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# 1

# Thermodynamics and Statistical Mechanics Review

This is a book about techniques, and the first few chapters are about the techniques you have to learn *before* you can learn the *real* techniques.

Your mastery of these crucial chapters will be presumed in subsequent ones. So go though them carefully, paying special attention to exercises whose answers are numbered equations.

I begin with a review of basic ideas from thermodynamics and statistical mechanics. Some books are suggested at the end of the chapter [1–4].

In the beginning there was thermodynamics. It was developed before it was known that matter was made of atoms. It is notorious for its multiple but equivalent formalisms and its orgy of partial derivatives. I will try to provide one way to navigate this mess that will suffice for this book.

## 1.1 Energy and Entropy in Thermodynamics

I will illustrate the basic ideas by taking as an example a cylinder of gas, with a piston on top. The piston exerts some pressure $P$ and encloses a volume $V$ of gas. We say the system (gas) is in equilibrium when nothing changes at the macroscopic level. In equilibrium the gas may be represented by a point in the $(P,V)$ plane.

The gas has an internal energy $U$. This was known even before knowing the gas was made of atoms. The main point about $U$ is that it is a *state variable*: it has a unique value associated with every state, i.e., every point $(P,V)$. It returns to that value if the gas is taken on a closed loop in the $(P,V)$ plane.

There are two ways to change $U$. One is to move the piston and do some mechanical work, in which case

$$dU = -PdV \tag{1.1}$$

by the law of conservation of energy. The other is to put the gas on a hot or cold plate. In this case some heat $\delta Q$ can be added and we write

$$dU = \delta Q, \tag{1.2}$$

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which acknowledges the fact that heat is a form of energy as well. The first law of thermodynamics simply expresses energy conservation:

$$dU = \delta Q - PdV. \tag{1.3}$$

I use $\delta Q$ and not $dQ$ since $Q$ is not a state variable. Unlike $U$, there is no unique $Q$ associated with a point $(P,V)$: we can go on a closed loop in the $(P,V)$ plane, come back to the same state, but $Q$ would have changed by the negative of the work done, which is the area inside the loop.

The second law of thermodynamics introduces another state variable, $S$, the *entropy*, which changes by

$$dS = \frac{\delta Q}{T} \tag{1.4}$$

when heat $\delta Q$ is added reversibly, i.e., arbitrarily close to equilibrium. It is a state variable because it can be shown that

$$\oint dS = 0 \tag{1.5}$$

for a quasi-static cyclic process.

Since $dU$ is independent of how we go from one point to another, we may as well assume that the heat was added reversibly, and write

$$dU = TdS - PdV, \tag{1.6}$$

which tells us that

$$U = U(S,V), \tag{1.7}$$

$$T = \left.\frac{\partial U}{\partial S}\right|_V, \tag{1.8}$$

$$-P = \left.\frac{\partial U}{\partial V}\right|_S. \tag{1.9}$$

For future use note that we may rewrite these equations as follows:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV, \tag{1.10}$$

$$S = S(U,V), \tag{1.11}$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_V, \tag{1.12}$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_U. \tag{1.13}$$

These equations will be recalled shortly when we consider statistical mechanics, in which macroscopic thermodynamic quantities like energy or entropy emerge from a microscopic description in terms of the underlying atoms and molecules.

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*The function $U(S,V)$, called the fundamental relation, constitutes complete thermodynamics knowledge of the system.*

This is like saying that the Hamiltonian function $H(x,p)$ constitutes complete knowledge of a mechanical system. However, we still need to find what $H$ is for a particular situation, say the harmonic oscillator, by empirical means.

As an example, let us consider $n$ moles of an ideal gas for which it is known from experiments that

$$U(S,V) = C\left[\frac{e^{S/nR}}{V}\right]^{2/3}, \tag{1.14}$$

where $R = 8.31\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is the universal gas constant and $C$ is independent of $S$ and $V$. From the definition of $P$ and $T$ in Eqs. (1.8) and (1.9), we get the *equations of state*:

$$P = -\left.\frac{\partial U}{\partial V}\right|_S = \frac{2}{3}\frac{U}{V}, \tag{1.15}$$

$$T = \left.\frac{\partial U}{\partial S}\right|_V = \frac{2}{3nR}U. \tag{1.16}$$

The two may be combined to give the more familiar $PV = nRT$.

