Notes for Lecture 2

Thermodynamics

The main result of the last lecture was that for a Carnot machine operating between the two thermal baths maintained at temperatures T_H and T_C ($T_C < T_H$) respectively, the heat transfer ratio is given by

$$\frac{Q_H}{Q_C} = \frac{T_H}{T_C} \tag{2.1}$$

whether or not the Carnot machine is operating in the engine mode (i.e. the forward mode) or in the refrigerator mode (i.e. the reverse mode). In the engine mode, $Q_H > 0$ and $Q_C > 0$, meaning that the heat Q_H is taken away from the hot body and the heat Q_C is deposited to the cold body. In the refrigerator mode, $Q_H < 0$ and $Q_C < 0$, meaning that the heat $|Q_H|$ is deposited to the hot body while the heat $|Q_C|$ is taken away from the cold body.

The above equation is in fact the definition of the absolute temperature scale (for T_H or T_C assuming that the other bath is a reference material). Also, we noted that as defined as above, the absolute temperature must be positive, assuming the reference temperature is taken to be positive[1].

This of course leads to the well-known result that the efficiency of a Carnot engine is given by $\frac{T_H - T_C}{T_H}$.

However, another grand result of the second law of thermodynamics is the concept of entropy, which we now describe. The entropy is the most fundamental concept in statistical mechanics.

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[1] However, beware that negative temperature states *can* and *do* exist, e.g. in spin systems. A negative temperature known in such a case is actually *higher* than a positive temperature, in the sense that heat flows from from negative T to positive T.

2.1 Entropy

Clausius theorem: For any cyclic transformation, $\oint đQ/T \leq 0$ where $đQ$ is the heat supplied to the system at T.

Proof: The proof is rather long. But let us make it very clear, since this is such a central theorem. Divide the system into many infinitesimal intervals. At a given fixed interval of time, we do the following.

For a given infinitesimal interval of time, let us say that the system exchanges work by $đW$ and heat by $đQ$. Whatever environment the system actually is interacting with in a given infinitesimal interval, it is possible to, at least theoretically (i.e. "virtually"), detach the system from the actual environment, then "re-connecting" the system to a purely mechanical system that will receive work by $đW$ (understanding that "will receive work by $đW$" would change to "will do work by $|đW|$" if $đW$ is actually negative) and likewise reconnecting the system to a Carnot engine, which will deposit heat by $đQ$ to the system (again, understanding that "deposit heat by $đQ$ to" will have to become "remove heat by $|đQ|$ from " if $đQ$ turns out to be negative). What is crucial is that we require that the Carnot engine is attached to a thermal reservoir at a *fixed temperature* T_0 (which can be any fixed non-zero value). Even under this constraint, it should be clear that by adjusting the size of the Carnot engine and the direction in which it is run at, we can run this Carnot machine just for one cycle during the infinitesimal time interval that it is needed, *just so that it exchanges the right amount of heat* $đQ$, no matter what sign $đQ$ may have and even if $đQ = 0$ (in the latter case, all we have to do is to make the Carnot machine very small).

Now that we have successfully replaced the system's environment with something that we can easily characterize, we go ahead and do the same for every small infinitesimal interval. So, we end up with a lot of Carnot machines, each of which run exactly only once (per one cycle of the system) at the assigned infinitesimal time interval.

The crucial point here is that we made it so that all Carnot machines connect to the same heat reservoir maintained at temperature T_0.

During an infinitesimal time interval, the corresponding Carnot engine must be exchanging heat with the T_0 reservoir. Let that be $đQ_0$. Then, we have, by Eq. 2.1,

$$đQ_0 = T_0 \frac{đQ}{T} \tag{2.2}$$

Considering all these Carnot engines and the system together as a new system, we see that this new system exchanges heat with the T_0 reservoir, $\oint đQ_0$, in its one cycle, which is identical with the cycle of the original system. In addition, the new system may do some work W, which is the combination of the work done by all Carnot engines and the original system. Kelvin's postulate would be violated if $\oint đQ_0 > 0$, as that would mean a perfect conversion of heat to work from a single source at a constant temperature throughout (T_0). We conclude, then, that $\oint đQ_0 \leq 0$. Therefore, by the above identity and the fact that

$T_0 > 0$,

$$\oint \frac{đQ}{T} \le 0 \tag{2.3}$$

QED.

