Statistical Mechanics

From First Principles to Macroscopic Phenomena

J. Woods Halley

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STATISTICAL MECHANICS

From First Principles to Macroscopic Phenomena

Based on the author's graduate course taught over many years in several physics departments, this book takes a "reductionist" view of statistical mechanics, while describing the main ideas and methods underlying its applications. It implicitly assumes that the physics of complex systems as observed is connected to fundamental physical laws represented at the molecular level by Newtonian mechanics or quantum mechanics. Organized into three parts, the first section describes the fundamental principles of equilibrium statistical mechanics. The next section describes applications to phases of increasing density and order: gases, liquids and solids; it also treats phase transitions. The final section deals with dynamics, including a careful account of hydrodynamic theories and linear response theory.

This original approach to statistical mechanics is suitable for a 1-year graduate course for physicists, chemists, and chemical engineers. Problems are included following each chapter, with solutions to selected problems provided.

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Preface

This book is based on a course which I have taught over many years to graduate students in several physics departments. Students have been mainly candidates for physics degrees but have included a scattering of people from other departments including chemical engineering, materials science and chemistry. I take a "reductionist" view, that implicitly assumes that the basic program of physics of complex systems is to connect observed phenomena to fundamental physical laws as represented at the molecular level by Newtonian mechanics or quantum mechanics. While this program has historically motivated workers in statistical physics for more than a century, it is no longer universally regarded as central by all distinguished users of statistical mechanics[1,2] some of whom emphasize the phenomenological role of statistical methods in organizing data at macroscopic length and time scales with only qualitative, and often only passing, reference to the underlying microscopic physics. While some very useful methods and insights have resulted from such approaches, they generally tend to have little quantitative predictive power. Further, the recent advances in first principles quantum mechanical methods have put the program of predictive quantitative methods based on first principles within reach for a broader range of systems. Thus a text which emphasizes connections to these first principles can be useful.

The level here is similar to that of popular books such as those by Landau and Lifshitz,[3] Huang[4] and Reichl.[5] The aim is to provide a basic understanding of the fundamentals and some pivotal applications in the brief space of a year. With regard to fundamentals, I have sought to present a clear, coherent point of view which is correct without oversimplifying or avoiding mention of aspects which are incompletely understood. This differs from many other books, which often either give the fundamentals extremely short shrift, on the one hand, or, on the other, expend more mathematical and scholarly attention on them than is appropriate in a one year graduate course. The chapters on fundamentals begin with a description of equilibrium for classical systems followed by a similar description for quantum

mechanical systems. The derivation of the equilibrium aspects of thermodynamics is then presented followed by a discussion of the semiclassical limit.

In the second part, I progress through equilibrium applications to successively more dense states of matter: ideal classical gases, ideal quantum gases, imperfect classical gases (cluster expansions), classical liquids (including molecular dynamics) and some aspects of solids. A detailed discussion of solids is avoided because, at many institutions, solid state physics is a separate graduate course. However, because magnetic models have played such a central role in statistical mechanics, they are not neglected here. Finally, in this second part, having touched on the main states of matter, I devote a chapter to phase transitions: thermodynamics, classification and the renormalization group.

The third part is devoted to dynamics. This consists first of a long chapter on the derivation of the equations of hydrodynamics. In this chapter, the fluctuation–dissipation theorem then appears in the form of relations of transport coefficients to dynamic correlation functions. The second chapter of the last part treats stochastic models of dynamics and dynamical aspects of critical phenomena.

There are problems in each chapter. Solutions are provided for many of them in an appendix. Many of the problems require some numerical work. Sample codes are provided in some of the solutions (in Fortran) but, in most cases, it is advisable for students to work out their own solutions which means writing their own codes. Unfortunately, the students I have encountered recently are still often surprised to be asked to do this but there is really no substitute for it if one wants a thorough mastery of simulation aspects of the subject.

I have interacted with a great many people and sources during the evolution of this work. For this reason acknowledging them all is difficult and I apologise in advance if I overlook someone. My tutelage in statistical mechanics began with a course by Allan Kaufman in Berkeley in the 1960s. With regard to statistical mechanics I have profited especially from interactions with Michael Gillan, Gregory Wannier (some personally but mainly from his book), Mike Thorpe, Aneesur Rahman, Bert Halperin, Gene Mazenko, Hisao Nakanishi, Nigel Goldenfeld and David Chandler. Obviously none of these people are responsible for any mistakes you may find, but they may be given some credit for some of the good stuff. I am also grateful to the many classes that were subjected to these materials, in rather unpolished form in the early days, and who taught me a lot. Finally I thank all my Ph.D. students and postdocs (more than 30 in all) through the years for being good company and colleagues and for stimulating me in many ways.

