully describe the microstate of a glass of water, we are all aware of useful macroscopic descriptions for such systems. Thermodynamics provides a theoretical framework for correlating the equilibrium properties of such systems. If the system is not at equilibrium, fluid mechanics is capable of predicting the macroscopic nonequilibrium behaviour of the system. In order for these macroscopic approaches to be useful their laws must be supplemented not only with a specification of the appropriate boundary conditions but with the values of thermophysical constants such as equation of state data and transport coefficients. These values cannot be predicted by macroscopic theory. Historically this data has been supplied by experiments. One of the tasks of statistical mechanics is to predict these parameters from knowledge of the interactions of the system's constituent molecules. This then is a major purpose for statistical mechanics. How well have we progressed?

Equilibrium classical statistical mechanics is relatively well developed. The basic ground rules - Gibbsian ensemble theory - have been known for the best part of a century (Gibbs, 1902). The development of electronic computers in the 1950's provided unambiguous tests of the theory of simple liquids leading to a consequently rapid development of integral equation and perturbation treatments of liquids (Barker and Henderson 1976). With the possible exceptions of phase equilibria and interfacial phenomena (Rowlinson and Widom, 1982) one could say that the equilibrium statistical mechanics of atomic fluids is a solved problem. Much of the emphasis has moved to molecular, even macromolecular liquids.

The nonequilibrium statistical mechanics of dilute atomic gases - kinetic theory - is likewise, essentially complete (Ferziger and Kaper, 1972). However attempts to extend

kinetic theory to higher densities have been fraught with severe difficulties. One might have imagined being able to develop a power series expansion of the transport coefficients in much the same way that one expands the equilibrium equation of state in the virial series. In 1965 Cohen and Dorfman (1965 and 1972) proved that such an expansion does not exist. The Navier-Stokes transport coefficients are nonanalytic functions of density.

It was at about this time that computer simulations began to have an impact on the field. In a celebrated 1957 paper, Kubo (1957) showed that linear transport coefficients could be calculated from a knowledge of the equilibrium fluctuations in the flux associated with the particular transport coefficient. For example the shear viscosity η, is defined as the ratio of the shear stress, $-P_{xy}$, to the strain rate, $\partial u_x / \partial y \equiv \gamma$,

$$P_{xy} \equiv -\eta\gamma \tag{1.1}$$

The Kubo relation predicts that the limiting, small shear rate, viscosity, is given by

$$\eta = \beta V \int_0^\infty ds \left\langle P_{xy}(0) P_{xy}(s) \right\rangle \tag{1.2}$$

where β is the reciprocal of the absolute temperature T, multiplied by Boltzmann's constant k_B, V is the system volume and the angle brackets denote an **equilibrium** ensemble average. The viscosity is then the infinite time integral of the equilibrium, autocorrelation function of the shear stress. Similar relations are valid for the other Navier-Stokes transport coefficients such as the self diffusion coefficient, the thermal conductivity and the bulk viscosity (see Chapter 4).

Alder and Wainwright (1956) were the first to use computer simulations to compute the transport coefficients of atomic fluids. What they found was unexpected. It was believed that at sufficiently long time, equilibrium autocorrelation functions should decay exponentially. Alder and Wainwright discovered that in two dimensional systems the velocity autocorrelation function which determines the self-diffusion coefficient, only decays as t^{-1}. Since the diffusion coefficient is thought to be the integral of this function, we were forced to the reluctant conclusion that the self diffusion coefficient does not exist for two dimensional systems. It is presently believed that each of the Navier-Stokes transport coefficients diverge in two dimensions (Pomeau and Resibois, 1975).

This does **not** mean that two dimensional fluids are infinitely resistant to shear flow. Rather, it means that the Newtonian constitutive relation (1.1), is an inappropriate definition of viscosity in two dimensions. There is no linear regime close to equilibrium where Newton's law (equation (1.1)), is valid. It is thought that at small strain rates, $P_{xy} \cong \gamma \log \gamma$. If this is the case then the limiting value of the shear viscosity $\lim_{\gamma \to 0} -\partial P_{xy} / \partial \gamma$ would be infinite. All this presupposes that steady laminar shear flow is stable in two dimensions. This would be an entirely natural presumption on the basis of our three dimensional experience. However there is some evidence that even this assumption may be wrong (Evans and Morriss, 1983). Recent computer simulation data suggests that in two dimensions laminar flow may be unstable at **small** strain rates.

