Chapter 5
The fundamental equation

5.1 Equilibrium and derivatives of the entropy

In Chapter 4, we saw that the entropy is a tool to find the most likely macroscopic state of a system, i.e., the macroscopic conditions that have the greatest number of microstates. We also saw that the conditions for equilibrium between two bodies are intimately linked to derivatives of the entropy. For two single-component systems 1 and 2, there are three types of equilibrium,

thermal equilibrium:
\[
\frac{\partial s_1}{\partial E_1} = \frac{\partial s_2}{\partial E_2} \rightarrow \frac{1}{T_1} = \frac{1}{T_2} \rightarrow T_1 = T_2
\]

mechanical (and thermal) equilibrium:
\[
\frac{\partial s_1}{\partial V_1} = \frac{\partial s_2}{\partial V_2} \rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow P_1 = P_2
\]

chemical (and thermal) equilibrium:
\[
\frac{\partial s_1}{\partial N_1} = \frac{\partial s_2}{\partial N_2} \rightarrow \frac{\mu_1}{T_1} = \frac{\mu_2}{T_2} \rightarrow \mu_1 = \mu_2
\]

How do we know that the derivatives of the entropy should involve the quantities \(T\), \(P\), and \(\mu\), and not something else? It is precisely because we use equilibrium to measure these quantities in reality. When we measure temperature, for example, we allow a thermometer to come to thermal equilibrium with another body with which it exchanges energy. We then use changes in the properties of the thermometer to characterize the point at which we have reached thermal equilibrium. We construct a scale called temperature that depends on these properties. Similarly, we measure pressure by placing a small measuring device in contact with another body such that the two can exchange volume—for example, through a piston attached to a spring or through liquid that is displaced in a column. We can measure the displacement at equilibrium and calculate the net force exerted by both systems, which must be equal.

Why do the entropy derivatives entail the specific quantities \(1/T\), \(P/T\), and \(-\mu/T\), where temperature and pressure are on an absolute scale? This will become clearer in our discussion of work and the first law in the next chapter, but consider for now the following rough argument. We could construct a temperature- or pressure-measuring device based on an ideal gas, for which we can determine an explicit, analytical form for the entropy (as we did roughly in Chapter 2 and will do more thoroughly in Chapter 9). We know that \((\partial S/\partial V)_{E,N} = Nk_B/V\) from this analysis, and experiments on ideal gas volumetric properties show that this must be equal to the quantity \(P/T\) that we measure in our defined units. If we bring the ideal gas device to equilibrium with another body, the derivative relations above must still hold. In this sense the ideal gas can serve as a reference point for the thermodynamic quantities that determine equilibrium conditions. The fact that the
derivatives of the entropy involve inverse temperatures, which may seem confusing at first, is merely an effect of how scales for measuring “hotness” developed historically. If we wanted, we could adopt a “coldness” scale instead based on $1/T$ where 0 represents an infinitely hot state and $+\infty$ is absolute zero.

One way that we know the $E, V, N$-derivatives of the entropy correspond to $1/T, P/T, -\mu/T$, respectively, is because these are the quantities that become equal between two bodies at equilibrium, and because any measurement of $T, P, \mu$ necessarily involves bringing a device into equilibrium with the system of interest. The fact that all of the derivatives involve inverse temperatures is due to the convention for measuring “hotness.”

5.2 Differential and integrated versions of the fundamental equations

As we saw in Chapter 2, a convenient summarization of the function $S(E, V, N)$ is the fundamental equation,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

(5.1)

We call this particular form of the fundamental equation the entropy version. An equivalent energy version can be made by rearranging the differentials,

$$dE = TdS - PdV + \mu dN$$

(5.2)

Here, this result describes the function $E(S, V, N)$, and it summarizes its partial derivatives as,

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T(S, V, N) \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -P(S, V, N) \quad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu(S, V, N)$$

(5.3)

All that we have done in going from the entropy to energy version is to switch out the independent variable from $E$ to $S$. It is as if we transformed the equation $w = f(x; y, z)$ by inverting to solve for $x$ as a function of $w$, that is, $x = g(w; y, z) = f^{-1}(w; y, z)$. Notice also that the $E$-derivatives depend on the independent variables $S, V, N$.

We must make a brief comment on our notation for the internal energy using the variable $E$. This convention is to keep consistency with the microscopic picture of matter, in which the internal energy is the sum of the atomic kinetic energy $K$ and potential energy $U$. An oft-seen alternate convention is the designation of the internal energy as $U$. In order to avoid confusion with the atomic potential energy, we will forgo this practice, and always write the total internal energy as $E$. 