## 1.2 Equilibrium as Maximum of Entropy

The second law of thermodynamics states that when equilibrium is disturbed, the entropy of the universe will either increase or remain the same. Equivalently,

*$S$ is a maximum at equilibrium.*

But I have emphasized that $S$, like $U$, is a state variable defined only in equilibrium! How can you maximize a function defined only at its maximum?

What this statement means is this. Imagine a box of gas in equilibrium. It has a volume $V$ and energy $U$. Suppose the box has a conducting piston that is held in place by a pin. The piston divides the volume into two parts of size $V_1 = \alpha V$ and $V_2 = (1-\alpha)V$. They are at some common temperature $T_1 = T_2 = T$, but not necessarily at a common pressure. The system is forced into equilibrium despite this due to a constraint, the pin holding the piston in place. The entropy of the combined system is just the sum:

$$S = S_1(V_1) + S_2(V_2) = S_1(\alpha V) + S_2((1-\alpha)V). \tag{1.17}$$

Suppose we now let the piston move. It may no longer stay in place and $\alpha$ could change. Where will it settle down? We are told it will settle down at the value that maximizes $S$:

$$0 = dS = dS_1 + dS_2 \tag{1.18}$$

$$= \frac{\partial S_1}{\partial V_1}dV_1 + \frac{\partial S_2}{\partial V_2}dV_2 \tag{1.19}$$

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$$= \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) d\alpha\ V \tag{1.20}$$

$$0 = \left(\frac{P_1 - P_2}{T}\right) d\alpha, \tag{1.21}$$

which is the correct physical answer: in equilibrium, when $S$ is maximized, the pressures will be equal.

So the principle of maximum entropy means that when a system held in equilibrium by a constraint becomes free to explore new equilibrium states due to the removal of the constraint, it will pick the one which maximizes $S$. In this example, where its options are parametrized by $\alpha$, it will pick

$$\frac{\partial S(\alpha)}{\partial \alpha} = 0 \overset{\text{def}}{=} \text{equilibrium}. \tag{1.22}$$

A subtle point: Suppose initially we had $\alpha = 0.1$, and finally $\alpha = 0.5$. In this experiment, only $S(\alpha = 0.1)$ and $S(\alpha = 0.5)$ are equilibrium entropies. However, we could define an $S(\alpha)$ by making any $\alpha$ into an equilibrium state by restraining the piston at that $\alpha$ and letting the system settle down. It is this $S(\alpha)$ that is maximized at the new equilibrium.

## 1.3 Free Energy in Thermodynamics

Temporarily, let $V$ be fixed, so that $U = U(S)$ and

$$T = \frac{dU}{dS}. \tag{1.23}$$

Since $U = U(S)$, this gives us $T$ as a function of $S$:

$$T = T(S). \tag{1.24}$$

Assuming that this relation can be inverted to yield

$$S = S(T), \tag{1.25}$$

let us construct a function $F(T)$, called the *free energy*, as follows:

$$F(T) = U(S(T)) - TS(T). \tag{1.26}$$

Look at the $T$-derivative of $F(T)$:

$$\frac{dF}{dT} = \frac{dU(S(T))}{dT} - S(T) - T\frac{dS(T)}{dT} \tag{1.27}$$

$$= \frac{dU}{dS} \cdot \frac{dS}{dT} - S(T) - T\frac{dS(T)}{dT} \tag{1.28}$$

$$= -S(T) \quad \text{using Eq. (1.8).} \tag{1.29}$$

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Thus we see that while $U$ was a function of $S$, with $T$ as the derivative, $F$ is a function of $T$, with $-S$ as its derivative. Equation (1.26), which brings about this exchange of roles, is an example of a *Legendre transformation*.

Let us manipulate Eq. (1.26) to derive a result that will be invoked soon:

$$F = U - ST \tag{1.30}$$

$$U = F + ST \tag{1.31}$$

$$= F - T\frac{dF}{dT} \quad \text{using Eq. (1.29).} \tag{1.32}$$

If we bring back $V$, which was held fixed so far, and repeat the analysis, we will find that

$$F = F(T,V), \tag{1.33}$$

$$-S = \left.\frac{\partial F}{\partial T}\right|_V, \tag{1.34}$$

$$-P = \left.\frac{\partial F}{\partial V}\right|_T, \tag{1.35}$$

$$dF = -SdT - PdV. \tag{1.36}$$

The following recommended exercise invites you to find $F(T,V)$ for an ideal gas by carrying out the Legendre transform.