In three dimensions the situation is better. The Navier-Stokes transport coefficients appear to exist. However the nonlinear Burnett coefficients, higher order terms in the Taylor series expansion of the shear stress in powers of the strain rate (§2.3, §9.5), are thought to diverge (Kawasaki and Gunton, 1973). These divergences are sometimes summarised in Dorfman's Lemma (Zwanzig, 1982): all relevant fluxes are nonanalytic functions of all relevant variables! The transport coefficients are thought to be nonanalytic functions of density, frequency and the magnitude of the driving thermodynamic force, the strain rate or the temperature gradient etc.

In this book we will discuss the framework of nonequilibrium statistical mechanics. We will not discuss in detail, the practical results that have been obtained. Rather we seek to derive a nonequilibrium analogue of the Gibbsian basis for equilibrium statistical mechanics. At equilibrium we have a number of idealisations which serve as standard models for experimental systems. Among these are the well known microcanonical, canonical and grand canonical ensembles. The real system of interest will not correspond exactly to any one particular ensemble, but such models furnish useful and reliable information about the experimental system. We have become so accustomed to mapping each real experiment onto its nearest Gibbsian ensemble that we sometimes forget that the canonical ensemble for example, does not exist in nature. It is an idealisation.

A nonequilibrium system can be modelled as a perturbed equilibrium ensemble, We will therefore need to add the perturbing field to the statistical mechanical description. The perturbing field does work on the system - this prevents the system from relaxing to equilibrium. This work is converted to heat, and the heat must be removed in order to obtain a well defined steady state. Therefore thermostats will also need to be included in our statistical mechanical models. A major theme of this book is the development of

a set of idealised nonequilibrium systems which can play the same role in nonequilibrium statistical mechanics as the Gibbsian ensembles play at equilibrium.

After a brief discussion of linear irreversible thermodynamics in Chapter 2, we address the Liouville equation in Chapter 3. The Liouville equation is the fundamental vehicle of nonequilibrium statistical mechanics. We introduce its formal solution using mathematical operators called propagators (§3.3). In Chapter 3, we also outline the procedures by which we identify statistical mechanical expressions for the basic field variables of hydrodynamics.

After this background in both macroscopic and microscopic theory we go on to derive the Green-Kubo relations for linear transport coefficients in Chapter 4 and the basic results of linear response theory in Chapter 5. The Green-Kubo relations derived in Chapter 4 relate *thermal* transport coefficients such as the Navier-Stokes transport coefficients, to equilibrium fluctuations. Thermal transport processes are driven by boundary conditions. The expressions derived in Chapter 5 relate *mechanical* transport coefficients to equilibrium fluctuations. A mechanical transport process is one that is driven by a perturbing external field which actually changes the mechanical equations of motion for the system. In Chapter 5 we show how the thermostatted linear mechanical response of many body systems is related to equilibrium fluctuations.

In Chapter 6 we exploit similarities in the fluctuation formulae for the mechanical and the thermal response, by deriving computer simulation algorithms for calculating the linear Navier-Stokes transport coefficients. Although the algorithms are designed to calculate linear thermal transport coefficients, they employ mechanical methods. The validity of these algorithms is proved using thermostatted linear response theory (Chapter 5) and the knowledge of the Green-Kubo relations provided in Chapter 4.

A diagrammatic summary of some of the common algorithms used to compute shear viscosity, is given in Figure 1.1. The Green-Kubo method simply consists of simulating an equilibrium fluid under periodic boundary conditions and making the appropriate analysis of the time dependent stress fluctuations using (1.2). Gosling, McDonald and Singer (1973) proposed performing a nonequilibrium simulation of a system subject to a sinusoidal transverse force. The viscosity could be calculated by monitoring the field induced velocity profile and extrapolating the results to infinite wavelength. In 1973 Ashurst and Hoover (1975), used external reservoirs of particles to induce a nearly planar shear in a model fluid. In the reservoir technique the viscosity is calculated by measuring the average ratio of the shear stress to the strain rate, in the bulk of the fluid, away from the reservoir regions. The presence of the reservoir regions gives rise to

significant inhomogeneities in the thermodynamic properties of the fluid and in the strain rate in particular. This leads to obvious difficulties in the calculation of the shear viscosity. Lees and Edwards (1972), showed that if one used 'sliding brick' periodic boundary conditions one could induce *planar* Couette flow in a simulation. The so-called Lees-Edwards periodic boundary conditions enable one to perform homogeneous simulations of shear flow in which the low-Reynolds number velocity profile is linear.

