2

Theoretical foundations of classical statistical mechanics

2.1 Overview

The field of thermodynamics began in precursory form with the work of Otto von Guericke (1602–1686) who designed the first vacuum pump in 1650 and with Robert Boyle (1627–1691) who, working with von Guericke's design, discovered an inverse proportionality between the pressure and volume of a gas at a fixed temperature for a fixed amount of gas. This inverse proportionality became known as Boyle's Law. Thermodynamics matured in the nineteenth century through the seminal work of R. J. Mayer (1814–1878) and J. P. Joule (1818–1889), who established that heat is a form of energy, of R. Clausius (1822–1888) and N. L. S. Carnot (1796–1832), who originated the concept of entropy, and of numerous others. This work is neatly encapsulated in what we now refer to as the laws of thermodynamics (see Section 2.2). As these laws are based on experimental observations, thermodynamics is a phenomenological theory of macroscopic matter, which has, nevertheless, withstood the test of time. The framework of thermodynamics is an elegantly self-consistent one that makes no reference to the microscopic constituents of matter. If, however, we believe in a microscopic theory of matter, then it must be possible to rationalize thermodynamics based on microscopic mechanical laws.

In Chapter 1, we presented the laws of classical mechanics and applied them to several simple examples. The laws of classical mechanics imply that if the positions and velocities of all the particles in a system are known at a single instant in time, then the past evolution of the system leading to that point in time and the future evolution of the system from that point forward are known. The example systems considered in Chapter 1 consisted of one or a small number of degrees of freedom with simple forces, and we saw that the past and future of each system could be worked out from Newton's second law of motion (see, for example, eqn. (1.2.10)). Thus, classical mechanics encodes all the information needed to predict the properties of a classical system at any instant in time.

In order to provide a rational basis for thermodynamics, we should apply the microscopic laws of motion to macroscopic systems. However, this idea immediately meets with two serious issues. First, macroscopic systems possess an enormous number of degrees of freedom (1 mole consists of $6.022 \times 10^{23}$ particles); second, real-world systems are characterized by highly nontrivial interactions. Hence, even though we should be able, in principle, to predict the microscopic detailed dynamics of any classical system knowing only the initial conditions, we quickly realize the hopelessness of this effort.
The highly nonlinear character of the forces in realistic systems means that an analytical solution of the equations of motion is not available. If we propose, alternatively, to solve the equations of motion numerically on a computer, the memory requirement to store just one phase space point for a system of $10^{23}$ particles exceeds what is available both today and in the foreseeable future. Thus, while classical mechanics encodes all the information needed to predict the properties of a system, the problem of extracting that information is seemingly intractable.

In addition to the problem of the sheer size of macroscopic systems, another, more subtle, issue exists. The second law of thermodynamics prescribes a direction of time, namely, the direction in which the entropy increases. This “arrow” of time is seemingly at odds with the microscopic mechanical laws, which are inherently reversible in time. This paradoxical situation, known as Loschmidt’s paradox, seems to pit thermodynamics against microscopic mechanical laws.

The reconciliation of macroscopic thermodynamics with the microscopic laws of motion required the development of a new field, statistical mechanics, the main topic of this book. Statistical mechanics began with ideas from Clausius and James C. Maxwell (1831–1879) but grew principally out of the work of Ludwig Boltzmann (1844–1906) and Josiah W. Gibbs (1839–1903). (Other significant contributors include Henri Poincaré, Albert Einstein, and later, Lars Onsager, Richard Feynman, Ilya Prigogine, Kenneth Wilson, and Benjamin Widom, to name just a few.) Early innovations in statistical mechanics derived from the realization that the macroscopic observable properties of a system do not depend strongly on the detailed dynamical motion of every particle in a macroscopic system but rather on gross averages that largely “wash out” these microscopic details. Thus, by applying the microscopic mechanical laws in a statistical fashion, a link can be provided between the microscopic and macroscopic theories of matter. Not only does this concept provide a rational basis for thermodynamics, it also leads to procedures for computing many other macroscopic observables. The principal conceptual breakthrough on which statistical mechanics is based is that of an ensemble, which refers to a collection of systems that share common macroscopic properties. Averages performed over an ensemble yield the thermodynamic quantities of a system as well as other equilibrium and dynamic properties.