J. Woods Halley
Minneapolis
July 2005

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Introduction

The problems of statistical mechanics are those which involve systems with a larger number of degrees of freedom than we can conveniently follow explicitly in experiment, theory or simulation. The number of degrees of freedom which can be followed explicitly in simulations has been changing very rapidly as computers and algorithms improve. However, it is important to note that, even if computers continue to improve at their present rate, characterized by Moore's "law," scientists will not be able to use them for a very long time to predict many properties of nature by direct simulation of the fundamental microscopic laws of physics. This point is important enough to emphasize.

Suppose that, T years from the present, a calculation requiring computation time t_0 at present will require computation time $t(T) = t_0 2^{-T/2}$ (Moore's "law,"[1] see Figure 1). Currently, state of the art numerical solutions of the Schrödinger equation for a few hundred atoms can be carried out fast enough so that the motion of these atoms can be followed long enough to obtain thermodynamic properties. This is adequate if one wishes to predict properties of simple homogeneous gases, liquids or solids from first principles (as we will be discussing later). However, for many problems of current interest, one is interested in entities in which many more atoms need to be studied in order to obtain predictions of properties at the macroscopic level of a centimeter or more. These include polymers, biomolecules and nanocrystalline materials for example. In such problems, one easily finds situations in which a first principles prediction requires following 10^6 atoms dynamically. The first principles methods for calculating the properties increase in computational cost as the number of atoms to a power between 2 and 3. Suppose they scale as the second power so the computational time must be reduced by a factor 10^8 in order to handle 10^6 atoms. Using Moore's law we then predict that the calculation will be possible T years from the present where $T = 16/\log_{10}2 = 53$ years. In fact, this may be optimistic because Moore's "law" may not continue to be valid for that long and also because 10^6 atoms will not be enough in many cases. What this means is that,

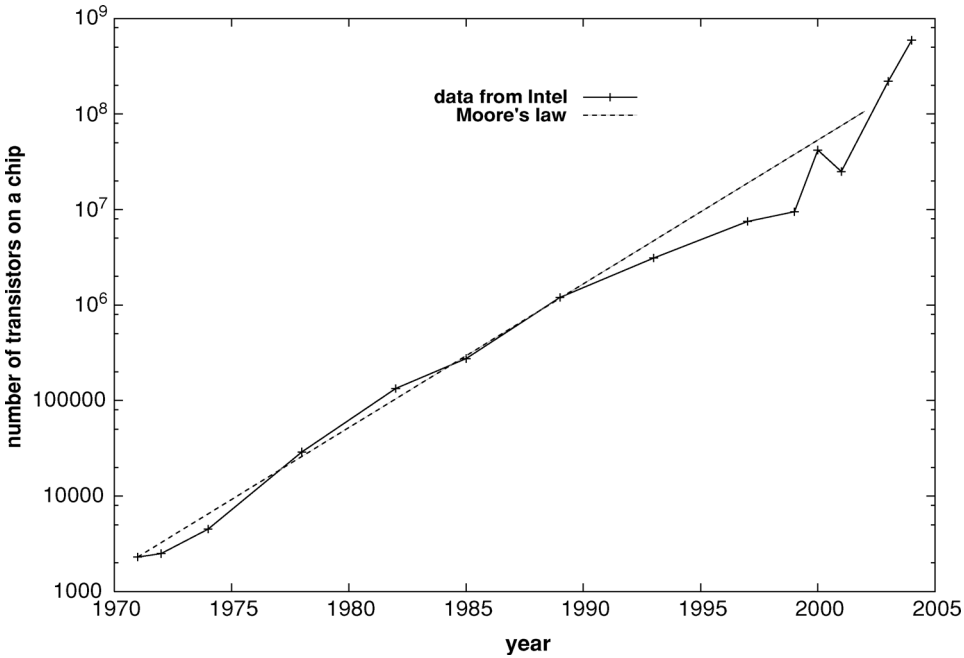

Figure 1 One version of Moore's "law."

for a long time, we will need means beyond brute force computation for relating the properties of macroscopic matter to the fundamental microscopic laws of physics.

Statistical mechanics provides the essential organizing principles needed for connecting the description of matter at large scales to the fundamental underlying physical laws (Figure 2). Whether we are dealing with an experimental system with intractably huge numbers of degrees of freedom or with a mass of data from a simulation, the essential goal is to describe the behavior of the many degrees of freedom in terms of a few "macroscopic" degrees of freedom. This turns out to be possible in a number of cases, though not always. Here, we will first describe how this connection is made in the case of equilibrium systems, whose average properties do not change in time. Having established (Part I) some principles of equilibrium statistical mechanics, we then provide (Part II) a discussion of how they are applied in the three most common phases of matter (gases, liquids and solids) and the treatment of phase transitions. Part III concerns dynamical and nonequilibrium methods.

