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# 1

# Introduction

## 1.1 Prologue

Engineers learn early on in their careers how to harness energy from nature, how to generate useful forms of energy, and how to transform between different energy forms. Engineers usually first learn how to do this in thermodynamics courses.

There are two fundamental concepts in thermodynamics, energy, $E$, and entropy, $S$. These are taught axiomatically in engineering courses, with the help of the two laws of thermodynamics:

(1) energy is always conserved, and
(2) the entropy difference for any change is non-negative.

Typically, the first law of thermodynamics for the energy of a system is cast into a balance equation of the form:

$$\begin{Bmatrix}\text{change of energy in the system}\\ \text{between times } t_1 \text{ and } t_2\end{Bmatrix} = \begin{Bmatrix}\text{energy that entered the system}\\ \text{between times } t_1 \text{ and } t_2\end{Bmatrix} - \begin{Bmatrix}\text{energy that exited the system}\\ \text{between times } t_1 \text{ and } t_2\end{Bmatrix} + \begin{Bmatrix}\text{energy generated in the system}\\ \text{between times } t_1 \text{ and } t_2\end{Bmatrix}. \tag{1.1}$$

The second law of thermodynamics for the entropy of a system can be presented through a similar balance, with the generation term never taking any negative values. Alternatively, the second law is presented with an inequality for the entropy, $\Delta S \geq 0$, where $\Delta S$ is the change of entropy of the system for a well-defined change of the system's state.

These laws have always served engineering disciplines well. They are adequate for purposes of engineering distillation columns, aircraft engines, power plants, fermentation reactors, or other large, macroscopic systems and processes. Sound engineering practice is inseparable from understanding the first principles underlying physical phenomena and processes, and the two laws of thermodynamics form a solid core of this understanding.

Macroscopic phenomena and processes remain at the heart of engineering education, yet the astonishing recent progress in fields like nanotechnology and genetics has shifted the focus of engineers to the microcosm. Thermodynamics is certainly applicable at the microcosm, but absent from the traditional engineering definitions is a molecular interpretation of energy and entropy. Understanding thermodynamic behavior at small scales can then be elusive.

The goal of this book is to present thermodynamics from a microscopic point of view, introducing engineers to the body of knowledge needed to apply thermodynamics and solve engineering challenges at the molecular level. Admittedly, this knowledge has been created in the physical and chemical sciences for more than one hundred years, with statistical thermodynamics. There have been hundreds of books published on this subject, since Josiah Willard Gibbs first developed his ensemble theory in the 1880s and published the results in a book in 1902. What then could another textbook have to offer?

I am hoping primarily three benefits:

1. A microscopic interpretation of thermodynamic concepts that engineers will find appropriate, one that does not dwell in the more esoteric concepts of statistical thermodynamics and quantum mechanics. I should note that this book does not shy away from mathematical derivations and proofs. I actually believe that sound mathematics is inseparable from physical intuition. But in this book, the presentation of mathematics is subservient to physical intuition and applicability and not an end in itself.
2. A presentation of molecular dynamics and Monte Carlo simulations as natural extensions of the theoretical treatment of statistical thermodynamics. I philosophically subscribe to the notion that computer simulations significantly augment our natural capacity to study and understand the natural world and that they are as useful and accurate as their underlying theory. Solidly founded on the theoretical concepts of statistical thermodynamics, computer simulations can become a potent instrument for assisting efforts to understand and engineer the microcosm.
3. A brief coverage of stochastic processes in general, and of stochastic reaction kinetics in particular. Many dynamical systems of scientific and technological significance are not at the thermodynamic limit (systems with very large numbers of particles). Stochasticity then emerges as an important feature of their dynamic behavior. Traditional continuous-deterministic models, such as reaction rate

ordinary differential equations for reaction kinetics, do not capture the probabilistic nature of small systems. I present the theory for stochastic processes and discuss algorithmic solutions to capture the probabilistic nature of systems away from the thermodynamic limit.