With the exception of the Green-Kubo method, these simulation methods all involve nonequilibrium simulations. The Green-Kubo technique is useful in that all linear transport coefficients can in principle be calculated from a single simulation. It is restricted though, to **only** calculating linear transport coefficients. The nonequilibrium methods on the other hand provide information about the nonlinear as well as the linear response of systems. They therefore provide a direct link with rheology.
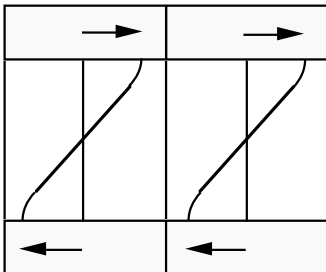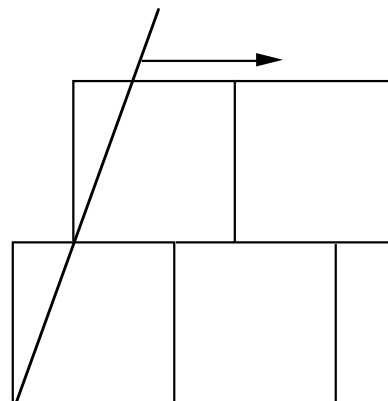
Methods for determining the Shear viscosity
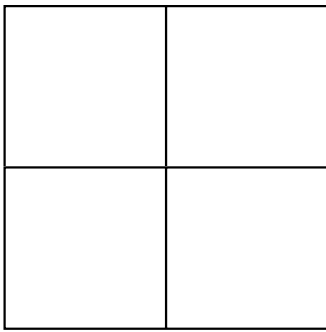
Green Kubo
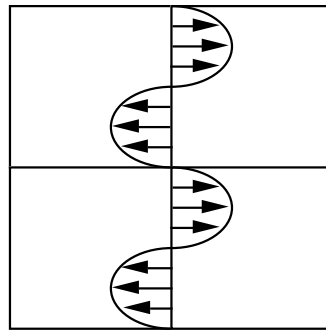
Sinusoidal Transverse Force

Momentum Resevoirs

Homogeneous shear

Figure 1.1.

The use of nonequilibrium computer simulation algorithms, so-called nonequilibrium molecular dynamics (NEMD), leads inevitably to the question of the large field, nonlinear response. Indeed the calculation of linear transport coefficients using NEMD proceeds by calculating the nonlinear response and extrapolating the results to zero field. One of our main aims will be to derive a number of nonlinear generalisations of the Kubo relations which give an exact framework within which one can calculate and characterise transport processes far from equilibrium (chapters 7 & 8). Because of the divergences alluded to above, the nonlinear theory cannot rely on power series expansions about the equilibrium state. A major system of interest is the nonequilibrium steady state. Theory enables one to relate the nonlinear transport coefficients and mechanical quantities like the internal energy or the pressure, to transient fluctuations in the thermodynamic flux which generates the nonequilibrium steady state (Chapter 7). We derive the Transient Time Correlation Function (TTCF, §7.3) and the Kawasaki representations (§7.2) of the thermostatted nonlinear response. These results are exact and do not require the nonlinear response to be an analytic function of the perturbing fields. The theory also enables one to calculate specific heats, thermal expansion coefficients and compressibilities from a knowledge of steady state fluctuations (Chapter 9). After we have discussed the nonlinear response, we present a resolution of the van Kampen objection to linear response theory and to the Kubo relations in Chapter 7.

An innovation in our theory is the use of reversible equations of motion which incorporate a deterministic thermostat (§3.1). This innovation was motivated by the needs imposed by nonequilibrium computer simulation. If one wants to use any of the nonequilibrium methods depicted in Figure 1.1 to calculate the shear viscosity one needs a thermostat so that one can accumulate reliable steady state averages. It is not clear how one could calculate the viscosity of a fluid whose temperature and pressure are increasing in time.

The first deterministic thermostat, the so-called Gaussian thermostat, was independently and simultaneously developed by Hoover and Evans (Hoover et. al., 1982, and Evans, 1983). It permitted homogeneous simulations of nonequilibrium steady states using molecular dynamics techniques. Hitherto molecular dynamics had involved solving Newton's equations for systems of interacting particles. If work was performed on such a system in order to drive it away from equilibrium the system inevitably heated up due to the irreversible conversion of work into heat.