It follows immediately, then, that $\oint \frac{đQ}{T} = 0$ for any reversible process, since in a reversible process, $đQ \to -đQ$.

For any reversible process, then, it must be possible to define a state function S such that $dS = đQ/T$.

$$\begin{aligned} dS &= \frac{đQ}{T} && \text{reversible} \qquad (2.4) \\ đQ &= T\,dS && \text{reversible} \qquad (2.5) \end{aligned}$$

S here is the *entropy.* It corresponds to the “displacement” for the temperature “force.”

Thus, for a reversible process (but see the paragraph labeled as “A very important remark” below), we get

$$dE = đQ + đW = T\,dS + \sum_j J_j\,dx_j \tag{2.6}$$

From this expression, it is recognized that, for n ways of doing mechanical work, we then have $n+1$ independent thermodynamic coordinates to describe the system, where the additional one can be taken as the temperature, entropy, or the energy, while the first n ones can be taken as x_j or J_j or any inhomogeneous mixture of them (but with no simultaneous choice of x_j and J_j for the same j).

Notice that the above way of defining the entropy function is reminiscent of how the potential energy is defined in classical mechanics.

A very important remark: although Eq. 2.6 is derived for a reversible process, the validity of the equation

$$dE = T\,dS + \sum_j J_j\,dx_j \tag{2.7}$$

can be extended to *any* transformation *as long as both the initial state and the final state are equilibrium states.* The difference between reversible and irreversible processes is that for irreversible processes $đQ \ne TdS$ (and thus $đW \ne \sum_j J_j dx_j$).

An example might be useful at this point. An expansion of a gas from a volume to a slightly larger volume. Let us assume that the additional volume claimed by the gas in the final state was initially vacuum. So, this is a free expansion problem. Since this is happening in vacuum, there is no heat involved in this process (we are ignoring the radiative heat transfer). Since the gas is not interacting with anything, there is no work involved either. So, $đW = đQ = 0$. And, so the energy is conserved, since $dE = đQ + đW = 0$. How about the entropy? It has increased. How does one know this? It is because we can apply $dE = TdS - PdV$ in this process, as long as all state variables are well defined *in the initial state and in the final state* even if *during* the process state variables may not even be well-defined. Since $dE = 0$ and $dV > 0$, $dS > 0$. Note that we do not need to make any assumption for the nature of gas – ideal or non-ideal – for this discussion.

Now, consider running a *reversible* process in which the initial state and the final state are exactly the same as those of the expansion process just described. How can such a process be carried out? First, one has to control the inflation process slowly, since any reversible process is necessarily a quasi-static process (LN 1). If you like you can assume that you contain the gas in a balloon, and allow the balloon to inflate gradually until it fills the required slightly larger volume, while you are pressing down on, and nearly balancing, the balloon at all times while you are allowing it to be inflated. Second, note that this controlled inflation will result in the gas doing work on the balloon and your hand and so the gas will lose energy. To make the same final state as above, then we need to inject some heat to make up for the lost energy. To be reversible, this heat injection process must be done with a heat source that is at just an infinitesimally higher temperature than the balloon (a heat transfer between two bodies with a finite temperature difference between them is irreversible). So, in this reversible process, we have achieved the same final state, while during the process $đW = -đQ < 0$.

For these two processes, $dE = TdS - PdV = 0$ is equally applicable since we have made sure that the initial state and the final state are the same between them.

So, what is the difference between process A (the first one, which is irreversible) and process B (the second one, which is reversible). In process B, the change to the final state, $dE = TdS - PdV = 0$, is achieved “in an honest deal” in the sense that work has been done to cause $-PdV$ and heat has been transferred to cause TdS. In process A, the same cannot be said. Instead, no work was done. The gas was literally enjoying a free ride. The final ledger said that the system spent a certain amount of “money” ($-PdV$) through work, but in fact during the process the system did not do any work! Where did that money go? It went into increasing the entropy (TdS). Perhaps it had some fun with that extra money! So, that is how it is for an irreversible process – some work has not resulted in changing mechanical parameters but instead gone into increasing the entropy. However, in process B, there is no such conversion of work to entropy. This is the sign that the process is reversible. Also, in process B, notice that *the total entropy did not change*, if one includes the heat bath

– this is also an important sign of a reversible process.

Back to a more formal discussion.