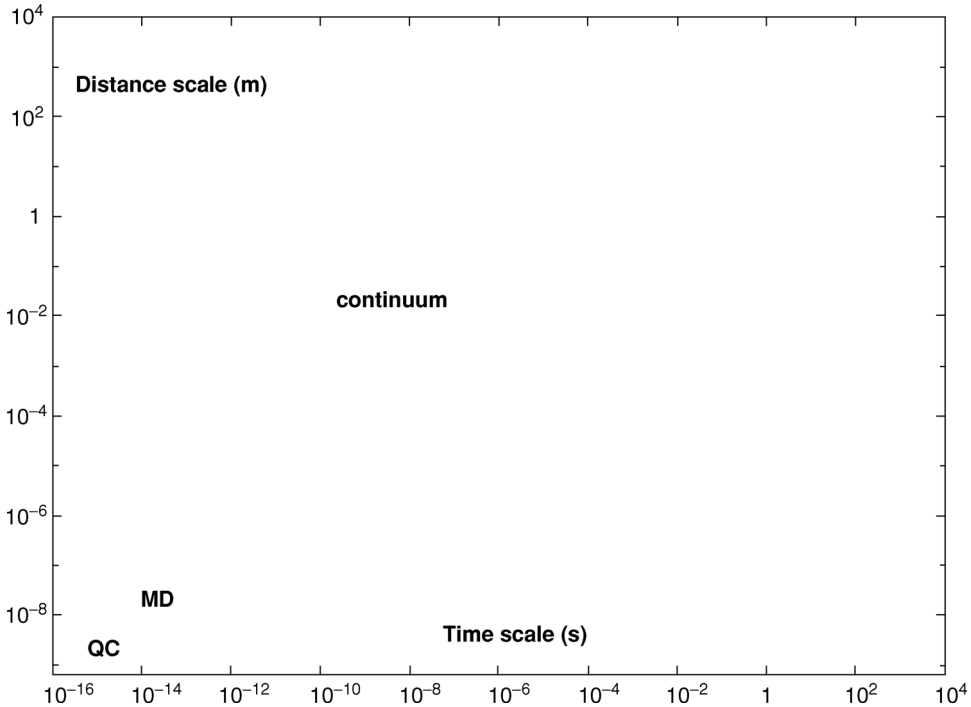

Figure 2 Computational length and time scales. QC stands for quantum chemistry methods in which the Schrödinger equation is solved. MD stands for molecular dynamics in which classical equations of motion for atomic motion are solved. Continuum includes thermodynamics, hydrodynamics, continuum mechanics, micromagnetism in which macroscopic variables describe the system. Statistical mechanics supplies the principles by which computations at these different scales are connected.

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Part I

Foundations of equilibrium statistical mechanics

1

The classical distribution function

Historically, the first and most successful case in which statistical mechanics has made the connection between microscopic and macroscopic description is that in which the system can be said to be in equilibrium. We define this carefully later but, to proceed, may think of the equilibrium state as the one in which the values of the macroscopic variables do not drift in time. The macroscopic variables may have an obvious relation to the underlying microscopic description (as for example in the case of the volume of the system) or a more subtle relationship (as for temperature and entropy). The macroscopic variables of a system in equilibrium are found experimentally (and in simulations) to obey historically empirical laws of thermodynamics and equations of state which relate them to one another. For systems at or near equilibrium, statistical mechanics provides the means of relating these relationships to the underlying microscopic physical description.

We begin by discussing the details of this relation between the microscopic and macroscopic physical description in the case in which the system may be described classically. Later we run over the same ground in the quantum mechanical case. Finally we discuss how thermodynamics emerges from the description and how the classical description emerges from the quantum mechanical one in the appropriate limit.

Foundations of equilibrium statistical mechanics

Here we will suppose that the systems with which we deal are nonrelativistic and can be described fundamentally by $3N$ time dependent coordinates labelled $q_i(t)$ and their time derivatives $\dot{q}_i(t)$ ($i = 1, \ldots, 3N$). A model for the dynamics of the system is specified through a Lagrangian $L(\{q_i\}, \{\dot{q}_i\})$ (not explicitly time dependent) from which the dynamical behavior of the system is given by the principle of least

action

$$\delta \int L \, \mathrm{d}t = 0 \tag{1.1}$$

or equivalently by the Lagrangian equations of motion

$$\frac{\partial L}{\partial q_i} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = 0 \tag{1.2}$$

Alternatively one may define momenta

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \tag{1.3}$$

and a Hamiltonian

$$H = \sum_{i=1}^{N} p_i \dot{q}_i - L \tag{1.4}$$

Expressing H as a function of the momenta p_i and the coordinates q_i one then has the equations of motion in the form

