

## VII. SOME BASICS OF THERMODYNAMICS

### A. Internal Energy $U$

In Thermodynamics, the **total energy**  $E$  of our system (as described by an empirical force field) is called **internal energy**  $U$ .  $U$  is a **state function**, which means, that the energy of a system depends only on the values of its parameters, e.g.  **$T$  and  $V$** , and not on the path in the parameters space, which led to the actual state.

This is important in order to establish a relation to the **microscopic energy**  $E$  as given by the force field. Here,  $E$  is completely determined by the actual coordinates and velocities, which define the **microscopic state**  $\{r_i, p_i\}$ .

The **first law of Thermodynamics** states the conservation of energy,

$$U = \text{const} \quad (\text{VII.1})$$

and we have used this in the microcanonical ensemble, where the total energy is fixed.

In **open systems**, **heat** ( $Q$ ) can be exchanged with the environment, and this situation is modeled in the **canonical ensemble**.

$$\Delta U = Q,$$

if the Volume  $V$  is constant. If the Volume is not fixed, **work** ( $W$ ) can be exchanged with the environment,

$$dW = -Fdz = -pdV \quad (\text{VII.2})$$

The first law therefore reads:

$$\boxed{dU = dQ + dW = dQ - pdV} \quad (\text{VII.3})$$



FIG. 37: Exchange of heat and work with the environment

### B. Entropy and Temperature

In Newtonian Mechanics, all processes are perfectly **reversible**, i.e. they can happen in forward and backward direction. An example is a stone falling down to earth. It could also go up, when someone has thrown it. This means, we can look at the 'movie' of this process and it would look right also when we would view it backwards in time.

However, in Thermodynamics there are many processes which would not 'look right' when being reversed although they obey the 1st law, two common examples can be found in Fig. 38.

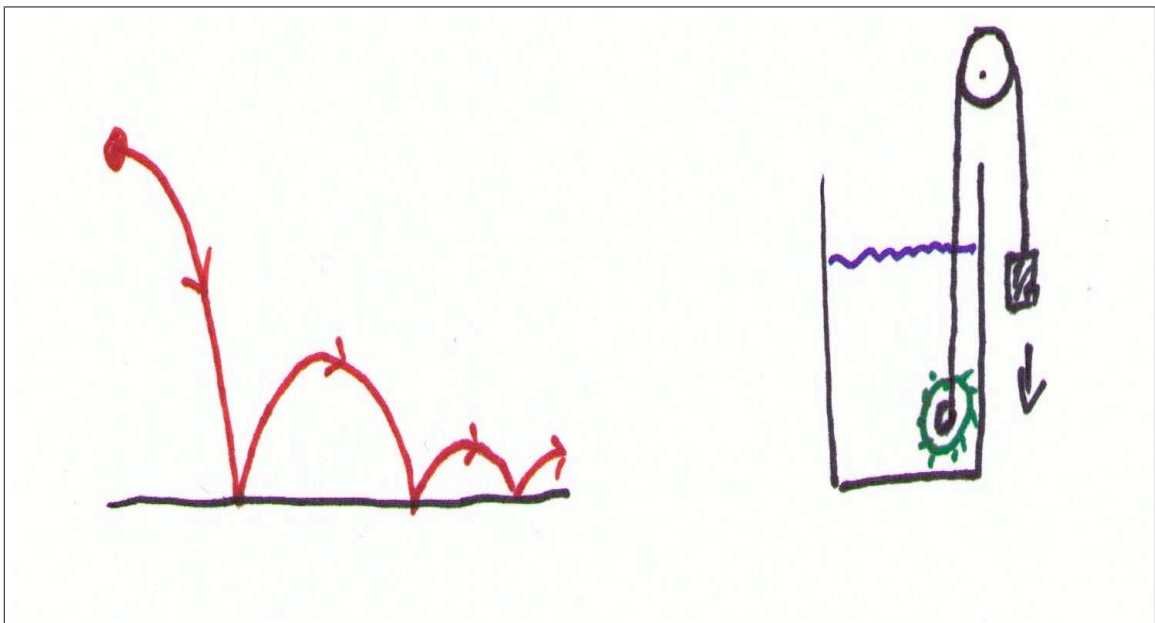


FIG. 38: Irreversible processes: the reverse direction would NOT violate the 1st law!