In this chapter, we will lay out the fundamental theoretical foundations of ensemble theory and show how the theory establishes the link between the microscopic and macroscopic realms. We begin with a discussion of the laws of thermodynamics and a number of important thermodynamic functions. Following this, we introduce the notion of an ensemble and the properties that an ensemble must obey. Finally, we will describe, in general terms, how to use an ensemble to calculate macroscopic properties. Specific types of ensembles and their use will be detailed in subsequent chapters.

\footnote{It can be easily shown, for example, that Newton’s second law retains its form under a time-reversal transformation $t \rightarrow -t$. Under this transformation, $\frac{d}{dt} \rightarrow -\frac{d}{dt}$, but $\frac{d^2}{dt^2} \rightarrow \frac{d^2}{dt^2}$. Time-reversal symmetry implies that if a mechanical system evolves from an initial condition $x_0$ at time $t = 0$ to $x_1$ at a time $t > 0$, and all the velocities are subsequently reversed ($v_1 \rightarrow -v_1$), the system will return to its initial microscopic state $x_0$. The same is true of the microscopic laws of quantum mechanics. Consequently, it should not be possible to tell if a “movie” made of a mechanical system is running in the “forward” or “reverse” direction.}
2.2 The laws of thermodynamics

Our discussion of the laws of thermodynamics will make no reference to the microscopic constituents of a particular system. Concepts and definitions we will need for the discussion are described below:

i. A thermodynamic system is a macroscopic system. Thermodynamics always divides the universe into the system and its surroundings. A thermodynamic system is said to be isolated if no heat or material is exchanged between the system and its surroundings and if the surroundings produce no other change in the thermodynamic state of the system.

ii. A system is in thermodynamic equilibrium if its thermodynamic state does not change in time.

iii. The fundamental thermodynamic parameters that define a thermodynamic state, such as the pressure $P$, volume $V$, the temperature $T$, and the total mass $M$ or number of moles $n$ are measurable quantities assumed to be provided experimentally. A thermodynamic state is specified by providing values of all thermodynamic parameters necessary for a complete description of a system.

iv. The equation of state of a system is a relationship among the thermodynamic parameters prescribing how these parameters vary from one equilibrium state to another. Thus, if $P$, $V$, $T$, and $n$ are the fundamental thermodynamic parameters of a system, the equation of state takes the general form

$$g(n, P, V, T) = 0. \tag{2.2.1}$$

As a consequence of eqn. (2.2.1), there are in fact only three independent thermodynamic parameters in an equilibrium state. When the number of moles remains fixed, the number of independent parameters is reduced to two. An example of an equation of state is that of an ideal gas, which is defined (thermodynamically) as a system whose equation of state is

$$PV = nRT = 0, \tag{2.2.2}$$

where $R = 8.315 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the gas constant. The ideal gas represents the limiting behavior of all real gases at sufficiently low density $\rho = n/V$.

v. A thermodynamic transformation is a change in the thermodynamic state of a system. In equilibrium, a thermodynamic transformation is effected by a change in the external conditions of the system. Thermodynamic transformations can be carried out either reversibly or irreversibly. In a reversible transformation, the change is carried out slowly enough that the system has time to adjust to each new external condition imposed along a prescribed thermodynamic path, so that the system can retrace its history along the same path between the endpoints of the transformation. If this is not possible, then the transformation is irreversible.

vi. A state function is any function $f(n, P, V, T)$ whose change under any thermodynamic transformation depends only on the initial and final states of the transformation and not on the particular thermodynamic path taken between these states (see Fig. 2.1).
Laws of thermodynamics always define the total mass of the thermodynamic system, the total amount of change in the thermodynamic state does not depend on the thermodynamic state, the total mass $M$ or provided experimentally if all thermodynamic parameters are known. The thermodynamic equilibrium state to which a dynamic parameters

(2.2.1)

An independent thermometer measures the number of moles remains constant for any two. An example of a thermodynamic system is a gas,

(2.2.2)

where $p$ is the pressure and $V$ is the volume. The thermodynamic state of a gas is described by the pressure, volume, and temperature.