Now, suppose that a small change in state can occur by two different processes, one a reversible process and the other a general (possibly reversible) process. Let us say that the heat absorbed by the system is $đQ_1$ in the first process and the heat absorbed by the system is $đQ$ in the second process. By our assumption, then $đQ_1 = TdS$. Now, combining the second process and the reverse of the first process, we form a cycle, and we see that during the cycle the total heat absorbed is $đQ - đQ_1 = đQ - TdS$. By Clausius theorem, this must be non-positive, and thus we conclude

$$dS \geq \frac{đQ}{T} \qquad \text{for any process} \tag{2.8}$$

What is the sense of all this? Namely, what is the entropy? Thermodynamics alone does not provide any answer to such a question, as at the level of thermodynamics the entropy remains a mysterious state function. This was the state of affairs at the beginning of the 20th century. Since then, much work has gone into shining light on the nature of the entropy.

Now, we know quite a lot on this, and, one can say that the entropy is the central quantity of the statistical mechanics. The next paragraph summarises some of what we have learned so far.

The entropy of a system is the logarithm of the number of all possible micro-states corresponding to the given macro-state, times the Boltzmann constant. The entropy provides a way to measure "disorder" (since, the higher the entropy, the more the system can "wander around" between all possible micro-states) or the *a priori probability* that the system will exist in a certain configuration as compared to other configurations. **For a closed system, the entropy can never decrease** (as is already clear from the above equation, since $đQ = 0$ for a closed system). For an irreversible process of a closed system, the entropy increases. For a reversible process of a closed system, the entropy remains the same. More generally, **for an adiabatic process (**$đQ = 0$**),** $dS = 0$ **implies reversibility and vice versa**[2]. **For a more general process,** $dS = đQ/T$ **for a reversible process while** $dS > đQ/T$ **for an irreversible process.** So, an irreversible process is where the entropy of the system increases more than the heat intake will imply. This means that some mechanical work has been converted to heat and gave rise to the extra entropy. Once

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[2] Notice that here, and more or less throughout this course, our focus is on the equilibrium thermodynamics, where the initial state and the final state are equilibrium states (otherwise, the entropy change, dS, will not be well-defined!). Read footnote 2, in page 6 of LN 1, for a slightly more general discussion.

the extra entropy has been generated this way, it can be passed around, but it cannot be annihilated.

For an open system, however, the entropy of the system can decrease or increase depending on how it interacts with the environment. A physicist's definition of life can start with a system which draws energy from, and emits heat to, the environment, while decreasing its entropy (metabolism; also this reminds me of what we do every morning, when we try to make ourselves presentable, i.e. not too disordered). Next time you feel like not cleaning up your room, remember this – the act of cleaning up your room is an act to remind yourself of what this mysterious thing that we call life is! However, it is important to note that, if one includes the environment and the open system together, then the above observation for a closed system applies – this is the most fundamental principle of statistical mechanics.

[Optional reading] The maximum entropy principle has a certain similarity with the way how classical mechanics emerges from quantum mechanics. Note that in the Feynman version of quantum mechanics, there is only one principle – all paths connecting the starting point to the ending point are *equally possible* – and the path integral that takes into account of all possible paths needs to be performed to obtain the probability amplitude for the particle to go from the starting point to the ending point. So, there is absolutely no difference between all paths, a priori. In the quantum regime, indeed all of those paths contribute significantly, and one can explore them by experiment. Yet, when such a path integral is performed with an energy value that is appropriate for a classical state (a very high energy to match the classical energy scale; such a state typically has to involve very many particles just to meet the energy requirement), the classical path (where the action ($\int L dt$) is stationary in agreement with the minimum action principle of classical mechanics) emerges as a sure path that satisfies Newton's laws since the probability amplitude for the classical path is just so singularly dominant over those of other paths. The key thing is that the density of paths around the classical path is divergent. This, along with the high energy, selects the classical path with an absolute certainty, and gives something as sure as Newton's laws. A similar thing happens in the maximum entropy principle. All states are born equal, in the sense that they are all equally likely, in a microscopic sense. And yet, when many particles are involved, a macroscopic state (the maximum entropy state) emerges with an absolute certainty, since a state with the highest entropy is just so dominant over others, for the only reason that the number of micro-states belonging in that state is singularly maximum. We will discuss this in more detail in upcoming lectures.