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \tag{1.5}$$

$$-\frac{\partial H}{\partial q_i} = \dot{p}_i \tag{1.6}$$

In examples, we will often be concerned with a system of identical particles with conservative pair interactions. Then it is convenient to use the various components of the positions of the particles $\vec{r}_1, \vec{r}_2, \ldots$ as the quantities q_i, and the Hamiltonian takes the form

$$H = \sum_k \vec{p}_k^{\,2}/2m + (1/2)\sum_{k \neq l} V(\vec{r}_k, \vec{r}_l) \tag{1.7}$$

where the sums run over particle labels and $\vec{p}_k = \nabla_{\dot{\vec{r}}_k} H$. Then the Hamiltonian equations reduce to simple forms of Newton's equation of motion. It turns out, however, that the more general formulation is quite useful at the fundamental level, particularly in understanding Liouville's theorem, which we will discuss later.

In keeping with the discussion in the Introduction, we wish to relate this microscopic description to quantities which are measured in experiment or which are conveniently used to analyze the results of simulations in a very similar way. Generically we denote these observable quantities as $\phi(q_i(t),\, p_i(t))$. It is also possible to consider properties which depend on the microscopic coordinates at more than one time. We will defer discussion of these until Part III. Generally, these quantities, for example the pressure on the wall of a vessel containing the system, are not constant

in time and what is measured is a time average:

$$\bar{\phi}_t = \frac{1}{\tau}\int_{t-\tau/2}^{t+\tau/2} \phi(q_i(t'), p_i(t'))\,\mathrm{d}t' \tag{1.8}$$

τ is an averaging time determined by the apparatus and the measurement made (or chosen for analysis by the simulator). Experience has shown that for many systems, an experimental situation can be achieved in which measurements of $\bar{\phi}_t$ are independent of τ for all $\tau > \tau_0$ for some finite τ_0. It is easy to show that, in such a case, $\bar{\phi}_t$ is also independent of t. If this is observed to be the case for the macroscopic observables of interest, then the system is said to be in equilibrium. A similar operational definition of equilibrium is applied to simulations. In practice it is never possible to test this equilibrium condition for arbitrarily long times, in either experiment or simulation. Thus except in the rare cases in which mathematical proofs exist for relatively simple models, the existence and nature of equilibrium states are hypothesized on the basis of partial empirical evidence. Furthermore, in experimental situations, we do not expect any system to satisfy the equilibrium condition for arbitrarily long times, because interactions with the surroundings will inevitably change the values of macroscopic variables eventually. Making the system considered ever larger and the time scales longer and longer does not help here, because there is no empirical evidence that the universe itself is in equilibrium in this sense. Nevertheless, the concept of equilibrium turns out to be an extremely useful idealization because of the strong evidence that many systems do satisfy the relevant conditions over a very wide range of averaging times τ and that, under sufficiently isolated conditions, many systems spontaneously evolve rapidly toward an approximately equilibrium state whose characteristics are not sensitive to the details of the initial microscopic conditions. These empirical statements lack mathematical proofs for most systems of experimental or engineering interest, though mathematicians have made progress in proving them for simple models.

For systems in equilibrium defined in this way we are concerned with the calculation of averages of the type

$$\bar{\phi}_t = \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} \phi(\{q_i(t')\}, \{p_i(t')\})\,\mathrm{d}t' \tag{1.9}$$

We will show that it is always possible in principle to write this average in the form

$$\bar{\phi}_t = \int \rho(\{q_i\}, \{p_i\})\phi(\{q_i\}, \{p_i\})\,\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p \tag{1.10}$$

in which $\rho(\{q_i\}, \{p_i\})$ is called the classical distribution function. The demonstration provides useful insight into the meaning of $\rho(\{q_i\}, \{p_i\})$. We consider the $6N$ dimensional space of the variables $\{q_i\}$, $\{p_i\}$, called phase space. In this space the time

evolution of the system is described by the motion of a point. Take a small region of this space whose volume is denoted $\Delta^{3N}p\Delta^{3N}q$ centered at the point (p, q). (Henceforth we denote $(p, q) \equiv (\{q_i\}, \{p_i\})$ and similarly $(\Delta p, \Delta q) \equiv (\{\Delta q_i\}, \{\Delta p_i\})$.) Consider the interval of time Δt defined as

$$\Delta t(q_0, p_0, t_0; q, p, t; \Delta p, \Delta q) \tag{1.11}$$

equivalent to the time which the point describing the system spends in the region $\Delta^{3N}p\Delta^{3N}q$ around (q, p) between t_0 and t if it started at the point (q_0, p_0) at time t_0.

