

CHAPTER 1

REVIEW OF THERMODYNAMICS

1.1 Thermodynamic variables

The purpose of thermodynamics is to describe the properties of various macroscopic systems at, or near, equilibrium. This is done with the help of several *state variables*, such as the internal energy E , the volume V , the pressure P , the number of particles N , the temperature T , the entropy S , the chemical potential μ , and others.

These state variables depend only on *what* the state of the system is, and not on *how* the system was brought to that state. The variables are not all independent, and thermodynamics provides general relations among them. Some of these relations are not specific to particular systems, but are valid for *all* macroscopic systems.

1.2 Equilibrium

A system is in equilibrium if its physical properties do not change with time. The state variables must therefore be constant in time. More precisely, a system is in equilibrium if there are no

- macroscopic motions (mechanical equilibrium)
- macroscopic energy fluxes (thermal equilibrium)
- unbalanced phase transitions or chemical reactions (chemical equilibrium)

occurring within the system.

We will see in Sec. 10 that the requirement for *mechanical* equilibrium is that P must be constant in time and uniform throughout the system. This is easily understood: a pressure gradient produces an unbalanced macroscopic force which, in turn, produces bulk motion within the system; such a situation does not represent equilibrium.

The requirement for *thermal* equilibrium is that T must be constant in time and uniform throughout the system. This also is easily understood: If one part of the system is hotter than the other, energy (in the form of heat) will flow from that part to the other; again such a situation does not represent equilibrium.

Finally, the requirement for *chemical* equilibrium is that μ must be constant in time and uniform throughout the system. The chemical potential is not a very familiar quantity, and this requirement can perhaps not be understood easily. But at least it is clear that unbalanced chemical reactions (we take this to include nuclear reactions as well) cannot occur in a system at equilibrium. Consider for example the reaction of β -decay:

$$n \rightarrow p + e^- + \bar{\nu}.$$

If this reaction is unbalanced (the reversed reaction can occur at sufficiently high densities), the number of neutrons in the system will keep on decreasing, while the number of protons, electrons, and anti-neutrinos will keep on increasing. Such a situation does not represent equilibrium.

A system which is at once in mechanical, thermal, and chemical equilibrium is said to be in *thermodynamic* equilibrium.

1.3 Equation of state

The *equation of state* of a thermodynamic system expresses the fact that not all of its state variables are independent.

Consider a system described by two state variables X and Y , apart from the temperature T . (For example, an ideal gas is described by the variables $X \equiv V$, $Y \equiv P$.) We suppose that the system is initially in equilibrium at temperature T .

We ask the question: Can X and Y be varied *independently*, so that the system remains in equilibrium after the transformation? The answer, which must be determined empirically, is: No! For the system to remain in equilibrium, a given variation of X must be accompanied by a *specific* variation in Y . If Y is not varied by this amount, the system goes out of equilibrium.

There must therefore exist an equation of state,

$$\boxed{f(X, Y, T) = 0}, \quad (1.1)$$

relating X , Y , and T for *all* equilibrium configurations. For non-equilibrium states, $f \neq 0$. [For example, the equation of state of an ideal gas is $f(V, P, T) = PV - NkT = 0$.]

The equation of state cannot be *derived* within the framework of thermodynamics. (This is one of the goals of statistical mechanics.) It must be provided as input, and determined empirically.

Suppose the system goes from one equilibrium configuration (X, Y, T) to a neighbouring one $(X + \delta X, Y + \delta Y, T)$. The temperature is kept constant for simplicity; it could also be varied. We can use the equation of state to calculate δY in terms of δX . We have $f(X, Y, T) = 0$ and $f(X + \delta X, Y + \delta Y, T) = 0$, since both these configurations are at equilibrium. So

$$f(X + \delta X, Y + \delta Y, T) - f(X, Y, T) = 0.$$

Expressing the first term as a Taylor series about (X, Y, T) , up to first order in the displacements δX and δY , gives

$$\left(\frac{\partial f}{\partial X}\right)_{Y,T} \delta X + \left(\frac{\partial f}{\partial Y}\right)_{X,T} \delta Y = 0.$$

Here, the subscript after each partial derivative indicates which quantities are to be held fixed when differentiating. This equation clearly shows that X and Y cannot be varied independently if the system is to remain in equilibrium during the transformation. (For an ideal gas, the previous equation reduces to $P\delta V + V\delta P = 0$.)

1.4 Quasi-static transformations

In general, changing the state of a thermodynamic system, initially in equilibrium, by a finite amount ($X \rightarrow X + \Delta X$) brings the system out of equilibrium. The free

expansion of a gas, resulting from removing a partition in a partially filled container, is a good example.