The transformation of a gas is described by the change in the state of the gas. The transformation of a gas is irreversible if the change in the state of the gas is irreversible. The transformation of a gas is reversible if the change in the state of the gas is reversible.

The quantity $\mu$ is called the chemical potential, defined to be the amount of work needed to add 1.0 mole of a substance to a system already containing that substance.

(2.2.3)

The amount of heat $dQ$ needed to change the temperature by an amount $dT$ in a reversible process is given by

(2.2.4)

The quantity $C$ is called the heat capacity, defined to be the amount of heat needed to change the temperature of 1.0 mole of a substance by 1.0 degree on a chosen scale. If heat is added at fixed pressure, then the heat capacity is denoted $C_p$. If heat is added at fixed volume, it is denoted $C_V$.

2.2.1 The first law of thermodynamics

The first law of thermodynamics is a statement of conservation of energy. We saw in Section 1.6 that performing work on a system changes its potential (or internal) energy (see Section 1.4). Thermodynamics recognizes that heat is also a form of energy. The
first law states that in any thermodynamic transformation, if a system absorbs an amount of heat $\Delta Q$ and has an amount of work $\Delta W$ performed on it, then its internal energy will change by an amount $\Delta E$ given by

$$\Delta E = \Delta Q + \Delta W.$$  \hspace{1cm} (2.2.5)

(Older books define the first law in terms of the heat absorbed and work done by the system. With this convention, the first law is written $\Delta E = \Delta Q - \Delta W$.) Although neither the heat absorbed $\Delta Q$ nor the work $\Delta W$ done on the system are state functions, the internal energy $E$ is a state function. Thus, the transformation can be carried out along either a reversible or irreversible path, and the same value of $\Delta E$ will result. If $E_1$ and $E_2$ represent the energies before and after the transformation respectively, then $\Delta E = E_2 - E_1$, and it follows that an exact differential $dE$ exists for the energy such that

$$\Delta E = E_2 - E_1 = \int_{E_1}^{E_2} dE.$$ \hspace{1cm} (2.2.6)

However, since $\Delta E$ is independent of the path of the transformation, $\Delta E$ can be expressed in terms of changes along either a reversible or irreversible path:

$$\Delta E = \Delta Q_{\text{rev}} + \Delta W_{\text{rev}} = \Delta Q_{\text{irrev}} + \Delta W_{\text{irrev}}.$$ \hspace{1cm} (2.2.7)

Suppose that reversible and irreversible transformations are carried out on a system with a fixed number of moles, and let the irreversible process be one in which the external pressure drops to a value $P_{\text{ext}}$ by a sudden volume change $\Delta V$, thus allowing the system to expand rapidly. It follows that the work done on the system is

$$\Delta W_{\text{irrev}} = -P_{\text{ext}} \Delta V.$$ \hspace{1cm} (2.2.8)

In such a process, the internal pressure $P > P_{\text{ext}}$. If the same expansion is carried out reversibly (slowly), then the internal pressure has time to adjust as the system expands. Since

$$\Delta W_{\text{rev}} = -\int_{V_1}^{V_2} P dV,$$ \hspace{1cm} (2.2.9)

where the dependence of the internal pressure $P$ on the volume is specified by the equation of state, and since $P_{\text{ext}}$ in the irreversible process is less than $P$ at all states visited in the reversible process, it follows that $-\Delta W_{\text{irrev}} < -\Delta W_{\text{rev}}$, or $\Delta W_{\text{irrev}} > \Delta W_{\text{rev}}$. However, because of eqn. (2.2.7), the first law implies that the amounts of heat absorbed in the two processes satisfy

$$\Delta Q_{\text{irrev}} < \Delta Q_{\text{rev}}.$$ \hspace{1cm} (2.2.10)

Eqn. (2.2.10) will be needed in our discussion of the second law of thermodynamics.

