Chapter 2

Thermodynamic Resume

Thermodynamics is the study of the macroscopic properties of many particle bodies. It consists of relating these macroscopic properties to one another and to specifying how the properties change when the constraints on the body change, e.g. when the volume or temperature is changed.

As noted earlier a goal of statistical mechanics is to derive the thermodynamic properties beginning from a microscopic picture. Some of the thermodynamic relations can also be derived from statistical mechanics. Particularly, we will be able to identify some parameters appearing in statistical mechanics from the similarity of the statistical mechanic relations and the thermodynamic relations. For this reason and to express thermodynamics in a view useful for subsequent chapters we briefly review some thermodynamics.

2.1 The First Law of Thermodynamics

Consider, for example, a gas or liquid of particles in a balloon. The first law states that if heat $dQ$ is added then this heat goes into increasing the internal energy $dU$ of the gas and into work done by the gas or liquid in the balloon,

$$dQ = dU + dW$$  \hspace{1cm} (2.1)

The most common idea is that the body does work by expanding against the external pressure, $p$

$$dW = pdV.$$  \hspace{1cm} (2.2)

In restricting ourselves to $dW = pdV$ we have neglected the work required to $dW = \gamma dA$ required to stretch the balloon.

The body might, however, be an atom having many electrons. There could be external work done on the atom such that the energy levels $\epsilon_s$ available to the electrons are changed. If there are $n_s$ electrons in each level the work done, by the body (atom) to increase the levels is

$$dW = - \sum_s n_s \, d\epsilon_s.$$  \hspace{1cm} (2.3)
The negative sign appears since positive work must be done on the body to
increase each level from \( \epsilon_s \) to \( \epsilon_s + d\epsilon_s \). This work might be done by squeezing
the atom to distort the levels, for example.

The first law is basically a statement of the conservation of energy.

2.2 The Second Law of Thermodynamics

We also observe, phenomenologically, that for a closed system, such as
the balloon, there is a perfect differential \( dS \) related to the heat transfer \( dQ \) by

\[
dQ = TdS.
\]

This equality holds for changes or processes that take place infinitely slowly and
that can be reversed with the equality still holding. For an arbitrary change of
the balloon walls, rapid or slow,

\[
TdS \geq dQ. \tag{2.4}
\]

This is the second law of thermodynamics. Combining the first and second laws
we have

\[
dQ = dU + dW \leq TdS
\]

or

\[
dU + pdV \leq TdS \tag{2.5}
\]

2.3 Equilibrium

We now see from (2.5) that if we perform a cyclic process on a body, that
is we return after manipulating the boundaries of the body to the same \( U \) and
\( V \), then

\[
TdS \geq 0. \tag{2.6}
\]

Thus the entropy \( S \) will either go on increasing or will reach an upper limit as
we continue these cyclic processes. We observe in practice that the body eventually
reaches a state from which no further changes occur, i.e. it returns after
subsequent cycles to the same internal state. From above the entropy \( S \) of this
state must be a maximum. Also for given boundary conditions we observe that
if we prepare the body in a special state then the body undergoes spontaneous
changes until no further changes take place. We define the equilibrium state
of the body as that state which is constant in time and from which no further
spontaneous changes occur.

2.4 Isolated System

We introduce now the idea of an isolated body. This body is isolated
from all other bodies. An example is a gas in a steel walled container suspended
by a long insulating string in a vacuum flask (Fig. 2.1). For this gas \( U \) and
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Figure 2.1: Isolated System.

\( V \) are constant, assuming the string is perfectly insulating and that reasonable changes in pressure in the gas cannot flex the walls of the container. Thus for a change in the gas,

\[
dU + pdV = 0 \leq TdS
\]  

(2.7)

If for example, we started the gas off in some special state, then changes would go on inside the container until in the end no more changes occur. We define, as above, the equilibrium state as that stationary state from which no further spontaneous change in the gas takes place. Since in the changes moving to equilibrium we have \( TdS \geq 0 \), then \( S \) increases until in the equilibrium state \( S \) is a maximum. Thus the equilibrium can be distinguished from all other states as that state for which \( S \) is a maximum. For an isolated body \( S \) is a maximum at equilibrium.

From the second law we see that \( S \) is a function of \( U \) and \( V \), \( S = S(U, V) \). Also, strictly, \( S \) is well defined only when the system is in its equilibrium state. Otherwise \( S \) would not be a single valued function of \( U \) and \( V \). If we now change the container in some way, for example, by expanding the walls of the container or by sending a heat pulse down the string, the body goes to a new equilibrium state. The equilibrium state depends solely on the boundary conditions.

We note also that the entropy is ideally suited to describing an isolated body since \( S \), in equilibrium, is solely a function of \( U \) and \( V \) and these are constant for an isolated body. The \( U \) and \( V \) are independent variables which specify the boundary conditions of the isolated body.