**Exercise 1.3.1** *For an ideal gas, start with Eq. (1.14) and show that*

$$T(S,V) = \frac{\partial U}{\partial S} = \frac{2}{3nR}U \tag{1.37}$$

*to obtain $U$ as a function of $T$. Next, construct $F(T,V) = U(T) - S(T,V)T$; to get $S(T,V)$, go back to Eq. (1.14), write $S$ in terms of $U$, and then $U$ in terms of $T$, and show that*

$$F(T,V) = \frac{3nRT}{2}\left[(1+\ln C) - \ln\frac{3nRT}{2} - \frac{2}{3}\ln V\right]. \tag{1.38}$$

*Verify that the partial derivatives with respect to $T$ and $V$ give the expected results for the entropy and pressure of an ideal gas.*

## 1.4 Equilibrium as Minimum of Free Energy

*Knowledge of $F(T,V)$ is as complete as the knowledge of $U(S,V)$.* Often $F(T)$ is preferred, since it is easier to control its independent variable $T$ than the entropy $S$ which enters $U(S)$. What does it mean to say that $F(V,T)$ has the same information as $U(V,S)$?

Start with the principle defining the equilibrium of an isolated system as the *maximum of $S$ at fixed $U$* (when a constraint is removed). It can equally well be stated as the *minimum of $U$ at fixed $S$*. After the Legendre transformation from $U$ to $F$, is there an equivalent principle that determines equilibrium? If so, what is it?

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It is that when a constraint is removed in a system in equilibrium with a reservoir at fixed $T$, *it will find a new equilibrium state that minimizes* $F$.

Let us try this out for a simple case. Imagine the same box of gas as before with an immovable piston that divides the volume into $V_1 = \alpha V$ and $V_2 = (1-\alpha)V$, but in contact with a reservoir at $T$. The two parts of the box are at the same temperature by virtue of being in contact with the reservoir, but at possibly different pressures. If we now remove the constraint, the pin holding the piston in place, where will the piston come to rest? The claim above is that the piston will come to rest at a position where the free energy $F(\alpha)$ is maximized. Let us repeat the arguments leading to Eq. (1.21) with $S$ replaced by $F$:

$$0 = dF = dF_1 + dF_2 \tag{1.39}$$

$$= \frac{\partial F_1}{\partial V_1} dV_1 + \frac{\partial F_2}{\partial V_2} dV_2 \tag{1.40}$$

$$0 = \left( \frac{-P_1 + P_2}{T} \right) d\alpha \tag{1.41}$$

$$P_1 = P_2, \tag{1.42}$$

which is the correct answer.

This completes our review of thermodynamics. We now turn to statistical mechanics.

## 1.5 The Microcanonical Distribution

Statistical mechanics provides the rational, microscopic foundations of thermodynamics in terms of the underlying atoms (and molecules). There are many equivalent formulations, depending on what is held fixed: the energy, the temperature, the number of particles, and so forth.

Consider an isolated system in equilibrium. It can be in any one of its possible *microstates* – states in which it is described in maximum possible detail. In the classical case this would be done by specifying the coordinate $x$ and momentum $p$ of every particle in it, while in the quantum case it would be the energy eigenstate of the entire system (energy being the only conserved quantity).

In statistical mechanics one abandons a microscopic description in favor of a statistical one, being content to give the probabilities for measuring various values of macroscopic quantities like pressure. One usually computes the average, and sometimes the fluctuations around the average.

Consider a system that can be in one of many microstates. Let the state labeled by an index $i$ occur with probability $p_i$, and in this state an observable $O$ has a value $O(i)$. The average of $O$ is

$$\langle O \rangle = \sum_i p_i O(i). \tag{1.43}$$

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One measure of fluctuations is the mean-squared deviation:

$$(\Delta O)^2 = \sum_i (O(i) - \langle O \rangle)^2 p_i = \langle O^2 \rangle - \langle O \rangle^2. \tag{1.44}$$

To proceed, we need $p_i$, the probability that the system will be found in a particular microstate $i$. This is given by the fundamental postulate of statistical mechanics: *A macroscopic isolated system in thermal equilibrium is equally likely to be found in any of its accessible microstates.* This "equal weight" probability distribution is called the *microcanonical distribution*.