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The reason for transforming to the energy fundamental equation is that it has a simpler connection to the physical quantities $T, P,$ and $\mu$. We will work more frequently with this version because of this simplicity. Note in particular that this equation involves both extensive and intensive quantities. 

An **extensive** quantity scales linearly with the size of the system. Some examples are $E, S, V,$ and $N$. An **intensive** quantity is independent of the size of the system upon scaling whilst maintaining the same equilibrium state, such as $T, P,$ and $\mu$.

All of the independent variables $S, V, N$ and $E$ itself are extensive, whereas the derivatives are intensive. This fact alone means that the function $E(S, V, N)$ has a very simple form according to a mathematical argument called Euler’s theorem. That form is,

$$E = TS - PV + \mu N$$

No longer expressed as a differential, this equation gives the **integrated form** of the fundamental equation. It shows that the function $E(S, V, N)$ is given by the sum of the independent variables times the derivatives of $E$ with respect to them. In this expression, it is important to keep in mind that $T$, $P$, and $\mu$ are not formally independent, but are functions of $S, V, N$. It is as if we were to write,

$$E = (\frac{\partial E}{\partial S})_{V,N} S + (\frac{\partial E}{\partial V})_{S,N} V + (\frac{\partial E}{\partial N})_{S,V} N$$

In other words, Euler’s theorem says that the function $E(S, V, N)$ has the special property that its value for any set of $S, V, N$ is also given by the sum on the right hand side of (5.5), involving derivatives of $E(S, V, N)$ evaluated at those values.

Euler’s theorem applies in this case because of the extensive behavior of the energy. The proof is as follows. Since $E$ scales linearly with system size,

$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N)$$

Taking the $\lambda$-derivative of both sides,

$$E(S, V, N) = \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial \lambda} \frac{\partial (\lambda S)}{\partial \lambda} + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda V)} \frac{\partial (\lambda V)}{\partial \lambda} + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda N)} \frac{\partial (\lambda N)}{\partial \lambda}$$

$$= \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda S)} S + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda V)} V + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda N)} N$$

Since $\lambda$ can be any arbitrary number, Eqn. (5.7) must hold for the case in which $\lambda = 1$,

$$E(S, V, N) = \frac{\partial E(S, V, N)}{\partial S} S + \frac{\partial E(S, V, N)}{\partial V} V + \frac{\partial E(S, V, N)}{\partial N} N$$

$$= T(S, V, N) S - P(S, V, N) V + \mu(S, V, N) N$$

$$= TS - PV + \mu N$$

$$= E$$
That concludes the proof. By an analogous argument, we can construct an integrated form for the entropy version of the fundamental equation. We can proceed by applying Euler’s theorem to the extensivity property $\lambda S(E,V,N) = S(\lambda E,\lambda V,\lambda N)$, or we can simply rearrange the integrated energy form. Either returns the same result,

$$S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T} \quad (5.9)$$

**EXAMPLE 6.1**

*Show that the Sackur-Tetrode equation, the exact expression for the entropy of a monatomic ideal gas with molecular mass $m$, obeys Euler’s theorem for the integrated form for the entropy. The Sackur-Tetrode equation is,*

$$S = Nk_B \ln \left[ \frac{E^{3/2}}{N} \right] + Nk_B C \quad \text{where} \quad C = \frac{5}{2} + \frac{3}{2} \ln \left( \frac{4\pi m}{3h^2} \right)$$

Note that the Sackur-Tetrode equation obeys extensive scaling, $S(\lambda E,\lambda V,\lambda N) = \lambda S(E,V,N)$. To check Euler’s theorem, we must compute the three partial derivatives of $S$,

$$\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{3Nk_B}{2E} \; ; \; \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk_B}{V} \; ; \; \left( \frac{\partial S}{\partial N} \right)_{E,V} = -\frac{5k_B}{2} + k_B \ln \left[ \frac{E^{3/2}}{N} \right] + k_B C$$

Now apply Euler’s theorem,

$$S = \left( \frac{\partial S}{\partial E} \right)_{V,N} E + \left( \frac{\partial S}{\partial V} \right)_{E,N} V + \left( \frac{\partial S}{\partial N} \right)_{E,V} N$$

$$= \left( \frac{3Nk_B}{2E} \right) E + \left( \frac{Nk_B}{V} \right) V + \left( -\frac{5k_B}{2} + k_B \ln \left[ \frac{E^{3/2}}{N} \right] + k_B C \right) N$$

$$= Nk_B \ln \left[ \frac{E^{3/2}}{N} \right] + Nk_B C$$

The result is the same, as we expected.