However, if the change occurs *sufficiently slowly*, the system will always stay arbitrarily close to equilibrium. The transformation will follow a sequence of equilibrium configurations, along which the equation of state is everywhere satisfied. A good example of such a transformation is the very slow expansion of a gas in a chamber, resulting from the slow displacement of a piston.

Such transformations, which do not take the system away from equilibrium, are called *quasi-static*. We will consider only quasi-static transformations in this course.

1.5 First law of thermodynamics

1.5.1 Formulation

The first law of thermodynamics is a statement of conservation of energy:

The internal energy E of a system can be increased by *either* letting the system absorb heat (denoted by Q), *or* doing work (denoted by W) on the system.

Mathematically,

$$\boxed{dE = \delta Q + \delta W} . \quad (1.2)$$

In this equation, δQ and δW are *inexact* differentials. This means that the integrals $\int_A^B \delta Q$ and $\int_A^B \delta W$ (where A and B represent the initial and final states of a transformation, respectively) depend not only on the endpoints A and B , but also on the *path* taken to go from A to B . (The path represents the precise way by which the system was taken from state A to state B .) In other words, there are *no* state variables Q and W such that $\int_A^B \delta Q = Q(B) - Q(A)$ and $\int_A^B \delta W = W(B) - W(A)$, independently of the path of integration. On the other hand, since E is a state variable, the equation $\int_A^B dE = E(B) - E(A)$ is always true, independently of the path.

1.5.2 Work

There are many ways of doing work on a system. One way is to compress (or decompress) the system. A good example of this is the compression of a gas in a chamber, resulting from the very slow (inward) displacement of a piston. The piston moves because of the application of a force F , which is counter-acted by the gas' pressure: $F = -PA$, where A is the piston's area. The work done during a displacement dx is then $\delta W = Fdx = -PA dx$. Since $A dx = dV$, this gives

$$\boxed{\delta W_{\text{compression}} = -P dV} . \quad (1.3)$$

The work done on the system is *positive* during a compression; it is *negative* during an expansion.

Another way of doing work is to inject new particles into the system. In this case it must be that $\delta W \propto dN$. The constant of proportionality defines the *chemical potential* μ , introduced earlier:

$$\boxed{\delta W_{\text{injection}} = \mu dN} . \quad (1.4)$$

The chemical potential is just the injection energy per particle.

There are many other forms of work (electric, magnetic, gravitational, shear, etc.). In general, a work term always take the form $f dX$, where X is one of the

physical variables describing the system (such as volume and number of particles), and f is the associated *generalized force* (such as pressure and chemical potential). Work is *always* associated with a change in one of the system's physical variables. (For example, the work done when stretching a rubber band is given by $\delta W = T d\ell$, where T is the tension and ℓ the length.)

1.5.3 Work depends on path

Consider the quasi-static expansion of an ideal gas, initially in equilibrium. We want to calculate the work done on the system while it is brought from the initial state A to the final state B . Equation (1.3) implies

$$W = - \int_A^B P dV.$$

But this cannot be integrated until the function $P(V)$ — the path — is specified. We shall consider two different transformations linking the same initial and final states.

In the first transformation, the gas is expanded at constant temperature T_A . Since the equation of state is always satisfied during a quasi-static transformation, we have $P(V) = NkT_A/V$. Integration yields

$$W_1 = -NkT_A \ln \frac{V_B}{V_A}.$$

In the second transformation, the gas is first expanded at constant pressure P_A , and then its pressure is decreased at constant volume V_B . No work is done during the second part of the transformation. In the first part, $P(V) = P_A = NkT_A/V_A$. Integration yields

$$W_2 = -NkT_A \left(\frac{V_B}{V_A} - 1 \right).$$

We see that the two answers are different, and that the work done on a system does indeed depend on the path.

1.5.4 Heat

By definition, adding heat to a system corresponds to increasing its internal energy *without* doing work, that is, without changing *any* of its physical variables (such as volume, number of particles, etc.). Heat is usually added by putting the system in thermal contact with another system at a higher temperature.

Heat also depends on the path, since work does, but internal energy does not.

1.5.5 Heat capacities

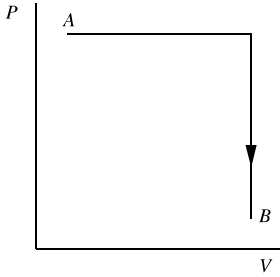
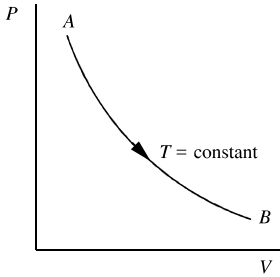
Adding heat to a system usually increases its temperature. A quantitative measure of this is provided by the *heat capacities*, which are defined according to which quantity is held fixed while heat is added.