A central result due to Boltzmann identifies the entropy of the isolated system to be

$$S = k \ln \Omega, \tag{1.45}$$

where $\Omega$ is the number of different microscopic states or *microstates* of the system compatible with its known macroscopic properties, such as its energy, volume, and so on. Boltzmann's constant $k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ is related to the macroscopically defined gas constant $R$, which enters

$$PV = nRT, \tag{1.46}$$

and Avogadro's number $N_\mathrm{A} \simeq 6 \times 10^{23}$ as follows:

$$R = N_\mathrm{A} k. \tag{1.47}$$

I will illustrate Eq. (1.45) by applying it to an ideal gas of non-interacting atoms, treated classically. I will compute

$$S(U,V,N) = k \ln \Omega(U,V,N), \tag{1.48}$$

where $\Omega(U,V,N)$ is the number of states in which every atomic coordinate of the $N$ atoms lies inside the box of volume $V$ and the momenta are such that the sum of the individual kinetic energies adds up to $U$.

For pedagogical reasons the complete dependence of $S$ on $N$ will not be computed here. We will find, however, that as long as $N$ is fixed, the partial derivatives of $S$ with respect to $U$ and $V$ can be evaluated with no error, and these will confirm beyond any doubt that Boltzmann's $S$ indeed corresponds to the one in thermodynamics, by reproducing $PV = NkT$ and $U = \frac{3}{2}NkT$.

First, consider the spatial coordinates. Because each atom is point-like in our description, its position is a point. If we equate the number of possible positions to the number of points inside the volume $V$, the answer will be infinite, no matter what $V$ is! So what one does is divide the box mentally into tiny cells of volume $a^3$, where $a$ is some tiny number determined by our desired accuracy in specifying atomic positions in practice. Let us say we choose $a = 10^{-6}$ m. In a volume $V$, there will be $V/a^3$ cells indexed by $i = 1, 2, \ldots, V/a^3$. We label the atoms $A, B, \ldots$, and say in which cell each one lies. If $A$ is in cell $i = 20$ and $B$ in cell $i = 98\,000$, etc., that's one microscopic arrangement or microstate.

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We can assign them to other cells, and if we permute them, say with $A \to B \to C \to D \to A$, that is counted as another arrangement (except when two exchanged atoms are in the same cell). Thus, when the gas is restricted to volume $V$, and each of the $N$ atoms has $V/a^3$ possible cell locations, the number of positional configurations is

$$\Omega_V = \left[\frac{V}{a^3}\right]^N, \tag{1.49}$$

and the entropy associated with all possible positions is

$$S_V = k\ln\left[\frac{V}{a^3}\right]^N = Nk\ln\frac{V}{a^3}. \tag{1.50}$$

Notice that $S_V$ depends on the cell size $a$. If we change $a$, we will change $S_V$ by a constant, because of the $\ln a^3$ term. This is unavoidable until quantum mechanics comes in to specify a unique cell size. However, *changes* in $S_V$, which alone are defined in classical statistical mechanics, will be unaffected by the varying $a$.

But Eq. (1.50) is incomplete. The state of the atom is not given by just its location, but also its momentum $\boldsymbol{p}$. Thus, $\Omega_V$ above should be multiplied by a factor $\Omega_p(U)$ that counts the number of momentum states open to the gas at a given value of $U$. Again, one divides the possible atomic momenta into cells of some size $b^3$. Whereas the atoms could occupy any spatial cell in the box independently of the others, now they can only assume momentum configurations in which the total kinetic energy of the gas adds up to a given fixed $U$. Thus, the formula to use is

$$\Omega = \left[\frac{V}{a^3}\right]^N \times \Omega_p(U), \tag{1.51}$$

$$S(U,V) = Nk\ln\frac{V}{a^3} + k\ln\Omega_p(U). \tag{1.52}$$

Now for the computation of $\Omega_p(U)$. The energy of an ideal gas is entirely kinetic and independent of the particle positions. The internal energy is (for the allowed configuration with every atom inside the box)

$$U = \sum_{i=1}^{N}\frac{1}{2}m|v_i|^2 = \sum_{i=1}^{N}\frac{|\boldsymbol{p}_i|^2}{2m} = \sum_{i=1}^{N}\frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m}, \tag{1.53}$$

where $\boldsymbol{p} = mv$ is the momentum.