Now consider the fraction of time that the system point spends in $\Delta^{3N}p\Delta^{3N}q$, denoted Δw:

$$\Delta w(q_0, p_0; q, p; \Delta p, \Delta q) = \lim_{t\to\infty}\left(\frac{\Delta t}{t - t_0}\right) \tag{1.12}$$

which is the fraction of the total time between t_0 and $t \to \infty$ which the system spends in the region $\Delta^{3N}p\Delta^{3N}q$ around (q, p).

Now we express the time average $\bar{\phi}_t$ of equation (1.9) in terms of Δw by dividing the entire phase space into small regions labelled by an index k and each of volume $\Delta^{3N}p\Delta^{3N}q$:

$$\bar{\phi}_t = \sum_k \phi(q_0, p_0; q_k, p_k)\Delta w(q_0, p_0; q_k, p_k; \Delta p, \Delta q) \tag{1.13}$$

We then suppose that $\Delta w(q_0, p_0; q, p; \Delta p, \Delta q)$ is a well behaved function of the arguments $(\Delta p, \Delta q)$ and write

$$\Delta w = \left[\frac{\partial^{6N}\Delta w}{\partial^{3N}\Delta q\,\partial^{3N}\Delta p}\right]_{\Delta p=\Delta q=0} \Delta^{3N}q\,\Delta^{3N}p + \cdots \tag{1.14}$$

Defining

$$\rho(q_0, p_0; q, p) = \left[\frac{\partial^{6N}\Delta w}{\partial^{3N}\Delta q\,\partial^{3N}\Delta p}\right]_{\Delta p=\Delta q=0} \tag{1.15}$$

we then have in the limit $\Delta p\Delta q \to 0$ that

$$\bar{\phi}_t = \int \rho(q_0, p_0; q, p)\phi(q, p)\,\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p \tag{1.16}$$

which is of the form (1.10). Several of the smoothness assumptions made in this discussion are open to question as we will discuss in more detail later.

Equation (1.16) is most useful if $\bar{\phi}_t$ depends only on a few of the $6N$ initial conditions q_0, p_0. Experimentally (and in simulations) it is found that the time averages of many macroscopic quantities measured in equilibrium systems are very insensitive to the way the system is prepared. We will demonstrate that under certain

conditions, the only way in which these averages can depend on the initial conditions is through the values of the energy, linear momentum and angular momentum of the entire system. The general study of the dependence of averages of the form (1.16) on the initial conditions is part of ergodic theory. An ergodic system is (loosely from a mathematical point of view) defined as an energetically isolated system for which the phase point eventually passes through every point on the surface in phase space consistent with its energy. It is not hard to prove that the averages $\bar{\phi}_t$ in such an ergodic system depend only on the energy of the system. It is worth pointing out that the existence of ergodic systems in phase space of more than two dimensions is quite surprising. The trajectory of the system in phase space is a topologically one dimensional object (a path, parametrized by one variable, the time) yet we want this trajectory to *fill* the $6N - 1$ dimensional surface defined by the energy. The possibility of space filling curves is known mathematically (for a semipopular account see reference 1). However, for a large system, the requirement is extreme: the trajectory must fill an enormously open space of the order of 10^{23} dimensions! By contrast the path of a random walk has dimension 2 (in any embedding dimension)! (Very briefly, the (fractal or Hausdorff–Besicovitch) dimension of a random walk can be understood to be 2 as follows. The dimension of an object in this sense is determined as D_{H} defined so that when one covers the object in question with spheres of radius η a minimum of $N(\eta)$ spheres is required and

$$L_{\mathrm{H}} = \lim_{\eta \to 0} N(\eta)\eta^{D_{\mathrm{H}}}$$

is finite and nonzero. For a random walk of mean square radius $\langle R^2 \rangle$, $N(\eta) = \langle R^2 \rangle / \eta^2$ and $D_{\mathrm{H}} = 2$. See reference 1 for details.) Nevertheless something like ergodicity is required for statistical mechanics to work, and so the paths in phase space of large systems must in fact achieve this enormous convolution in order to account for the known facts from experiment and simulation. It is not true that every system consisting of small numbers of particles is ergodic. Some of the problems at the end of this section illustrate this point. For example, a one dimensional harmonic oscillator is ergodic, but a billiard ball on a two dimensional table is not (Figure 1.1). On the other hand, in the latter case, the set of initial conditions for which it is not ergodic is in some sense "small." Another instructive example is a two dimensional harmonic oscillator (Problem 1.1).