The *heat capacity at constant volume* is defined as

$$C_V = \left(\frac{dQ}{dT} \right)_{V,N}. \quad (1.5)$$

The *heat capacity at constant pressure* is defined as

$$C_P = \left(\frac{dQ}{dT} \right)_{P,N}. \quad (1.6)$$



In the framework of thermodynamics, the heat capacities of a given system must be empirically determined (as functions of temperature), and given as input; they cannot be derived. (To theoretically predict the value of the heat capacities is another goal of statistical mechanics.)

However, a general relationship between the heat capacities *can* be derived within thermodynamics, without any need for statistical mechanics. We simply quote the result here:

$$C_P - C_V = -T \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2 \left(\frac{\partial P}{\partial V} \right)_T.$$

The derivation of this result can be found in Sec. 5.7 of Reif's book.

Now, it is true for all substances that $(\partial P/\partial V)_T < 0$: pressure *must* increase as volume is decreased at constant temperature. (The opposite sign would imply instability.) Since the first factor is evidently positive, we conclude that $C_P > C_V$. This is a very general result, which illustrates the power and usefulness of thermodynamics. For an ideal gas, it is easy to use the equation of state $PV = NkT$ to show that $C_P - C_V = Nk$. (Once we have mastered the tools of statistical mechanics, we will be able to calculate that for an ideal gas, $C_P = \frac{5}{2}Nk$ and $C_V = \frac{3}{2}Nk$.)

1.5.6 Heat reservoir

In the sequel we will frequently make use of the idealization of a *reservoir*.

We define a *heat reservoir* (or heat bath) to be a system (in thermal equilibrium) that is so large that to extract any amount of heat from it never affects its temperature. (This works also if heat is delivered to the reservoir.) In other words, a heat reservoir is a system with virtually infinite heat capacity.

We define a *volume reservoir* to be a system (in mechanical equilibrium) that is so large that to vary its volume never affects its pressure.

Finally, we define a *particle reservoir* to be a system (in chemical equilibrium) that is so large that to extract particles from it never affects its chemical potential.

These three idealizations can be combined into a single one, the (unqualified) *reservoir*. This is defined to be a system (in thermodynamic equilibrium) that is so large that interactions with other systems never affect its temperature T , its pressure P , nor its chemical potential μ . It is of course implied that these interactions never take the reservoir away from thermodynamic equilibrium.

1.6 Second law of thermodynamics

1.6.1 Two statements

The second law of thermodynamics is typically formulated in two different ways. The *Kelvin* statement is:

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a system and to convert it entirely into work.

The *Clausius* statement is:

There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a colder system and to deliver it to a hotter system.

These two statements have been shown to be completely equivalent.

1.6.2 Reversible, irreversible, and cyclic transformations

A *reversible* transformation from state A to state B is one which can be performed equally well in the opposite direction (from state B to state A), *without introducing any other changes in the thermodynamic system or its surroundings*. As an example of a reversible transformation, consider the quasi-static compression of a gas. The work done on during the compression can be extracted again by letting the gas expand back to its original volume. Since both the gas and the agent responsible for the compression then return to their original states, the transformation is reversible.

An *irreversible* transformation from state A to state B is one which can be performed only in this direction; the reversed transformation would introduce additional changes in the system or its surroundings. As an example of an irreversible transformation, consider the free expansion of a gas caused by the removal of a partition. This transformation is clearly irreversible: replacing the partition once the gas has completely filled the chamber does not make the gas return back to its original volume.

The transfer of heat generally occurs irreversibly. Consider two systems, initially well separated and at different temperatures. The systems are put in thermal contact, and heat flows from the hotter body to the colder one, until they achieve a common temperature. At this point the systems are separated again; this is the final state. The transformation from the initial state to the final state is clearly irreversible: even if the two systems are again put in thermal contact, they have the same temperature, and they can never restore themselves to their initial temperatures. (This would imply a violation of the Clausius statement of the second law.)

In the discussion of the last paragraph, the two systems are completely arbitrary. If one of them turns out to be a heat reservoir, the conclusion would be unaltered. If, however, the reservoir has a temperature that differs by an *infinitesimal* amount from the temperature of the other system, then the transformation would be *reversible*. (We shall prove this in subsection f.) It is therefore possible to add a finite amount of heat to a system in a reversible manner: the system must be put in thermal contact with a succession of heat reservoirs, each at an infinitesimally larger temperature than the previous one. (We show, also in subsection f, that such a procedure is indeed reversible.)

A *cyclic* transformation is one which brings the system back to its original state, irrespective of what may happen to the system's surroundings. In other words, the system's final and initial states are one and the same. Cyclic transformations can be both reversible and irreversible. An example of a reversible cyclic transformation is the quasi-static compression, and then re-expansion, of a gas. An example of an irreversible cyclic transformation is the free expansion of a gas, followed by a slow compression back to its original volume.