Of course, since the thermodynamic universe is, by definition, an isolated system (it has no surroundings), its energy is conserved. Therefore, any change $\Delta E_{\text{sys}}$ in a system must be accompanied by an equal and opposite change $\Delta E_{\text{surr}}$ in the surroundings so that the net energy change of the universe $\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$. 


2.2.2 The second law of thermodynamics

Before discussing the second law of thermodynamics, it is useful to review the Carnot cycle. The Carnot cycle is the thermodynamic cycle associated with an ideal device or "engine" that takes in heat at a high temperature $T_h$, expels heat at a low temperature $T_l$, and over the cycle, delivers a net amount of useful work. The ideal engine provides an upper bound on the efficiency that can be achieved by a real engine.

The thermodynamic cycle of a Carnot engine is shown in Fig. 2.2, which is a plot of the process in the $P$–$V$ plane. In the cycle, each of the four transformations (curves

![Fig. 2.2 The Carnot cycle.](image)

AB, BC, CD and DA in Fig. 2.2) is assumed to be performed reversibly on an ideal gas. The four stages of the cycle are defined as follows:

- **Path AB**: An amount of heat $Q_h$ is absorbed at a high temperature $T_h$, and the system undergoes an isothermal expansion at this temperature.
- **Path BC**: The system further expands adiabatically so that no further heat is gained or lost.
- **Path CD**: The system is compressed at a low temperature $T_l$, and an amount of heat $Q_l$ is released by the system.
- **Path DA**: The system undergoes a further adiabatic compression in which no further heat is gained or lost.

Since the cycle is closed, the change in the internal energy in this process is $\Delta E = 0$. Thus, according to the first law of thermodynamics, the net work output by the Carnot engine is given by
\[ -W_{\text{net}} = \Delta Q = Q_h + Q_l. \quad (2.2.11) \]

The efficiency of any engine \( \epsilon \) is defined as the ratio of the net work output to the heat input
\[ \epsilon = -\frac{W_{\text{net}}}{Q_h}, \quad (2.2.12) \]
from which it follows that the efficiency of the Carnot engine is
\[ \epsilon = 1 + \frac{Q_l}{Q_h}. \quad (2.2.13) \]

On the other hand, the work done on (or by) the system during the adiabatic expansion and compression phases cancels, so that the net work comes from the isothermal expansion and compression segments. From the ideal gas law, eqn. (2.2.2), the work done on the system during the initial isothermal expansion phase is simply
\[ W_h = -\int_{V_a}^{V_b} PdV = -\int_{V_a}^{V_b} \frac{nRT_h}{V} dV = -nRT_h \ln \left( \frac{V_b}{V_A} \right), \quad (2.2.14) \]
while the work done on the system during the isothermal compression phase is
\[ W_l = -\int_{V_C}^{V_D} \frac{nRT_l}{V} dT = -nRT_l \ln \left( \frac{V_D}{V_C} \right). \quad (2.2.15) \]

However, because the temperature ratio for both adiabatic phases is the same, namely, \( T_h/T_l \), it follows that the volume ratios \( V_C/V_B \) and \( V_D/V_A \) are also the same. Since \( V_C/V_B = V_D/V_A \), it follows that \( V_B/V_A = V_C/V_D \), and the net work output is
\[ -W_{\text{net}} = nR(T_h - T_l) \ln \left( \frac{V_B}{V_A} \right). \quad (2.2.16) \]