Hoover and Evans showed that if such a system evolved under their thermostatted equations of motion, the so-called Gaussian isokinetic equations of motion, the

dissipative heat could be removed by a thermostatting force which is part of the equations of motion themselves. Now, computer simulators had been simulating nonequilibrium steady states for some years but in the past the dissipative heat was removed by simple ad-hoc rescaling of the second moment of the appropriate velocity. The significance of the Gaussian isokinetic equations of motion was that since the thermostatting was part of the equations of motion it could be analysed theoretically using response theory. Earlier ad-hoc rescaling or Andersen's stochastic thermostat (Andersen, 1980), could not be so easily analysed. In Chapter 5 we prove that while the adiabatic (ie unthermostatted) linear response of a system can be calculated as the integral of an unthermostatted (ie Newtonian) equilibrium time correlation function, the thermostatted linear response is related to the corresponding thermostatted equilibrium time correlation function. These results are quite new and can be proved only because the thermostatting mechanism is reversible and deterministic.

One may ask whether one can talk about the 'thermostatted' response without referring to the details of the thermostatting mechanism. Provided the amount of heat Q, removed by a thermostat within the characteristic microscopic relaxation time τ, of the system is small compared to the enthalpy I, of the fluid (ie. $(\tau \, dQ/dt)/I < 1$), we expect that the microscopic details of the thermostat will be unimportant. In the linear regime close to equilibrium this will always be the case. Even for systems far (but not too far), from equilibrium this condition is often satisfied. In §5.4 we give a mathematical proof of the independence of the linear response to the thermostatting mechanism.

Although originally motivated by the needs of nonequilibrium simulations, we have now reached the point where we can simulate equilibrium systems at constant internal energy E, at constant enthalpy I, or at constant temperature T, and pressure p. If we employ the so-called Nosé-Hoover (Hoover, 1985) thermostat, we can allow fluctuations in the state defining variables while controlling their mean values. These methods have had a major impact on computer simulation methodology and practice.

To illustrate the point: in an ergodic system at equilibrium, Newton's equations of motion *generate* the molecular dynamics ensemble in which the number of particles, the total energy, the volume and the total linear momentum are all precisely fixed (N, E, V, $\sum \mathbf{p}_i$). Previously this was the only equilibrium ensemble accessible to molecular dynamics simulation. Now however we can use Gaussian methods to generate equilibrium ensembles in which the precise value of say, the enthalpy and pressure are fixed (N, I, p, $\sum \mathbf{p}_i$). Alternatively, Nosé-Hoover equations of motion could be used which generate the canonical ensemble ($e^{-\beta H}$). Gibbs proposed the

various ensembles as statistical *distributions* in phase space. In this book we will describe *dynamics* that is capable of generating each of those distributions.

A new element in the theory of nonequilibrium steady states is the abandonment of Hamiltonian dynamics. The Hamiltonian of course plays a central role in Gibbs' equilibrium statistical mechanics. It leads to a compact and elegant description. However the existence of a Hamiltonian which generates dynamical trajectories is, as we will see, not essential.

In the space of relevant variables, neither the Gaussian thermostatted equations of motion nor the Nosé-Hoover equations of motion can be derived from a Hamiltonian. This is true even in the absence of external perturbing fields. This implies in turn that the usual form of the Liouville equation, $df/dt = 0$, for the N-particle distribution function f, is invalid. Thermostatted equations of motion necessarily imply a compressible phase space.

The abandonment of a Hamiltonian approach to particle dynamics had in fact been forced on us somewhat earlier. The Evans-Gillan equations of motion for heat flow (§6.5), which predate both the Gaussian and Nosé-Hoover thermostatted dynamics, cannot be derived from a Hamiltonian. The Evans-Gillan equations provide the most efficient presently known dynamics for describing heat flow in systems close to equilibrium. A synthetic external field was invented so that its interaction with an N-particle system precisely mimics the impact a real temperature gradient would have on the system. Linear response theory is then used to prove that the response of a system to a real temperature gradient is identical to the response to the synthetic Evans-Gillan external field.

We use the term *synthetic* to note the fact that the Evans-Gillan field does not exist in nature. It is a mathematical device used to transform a difficult boundary condition problem, the flow of heat in a system bounded by walls maintained at differing temperatures, into a much simpler mechanical problem. The Evans-Gillan field acts upon the system in a homogeneous way permitting the use of periodic rather than inhomogeneous boundary conditions. This synthetic field exerts a force on each particle which is proportional to the difference of the particle's enthalpy from the mean enthalpy per particle. The field thereby induces a flow of heat in the absence of either a temperature gradient or of any mass flow. No Hamiltonian is known which can generate the resulting equations of motion.