This means, the first law is not enough to characterize thermodynamics processes, the **second law** is crucial:

$$\Delta S \geq 0$$

Microscopically, the second law results from the fact, that the most probable distribution dominates, i.e., the energy will be distributed over the possible states (in the example in the last chapter) in order to maximize the number of micro-states.

The entropy of a system depends therefore on the energy  $E$  and other parameters  $x_\alpha$ , like Volume, particle number etc.,

$$S = S(E, V, \dots) = k \ln W(E, V, \dots).$$

For a given system, the driving force therefore is not energy minimization (as in geometry optimization), since the energy is constant due to the first law, but the maximization of the entropy!

To introduce **Temperature** in the framework of Statistical Mechanics, two ways can be usually found:

The first way is to use the knowledge from Thermodynamics. From there, we know that

$$\frac{\partial S}{\partial E} = \frac{1}{T}.$$

This would motivate us, to define a microscopic quantity:

$$\beta = \frac{\partial \ln W}{\partial E}$$

Since  $S = k \ln W$ , we see immediately, that  $\beta^{-1} = kT$ . Note, that in this way Thermodynamics is used to define quantities of Statistical Mechanics!

A different route is to examine the equilibration process. Consider systems A and A' in thermal contact as in Fig. 39. The equilibration will be driven by the maximization of entropy,

$$S = S_1 + S_2 = \text{max.}$$

Therefore, in equilibrium, the entropy change will be zero, i.e.

$$dS = dS_1 + dS_2 = 0$$

which is:

$$\frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial S_2}{\partial U_2} dU_2 = 0$$

which leads to ( $dU_1 = -dU_2$ ):

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}$$

or:

$$\beta_1 = \beta_2.$$

Therefore, equilibrium forces the equality for the  $\beta$ -parameters (and other properties not discussed here) leads to the identification of  $\beta$  with the Temperature  $T$ .

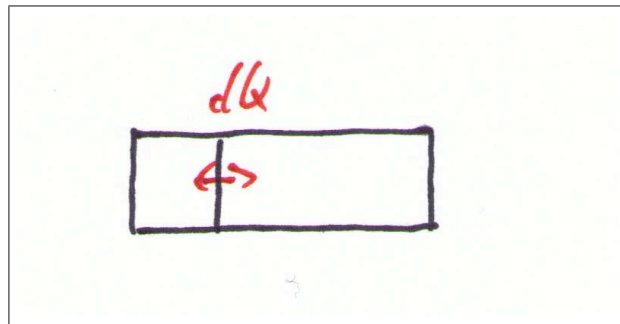


FIG. 39: Two systems A and A' exchanging a small amount of heat  $dQ$

Consider our system A in contact with a heat bath A', exchanging an infinitesimal amount of heat  $dQ$ . The number of states in A' therefore changes by:

$$d \ln W(E') = \ln W(E' + dQ) - \ln W(E') \approx \frac{\partial \ln W}{\partial E} dQ = \beta dQ. \quad (\text{VII.4})$$

Abbreviating:

$$\frac{\partial \ln W}{\partial E} = \beta = \frac{1}{k} \frac{\partial S}{\partial E}$$

leads to the well know expression for the **reversible entropy change**:

$$dS = k d \ln W(E) = \frac{\partial S}{\partial E} dQ = \frac{dQ}{T} \quad (\text{VII.5})$$

- In Thermodynamics, this relation is called the **reversible entropy change**, which is applicable in **quasi-static processes**. In this process, the transfer of heat or work is infinitesimally slow, that the system is always in equilibrium, i.e. a temperature is defined. Reversible means that the process can be reversed without changing the (entropy of the) environment.
- We can understand this formular microscopically e.g. for our example in the last chapter: by heating, we e.g. introduce one more energy quantum into the system, now having four energy quanta. It is obvious, that the number of possible microstates increases, i.e. the entropy increases. And it increases, depending on how much energy (Temperature) is already in the system. So, the increase will be smaller when going from 1000 to 1001 energy quanta than going from 3 to 4!
- Using the first law, we can rewrite the internal energy as:

$$dU = dQ = TdS$$

Therefore, we changed the dependence of the internal energy from  $U(T)$  to  $U(S)$ .

Including volume change, we can write:

$$dQ = TdS = dU - dW \tag{VII.6}$$

### C. Reversible and irreversible processes

Consider two examples as shown in Fig. 40. Heating a system by keeping the volume constant changes the distribution, i.e. the entropy is changed:

$$dU = dQ = TdS$$

or

$$dS = \frac{dQ}{T}.$$

When moving the piston infinitesimally slow, the distribution function will remain the same and only the spacing between the states will change, therefore, no heat will be transferred and  $dS=0$ .