Let us now form a vector $\boldsymbol{P}$ with $3N$ components,

$$\boldsymbol{P} = (p_{1x}, p_{1y}, p_{1z}, p_{2x}, \dots, p_{Nz}), \tag{1.54}$$

which is simply the collection of the 3 components of the $N$ momentum vectors $\boldsymbol{p}_i$. If we renumber the components of $\boldsymbol{P}$ with an index $j = 1, \dots, 3N$,

$$\boldsymbol{P} = (P_1, P_2, \dots, P_{3N}), \tag{1.55}$$

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that is to say,

$$P_1 = p_{1x}, P_2 = p_{1y}, P_3 = p_{1z}, P_4 = p_{2x}, \ldots, P_{3N} = p_{Nz}, \tag{1.56}$$

we may write

$$U = \sum_{j=1}^{3N} \frac{P_j^2}{2m}. \tag{1.57}$$

Regardless of their position, the atoms can have any momentum as long as the components satisfy Eq. (1.57). So we must see how many possible momenta exist obeying this condition. The condition may be rewritten as

$$\sum_{j=1}^{3N} P_j^2 = 2mU. \tag{1.58}$$

This is the equation for a hypersphere of radius $\mathcal{R} = \sqrt{2mU}$ in $3N$ dimensions. By dimensional analysis, a sphere of radius $\mathcal{R}$ in $d$ dimensions has an area that goes as $\mathcal{R}^{d-1}$. In our problem, $\mathcal{R} = \left[\sqrt{2mU}\right]$ and $d = 3N - 1 \simeq 3N$. If we divide the individual momenta into cells of size $b^3$, which, like $a^3$, is small but arbitrary, the total number of states allowed to the gas behaves as

$$\Omega(V,U) = V^N U^{3N/2} f(m,N,a,b), \tag{1.59}$$

where we have focused on the dependence on $U$ and $V$ and lumped the rest of the dependence on $m$, $a$, $b$, and $N$ in the unknown function $f(m,N,a,b)$. We do not need $f$ because we just want to take

$$S = k\ln\Omega = k\left[N\ln V + \frac{3N}{2}\ln U\right] + k\ln f(m,N,a,b) \tag{1.60}$$

and find its $V$ and $U$ partial derivatives, to which $f$ makes no contribution. These derivatives are

$$\left.\frac{\partial S}{\partial V}\right|_U = \frac{kN}{V}, \tag{1.61}$$

$$\left.\frac{\partial S}{\partial U}\right|_V = \frac{3kN}{2U}. \tag{1.62}$$

If $S = k\ln\Omega$ were indeed the $S$ of thermodynamics, it should obey

$$\left.\frac{\partial S}{\partial V}\right|_U = \frac{P}{T}, \tag{1.63}$$

$$\left.\frac{\partial S}{\partial U}\right|_V = \frac{1}{T}. \tag{1.64}$$

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We will see that assuming this indeed gives us the correct ideal gas equation:

$$\frac{kN}{V} = \frac{P}{T} \quad \text{which is just } PV = NkT; \tag{1.65}$$

$$\frac{3kN}{2U} = \frac{1}{T} \quad \text{which is just } U = \tfrac{3}{2}NkT. \tag{1.66}$$

Thus we are able derive these *equations of state* of the ideal gas from the Boltzmann definition of entropy. Going forward, remember that the (inverse) temperature is the derivative of Boltzmann's entropy with respect to energy, exactly as in thermodynamics:

$$\left.\frac{\partial S}{\partial U}\right|_V = \frac{1}{T}. \tag{1.67}$$

Dividing both sides by $k$, we obtain another important variable, $\beta$:

$$\beta = \left.\frac{\partial \ln \Omega(U)}{\partial U}\right|_V = \frac{1}{kT}. \tag{1.68}$$

With more work we could get the full $N$-dependence of $\Omega$ as well. It has interesting consequences, but I will not go there, leaving it to you to pursue the topic on your own.

While

$$S = k \ln \Omega \tag{1.69}$$

is valid for any thermodynamic system, computing $\Omega$ is generally impossible except for some idealized models, like the ideal gas.

Finally, consider two systems that are independent. Then

$$\Omega = \Omega_1 \times \Omega_2, \tag{1.70}$$

i.e., the number of options open to the two systems is the product of the numbers open to each. This ensures that the total entropy, $S$, is additive:

$$S = S_1 + S_2. \tag{1.71}$$

## 1.6 Gibbs's Approach: The Canonical Distribution

In contrast to Boltzmann, who gave a statistical description of isolated systems with a *definite energy* $U$, Gibbs wanted to describe systems at a *definite temperature* by virtue of being in thermal equilibrium with a heat reservoir at a fixed $T$. For example, the system could be a gas, confined to a heat-conducting box, placed inside a gigantic oven at that $T$. By definition, the temperature of the reservoir remains fixed no matter what the system does.

What is the probability $p_i$ that the system will be in microstate $i$? We do not need a new postulate for this. The system and reservoir may exchange heat but the two of them are isolated from everything else and have a total conserved energy $U_0$. *So, together, they obey*