In a similar way Kawasaki showed that the boundary condition which corresponds to planar Couette shear flow can be incorporated exactly into the equations of motion. These equations are known as the SLLOD equations (§6.3). They give an exact description of the shearing motion of systems arbitrarily far from equilibrium. Again no Hamiltonian can be found which is capable of generating these equations.

When external fields or boundary conditions perform work on a system we have at our disposal a very natural set of mechanisms for constructing nonequilibrium ensembles in which different sets of thermodynamic state variables are used to constrain or define, the system. Thus we can generate on the computer or analyse theoretically, nonequilibrium analogues of the canonical, microcanonical or isobaric-isoenthalpic ensembles.

At equilibrium one is used to the idea of pairs of conjugate thermodynamic variables generating conjugate equilibrium ensembles. In the canonical ensemble particle number N, volume V, and temperature T, are the state variables whereas in the isothermal-isobaric ensemble the role played by the volume is replaced by the pressure, its thermodynamic conjugate. In the same sense one can generate conjugate pairs of nonequilibrium ensembles. If the driving thermodynamic force is X, it could be a temperature gradient or a strain rate, then one could consider the N, V, T, X ensemble or alternatively the conjugate N, p, T, X ensemble.

However in nonequilibrium steady states one can go much further than this. The dissipation, the heat removed by the thermostat per unit time dQ/dt, can always be written as a product of a thermodynamic force, X, and a thermodynamic flux, $J(\Gamma)$. If for example the force is the strain rate, γ, then the conjugate flux is the shear stress, $-P_{xy}$ One can then consider nonequilibrium ensembles in which the thermodynamic flux rather than the thermodynamic force is the independent state variable. For example we could define the nonequilibrium steady state as an N, V, T, J ensemble. Such an ensemble is, by analogy with electrical circuit theory, called a Norton ensemble, while the case where the force is the state variable N, V, T, X, is called a Thévenin ensemble. A major postulate in this work is the macroscopic equivalence of corresponding Norton and Thévenin ensembles.

The Kubo relations referred to above, only pertain to the Thévenin ensembles. In §6.6 we will discuss the Norton ensemble analogues of the Kubo relations and show how deep the duality between the two types of ensembles extends. The generalisation of Norton ensemble methods to the nonlinear response leads for the first time, to analytic expressions for the nonlinear Burnett coefficients. The nonlinear Burnett coefficients

are simply the coefficients of a Taylor series expansion, about equilibrium, of a thermodynamic flux in powers of the thermodynamic force. For Navier-Stokes processes, these coefficients are expected to diverge. However since until recently no explicit expressions were known for the Burnett coefficients, simulation studies of this possible divergence were severely handicapped. In Chapter 9 we discuss Evans and Lynden-Bell's (1988) derivation of, equilibrium time correlation functions for the inverse Burnett coefficients. The inverse Burnett coefficients are so-called because they refer to the coefficients of the expansion of the forces in terms of the thermodynamic fluxes rather than vice versa.

In the last Chapter we introduce material which is quite recent and perhaps controversial. We attempt to characterise the phase space distribution of nonequilibrium steady states. This is essential if we are ever to be able to develop a thermodynamics of nonequilibrium steady states. Presumably such a thermodynamics, a nonlinear generalisation of the conventional linear irreversible thermodynamics treated in Chapter 2, will require the calculation of a generalised entropy. The entropy and free energies are functionals of the distribution function and thus are vastly more complex to calculate than nonequilibrium averages.

What we find is surprising. The steady state nonequilibrium distribution function seen in NEMD simulations, is a fractal object. There is now ample evidence that the *dimension* of the phase space which is accessible to nonequilibrium steady states is *lower* than the dimension of phase space itself. This means that the volume of accessible phase space as calculated from the ostensible phase space, is zero. This means that the fine grained entropy calculated from Gibbs' relation,

$$ S = -k_B \int_{\text{all } \Gamma \text{ space}} d\Gamma \ f(\Gamma,t) \ln f(\Gamma,t) \tag{1.3} $$

diverges to negative infinity. (If no thermostat is employed the corresponding nonequilibrium entropy is, as was known to Gibbs (1902), a constant of the motion!) Presumably the thermodynamic entropy, if it exists, must be computed from *within* the lower dimensional, accessible phase space rather than from the full phase space as in (1.3). We close the book by describing a new method for computing the nonequilibrium entropy.

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