2.5 System in Contact with a Heat Bath

An isolated body is an idealization. All bodies have at least some thermal contact with their surroundings. The exchange of heat then takes place between the body and its surroundings and this brings the two to the same temperature eventually. It is therefore more realistic to consider a body in equilibrium at constant temperature than to consider one in equilibrium at constant energy.

For this reason we now examine a system in contact with a large heat bath at constant temperature. The bath serves to supply or extract heat from the body (system) and is large enough so that its temperature remains constant during these transfers of heat. We could imagine constructing our system and
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Figure 2.2: LHS: Closed system in contact with a heat bath. RHS: Open system in contact with a heat bath and a particle bath.

heat bath from the isolated gas considered in section 2.4 in the following way. We partition a small part of the gas by enclosing it in a thin walled metal container. The small container has a constant volume but heat is exchanged freely through the container walls between the partitioned gas and the remainder of the gas. The smaller container of gas constitutes the system and the remainder of the gas the heat bath. This is depicted schematically in Fig. 2.2 (LHS). The whole gas can be regarded as isolated as before.

To identify the equilibrium state of a body (system) in contact with a heat bath at constant temperature, we extract heat \( dQ_o \) from the heat bath and transfer it to the body. In this change,

\[
-dQ_o = dQ = dU + pdV \leq TdS
\]

(2.8)

or since \( dV = 0 \)

\[
dU - TdS \leq 0.
\]

Since the transfer takes place at constant temperature,

\[
d(U - TS) \leq 0
\]

(2.9)

We now introduce the Helmholtz free energy

\[
F = U - TS = F(T, V)
\]

(2.10)

and for changes at constant \( T \) and \( V \),

\[
dF \leq 0
\]

(2.11)

This means that if we prepared the body in some special state, then in spontaneous changes as the body goes toward the equilibrium state \( dF \leq 0 \). That is, \( F \) always decreases. When we reach the final state from which no further changes takes place, \( dF = 0 \). Thus in equilibrium, \( F \) is a minimum for a body at constant \( T \) and \( V \).

We also see from (2.10) that \( F \) is a natural thermodynamic function to describe a body at constant \( T \) and \( V \). The equilibrium state depends upon the values of \( T \) and \( V \); that is, on the boundary conditions. Once these boundary conditions are set, then the equilibrium value of \( F \) is also set, for \( F \) is a function of \( T \) and \( V \) as independent variables. Also strictly \( F \) is defined only at equilibrium. Otherwise \( F \) would not be a single valued function of \( T \) and \( V \). Thus
we regard $F$ as defined at equilibrium and for small, slow changes in $T$ and $V$ the body goes from equilibrium state to equilibrium state. In this way we could return to the initial values of $T$ and $V$ and arrive again at the initial value of $F(T,V)$. For the special case of $T = 0\ K$, we have from (2.11)

$$dU \leq 0 \quad (T = 0\ K)$$

Thus we arrive at the mechanical condition that $U$ is a minimum at equilibrium at $T = 0\ K$.

Both the isolated system and the system in contact with a heat reservoir that we have considered so far are closed systems. That is, they are enclosed by a boundary that prevents particles from moving in or out of the system. Thus the number $N$ of particles (e.g. atoms) in the system is constant. We could follow the above arguments for systems with different values of $N$ and we would obtain different values of $S$ and $F$. Since $N$ is constant in each case we examine, we may consider the entropy as a function of $N$ as an independent variable as well as $U$ and $V$, $S = S(U,V,N)$, and $F$ as a function of $N$ as well as $T$ and $V$, $F = F(T,V,N)$. Thus $S(U,V,N)$ and $F(T,V,N)$ are functions of three independent variables.

### 2.6 System in Contact with a Heat and Particle Bath

We now consider a body in contact with a heat and particle bath. In this case both heat and particles can be exchanged between the body and the reservoir. This is depicted schematically in Fig. 2.2 (RHS). We could construct an example of this case from the above by enclosing a small part of the whole gas in a permeable walled container. The remainder of the gas would act as the reservoir. Heat and particles could be transferred through the walls of the container to and from the small body of gas.

To describe this open system thermodynamically we need to introduce the chemical potential, $\mu$. If we add $dN$ particles to the body, the external work done on the body to add the particles is

$$dW_{ext} = \mu \, dN.$$  \hspace{1cm} (2.13a)

This can be regarded as the defining relation for $\mu$. An example is a battery. If we take $dN$ electrons from the negative terminal and transfer them to the positive terminal we must do work. In this case $\mu$ is the voltage (potential) of the battery, 12.6 volts in the case of a car battery. We have had to do work to change the chemical state (chemical potential) of the electrons. The chemical potential is the thermodynamic analogy of the mechanical potential energy of the particles in a body (with the potential of the particles in the reservoir taken as zero). The work done by the body when $dN$ particles are added to it is

$$dW = -\mu \, dN.$$  \hspace{1cm} (2.13b)
In many practical cases, such as a battery, \( \mu \) is a constant so that we take \( \mu \) as constant. In fact in many cases the driving force for adding or removing particles is to keep \( \mu \) constant and the same as the value in the heat bath. For example, if \( \mu \) increases in the body for some reason, particles will leave the body to lower its thermodynamic potential.