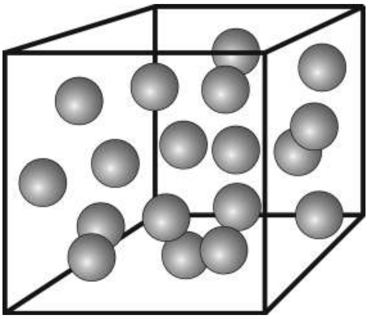
To provide an outline of the topics discussed in the book, I present a summary of the salient concepts of statistical thermodynamics in the following section.

## 1.2 If we had only a single lecture in statistical thermodynamics

The overarching goal of classical statistical thermodynamics is to explain thermodynamic properties of matter in terms of atoms. Briefly, this is how:

Consider a system with $N$ identical particles contained in volume $V$ with a total energy $E$. Assume that $N$, $V$, and $E$ are kept constant. We call this an $NVE$ system (Fig. 1.1). These parameters uniquely define the macroscopic state of the system, that is all the rest of the thermodynamic properties of the system are defined as functions of $N$, $V$, and $E$. For example, we can write the entropy of the system as a function $S = S(N, V, E)$, or the pressure of the system as a function $P = P(N, V, E)$. Indeed, if we know the values of $N$, $V$, and $E$ for a single-component, single-phase system, we can in principle find the values of the enthalpy $H$, the Gibbs free energy $G$, the Helmholtz free energy $A$, the chemical potential $\mu$, the entropy $S$, the pressure $P$, and the temperature $T$. In Appendix B, we summarize important elements of thermodynamics, including the fundamental relations between these properties.

Figure 1.1 System with $N$ particles contained in volume $V$ with a total energy $E$.



A fundamentally important concept of statistical thermodynamics is the microstate of a system. We define a microstate of a system by the values of the positions and velocities of all the $N$ particles. We can concisely describe a microstate with a $6N$-dimensional vector

$$\underline{X} = (\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N, \dot{\underline{r}}_1, \dot{\underline{r}}_2, \ldots, \dot{\underline{r}}_N). \tag{1.2}$$

In Eq. 1.2, $\underline{r}_i$ are the three position coordinates and $\dot{\underline{r}}_i$ are the three velocity coordinates of particle $i$, respectively, with $i = 1, 2, \ldots, N$. By definition, $\dot{\underline{r}}_i = d\underline{r}_i/dt$. Note that the positions and the velocities of atoms do not depend on one another.

An important postulate of statistical thermodynamics is that each macroscopic property $M$ of the system (for example the enthalpy $H$, or the pressure $P$) at any time $t$ is a function of the positions and velocities of the $N$ particles at $t$, i.e., $M(t) = M(\underline{X}(t))$. Then, any observed, experimentally measured property $M_{\text{observed}}$ is simply the time average of instantaneous values $M(t)$,

$$M_{\text{observed}} = \langle M \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T M(\underline{X}(t))dt, \tag{1.3}$$

where $T$ is the time of the experimental measurement.

Equation (1.3) provides a bridge between the observable macroscopic states and the microscopic states of any system. If there were a way to know the microscopic state of the system at different times then all thermodynamic properties could be determined. Assuming a classical system of point-mass particles, Newtonian mechanics provides such a way. We can write Newton's second law for each particle $i$ as follows:

$$m_i \ddot{\underline{r}}_i = \underline{F}_i, \tag{1.4}$$

where $m_i$ is the mass of particle $i$, $\ddot{\underline{r}}_i = d^2\underline{r}_i/dt^2$, and $\underline{F}_i$ is the force vector on particle $i$, exerted by the rest of the particles, the system walls, and any external force fields.