1.6.3 Clausius' theorem

This theorem by Clausius follows from the second law:

The inequality

$$\oint \frac{\delta Q}{T} \leq 0 \quad (1.7)$$

holds for *any* cyclic transformation; equality holds if and only if the transformation is *reversible*.

We will not prove the theorem here, but we will use it to introduce a new state variable, the *entropy*.

1.6.4 Entropy

Consider any cyclic, *reversible* path, taking some thermodynamic system from an initial state A to some state B , and then back to state A . The Clausius theorem implies $0 = \oint \dot{d}Q/T = \int_A^B \dot{d}Q/T + \int_B^A \dot{d}Q/T$, or

$$0 = \int_A^B \frac{\dot{d}Q}{T} - \int_A^B \frac{\dot{d}Q}{T}.$$

Here, the two integrals are evaluated along two different paths. If we denote these paths C_1 and C_2 , we have

$$\int_{C_1} \frac{\dot{d}Q}{T} = \int_{C_2} \frac{\dot{d}Q}{T}.$$

The integral is therefore *independent* of the path taken to go from state A to state B , so long as it is *reversible*.

There must therefore exist a *state variable* S such that $\int_A^B \dot{d}Q/T = S(B) - S(A)$, independently of the (reversible) path of integration. This state variable is called the *entropy*, and is such that along any reversible path, $dS = \dot{d}Q/T$ is an exact differential.

The entropy is always defined with respect to some reference state, which we denote O . In terms of this state, the entropy of any other state A is given by

$$\boxed{S(A) = S(O) + \int_R \frac{\dot{d}Q}{T}}, \quad (1.8)$$

where the path R is *any* reversible path connecting the states O and A .

1.6.5 Properties of the entropy

For *arbitrary* transformations, bringing a thermodynamic system from state A to state B , the change in entropy is related to the integral of $\dot{d}Q/T$ by

$$\boxed{S(B) - S(A) \geq \int_A^B \frac{\dot{d}Q}{T}}; \quad (1.9)$$

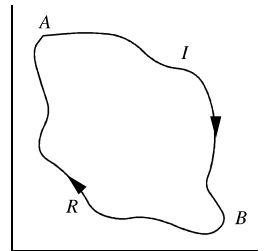
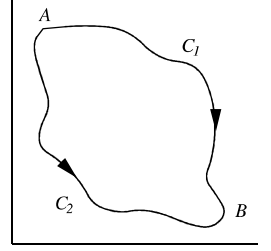
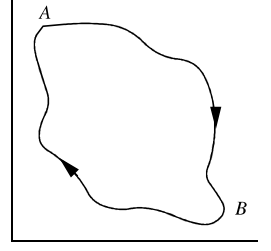
equality holds for reversible transformations.

The proof of this statement involves Clausius' theorem, with the following cyclic path: the system is first brought from state A to state B along an arbitrary path I , and then brought back to A along a reversible path R . The theorem implies $0 \geq \oint \dot{d}Q/T = \int_I \dot{d}Q/T + \int_R \dot{d}Q/T$. But since $\dot{d}Q/T = dS$ along R , we have $0 \geq \int_I \dot{d}Q/T + \int_R dS = \int_I \dot{d}Q/T + S(A) - S(B)$. This is the same statement as Eq. (1.9).

A special case of this statement holds for an *isolated* system, that is, a system that does not exchange heat with its surroundings. For such a system, Eq. (1.9) implies $S(B) - S(A) \geq 0$, since $\dot{d}Q \equiv 0$. In other words,

$$\boxed{\text{The entropy of an isolated system never decreases.}} \quad (1.10)$$

This is often taken as the statement of the second law. As we can see, however, the Kelvin and Clausius statements lead to the more general result (1.9). We note that for reversible transformations involving isolated systems, $S(B) = S(A)$. In other words, *the entropy of an isolated system stays constant during a reversible transformation*.



1.6.6 Example: system interacting with a heat reservoir

Consider a system A , which initially is in equilibrium at a temperature T_A , but is then put in thermal contact with a heat reservoir B at a higher temperature T_B . As a result of the interaction, heat flows into A from B , and A 's temperature eventually increases to T_B . This transformation is clearly irreversible, and since the combined system $A + B$ is isolated, the change in the total entropy $S_A + S_B$ must be strictly positive.

It is easy to show (this is a homework problem) that for this transformation, the change in total entropy is given by

$$\Delta S = C(x - 1 - \ln x),$$

where C is A 's heat capacity, and $x \equiv T_A/T_B$. It is also easy to prove that $x - 1 - \ln x > 0$ for $x < 1$, which establishes that ΔS is strictly positive, as claimed.