The internal energy of an ideal gas is \( E = 3nRT/2 \), and therefore the energy change during an isothermal process is \( \Delta E = 0 \). Hence, for the initial isothermal expansion phase, \( \Delta E = 0 \) and \( W_h = -Q_h = nRT_h \ln(V_B/V_A) \). The efficiency can also be expressed in terms of the temperatures as
\[ \epsilon = -\frac{W_{\text{net}}}{Q_h} = -\frac{nR(T_h - T_l) \ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)} = 1 - \frac{T_l}{T_h}. \quad (2.2.17) \]

Equating the two efficiency expressions, we have
\[ 1 + \frac{Q_l}{Q_h} = 1 - \frac{T_l}{T_h} \]
\[ \frac{Q_l}{Q_h} = -\frac{T_l}{T_h} \]
\[ \frac{Q_h}{T_h} + \frac{Q_l}{T_l} = 0. \quad (2.2.18) \]
Eqn. (2.2.18) indicates that there is a quantity \( \Delta Q_{\text{rev}} / T \) whose change over the closed cycle is 0. The “rev” subscript serves as a reminder that the Carnot cycle is carried out using reversible transformations. Thus, the quantity \( \Delta Q_{\text{rev}} / T \) is a state function, and although we derived this fact using an idealized Carnot cycle, it turns out that this quantity is always a state function. This means that there is an exact differential \( dS = dQ_{\text{rev}} / T \) such that \( S \) is a state function. The quantity \( \Delta S \), defined by

\[
\Delta S = \int_1^2 \frac{dQ_{\text{rev}}}{T},
\]  

(2.2.19)

is therefore independent of the path over which the transformation from state “1” to state “2” is carried out. The quantity \( S \) is the entropy of the system.

The second law of thermodynamics is a statement about the behavior of the entropy in any thermodynamic transformation. From eqn. (2.2.10), which implies that \( dQ_{\text{irrev}} < dQ_{\text{rev}} \), we obtain

\[
dS = \frac{dQ_{\text{rev}}}{T} > \frac{dQ_{\text{irrev}}}{T},
\]  

(2.2.20)

which is known as the Clausius inequality. If this inequality is now applied to the thermodynamic universe, an isolated system that absorbs and releases no heat \( (dQ = 0) \), then the total entropy \( dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{sur}} \) satisfies

\[
dS_{\text{tot}} \geq 0.
\]  

(2.2.21)

That is, in any thermodynamic transformation, the total entropy of the universe must either increase or remain the same. \( dS_{\text{tot}} > 0 \) pertains to an irreversible process while \( dS_{\text{tot}} = 0 \) pertains to a reversible process. Eqn. (2.2.21) is the second law of thermodynamics.

Our analysis of the Carnot cycle allows us to understand two equivalent statements of the second law. The first, attributed to William Thomson (1824–1907), known later as the First Baron Kelvin or Lord Kelvin, reads: There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a high-temperature source and convert it entirely into work. In fact, some of the heat absorbed at \( T_h \) is always lost in the form of waste heat, which in the Carnot cycle is the heat \( Q_h \) released at \( T_i \). The loss of waste heat means that \( -W_{\text{net}} < -W_h \) or that the net work done by the system must be less than the work done during the first isothermal expansion phase.

Now suppose we run the Carnot cycle in reverse so that an amount of heat \( Q_i \) is absorbed at \( T_i \) and released as \( Q_h \) at \( T_h \). In the process, the amount of work \( W_{\text{net}} \) is consumed by the system. Thus, the Carnot cycle operated in reverse performs as a refrigerator, moving heat from a cold source to a hot source. This brings us to the second statement of the second law, attributed to Clausius: There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a cold source and deliver it to a hot source. That is, heat does not flow spontaneously from cold to hot; moving heat in this direction requires that work be done.
2.2.3 The third law of thermodynamics

As with any state function, it is only possible to measure changes in the entropy, which does not inherently require an absolute entropy scale. The third law of thermodynamics defines an absolute scale of entropy: The entropy of a system at the absolute zero of temperature is a universal constant, which can be taken to be zero. Absolute zero of temperature is defined as $T = 0$ on the Kelvin scale; it is a temperature that can never be physically reached. The unattainability of absolute zero is sometimes taken as an alternative statement of the third law. A consequence of the unattainability of absolute zero temperature is that the ideal (Carnot) engine can never be one-hundred percent efficient, since this would require sending $T_1 \to 0$ in eqn. (2.2.17), which is not possible. As we will see in Chapter 10, the third law of thermodynamics is actually a macroscopic manifestation of quantum mechanical effects.