We can define the microscopic kinetic and potential energies, $K$ and $U$, respectively so that $E = K + U$. The kinetic energy is

$$K = K(\dot{\underline{r}}_1, \dot{\underline{r}}_2, \ldots, \dot{\underline{r}}_N) = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\underline{r}}_i^2. \tag{1.5}$$

The potential energy is

$$U = U(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N), \tag{1.6}$$

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so that (for conservative systems)

$$\underline{F}_i = -\frac{\partial U}{\partial \underline{r}_i}. \tag{1.7}$$

Albert Einstein attempted to infer the laws of thermodynamics from Newtonian mechanics for systems with large but finite degrees of freedom. In principle, a set of initial conditions at $t = 0$, $\underline{X}(0)$, would suffice to solve the second law of motion for each particle, determine $\underline{X}(t)$ and through Eq. (1.3) determine thermodynamic properties. Einstein was, however, unsuccessful in his quest. A simple reason is that it is not practically feasible to precisely determine the initial microscopic state of a system with a large number of particles $N$, because it is not possible to conduct $6N$ independent experiments simultaneously.

The impossibility of this task notwithstanding, even if the initial conditions of a system could be precisely determined in a careful experiment at $t = 0$ , the solution of $6N$ equations of motion in time is not possible for large numbers of particles. Had Einstein had access to the supercomputing resources available to researchers today, he would still not be able to integrate numerically the equations of motion for any system size near $N = 10^{23}$. To appreciate the impossibility of this task, assume that a computer exists that can integrate for one time step 10 000 coupled ordinary differential equations in one wall-clock second. This computer would require $10^{20}$ seconds to integrate around $10^{24}$ equations for this single time step. With the age of the universe being, according to NASA, around 13.7 billion years, or around $432 \times 10^{15}$ seconds, the difficulty of directly connecting Newtonian mechanics to thermodynamics becomes apparent.

Thankfully, Josiah Willard Gibbs* developed an ingenious conceptual framework that connects the microscopic states of a system to macroscopic observables. He accomplished this with the help of the concept of phase space (Fig. 1.2). For a system with $N$ particles, the phase space is a $6N$ dimensional space where each of the $6N$ orthogonal axes corresponds to one of the $6N$ degrees of freedom, i.e., the positions and velocities of the particles. Each point in phase space is identified by a vector

$$\underline{X} = (\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N, \dot{\underline{r}}_1, \dot{\underline{r}}_2, \ldots, \dot{\underline{r}}_N), \tag{1.8}$$

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* It is noteworthy that Gibbs earned a Ph.D. in Engineering from Yale in 1863. Actually, his was the first engineering doctorate degree awarded at Yale. Gibbs had studied Mathematics and Latin as an undergraduate and stayed at Yale for all of his career as a Professor in Mathematical Physics.

or equivalently by a vector

$$\underline{X} = (\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N, \underline{p}_1, \underline{p}_2, \ldots, \underline{p}_N), \tag{1.9}$$

where $\underline{p}_i = m_i \dot{\underline{r}}_i$, is the momentum of particle $i$.

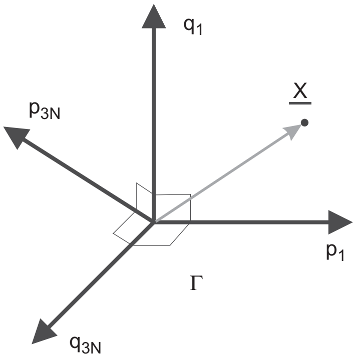
Consequently, each point in phase space represents a microscopic state of the system. For an $NVE$ system the phase space is finite, since no position axis can extend beyond the confines of volume $V$ and no momentum axis can extend beyond a value that yields the value of the total kinetic energy.

In classical mechanics the phase space is finite, of size $\Sigma$, but because it is continuous, the number of microscopic states is infinite. For each state identified with a point $\underline{X}$, a different state can be defined at $\underline{X} + d\underline{X}$, where $d\underline{X}$ is an infinitesimally small distance in $6N$ dimensions.

Thanks to quantum mechanics, we now know that this picture of a continuous phase space is physically unattainable. Werner Heisenberg's uncertainty principle states that the position and momentum of a particle cannot be simultaneously determined with infinite precision. For a particle confined in one dimension, the uncertainties in the position, $\Delta x$, and momentum, $\Delta p$, cannot vary independently: $\Delta x \Delta p \geq h/4\pi$, where $h = 6.626 \times 10^{-34}$ m$^2$ kg/s is Planck's constant.