Let's consider the special case for which T_B differs from T_A by a very small amount: $T_B = T_A + \delta T$. In this limit, we have $x = 1 - \delta T/T_B$ and $\ln x = -\delta T/T_B - \frac{1}{2}(\delta T/T_B)^2 + \dots$. This gives

$$\Delta S \simeq \frac{C}{2} \left(\frac{\delta T}{T_B} \right)^2,$$

which is *second order* in the small quantity δT . This proves the statement made earlier, in subsection b, that a system in thermal contact with a heat reservoir at a slightly higher temperature receives heat in a virtually reversible manner.

Any system can be brought *reversibly* from a lower temperature T_1 to a higher temperature T_2 . The procedure to follow is to first put the system in thermal contact with a slightly hotter reservoir ($T = T_1 + \delta T$), then with another one, slightly hotter than the previous one ($T = T_1 + 2\delta T$), and so on, until the final temperature is reached. At the end of the process, the overall change in total entropy is given by the immediate generalization of the previous result:

$$\Delta S \simeq \frac{C\delta T}{2} \left[\frac{\delta T}{(T_1 + \delta T)^2} + \frac{\delta T}{(T_1 + 2\delta T)^2} + \dots + \frac{\delta T}{T_2^2} \right].$$

The sum within the square brackets is obviously equal to the integral

$$\int_{T_1}^{T_2} \frac{dT}{T^2} = \frac{1}{T_1} - \frac{1}{T_2}$$

when δT is sufficiently small. We finally obtain

$$\Delta S \simeq \frac{C\delta T}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

By choosing δT sufficiently small, ΔS can be made as small as desired. In the limit $\delta T \rightarrow 0$, the transformation is reversible.

1.6.7 Third law of thermodynamics

Another property of the entropy, which must be derived empirically within the framework of thermodynamics, but can be proven using the tools of statistical mechanics, is known as the third law of thermodynamics. It states:

The entropy of a thermodynamic system at zero temperature is zero.

We will get back to this later on in the course.

1.7 Thermodynamic potentials

In this and the remaining sections we will consider reversible transformations *only*. For such transformations, it is always true that $\delta Q = T dS$.

1.7.1 Energy

For reversible transformations, the first law of thermodynamics reads

$$\boxed{dE = T dS - P dV + \mu dN} . \quad (1.11)$$

When looked at from a purely mathematical point of view, this equation tells us that E can be expressed as a function of S , V , and N : $E = E(S, V, N)$. Indeed, if such a function exists, then purely mathematically,

$$dE = \left(\frac{\partial E}{\partial S} \right)_{V,N} dS + \left(\frac{\partial E}{\partial V} \right)_{S,N} dV + \left(\frac{\partial E}{\partial N} \right)_{S,V} dN.$$

This has the same form as Eq. (1.11), and it gives us formal *definitions* for T , P , and μ :

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

Thus, if E is known as a function of S , V , and N , then the related quantities T , P , and μ can be calculated.

The interpretation of the equation $E = E(S, V, N)$ is that S , V , and N can be considered to be the *independent* state variables, and that E is a *dependent* quantity; T , P , and μ are also dependent quantities. For fixed N , an equilibrium configuration is fully specified by giving the values of S and V . Alternatively, $E = E(S, V, N)$ could be inverted to give $S = S(E, V, N)$, which would make E an independent variable, and S a dependent one. The point is that the four quantities E , S , V , and N are not all independent, and that T , P , and μ can be derived from the equation relating them.

The function $E(S, V, N)$ is the first instance of a *thermodynamic potential*, a function that generates other thermodynamic variables (such as T , P , and μ) by partial differentiation. Other instances are obtained by considering other choices of independent variables. The usefulness of all this will become apparent below.

1.7.2 Enthalpy

We define the enthalpy as

$$\boxed{H = E + PV} . \quad (1.12)$$

This equation, when combined with Eq. (1.11), implies

$$dH = T dS + V dP + \mu dN,$$

which states that $H = H(S, P, N)$. We also obtain formal definitions for T , V , and μ :

$$T \equiv \left(\frac{\partial H}{\partial S} \right)_{P,N}, \quad V \equiv \left(\frac{\partial H}{\partial P} \right)_{S,N}, \quad \mu \equiv \left(\frac{\partial H}{\partial N} \right)_{S,P}.$$

1.7.3 Helmholtz free energy

We define the Helmholtz free energy as

$$\boxed{F = E - TS} . \quad (1.13)$$

This equation, when combined with Eq. (1.11), implies

$$dF = -S dT - P dV + \mu dN,$$

which states that $F = F(T, V, N)$. We also obtain formal definitions for S , P , and μ :

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

This choice of independent variables, (T, V, N) , seems more natural than (S, V, N) or (S, P, N) . We will see in Sec. 11 that the Helmholtz free energy has an important physical meaning; we will encounter it again later.

