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More information

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 1950s 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

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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. Dorfman and Cohen (1965; 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 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 shear 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:

$$\eta = \beta V \int_0^\infty \mathrm{d}s \, \langle P_{xy}(0) P_{xy}(s) \rangle, \tag{1.2}$$

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).

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This does *not* mean that two-dimensional fluids are infinitely resistant to shear flow. Rather, it means that the Newtonian constitutive relation Equation (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 were 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, 1983b). 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 (Section 2.3, Section 9.5), are thought to diverge (Kawasaki and Gunton, 1973). These divergences are sometimes summarized 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 analog of the Gibbsian basis for equilibrium statistical mechanics. At equilibrium we have a number of idealizations 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 idealization.

A nonequilibrium system can be modeled 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 idealized nonequilibrium systems which can play the same role in nonequilibrium statistical mechanics as the Gibbsian ensembles play at equilibrium.

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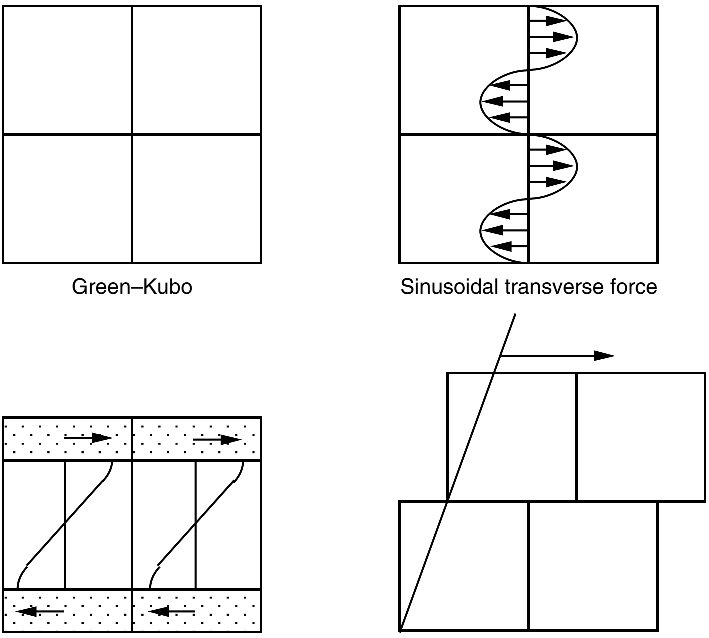
After a brief discussion of linear irreversible thermodynamics in Chapter 2, we address the Liouville equation in Chapter 3. The Liouville equation is the fundamental vehicle of nonequilibrium statistical mechanics. We introduce its formal solution using mathematical operators called propagators (Section 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 Equation (1.2). Gosling *et al*. (1973) proposed performing a nonequilibrium simulation of a system subject to a sinusoidal transverse force. Monitoring the field-induced velocity profile and extrapolating the results to infinite wavelength, the viscosity can be calculated. Hoover and Ashurst (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



Green–Kubo

Sinusoidal transverse force

Momentum reservoirs

Homogeneous shear

Figure 1.1 Methods of determining the shear viscosity

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.

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 generalizations of the Kubo relations which give an exact framework within which one can calculate and characterize transport processes far from equilibrium (Chapter 7). 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 us 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, Section 7.3) and the Kawasaki representations (Section 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 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 (Section 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 to achieve a reliable steady-state average. It is not clear how to 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 (1983a). 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. As work was performed on such a system in order to drive it away from equilibrium, the system inevitably heated with 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 was 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 analyzed theoretically using response theory. Earlier ad hoc rescaling or Andersen's stochastic thermostat (Andersen, 1980), could not be so easily analyzed. In Chapter 5 we prove that while the adiabatic (i.e. unthermostatted) linear response of a system can be calculated as the integral of an unthermostatted (i.e. 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.

It is natural to ask whether the “thermostatted” response depends upon 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 (i.e. $(\tau\, \mathrm{d}Q/\mathrm{d}t)/I < 1$), 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 Section 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 (Nosé, 1984b; 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 ($N, E, V, \Sigma\mathbf{p}_i$). 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 ($N, E, p, \Sigma\mathbf{p}_i$). Alternatively, Nosé–Hoover equations of motion could be used which generate the canonical ensemble ($\exp[-\beta H]$). Gibbs proposed the various ensembles as idealized statistical *distributions* in phase space. Now we have the *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, $\mathrm{d}f/\mathrm{d}t = 0$, 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 (Section 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 a 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 that corresponds to planar Couette shear flow can be incorporated exactly into the equations of motion. These equations are known as the SLLOD equations (Section 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 analyze theoretically, nonequilibrium analogs 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, and 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 $\mathrm{d}Q/\mathrm{d}t$, can always be written as a product of a thermodynamic force, X, and a thermodynamic flux, $J(\Gamma)$.

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If, for example, the force is the shear 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 equations of motion for a system of particles which undergo collisions are usually chaotic (although there are examples, like the wind-tree model, that are not). The application of the ideas of modern dynamical systems theory has had a large impact on nonequilibrium statistical mechanics in the last 15 to 20 years. The books by Gaspard (1998), Dorfman (1999), Ott (2002) and Sprott (2003) are more comprehensive than the development that we present in Chapter 8. However, our approach is to begin with the characterization of chaos in a dynamical system, and then to use the ideas of Ruelle (1978), Cvitanovic, and others (2005) to show how to develop an understanding of the time evolution of both the probability distribution and an arbitrary phase variable. Surprisingly, just the structure of the theory gives a simple argument to show that the transport coefficients must be non-negative.

The discovery of relations satisfied by the fluctuations in nonequilibrium steady states has become a major area of activity in the last decade. The discovery of the fluctuation theorem by Evans *et al*. (1993a), the derivations by Evans and Searles (1994) and Gallavotti and Cohen (1995a) have sparked a great deal of interest and controversy. The subsequent discovery of methods of calculating free-energy differences using arbitrary nonequilibrium paths by Jarzynski (1997) and Crooks (1998) has stimulated many experiments designed both to confirm the theoretical predictions and to use the techniques in physical and biological systems.

In the last chapter we introduce material which is quite recent and perhaps controversial. We attempt to develop a thermodynamics of nonequilibrium steady states which may be considered a nonlinear generalization of the conventional linear irreversible thermodynamics treated in Chapter 2. The difficulty is extending our notions of temperature and entropy to nonequilibrium systems. We take as an axiom, the observation from computer simulation studies, that the internal energy of the system is also a function of the field that perturbs the system from equilibrium. Thus the internal energy U is a function of temperature, volume, and the shear rate for a system undergoing Couette flow. We consider two approaches; the first using the assumption of linear viscoelasticity, and the second using a purely statistical mechanical treatment.

What is surprising is that the steady-state nonequilibrium distribution function is a singular and fractal object. This implies that the fine grained Gibbs entropy:

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

diverges to negative infinity. (If no thermostat is employed, the nonequilibrium entropy is a constant of the motion Gibbs (1902)). The question of the expression for the nonequilibrium entropy, and how to calculate it, remain unresolved.