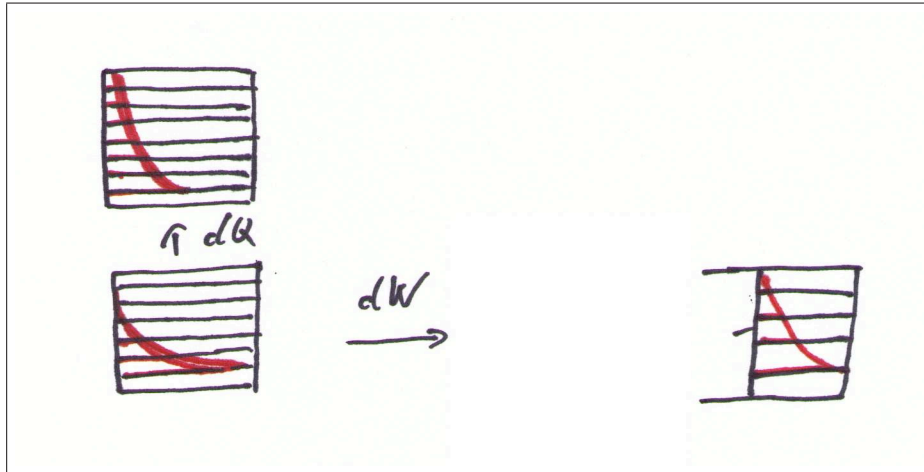


FIG. 40: Heating a system changes the distribution, thereby changing entropy. Reversible work only changes the states, not the occupation.

Both **reversible** processes are infinitesimally slow. If we move the piston very fast, we will get changes of the occupation and thereby a **non-reversible** entropy change. This entropy change can not be reversed, without changing the environment in a way, that the total entropy is increased.

Therefore, we have the **reversible entropy change of  $dS_{rev} = \frac{dQ}{T}$  and an irreversible part.** The second law states, that the entropy production is positive, i.e. we can write:

$$dS - \frac{dQ}{T} \geq 0.$$

$dS$  is the total entropy-change and  $dQ/T$  is the reversible part. If we have  $dV=0$ , we can write:

$$TdS - dU \geq 0.$$

This is the condition, that a **process happens spontaneously**. I.e., processes will happen in a way, that the property  $TS-U$  becomes a maximum, or, vice versa,

$$U - TS = \min.$$

I.e., nature minimizes the value of  $U-TS$  in its processes.

We could interpret this as follows:

Nature allows processes, which minimize the internal energy  $U$  of a system and its entropy  $S$  simultaneously. However, this is not completely right!

We always have to consider the system and its environment. If  $U$  of the system changes, energy is transferred to the environment, according to the first law the total energy is unchanged! Therefore, minimization of the system energy  $U$  is **no driving force** in nature. Energy minimization has NO meaning!

Since the total energy is conserved, the only driving force is the second law, the entropy will be maximized.

$$dS = dS_1 + dS_2 \geq 0$$

(1 is the system, 2 the environment) The entropy change of the environment,  $dS_2$  is given by the heat exchanged,

$$dS_2 = \frac{dQ}{T} = -\frac{dU_1}{T}$$

( $U_1$  is the change of internal energy of the system). Therefore,

$$-\frac{dU_1}{T} + dS_1 \geq 0$$

combines the 1st and 2nd law to derive the driving force for the system 1 (remember, that we have  $V=\text{const.}$  in the whole discussion!).

The driving force for complex processes is the maximization of the entropy of the total system. Since we can not handle the whole universe in all our calculations, we found a way to concentrate on our subsystem by looking at  $U$ - $TS$ . This is called the [Helmholz free energy](#):

$$F = U - TS \tag{VII.7}$$

This is the fundamental property we are interested in, because:

- $F = F(T, V)$ :  $F$  depends on the variables  $T$  and  $V$ , which are experimentally controllable, while  $U = U(S, V)$  depends on  $S$  and  $V$ . We do not know, how to control entropy in experiments. In particular,  $F$  is the energetic property which is measured when  $T$  and  $V$  are constant, a situation we often model in our simulations.
- $\Delta F = F_f - F_i = W_{max}$  is the maximum amount of work a system can release between an initial (i) and final (f) state. In the first law  $dU = dQ + dW$ , we can substitute  $dQ$

by  $TdS$ , since the latter is always large due to second law  $TdS \geq dQ$  to get:

$$dU \leq TdS + dW,$$

or:

$$dW \geq dU - TdS = dF$$

Therefore, the maximal work is always greater or equal the free energy. In other words, a certain amount of internal energy  $dU$  can **never** be converted completely into work, a part is always lost due to entropy production.