1.7.4 Gibbs free energy

We define the Gibbs free energy as

$$\boxed{G = E - TS + PV} . \quad (1.14)$$

This equation, when combined with Eq. (1.11), implies

$$dG = -S dT + V dP + \mu dN,$$

which states that $G = G(T, P, N)$. We also obtain formal definitions for S , V , and μ :

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

This choice of independent variables also seems quite natural, and the Gibbs free energy also has an important physical meaning. This will be described in Sec. 11.

1.7.5 Landau potential

As a final example, we consider the Landau potential, which is defined as

$$\boxed{\Omega = E - TS - \mu N} . \quad (1.15)$$

This equation, when combined with Eq. (1.11), implies

$$d\Omega = -S dT - P dV - N d\mu,$$

which states that $\Omega = \Omega(T, V, \mu)$. We also obtain formal definitions for S , P , and N :

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

We will put the Landau potential to good use in a later portion of this course.

1.8 Maxwell relations

The formal definitions for T , S , V , P , μ , and N in terms of the potentials E , H , F , G , and Ω can be used to generate many relations between the various derivatives of these quantities.

For example, Eq. (1.11) implies that $T = \partial E / \partial S$ and $P = -\partial E / \partial V$. This, in turn, gives $\partial T / \partial V = \partial^2 E / \partial V \partial S$. But since the order in which we take the partial derivatives does not matter, we obtain $\partial T / \partial V = \partial^2 E / \partial S \partial V = -\partial P / \partial S$. In other words,

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

This is the first instance of what is known as a Maxwell relation.

Other relations follow just as easily from the other thermodynamic potentials. For example, you may derive these:

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

and

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

The Maxwell relations are extremely general, they hold for *any* thermodynamic system. This is another illustration of the power of thermodynamics.

1.9 Scaling properties

Consider two systems in thermodynamic equilibrium. Both systems are identical in every way, except that one is a factor λ larger than the other. We say that the second system is *scaled* by a factor λ with respect to the first system. We ask: How are the state variables of the two systems related? Or, in other words, how do the state variables of a thermodynamic system scale under a scaling of the system?

Clearly, if the system is scaled by a factor λ , it must mean that E , V , and N are all scaled by such a factor: $E \rightarrow \lambda E$, $V \rightarrow \lambda V$, and $N \rightarrow \lambda N$. On the other hand, if the scaled system is otherwise identical to the original system, it must be true that T stays the same: $T \rightarrow T$. How about S , P , and μ ? The answer comes from the first law: $dE = T dS - P dV + \mu dN$. If E scales but T does not, it must be true that S scales: $S \rightarrow \lambda S$. Similarly, if both E and V scale, it must be true that P does not: $P \rightarrow P$. And finally, if both E and N scale, it must be true that μ does not: $\mu \rightarrow \mu$.

We can therefore separate the thermodynamic variables into two groups. The first group contains the variables that scale under a scaling of the system; such variables are called *extensive*. The second group contains the variables that do not scale under a scaling of the system; such variables are called *intensive*. We have found that E , S , V , and N are extensive variables, and that T , P , and μ are intensive variables.

These scaling properties lead to an interesting consequence when we recall that $E = E(S, V, N)$. Upon scaling, this equation implies

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

whatever the function $E(S, V, N)$ happens to be, it must satisfy this scaling equation. Let $\lambda = 1 + \epsilon$, where $\epsilon \ll 1$. Then $E(S + \epsilon S, V + \epsilon V, N + \epsilon N) = (1 + \epsilon)E(S, V, N)$.

Expanding the left-hand side of this equation in powers of ϵ , up to first order, we arrive at

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

Or, recalling the formal definitions for T , P , and μ ,

$$\boxed{E = TS - PV + \mu N}. \quad (1.16)$$

Now for another interesting result. If we differentiate Eq. (1.16) and substitute Eq. (1.11), we quickly obtain

$$\boxed{N d\mu = -S dT + V dP}. \quad (1.17)$$

This states that the intensive variables are not all independent: $\mu = \mu(T, P)$. Equation (1.17) is known as the *Gibbs-Duhem relation*.

1.10 Equilibrium conditions for isolated, composite systems

We now turn from formal considerations to more physical ones. In this section we consider two thermodynamic systems, A and B , which initially are separated and in equilibrium. The systems are then brought together to form a composite system C , and are allowed to interact. In general, C is not initially in equilibrium. For example, if A and B are at a different temperature, heat will flow from the hotter part of C to the colder part, and this cannot represent an equilibrium situation. However, interactions between the two subsystems will give rise to an irreversible transformation from C 's original state to a final, equilibrium state. In our example, A and B will eventually reach a common temperature, at which point equilibrium will be re-established.