There are several rationally equivalent ways of talking about equation (1.10). These occur in textbooks and other discussions and reflect the history of the subject as well as useful approaches to its extension to nonequilibrium systems. What we have discussed so far may be termed the Boltzmann interpretation of ρ (in which ρ is related to the time which the system phase point spends in each region of phase space). This is closely related to the *probability* interpretation of ρ because the

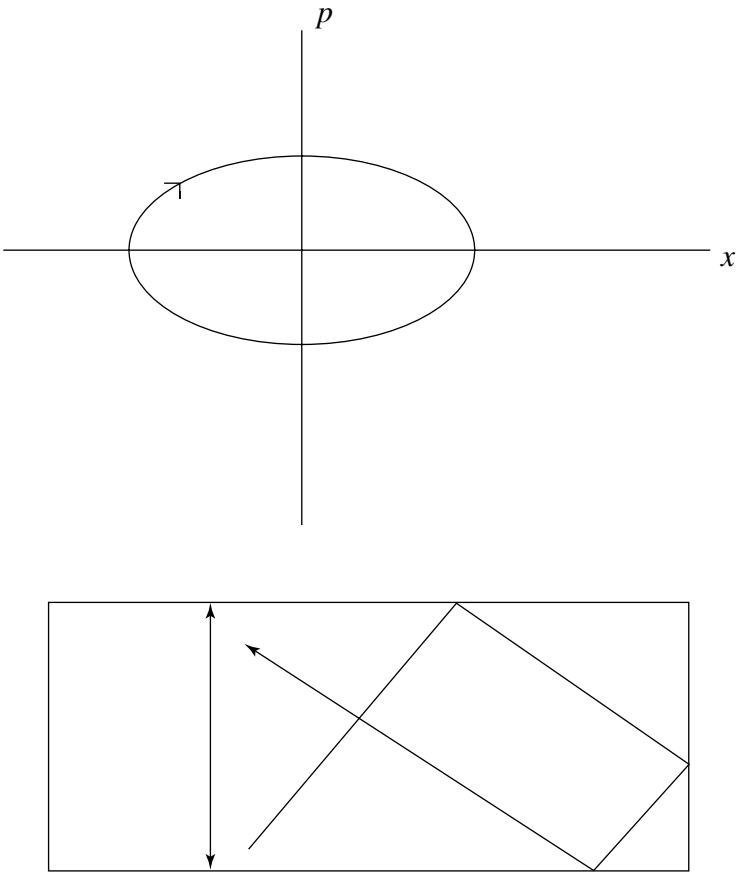

Figure 1.1 Phase space trajectory of a one dimensional oscillator fills the energy surface. For some initial conditions, a ball on a billiard table with elastic specularly reflecting walls is not ergodic.

probability that the system is found in $\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p$ is just $\rho\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p$ according to the standard observation frequency definition of probability. In such an interpretation, one takes no interest in the question of how the system got into each phase space region and could as well imagine that it hopped discontinuously from one to another for some purposes. Indeed such discontinuous hops (which we do not believe occur in real experimental systems obeying classical mechanics to a good approximation) do occur in certain numerical methods of computing the integrals (1.10) once the form of ρ is known. Regarding $\rho\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p$ as a probability opens the way to the use of information theoretic methods for approximating its form under all sorts of conditions in which various constraints are applied. For mechanical systems in equilibrium this approach leads to the same forms which we will obtain and use here. The reader is referred to the book by Katz[2] and to many papers by Jaynes

for accounts of the information theoretic approach.[3,4] A third interpretation regards the integral (1.10) as describing an average over a large number (an *ensemble*) of different systems, all specified macroscopically in the same way. Specifically we may suppose that there are $\mathcal{N}$ systems with $\mathcal{N}\rho \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p$ in each small region. Then the right hand side of (1.10) may be regarded as averaging ϕ over all $\mathcal{N}$ systems and the equality in (1.10) as stating the equality of time averages and ensemble averages. This was the approach taken by Gibbs in the first development of the foundations of the subject.[5] Gibbs regarded the equivalence of temporal and ensemble averages as a postulate and did not attempt a proof. The ensemble interpretation is of mainly historical interest but we will find its language useful in discussing Liouville's theorem below and the language of statistical mechanics contains many vestiges of it.

In statistical physics, we are mainly interested in large systems and will usually make assumptions appropriate for them. The path we will follow in order to obtain the standard forms (microcanonical, canonical and grand canonical) for the distribution function ρ which successfully describe experimental and simulated equilibrium systems is as follows. (These materials come from a variety of sources but follow mainly the lines in Landau and Lifshitz' book.[6])

(1) We prove (in a physicist's manner, but following lines which can be made rigorous) the Liouville theorem, which shows that ρ must be invariant in time, that is it is a constant of the motion.
(2) For large enough systems with finite range interactions, we then establish that ρ can depend only on *additive* constants of the motion.
(3) Accepting that the additive constants are energy, linear and angular momentum (only) we obtain the canonical distribution. This leads to an apparent contradiction for an isolated system.
(4) We resolve this by demonstrating that the fluctuations in the energy in the canonical distribution become arbitrarily small in large enough systems.