- If the system is in contact to environment, there is no more a minimum (internal) energy principle available. In principle, energy minimization as we have discussed before, does not make any sense, neither for the subsystem, not for the whole. Energy is simply conserved and we have a micro-canonical ensemble, however, including the whole universe. The free energy however, restores a minimization procedure again: Systems will evolve in order to minimize the free energy. This, however, is nothing else than entropy maximization of the whole system.

The latter point is in particular important if we want to study chemical reactions and energy profiles along reaction coordinates. We are used to look to minima of total (internal) energies, as e.g. drawn in Fig. 43. The minima of the total/internal energy, however, may have no more meaning, while the minima of the free energy have!

Question: why do we still use energy minimized structures in many cases? (Exercises!)



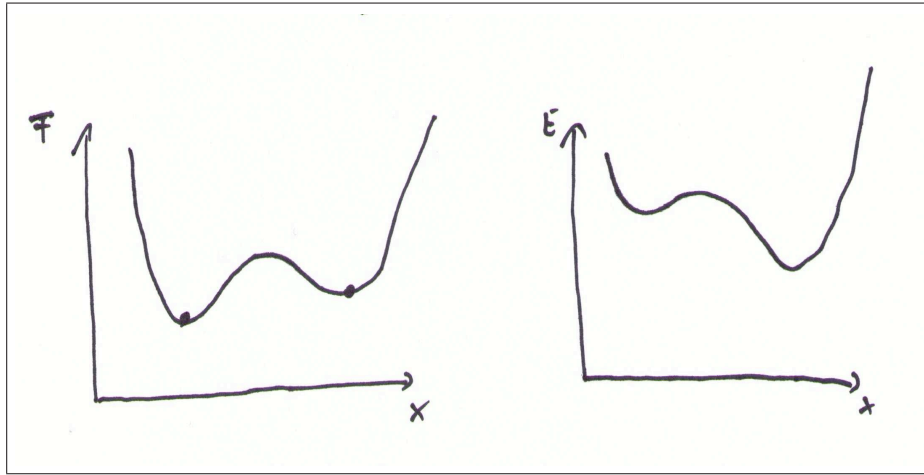


FIG. 41: Minima and transition states along a reaction coordinate for the free energy  $F$  and the internal energy  $U$

#### D. State functions and relation of Statistical Mechanics to Thermodynamics

##### Complete differential

Consider an infinitesimal change of a function  $F(x,y)$ ,

$$dF = F(x + dx, y + dy) - F(x, y) = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = A dx + B dy$$

Integrating  $F$  between two points

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f (A dx + B dy)$$

leads to a value  $\Delta F$ , which is not dependent on the integration pathway. In this case, we call  $F$  (in Thermodynamics) a **state function**.  $F$  is also called an complete differential (vollständiges Differential). A function  $F$  is a state function, when it is a complete differential, which mathematically means

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} \rightarrow \frac{\partial B}{\partial x} = \frac{\partial A}{\partial y}$$

$U(S,V)$  is a state function, it depends only on the values of the parameters, not on the path the state has been reached. Microscopically,  $U$  depends on the set of coordinates and velocities, which also only depend on the actual state and not on history.

$S(E,V) = k \ln W(E,V)$  also is a state function, while the work and heat exchanged along a certain path are not.

## Internal energy U

Using the expression for the reversible entropy, we can rewrite the internal energy:

$$dQ = TdS = dU + pdV,$$

or:

$$dU = TdS - pdV.$$

Now, U depends on the variables S and V,

$$U = U(S, V)$$

First derivatives:

$$dU = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV,$$

$$T = \frac{\partial U}{\partial S} \quad p = -\frac{\partial U}{\partial V}$$

Second derivatives (Maxwell relations):

$$\frac{\partial p}{\partial S} = \frac{\partial T}{\partial V}$$

## Enthalpy H

Consider a function  $H = U + pV$ , using  $d(pV) = pdV + Vdp$ :