We wish to derive the conditions under which a composite system will be in equilibrium. We proceed as follows:

Because C is an isolated system and the transformation is irreversible, its entropy must be increasing during the transformation:

$$dS_C = dS_A + dS_B \geq 0;$$

the equality sign takes over when equilibrium is established. Now, the change in entropy in subsystem A , dS_A , can be computed by considering *any* reversible transformation that relates the same initial and final states as the *actual*, irreversible transformation: we just apply Eq. (1.8). Along such a path, $T_A dS_A = \bar{d}Q_A = dE_A - \bar{d}W_A = dE_A + P_A dV_A - \mu_A dN_A$. Similarly, $T_B dS_B = dE_B + P_B dV_B - \mu_B dN_B$. The final step of the derivation is to notice that since C is an isolated system, its total energy must be conserved: $0 = dE_C = dE_A + dE_B$. Similarly, $dV_A + dV_B = 0$, and $dN_A + dN_B = 0$. Combining these results, we easily obtain the fundamental equation

$$\boxed{\left(\frac{1}{T_A} - \frac{1}{T_B}\right) dE_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dN_A \geq 0}. \quad (1.18)$$

As before, equality holds at equilibrium.

To extract the equilibrium conditions from Eq. (1.18), we consider some special cases.

We first consider a purely *thermal* interaction between the subsystems A and B . This means that the partition separating A and B allows for the exchange

of heat, but it cannot move, and it does not allow particles to pass through. In other words, the interaction leaves V_A and N_A fixed. Equation (1.18) then implies $(1/T_A - 1/T_B)dE_A \geq 0$. During the approach to equilibrium, the inequality sign applies. We therefore find that $dE_A > 0$ if $T_A < T_B$, while $dE_A < 0$ if $T_A > T_B$. This certainly conforms to our physical intuition. On the other hand,

$$T_A = T_B$$

at equilibrium. This also conforms to physical intuition.

We next consider a purely *mechanical* interaction between A and B , now imagined to have equal temperatures. This means that the partition separating A and B is now able to move, so that V_A might change during the interaction. In other words, the interaction leaves only N_A fixed, and $T_A = T_B$. For such a situation, Eq. (1.18) implies $(P_A - P_B)dV_A \geq 0$. The inequality sign holds during the approach to equilibrium, and we find that $dV_A > 0$ if $P_A > P_B$, while $dV_A < 0$ if $P_A < P_B$. This makes sense: the subsystem with the larger pressure pushes the partition outward. We also find that

$$P_A = P_B$$

at equilibrium, which also makes good physical sense.

Finally, we consider a purely *chemical* interaction between A and B , now imagined to have identical temperatures and pressures ($T_A = T_B$ and $P_A = P_B$). This means that particles can now pass through the partition separating A from B . Equation (1.18) now gives $(\mu_A - \mu_B)dN_A \leq 0$. This means that a difference in the chemical potentials gives rise to a flux of particles from one subsystem to the other. This also implies that

$$\mu_A = \mu_B$$

at equilibrium.

To summarize, we have found that the composite system achieves equilibrium when, as a result of the interaction between the subsystems, the temperatures, pressures, and chemical potentials have all equalized. This means that at equilibrium, the temperature, pressure, and chemical potential must be *uniform* throughout the system. This conclusion holds for any composite system in isolation; the number of parts is irrelevant. This conclusion also holds for any isolated system, since such a system can always be partitioned into two or more parts (this partitioning can be real or fictitious). We therefore have derived the equilibrium conditions first introduced in Sec. 2.

1.11 Equilibrium for interacting systems

The equilibrium conditions derived in the preceding section are appropriate for isolated systems. Here we wish to derive equilibrium conditions that are appropriate for systems interacting with a *reservoir*. We recall from Sec. 5f that a reservoir is a system so large that interactions with other systems never affect its *intensive* variables (temperature, pressure, and chemical potential).

We consider a system A , initially isolated and in equilibrium, but then made to interact with a reservoir R at temperature T_R , pressure P_R , and chemical potential μ_R . The combined system $C = A + R$, which is isolated, is initially not in equilibrium. However, interactions between A and R give rise to an irreversible transformation from C 's original state to its final, equilibrium state. We seek the conditions that hold when equilibrium is established.

The derivation proceeds much as before. We first use the fact that the combined system is isolated to write $dE_A + dE_R = dV_A + dV_R = dN_A + dN_R = 0$. Next, we

calculate that the change in the reservoir's entropy is given by

$$\begin{aligned} T_R dS_R &= dE_R + P_R dV_R - \mu_R dN_R \\ &= -dE_A - P_R dV_A + \mu_R dN_A. \end{aligned}$$

Next, we write $T_R(dS_A + dS_R) = T_R dS_A - dE_A - P_R dV_A + \mu_R dN_A$, and notice that the left-hand side must be non-negative. This gives us our fundamental equation:

$$\boxed{dE_A - T_R dS_A + P_R dV_A - \mu_R dN_A \leq 0}. \quad (1.19)$$

This equation holds for *any* kind of interaction between a system A and a reservoir R ; equality holds at equilibrium.