The implication for statistical mechanics is significant. What the quantum mechanical uncertainty principle does is simply to discretize the phase space (Fig. 1.3). For any $NVE$ system, instead of an infinite number of possible microscopic states, there is a finite number of microscopic states corresponding to the macroscopic $NVE$ system. Let us call this number $\Omega$ and write $\Omega(N, V, E)$ to denote that it is determined by the macroscopic state.

Figure 1.2 Phase space $\Gamma$. Each microscopic state of a macroscopic $NVE$ system is represented by a single point in $6N$ dimensions.



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Another fundamental postulate of statistical thermodynamics is that all these Ω microscopic states have the same probability of occurring. This probability is then

$$P = 1/\Omega. \tag{1.10}$$

Ludwig Boltzmann showed around the same time as Gibbs that the entropy of an $NVE$ system is directly related to the number of microscopic states Ω. Gibbs and Boltzmann were thus able to provide a direct link between microscopic and macroscopic thermodynamics, one that proved to be also useful and applicable. The relation between entropy $S(N, V, E)$ and the number of microscopic states $\Omega(N, V, E)$ has been determined by numerous different methods. We will present a concise one that Einstein proposed:

1. Assume there generally exists a specific function that relates the entropy of an $NVE$ system to the number of microscopic states that correspond to this $NVE$ macroscopic state. The relation can be written as

$$S = \phi(\Omega). \tag{1.11}$$

2. Consider two independent systems $A$ and $B$. Then

$$S_A = \phi(\Omega_A), \tag{1.12}$$

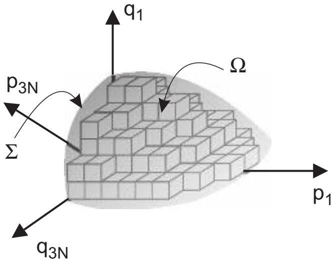
and

$$S_B = \phi(\Omega_B). \tag{1.13}$$

3. Consider the composite system of $A$ and $B$. Call it system $AB$. Since entropy is an extensive property, the entropy of the composite system is

$$S_{AB} = \phi(\Omega_{AB}) = S_A + S_B = \phi(\Omega_A) + \phi(\Omega_B). \tag{1.14}$$

Figure 1.3 The available phase space to any macroscopic state is an ensemble of discrete microscopic states. The size of the available phase space is Σ, and the number of microscopic states is Ω.



4. Since the systems are independent, the probability of the composite system being in a particular microscopic state is equal to the product of probabilities that systems $A$ and $B$ are in their respective particular microscopic state, i.e.,

$$P_{AB} = P_A P_B. \tag{1.15}$$

Therefore the number of microscopic states of the composite system can be written as

$$\Omega_{AB} = \Omega_A \Omega_B. \tag{1.16}$$

5. Combining the results in the two previous steps,

$$\phi(\Omega_{AB}) = \phi(\Omega_A \Omega_B) = \phi(\Omega_A) + \phi(\Omega_B). \tag{1.17}$$

The solution of this equation is

$$\phi(\Omega) = k_B \ln(\Omega), \tag{1.18}$$

and thus

$$S = k_B \ln(\Omega), \tag{1.19}$$

where $k_B = 1.38065 \times 10^{-23}\ \mathrm{m^2 kg\, s^{-2} K^{-1}}$ is Boltzmann's constant.

This equation, which is called Boltzmann's equation, provides a direct connection between microscopic and macroscopic properties of matter. Importantly, the entropy of $NVE$ systems is defined in a way that provides a clear physical interpretation.

Looking at the phase space not as a succession in time of microscopic states that follow Newtonian mechanics, but as an ensemble of microscopic states with probabilities that depend on the macroscopic state, Gibbs and Boltzmann set the foundation of statistical thermodynamics, which provides a direct connection between classical thermodynamics and microscopic properties.