### 5.3 Intensive forms and state functions

It is often convenient to make intensive versions of extensive variables. The recipe is simple: take the ratio of two extensive quantities, such as the energy per particle or the number of molecules per volume. A common way to construct intensive variables is to use a per-molecule or per-mole basis, although a per-volume basis would be no less valid. We will define the energy per particle as follows,

$$e \equiv \frac{E}{N} \quad (5.10)$$

Since the energy is extensive, we can let $\lambda = 1/N$ in (5.6) to find that,
In other words, \( e \) depends only on the intensive entropy \( s = S/N \) and volume \( v = V/N \). Therefore, we can write that \( e \) is a function of two independent variables,

\[
e = e(s, v)
\] (5.12)

In going from an extensive to an intensive energy, we reduced the number of independent variables by one. This occurs because we give up information about the system, and that information is precisely the system size.

We now seek a fundamental differential equation for \( e(s, v) \) by finding the partial derivatives. Note that,

\[
e(s, v) = \frac{E(sN, vN, N)}{N}
\] (5.13)

Taking the \( s \) derivative,

\[
\left( \frac{\partial e}{\partial s} \right)_v = \frac{\partial}{\partial s} \frac{E(sN, vN, N)}{N} = \frac{1}{N} \frac{dE(sN, vN, N)}{\partial (sN)} \frac{\partial (sN)}{\partial s} = \frac{1}{N} \frac{\partial E}{\partial s} = T
\] (5.14)

and then the \( v \) derivative,

\[
\left( \frac{\partial e}{\partial v} \right)_s = \frac{\partial}{\partial v} \frac{E(sN, vN, N)}{N} = \frac{1}{N} \frac{dE(sN, vN, N)}{\partial (vN)} \frac{\partial (vN)}{\partial v} = \frac{1}{N} \frac{\partial E}{\partial v} = -P
\] (5.15)

we find that we can write,

\[
de = T \, ds - P \, dv
\] (5.16)

What happened to the chemical potential when we went to the extensive version? Because we used the variable \( N \) to make all quantities intensive, the chemical potential is no longer a partial of the energy function. Instead, we can recover it using the integrated form of the fundamental equation,
Rearranging,

\[ \frac{E}{N} = \frac{TS}{N} - \frac{PV}{N} + \frac{\mu N}{N} \]  \hspace{1cm} (5.17)

This shows that we can still compute the chemical potential from the function \( e(s, v) \). Therefore, the intensive form of the fundamental equation still contains a relationship to all intensive variables. This fact has significant implications:

Once \( s \) and \( v \) are given, the values of all other intensive variables are fixed at equilibrium in an isolated, single-component system. \( e \) is found from \( e(s, v) \), \( T \) and \( P \) stem from derivatives of \( e(s, v) \), and the chemical potential is given by \( \mu = e - Ts + Pv \). Thus we only need to know two pieces of intensive information to completely specify the thermodynamic state of the system, that is, the values of all other intensive variables.

For extensive variables, we need one additional piece of information, the size of the system \( N \).

For systems with more than one component, there will be multiple chemical potentials \( \partial E / \partial N_1 = \mu_1 \), \( \partial E / \partial N_2 = \mu_2 \), etc. Therefore, we would need \( C - 1 \) more pieces of information to specify the intensive state of a system of \( C \) components.

The crux of these statements is very general and powerful: for \( C \) components, we need \( C + 1 \) pieces of information to tell us the macroscopic, equilibrium state of a single-phase, non-reacting system. For multiphase systems, the mere fact that there exists two phases in equilibrium can serve as one piece of information. For reactive systems, equilibrium constants serve as additional information. We will learn more about such cases in later chapters.