We now consider a few special cases.

First, we consider an *isolated system*. An isolated system can always be considered to be interacting, though the “interaction” involves no change in energy, volume, or number of particles. In other words, we consider an “interaction” that keeps E_A , V_A , and N_A fixed. For such a case Eq. (1.19) implies $dS_A \geq 0$, which is nothing but the compact mathematical statement of the second law of thermodynamics. In other words:

For interactions that leave E , V , and N fixed — that is, for isolated systems — the entropy S is maximized at equilibrium.

Second, we consider a purely *thermal* interaction, which keeps V_A and N_A fixed. For such a case Eq. (1.19) implies $d(E_A - T_R S_A) \leq 0$, which states that at equilibrium, the quantity $E_A - T_R S_A$ is minimized. But since we already know that temperature must be uniform at equilibrium ($T_A = T_R$), we obtain the following statement:

For interactions that leave V and N fixed — that is, for thermal interactions — the Helmholtz free energy $F = E - TS$ is minimized at equilibrium.

Third, we consider a *thermo-mechanical* interaction, during which only N_A is kept fixed. For such a case Eq. (1.19) implies $d(E_A - T_R S_A + P_R V_A) \leq 0$, which states that at equilibrium, the quantity $E_A - T_R S_A + P_R V_A$ is minimized. But since we know that temperature and pressure must both be uniform at equilibrium ($T_A = T_R$, $P_A = P_R$), we obtain the following statement:

For interactions that leave N fixed — that is, for thermo-mechanical interactions — the Gibbs free energy $G = E - TS + PV$ is minimized at equilibrium.

Fourth, and last, we consider a *thermo-chemical* interaction, during which only V_A is kept fixed. For this case Eq. (1.19) implies $d(E_A - T_R S_A - \mu_R N_A) \leq 0$, which states that at equilibrium, the quantity $E_A - T_R S_A - \mu_R N_A$ is minimized. But since we know that temperature and chemical potential must both be uniform at equilibrium ($T_A = T_R$, $\mu_A = \mu_R$), we obtain the following statement:

For interactions that leave V fixed — that is, for thermo-chemical interactions — the Landau potential $\Omega = E - TS - \mu N$ is minimized at equilibrium.

These various equilibrium conditions give physical meaning to the thermodynamic potentials introduced in Sec. 7.

1.12 Limitations of thermodynamics

The laws of thermodynamics can be used to derive very general relations among the various state variables and their derivatives. These relations are not specific to particular systems, but hold for *all* macroscopic systems at equilibrium.

However, because thermodynamics makes no contact with the microphysics of the systems it studies, it cannot give a complete picture. For example, thermodynamics alone cannot provide an expression for a system's equation of state, nor can it provide the function $S(E, V, N)$, and it cannot provide values for the heat capacities.

The role of statistical mechanics is to make contact with the microphysics. Its role is not to *derive* the laws of thermodynamics. In fact, thermodynamics stands very well on its own. The role of statistical mechanics is to *extend* and *complement* the framework of thermodynamics. It also makes the language of thermodynamics much more concrete, by providing a way of *computing* the equation of state, the function $S(E, V, N)$, and the heat capacities.

1.13 Brief summary of thermodynamics

- The *first law of thermodynamics* states that the internal energy E of a system can be increased by either adding heat or doing work. Mathematically,

$$dE = dQ + dW.$$

Here, dQ and dW are *inexact differentials*, meaning that the integrals $\int_A^B dQ$ and $\int_A^B dW$ depend not only on the endpoints, but also on the path taken to go from state A to state B . On the other hand, because E is a *state function*, $\int_A^B dE = E(B) - E(A)$, independently of the path.

- The *second law of thermodynamics* states that there exists a state function S , called the entropy, which satisfies the inequality

$$dS \geq \frac{dQ}{T};$$

equality holds for *reversible* transformations. For *thermally isolated* systems (such that $dQ \equiv 0$), the entropy satisfies $dS \geq 0$: The entropy of an isolated system can never decrease, and stays constant during reversible transformations.

- When heat is applied to a system, its temperature generally increases. A quantitative measure of this is given by the *heat capacities*:

$$C_V = \left(\frac{dQ}{dT} \right)_{V,N}, \quad C_P = \left(\frac{dQ}{dT} \right)_{P,N}.$$

It is true for *all* thermodynamic systems that $C_P > C_V$.

- During reversible transformations ($dQ = TdS$), the first law of thermodynamics reads

$$dE = T dS - P dV + \mu dN.$$

This shows that E can be regarded as a function of S , V , and N . If the function $E(S, V, N)$ is known, then it can be used to *define* T , P , and μ :

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