An example is a liquid in equilibrium with its vapor. We might regard the liquid as the body and the vapor as the particle bath. In equilibrium the number of particles in the liquid is constant and \( \mu \) is the same in the liquid and in the vapor. If the temperature increases a number of particles evaporate into the vapor until \( \mu \) is again equal in the liquid and vapor.

In applying the first and second law to thermodynamic changes we must now include this additional work. That is,

\[
dQ = dU + dW = dU + p\,dV - \mu dN \tag{2.14}
\]

(first law) and again (second law)

\[
dQ \leq T\,dS.
\]

For an exchange of heat and particles taking place at constant, \( V \), \( T \) and \( \mu \), the body undergoes a change,

\[
dU - \mu dN \leq TdS.
\]

or

\[
dU - TdS - \mu dN \leq 0
\]

and

\[
d(F - \mu N) \leq 0 \tag{2.15}
\]

We now define the thermodynamic potential

\[
\Omega \equiv F - \mu N = \Omega (T, V, \mu) \tag{2.16}
\]

Hence for spontaneous changes in a body at constant \( V \) in which heat and particles can be exchanged with a reservoir at constant \( T \) and \( \mu \),

\[
d\Omega \leq 0. \tag{2.17}
\]

The equilibrium or final state from which no further changes take place at constant \( T \) and \( \mu \) is the state for which the thermodynamic potential is a minimum.

We see also from (2.16) that the thermodynamic potential is a natural thermodynamic function to describe a body at constant \( T \) and \( \mu \). With these independent variables held constant, \( \Omega \) must be constant. As with \( S \) and \( F \), \( \Omega \) is strictly defined only for the equilibrium state so that it is a single valued function of \( T \) and \( \mu \). The equilibrium state is determined by the boundary conditions on the body (the values of \( T \) and \( \mu \)) and once these are given the thermodynamic equilibrium value of \( \Omega \) is set. Changes in \( T \) and \( \mu \) should take
place slowly enough that the body goes from equilibrium state to equilibrium state with $\Omega$ taking its equilibrium value at each stage during the change.

Strictly we should also state explicitly that $F$ is a function of $N$, i.e.,

$$\Omega (T, V, \mu) = F (T, V, N) - \mu N.$$  

This also emphasizes that in going from $F$ to $\Omega$ we have simply transformed to a function $\Omega$ which has $\mu$ rather than $N$ as the independent variable. This type of transformation is called a Legendre transformation. The transformation is useful since $\mu$ in the open system $\mu$ rather than $N$ is constant. With $T, V$ and $\mu$ constant, $\Omega (T, V, \mu)$ will be constant in equilibrium.

We could also write the relation $F = U - TS$ in a form which emphasizes that for a body at constant $T$, $F$ is more convenient than $S$, i.e.

$$\frac{1}{T} F (T, V, N) = -S (U, V, N) + \frac{U}{T}.$$

We implicitly made this transformation in (2.10) when we considered a body at constant $T$ rather than at constant $U$ (isolated).

Finally, using the defining relation (2.13b) we can relate $\mu$ to other thermodynamic functions. For example,

$$dF = dU - SdT - TdS$$  

Employing the first and second law,

$$TdS = dU + dW = dU + pdV - \mu dN$$  

we find

$$dF = -pdV - SdT + \mu dN.$$  

Thus

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

Similarly, we will find

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,p} = \left( \frac{\partial H}{\partial N} \right)_{S,p}$$  

where $G \equiv F + pV$ is the Gibbs free energy and $H \equiv U + pV$ is the Enthalpy.

The Gibbs free energy and $\mu$ are related in a special way. From the definition of $G$ we have

$$dG = dF + pdV + Vdp$$

and using (2.21) we find

$$dG = Vdp - SdT + \mu dN$$
That is
\[ G = G(p, T, N). \] (2.24)

Since \( p \) and \( T \) are intensive quantities and \( G \) is an extensive quantity (proportional to \( N \)) we must have
\[ G = N f(p, T) \] (2.25)

where \( f(p, T) \) is some function of \( p \) and \( T \). From (2.25)
\[ \mu = \left( \frac{\partial G}{\partial N} \right)_{T,p} = f(p, T) \] (2.26)

Therefore
\[ G = \mu N \] (2.27)

and the chemical potential is the Gibbs free energy per particle in a many particle system.