Must the two pieces of information specifying the thermodynamic state of a system be \( v \) and \( s \) specifically? It turns out that we can use other sets of parameters by swapping these variables for their conjugates, the variables that relate to them in the partial derivatives of the fundamental equation. For example, we can swap \( s \) for \( T \). This is because we can always regain the value of \( s \) by solving the following equation at fixed values of \( T \) and \( v \),

\[ \frac{\partial e(s, v)}{\partial s} = T \]  \hspace{1cm} (5.19)
While one might be worried that there are multiple solutions for $s$ that satisfy this equality, the concavity condition on the entropy guarantees that there is only a single one. Similarly, we can swap $P$ for $v$ since we could solve,

$$\frac{\partial e(s,v)}{\partial v} = -P$$

(5.20)

to find $v$ as a function of $s$ and $P$. Here, the concavity condition also guarantees a single solution. On the other hand, we cannot swap $s$ for $P$ because $P$ is conjugate to $v$ and not $s$. In that case, there is no concavity condition that could guarantee a unique solution for $s$. Thus, each piece of information used to specify the thermodynamic state must originate from different conjugate variable pairs. The same is true if we switch to other intensive versions of the fundamental equation, e.g., the energy per volume.

The $C + 1$ intensive pieces of information specifying the thermodynamic state of a system must originate from different conjugate pairs. A conjugate pair appears as an independent variable and its derivative in a fundamental equation. Examples include $(s,T)$ and $(v,P)$, which stem from $e(s,v)$. In general, $x$ and $y$ are intensive conjugate pairs if $y = (\partial f / \partial x)_z$ where $f(x,z)$ is any intensive fundamental equation.

All thermodynamic variables studied thus far are called state functions, meaning their values in intensive form are exactly specified once given the $C + 1$ pieces of information required to specify the equilibrium state. For example, if one prepares a certain single-component system with specific values of $s$ and $v$, there is one and only one pressure that system can exhibit at true equilibrium; no other value will be detected in that system as long as $s$ and $v$ remain fixed, unless it strays from equilibrium or, as we will see later, is metastable. It doesn’t matter what processes a system experienced beforehand, or how it was prepared, the values of state functions will always be the same at the same thermodynamic state.

The values of state functions are completely determined by the thermodynamic state of the system, regardless of its history or preparation. State functions include $S, E, V, N, T, P, \mu$ and intensive versions thereof.

**EXAMPLE 6.2**

The energy of a perfect crystal at very low temperatures near absolute zero, and at constant $V$ and $N$ conditions, is found to obey $E = E_0 + \alpha T^4$ where $E_0$ and $\alpha$ are constants (both proportional to system size to maintain extensivity). Compute $S(T)$ and $S(E)$.

From the fundamental equation we have,

$$dE = TdS - PdV + \mu dN$$

$$= TdS \quad \text{(constant } V \text{ and } N)$$

Taking the $T$-derivative,
Substituting the measured energy relation,

\[ 4\alpha T^3 = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \]

Now, we integrate,

\[
\int dS = \int 4\alpha T^2 dT \quad \text{(constant } V \text{ and } N) \\
S = S_0(V, N) + \frac{4}{3} \alpha T^3
\]

where \( S_0 \) is an integration constant. It depends on \( V \) and \( N \) because those were held constant during the integration. This completes the determination of \( S(T) \). To obtain \( S(E) \), we back-substitute for \( T \) using the measured relation,

\[ T = \left( \frac{E - E_0}{\alpha} \right)^{\frac{1}{4}} \]

so that,

\[ S = S_0(V, N) + \frac{4}{3} \frac{1}{\alpha} (E - E_0)^{\frac{3}{4}} \]

Alternatively, we could have substituted for \( T \) before integration using,

\[
\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} = \left( \frac{E - E_0}{\alpha} \right)^{-\frac{1}{4}}
\]

And then the integration would look like,

\[
\int dS = \int \left( \frac{E - E_0}{\alpha} \right)^{\frac{1}{4}} dE
\]

The final answer is the same as before.

**EXAMPLE 6.3**

Find the pressure from the above example as \( P(T, V, N) \). This is the equation of state. Note that, in general, \( E_0 \) and \( \alpha \) are \( V \) - and \( N \)-dependent.

There are two approaches. First we proceed by method 1,

\[
P = T \left( \frac{\partial S}{\partial V} \right)_E = T \frac{\partial}{\partial V} \left[ S_0 + \frac{4}{3} \alpha \frac{1}{4} (E - E_0)^{\frac{3}{4}} \right]_E
\]
Next we use the different, but ultimately equivalent, method 2, 

\[ dE = TdS - PdV + \mu dN \]

Taking the \( V \)-derivative at constant \( T \) and using constant \( N \) conditions,

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \]

Rearranging, we have,

\[
\begin{align*}
P &= -\left( \frac{\partial E}{\partial V} \right)_T + T \left( \frac{\partial S}{\partial V} \right)_T \\
&= -\left[ \frac{\partial E_0}{\partial V} + \frac{\partial \alpha}{\partial V} T^4 \right] + T \left[ \frac{\partial S_0}{\partial V} + \frac{4}{3} \frac{\partial \alpha}{\partial V} \right] \\
&= T \frac{\partial S_0}{\partial V} + \frac{1}{3} T^4 \frac{\partial \alpha}{\partial V} - \frac{\partial E_0}{\partial V}
\end{align*}
\]

which is the same as before.