$$d(U + pV) = dU + pdV + Vdp = TdS + Vdp$$

This means, H depends on the variables p and S. First derivatives:

$$dH = \frac{\partial H}{\partial S}dS + \frac{\partial H}{\partial p}dp,$$

$$T = \frac{\partial H}{\partial S} \quad V = \frac{\partial H}{\partial p}$$

Second derivatives (Maxwell relations):

$$\frac{\partial V}{\partial S} = \frac{\partial T}{\partial p}$$

The variables of the Thermodynamic Potentials connect to the experimental conditions. Since it is experimentally difficult to control the entropy, while it is easy to control temperature, volume or pressure, it is convenient to introduce further potentials.

Free energy  $F$

$$F = U - TS, \quad d(TS) = TdS + SdT,$$

$$dF = d(U - TS) = dU - TdS - SdT = TdS - pdV - TdS - SdT = -pdV - SdT$$

$F=F(V,T)$ , first derivatives:

$$\begin{aligned} dF &= \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial V}dV, \\ -S &= \frac{\partial F}{\partial T} & -p &= \frac{\partial F}{\partial V} \end{aligned}$$

Second derivatives (Maxwell relations):

$$\frac{\partial S}{\partial V} = \frac{\partial p}{\partial T}$$

This is the property we simulate in a canonical ensemble, keeping temperature and  $V$  constant.

## E. Equilibrium

We are interested in the equilibrium of a system, i.e. the state the system approaches after some time (equilibration). Lets look into the change of the thermodynamic potentials  $U$ ,  $H$  and  $F$ :

$$dU = dQ - pdV$$

$$dH = dQ + VdP$$

$$dF = dQ - TdS - SdT - pdV$$

Using

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

we find:

$$dU \leq TdS - pdV$$

$$dH \leq TdS + VdP$$

$$dF \leq -SdT - pdV$$

The change of the potential in a process is always smaller than the right hand side. In particular, if we fix parameters in an experimental situation, the change is always smaller than zero, and the energy runs into a **minimum**, which is defined by **thermal equilibrium**.

$$dU \leq 0, \quad \text{for } S = \text{const}, V = \text{const}$$

Therefore, we could search for the Minimum of the internal energy, if we would keep the entropy and Volume constant. But how to do that?

$$dH \leq 0, \quad \text{for } S = \text{const}, p = \text{const}$$

$$dF \leq 0, \quad \text{for } T = \text{const}, V = \text{const}$$

As discussed above, this is easy to realize, therefore, we look for the minima of the free energy.

### F. Relation to the partition function

Consider the canonical distribution ( $\beta^{-1} = kT$ ):

$$p_i = \frac{1}{Z} \exp(-\beta E_i)$$

The expectation value of the energy is:

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i)$$

A nice mathematical trick is:

$$-\frac{\partial}{\partial \beta} Z = - \sum_i \frac{\partial}{\partial \beta} \exp(-\beta E_i) = \sum_i E_i \exp(-\beta E_i).$$

Therefore,

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z = -\frac{\partial \ln Z}{\partial \beta} \quad (\text{VII.8})$$

To relate the free energy to  $Z$ , the easiest way is to use the thermodynamic relation:

$$F = U - TS.$$

Multiplying with  $\beta$ ,

$$\beta F = \beta U - S/k$$

Taking the derivative

$$\frac{\partial(\beta F)}{\partial \beta} = U = \langle E \rangle$$

and comparing with eq. VII.8 gives the expression for the **free energy**:

$$F = -kT \ln Z \quad (\text{VII.9})$$

and for the **entropy**  $S = -F/T - U/T$ :

$$S = k \ln Z + k\beta \langle E \rangle \quad (\text{VII.10})$$

This is a remarkable result, since the only thing we have to do in our simulations it to get the partition function  $Z$ , i.e. we have to get the phase space distribution  $\rho$ , i.e. the density of points in phase space from the simulation and then integrate it over phase space to get  $Z$ . Everything follows from there.

### G. Exercises

1. Consider the Thermodynamic Potential  $G(p, V)$ . Derive it using a coordinate transformation and write down the corresponding Maxwell relations.
2. Why do we still use energy minimized structures in many cases?
3. Calculate the energy of a **quantum** harmonic oscillator at temperature  $T$  using eq. VII.8,  $E_n = (n + 0.5)\hbar\omega$ . Determine  $Z$  first by using the formula for the geometrical series.