2.3 The ensemble concept

We introduced the laws of thermodynamics without reference to the microscopic origin of macroscopic thermodynamic observables. Without a microscopic basis, thermodynamics must be regarded as a phenomenological theory. We now wish to provide this microscopic basis and establish a connection between the macroscopic and microscopic realms. As we remarked at the beginning of the chapter, we cannot solve the classical equations of motion for a system of $10^{23}$ particles with the complex, nonlinear interactions that govern the behavior of real systems. Nevertheless, it is instructive to pose the following question: If we could solve the equations of motion for such a large number of particles, would the vast amount of detailed microscopic information generated be necessary to describe macroscopic observables?

Intuitively, we would answer this question with "no." Although the enormous quantity of microscopic information is certainly sufficient to predict any macroscopic observable, there are many microscopic configurations of a system that lead to the same macroscopic properties. For example, if we connect the temperature of a system to an average of kinetic energy of the individual particles composing the system, then there are many ways to assign the velocities of the particles consistent with a given total energy such that the same total kinetic energy and, hence, the same measure of temperature is obtained. Nevertheless, each assignment corresponds to a different point in phase space and, therefore, a different and unique microscopic state. Similarly, if we connect the pressure to the average force per unit area exerted by the particles on the walls of the container, there are many ways of arranging the particles such that the forces between them and the walls yields the same pressure measure, even though each assignment corresponds to a unique point in phase space and hence, a unique microscopic state. Suppose we aimed, instead, to predict macroscopic time-dependent properties. By the same logic, if we started with a large set of initial conditions drawn from a state of thermodynamic equilibrium, and if we launched a trajectory from each initial condition in the set, then the resulting trajectories would all be unique in phase space. Despite their uniqueness, these trajectories should all lead, in the long time limit, to the same macroscopic dynamical observables such as vibrational spectra, diffusion constants, and so forth.
The idea that the macroscopic observables of a system are not sensitive to precise microscopic details is the basis of the ensemble concept originally introduced by Gibbs. More formally, an ensemble is a collection of systems described by the same set of microscopic interactions and sharing a common set of macroscopic properties (e.g., the same total energy, volume, and number of moles). Each system evolves under the microscopic laws of motion from a different initial condition so that at any point in time, every system has a unique microscopic state. Once an ensemble is defined, macroscopic observables are calculated by performing averages over the systems in the ensemble. Ensembles can be defined for a wide variety of thermodynamic situations. The simplest example is a system isolated from its surroundings. However, ensembles also describe systems in contact with heat baths, systems in contact with particle reservoirs, systems coupled to pressure control mechanisms such as mechanical pistons, and various combinations of these influences. Such ensembles are useful for determining static properties such as temperature, pressure, free energy, average structure, etc. Thus, the fact that the systems in the ensemble evolve in time does not affect properties of this type, and we may freeze the ensemble at any instant and perform the average over the ensemble at that instant. These ensembles are known as equilibrium ensembles, and we will focus on them up to and including Chapter 12. Finally, ensembles can also be defined for systems driven by external forces or fields for the calculation of transport coefficients and other dynamical properties. These are examples of non-equilibrium ensembles, which will be discussed in Chapters 13 and 14.