**EXAMPLE 6.4**

At constant \( T \) and \( P \), a liquid at its boiling point can also be a vapor or gas. This is similar to the situation in which there are two “systems”—two phases—that are in equilibrium with each other and can exchange energy, volume, and particles as the liquid and vapor phases interact. In terms of the intensive energies \( e_L \) and \( e_G \) and volumes \( v_L \) and \( v_G \) (\( L = \text{liquid}, \ G = \text{gas} \)), write an expression for the entropy difference \( \Delta s = s_G - s_L \).

Notice here that the two phases reach equilibrium with each other by sharing energy, volume, and particles. Thus the conditions for thermal, mechanical, and chemical equilibrium apply, meaning that \( T_L = T_G, P_L = P_G, \) and \( \mu_L = \mu_G \). If these conditions were not met, phase coexistence would not be possible; one of the phases would shrink away and the system would become single-phase. Therefore, we can define the temperatures, pressures, and molar volumes using subscript-less variables: \( T_L = T_G = T, P_L = P_G = P, \) and \( \mu_L = \mu_G = \mu \).

We write out the integrated fundamental equation for \( E \) for each phase,

\[
E_L = TS_L - PV_L + \mu N_L \quad \text{and} \quad E_G = TS_G - PV_G + \mu N_G
\]

Dividing each side through by the respective \( N \) variable,

\[
e_L = T s_L - P v_L + \mu \quad \text{and} \quad e_G = T s_G - P v_G + \mu
\]

Now, we can subtract to find,

\[ \Delta e = T \Delta s - P \Delta v \]

Notice that the \( \mu \) terms vanished, since \( \mu_L = \mu_G = \mu \). Rearranging the expression,
\[ \Delta s = \frac{\Delta e + P \Delta v}{T} \]

We could also write this expression as

\[ \Delta s = \frac{\Delta (e + P v)}{T} \]

The quantity \( e + P v \) appears frequently in thermodynamics, and it is called the molar enthalpy or per-particle enthalpy, \( h = H/N \equiv (E + PV)/N \). We will learn more about the enthalpy in later chapters, and why it emerges as useful in thermodynamics. For now, we simply show that it relates conveniently to the entropy associated with a phase transition,

\[ \Delta s = \frac{\Delta h}{T} \]
Problems

Conceptual and thought problems

1. Starting from the fundamental equation, show that \( T, P, \mu \) are all intensive, i.e., independent of the size of the system. Use the relation \( E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N) \) to show that \( T, P, \mu \) are independent of \( \lambda \).

2. A friend suggests that the intensive pair \((e, T)\) is enough information to determine the state of a single-phase, single-component system. Is he or she right or wrong? Explain.

3. For a single-component system, prove that \( (\partial V/\partial N)_{T,P} = v \). In general, prove that \( (\partial X/\partial N)_{T,P} \) where \( X \) is any extensive quantity.

Fundamentals problems

4. Find the fundamental equation for the intensive quantity \( \hat{e} = E/V \), in differential form. Also give an expression for the pressure \( P \) in terms of \( \hat{e} \) and \( \hat{s} = S/V \). Define \( \rho \equiv v^{-1} = N/V \).

5. An experimentalist measures the molar heat capacity of a system and finds the relation \( c_v(T, v) = \alpha(v)T^2 \). It is also known that the energy and entropy are both zero at absolute zero. Write an expression for the energy as a function of entropy, \( e(s, v) \). Write an expression for the equation of state, \( P(T, v) \).

Applied problems

6. The term photon gas describes a system in which radiation is inside a rigid container that is maintained at constant temperature \( T \). In this particular case, the number of photons is not conserved as they can be created and destroyed. Therefore, it is impossible to fix the particle number \( N \) and the chemical potential is always zero. It is also found that the pressure obeys the relation \( P = \frac{1}{3} E/V \). With these constraints only, show that the entropy and energy are given by the following, where \( c \) is a volume-dependent constant:

\[
E = (3/4)cT^4
\]

\[
S = cT^3
\]