Before proceeding let me explain why I think it worthwhile to spend time on these aspects of fundamentals. Most books of this sort simply write down the canonical distribution function and start calculating. Firstly, simulation usually uses an approach related to the microcanonical distribution, not the canonical one, whereas analytical theories almost always work with the canonical or grand canonical distribution function. Thus a firm grasp of why and when these are equivalent is of daily use in theoretical work which combines theory and simulation. Second, the proofs (inasfar as they exist) of the legitimacy of the standard distribution functions depend at several points on the largeness of the system involved, whereas simulations are necessarily constricted to quite finite systems and experiments too are increasingly interested in small systems for technical reasons. Finally, research on

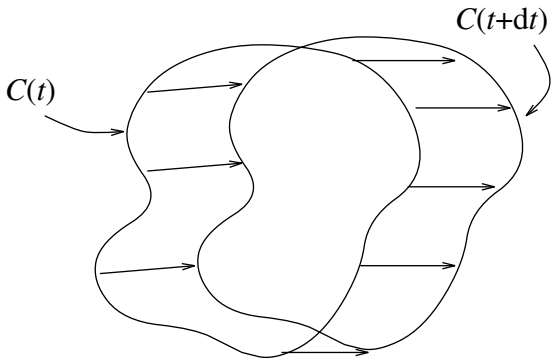

Figure 1.2 Schematic sketch of the evolution of the boundary $C(t)$ in phase space.

nonequilibrium systems will be informed by an understanding of the conditions under which an equilibrium description is expected to work.

Liouville's theorem

The theorem states that the function $\rho(q_0, p_0; q, p)$ does not change if the phase point q, p evolves in time as it does when the coordinates and momenta obey the Hamiltonian equations of motion in time. (When we actually use (1.10) to calculate an average, we do not regard the arguments q, p as functions of time, but just integrate over them.) To demonstrate this, we use the ensemble interpretation. Consider a cloud of $\mathcal{N}$ phase points distributed over the phase space with density ρ. Consider a small but finite region in the phase space surrounded by a $6N-1$ dimensional surface $C(t)$ around the point $p(t), q(t)$. The volume of the small region is

$$\Delta p \Delta q(t) = \int_{\text{inside } C(t)} \mathrm{d}^{3N} q(t)\, \mathrm{d}^{3N} q(t) \tag{1.17}$$

The surface $C(t)$ may be regarded as defined by the system points on it, which we regard as moving along trajectories according to Hamilton's equations as well. Thus the surface will move in time and so will the points inside it. At time t, the number of system points inside $C(t)$ is

$$\Delta\mathcal{N}(t) = \mathcal{N}\rho(q(t), p(t))\Delta q(t)\Delta p(t) \tag{1.18}$$

if the region is small.

Now let time evolve to $t + \mathrm{d}t$ (Figure 1.2).

The points in the boundary $C(t)$ move to form a new boundary $C(t + \mathrm{d}t)$. The points inside $C(t)$ also move along their trajectories. But, because the solutions to the Hamiltonian equations are unique, *no trajectories cross*. Therefore the same points

that lay inside $C(t)$ now lie inside $C(t+\mathrm{d}t)$ and the number of points $\Delta\mathcal{N}(t+\mathrm{d}t)$ lying inside $C(t+\mathrm{d}t)$ is the same as the number $\Delta\mathcal{N}(t)$. But by the same argument used at time t,

$$\Delta\mathcal{N}(t+\mathrm{d}t) = \mathcal{N}\rho(q(t+\mathrm{d}t),\, p(t+\mathrm{d}t))\Delta q(t+\mathrm{d}t)\Delta p(t+\mathrm{d}t) \tag{1.19}$$

where

$$\Delta q(t+\mathrm{d}t)\Delta p(t+\mathrm{d}t) = \int_{\text{inside } C(t+\mathrm{d}t)} \mathrm{d}^{3N}q(t+\mathrm{d}t)\,\mathrm{d}^{3N}q(t+\mathrm{d}t) \tag{1.20}$$

Combining (1.17), (1.18), (1.19), and (1.20) with the condition $\Delta\mathcal{N}(t+\mathrm{d}t) = \Delta\mathcal{N}(t)$ gives

$$\begin{aligned}\rho(q(t),\, p(t)) &\int_{\text{inside } C(t)} \mathrm{d}^{3N}q(t)\,\mathrm{d}^{3N}q(t) \\ &= \rho(q(t+\mathrm{d}t),\, p(t+\mathrm{d}t)) \int_{\text{inside } C(t+\mathrm{d}t)} \mathrm{d}^{3N}q(t+\mathrm{d}t)\,\mathrm{d}^{3N}q(t+\mathrm{d}t)\end{aligned} \tag{1.21}$$