In classical ensemble theory, every macroscopic observable of a system is directly connected to a microscopic function of the coordinates and momenta of the system. A familiar example of this comes from the kinetic theory, where the temperature of a system is connected to the average kinetic energy. In general, we will let $A$ denote a macroscopic equilibrium observable and $a(x)$ denote a microscopic phase space function that can be used to calculate $A$. According to the ensemble concept, if the ensemble has $Z$ members, then the “connection” between $A$ and $a(x)$ is provided via an averaging procedure, which we write heuristically as

$$ A = \frac{1}{Z} \sum_{\lambda=1}^{Z} a(x_\lambda) \equiv \langle a \rangle. \quad (2.3.1) $$

This definition is not to be taken literally, since the sum may well be a continuous “sum” or integral. However, eqn. (2.3.1) conveys the notion that the phase space function $a(x)$ must be evaluated for each member of the ensemble at that point in time when the ensemble is frozen. Finally, $A$ is obtained by performing an average over the ensemble. (The notation $\langle a \rangle$ in eqn. (2.3.1) will be used throughout the book to denote an ensemble average.)

Let us recall the question we posed earlier: If we could solve the equations of motion for a very large number of particles, would the vast amount of detailed microscopic information generated be necessary to describe macroscopic observables? Previously, we answered this in the negative. However, the other side can also be argued if we take a purist’s view. That is, all of the information needed to describe a physical system is encoded in the microscopic equations of motion. Indeed, there are many
physical and chemical processes for which the underlying atomic and molecular mechanics are of significant interest and importance. In order to elucidate these, it is necessary to know how individual atoms and molecules move as the process occurs. Experimental techniques such as ultrafast laser spectroscopy can resolve processes at increasingly short time scales and thus obtain important insights into such motions. (The importance of such techniques was recognized by the award of the 1999 Nobel Prize in chemistry to the physical chemist Ahmed Zewail for his pioneering work in their development.) While we cannot expect to solve the equations of motion for $10^{23}$ particles, we actually can solve them numerically for systems whose particle numbers range from $10^2$ to $10^6$, depending on the complexity of the interactions in a particular physical model. The technique of solving the equations of motion numerically for small representative systems is known as molecular dynamics, a method that has become one of the most important theoretical tools for solving statistical mechanical problems. Although the system sizes currently accessible to molecular dynamics calculations are not truly macroscopic, they are large enough to capture the macroscopic limit for certain properties. Thus, a molecular dynamics calculation, which can be viewed as a kind of detailed "thought experiment" performed in silico, can yield important microscopic insights into complex phenomena including the catalytic mechanisms of enzymes, details of protein folding and misfolding processes, formation supramolecular structures, and many other fascinating phenomena.

We will have more to say about molecular dynamics and other methods for solving statistical mechanical problems throughout the book. For the remainder of this chapter, we will focus on the fundamental underpinnings of ensemble theory.

### 2.4 Phase space volumes and Liouville's theorem

As noted previously, an ensemble is a collection of systems with a set of common macroscopic properties such that each system is in a unique microscopic state at any point in time as determined by its evolution under some dynamical rule, e.g., Hamilton's equations of motion. Given this definition, and assuming that the evolution of the collection of systems is prescribed by Hamilton's equations, it is important first to understand how a collection of microscopic states (which we refer to hereafter simply as "microstates") moves through phase space.

Consider a collection of microstates in a phase space volume element $dx_0$ centered on the point $x_0$. The "0" subscript indicates that each microstate in the volume element serves as an initial condition for Hamilton's equations, which we had written in eqn. (1.6.23) as $\dot{x} = \eta(x)$. The equations of motion can be generalized to the case of a set of driven Hamiltonian systems by writing them as $\dot{x} = \eta(x, t)$. We now ask how the entire volume element $dx_0$ moves under the action of Hamiltonian evolution. Recall that $x_0$ is a complete set of generalized coordinates and conjugate momenta:

$$x_0 = (q_1(0), ..., q_{3N}(0), p_1(0), ..., p_{3N}(0)).$$

(We will refer to the complete set of generalized coordinates and their conjugate momenta collectively as the phase space coordinates.) If we follow the evolution of this volume element from $t = 0$ to time $t$, $dx_0$ will be transformed into a new volume element $dx_t$ centered on a point $x_t$ in phase space. The point $x_t$ is the phase space...