This has been accomplished not only for $NVE$ systems, but for $NVT$, $NPT$, and $\mu VT$ systems among others. Indeed, for any system in an equilibrium macroscopic state, statistical thermodynamics focuses on the determination of the probabilities of all the microscopic states that correspond to the equilibrium macrostate. It also focuses on the enumeration of these microscopic states. With the information of how many microscopic states correspond to a macroscopic one and of what their probabilities are, the thermodynamic state and behavior of the system can be completely determined.

Remembering from thermodynamics that

$$dE = TdS - PdV + \mu dN, \tag{1.20}$$

we can write, for the $NVE$ system

$$\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}, \tag{1.21}$$

or

$$\left.\frac{\partial \ln(\Omega)}{\partial E}\right|_{N,V} = \frac{1}{k_B T}. \tag{1.22}$$

Similarly,

$$\left.\frac{\partial \ln(\Omega)}{\partial V}\right|_{N,E} = \frac{P}{k_B T}, \tag{1.23}$$

and

$$\left.\frac{\partial \ln(\Omega)}{\partial N}\right|_{E,V} = -\frac{\mu}{k_B T}. \tag{1.24}$$

In this book I present the theory for enumerating the microscopic states of equilibrium systems and determining their probabilities. I then discuss how to use this knowledge to derive thermodynamic properties, using Eqs. 1.21–1.24, or other similar ones for different ensembles.

As an example, consider an ideal gas of $N$ particles, in volume $V$, with energy $E$. The position of any of these non-interacting particles is independent of the positions of the rest of the particles. We discuss in Chapter 4 that in this case we can enumerate the microscopic states. In fact we find that

$$\Omega(N, V, E) \propto V^N. \tag{1.25}$$

Using Eq. 1.23 we can then write

$$\frac{P}{k_B T} = \frac{N}{V}, \tag{1.26}$$

and rearranging

$$PV = Nk_B T. \tag{1.27}$$

We can show that the Boltzmann constant is equal to the ratio of the ideal gas constant over the Avogadro number, $k_B = R/N_A$. Then for ideal gases

$$PV = nRT, \tag{1.28}$$

where $n$ is the number of moles of particles in the system.

First stated by Benoît Paul Emile Clapeyron in 1834, the ideal gas law, an extraordinary and remarkably simple equation that has since guided understanding of gas thermodynamics, was originally derived empirically. With statistical thermodynamics the ideal gas law is derived theoretically from simple first principles and statistical arguments.

I discuss how other equations of state can be derived theoretically using information about the interactions at the atomic level. I do this analytically for non-ideal gases, liquids, and solids of single components of monoatomic and of diatomic molecules. I then introduce computer simulation techniques that enable us numerically to connect the microcosm with the macrocosm for more complex systems, for which analytical solutions are intractable.

In Chapter 2, I present the necessary elements of probability and combinatorial theory to enumerate microscopic states and determine their probability. I assume no prior exposure to statistics, which is regretfully true for most engineers.

I then discuss, in Chapter 3, the classical mechanical concepts required to define microscopic states. I introduce quantum mechanics in order to discuss the notion of a discrete phase space. In Chapter 4, I introduce the classical ensemble theory, placing emphasis on the $NVE$ ensemble.

In Chapter 5, I define the canonical $NVT$ ensemble. In Chapter 6, fluctuations and the equivalence of various ensembles is presented. Along the way, we derive the thermodynamic properties of monoatomic ideal gases.

Diatomic gases, non-ideal gases, liquids, crystals, mixtures, reacting systems, and polymers are discussed in Chapters 7–11.

I present an introduction to non-equilibrium thermodynamics in Chapter 12, and stochastic processes in Chapter 13.

Finally, in Chapters 14–18, I introduce elements of Monte Carlo, molecular dynamics and stochastic kinetic simulations, presenting them as the natural, numerical extension of statistical mechanical theories.