Thus to show that ρ is constant we need to show that the integrals on the two sides of (1.21) are equal. To do that we transform the variables of integration on the right hand side to those on the left by use of the Jacobian:

$$\begin{aligned}\frac{\partial(q(t+\mathrm{d}t),\, p(t+\mathrm{d}t))}{\partial(q(t),\, p(t))} &= \begin{vmatrix} 1+\frac{\partial\dot{q}_1(t)}{\partial q_1(t)}\mathrm{d}t & \frac{\partial\dot{q}_1(t)}{\partial q_2(t)}\mathrm{d}t & \dots & \dots \\ \frac{\partial\dot{q}_1(t)}{\partial q_2(t)}\mathrm{d}t & 1+\frac{\partial\dot{q}_2(t)}{\partial q_2(t)}\mathrm{d}t & \dots & \dots \\ \cdot & \cdot & \cdot & \dots \\ \cdot & \cdot & \cdot & \dots \\ \cdot & \cdot & \cdot & \dots \\ \dots & \dots & \dots & \text{same for } p \end{vmatrix} \\ &= \prod_{i=q}^{3} N\left(1+\frac{\partial\dot{q}_i(t)}{\partial q_i(t)}\mathrm{d}t\right)\left(1+\frac{\partial\dot{p}_i(t)}{\partial p_i(t)}\mathrm{d}t\right) + \mathcal{O}((\mathrm{d}t)^2) \\ &= 1+\sum_{i}^{3N}\left(\frac{\partial\dot{q}_i(t)}{\partial q_i(t)}+\frac{\partial\dot{p}_i(t)}{\partial p_i(t)}\right)\mathrm{d}t + \mathcal{O}((\mathrm{d}t)^2)\end{aligned} \tag{1.22}$$

From the Hamiltonian equations of motion

$$\frac{\partial\dot{q}_i(t)}{\partial q_i(t)} = \frac{\partial^2 H}{\partial q_i\,\partial p_i} \tag{1.23}$$

$$\frac{\partial\dot{p}_i(t)}{\partial p_i(t)} = -\frac{\partial^2 H}{\partial p_i\,\partial q_i} \tag{1.24}$$

Thus if the Hamiltonian is analytic

$$\frac{\partial(q(t+\mathrm{d}t),\, p(t+\mathrm{d}t))}{\partial(q(t),\, p(t))} = 1 + \mathcal{O}((\mathrm{d}t)^2) \tag{1.25}$$

Thus from (1.21)

$$\begin{aligned}\frac{\mathrm{d}\rho(q(t),\, p(t))}{\mathrm{d}t} &= \lim_{\mathrm{d}t\to 0} \frac{\rho(q(t+\mathrm{d}t),\, p(t+\mathrm{d}t)) - \rho(q(t),\, p(t))}{\mathrm{d}t} \\ &= \lim_{\mathrm{d}t\to 0} \mathcal{O}(\mathrm{d}t^2/\mathrm{d}t) = 0 \end{aligned} \tag{1.26}$$

With suitable mathematical tightening of the various steps, this line of reasoning rigorously proves the Liouville theorem (see for example Kurth[7]). The proof depends essentially on the choice of the variables q_i and p_i as the coordinates of phase space. For example, if one were to work in the space $\{q_i\}$, $\{\dot{q}_i\}$, the corresponding density would not be constant for every Lagrangian system.

The distribution function depends only on additive constants of the motion

The preceding section sketches the proof that the density distribution function ρ is a constant of the motion defined by Hamilton's equations of motion. That theorem is quite robust and in particular does not require that the system be large for its validity. To go further we need to suppose that the system has a large number of degrees of freedom. Furthermore we will assume that the interactions between the entities, usually atoms or molecules, in the system are short range in the following sense. We imagine dividing the system when it is in equilibrium into two parts both containing a large number of entities, say by designating a smooth two dimensional surface which divides the region of accessible values of each of the (q_i, p_i) in two and assigning all the variables on one side of the surface at some time to one subsystem and all those on the other side to the other. If the interactions are of short range then the effects of the partition are only felt over a finite distance from the partition (which is actually somewhat larger than the range of the interaction, but which can be made much smaller than the dimension of each part). Let this distance be d and the size of each partition be of order L. Then the magnitude of the effects of inserting the partition to the magnitude of effects from the bulk of each subsystem is roughly $L^2 d/L^3 \to 0$ as $L \to \infty$. Thus, effectively, we can calculate average properties as well from the partitioned system as from the original system, as long as the properties ϕ which we are averaging treat every allowed region of phase space with equal weight. (The last condition means, for example, that ϕ could be the total energy or the average density, but not the density near the partition.)

Let the distribution function for the entities on one side of the partition be ρ_1 and let it depend on coordinates and momenta q_1, p_1 and similarly for the other