2.2 Equilibrium and maximum entropy

The maximum entropy principle is the major principle of the statistical mechanics along with other conservation principles. Let us consider the case when the system consists of two sub systems in contact.

We shall assume that while the two parts interact with each other (so that they can establish a mutual equilibrium) the interaction at the interface between the two systems is weak enough so that the total entropy can be written as

$$S = S_1 + S_2 \tag{2.9}$$

Furthermore, we shall consider, as independent thermodynamic variables, E (energy) and x (displacement), both of which we assume are conserved. So, x can be volume or particle number, for example.

Let us suppose that the system as a whole found an equilibrium. By the maximum entropy principle, we then see that the entropy must be stationary around the equilibrium point. Considering a small change from the equilibrium, we can write

$$S = S_1(E_1 + \delta E_1, x_1 + \delta x_1) + S_2(E_2 + \delta E_2, x_2 + \delta x_2) \tag{2.10}$$

However, as E and x are conserved, we have $\delta E_2 = -\delta E_1$ and $\delta x_2 = -\delta x_1$. Using this, and then differentiating the above expression, then we get

$$\delta S = \left(\left.\frac{\partial S_1}{\partial E_1}\right|_{x_1} - \left.\frac{\partial S_2}{\partial E_2}\right|_{x_2} \right) \delta E_1 + \left(\left.\frac{\partial S_1}{\partial x_1}\right|_{E_1} - \left.\frac{\partial S_2}{\partial x_2}\right|_{E_2} \right) \delta x_1 \tag{2.11}$$

From $dS = (dE - Jdx)/T$, $(\partial S/\partial E)_x = 1/T$ and $(\partial S/\partial x)_x = -J/T$. And so, we get

$$\delta S = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 - \left(\frac{J_1}{T_1} - \frac{J_2}{T_2} \right) \delta x_1 \tag{2.12}$$

For S to be maximum at the equilibrium, we see that this must vanish for any values of δE_1 and δE_2. So, the coefficient for δE_1 and the coefficient for δx_1 must vanish separately. Thus, we get the following conditions for the equilibrium

$$T_1 = T_2 \tag{2.13}$$

$$J_1 = J_2 \tag{2.14}$$

This is a familiar result. When $x = V$, $J = -P$ (pressure) and when $x = N$, $J = \mu$ (chemical potential).

2.3 Thermodynamic potentials

For a closed system, the entropy is maximized towards the equilibrium. This maximum entropy principle is the origin of the arrow of time as we understand it. What if a system is not closed? In such a case, other various thermodynamic potentials are useful.

Note on notations: (1) Below, δ means a general change involving non-equilibrium states, while d means a change between equilibrium states. (2) The subscript R means reservoir.

Helmholtz free energy F For isothermal process and constant displacement (no work), the Helmholtz free energy, $F \equiv E - TS$ is minimized. $\delta F = \delta E - T\delta S = đQ - T\delta S \le 0$ (by Eq. 2.8).

The total entropy change is given by $dS_{tot} = dS + dS_R$. $dS_R = -dE/T$. And so, $dS_{tot} = dS - dE/T = -dF/T$. So, in this case, the maximum entropy principle is equivalent to the minimum Helmholtz free energy.

Gibbs free energy G For isothermal process with constant external force, the Gibbs free energy, $G \equiv F - Jx$ is minimized. $\delta G = \delta F - T\delta S - đW - J\delta x \le 0$ (by Eq. 2.8 and the same argument for $đW \le J\delta x$ as for the enthalpy).

The total entropy change is given by $dS_{tot} = dS + dS_R$ with $dS_R = (-dE + Jdx)/T$ and so $dS_{tot} = -dG/T$. So, the maximum entropy principle is equivalent to the minimum Gibbs free energy.

Grand potential Φ When the force is the chemical potential, traditionally the case is treated separately. The corresponding free energy is called "the grand potential" $\Phi \equiv E - TS - \mu N$. Instead of Φ, Ω_G is often used also. This is the potential that is minimized when the chemical potential is constrained to be constant (and thus the particle number can change) in an isothermal process. Similar to free energies, the minimization of the grand potential corresponds to the maximization of the total entropy.

Enthalpy H Let us consider a system coupled to a constant external force. Mass on a vertical spring, or a system of gas with a movable lid on top of it would be an example. In the first example, the constant force is mg from the earth gravity, and in the second example it would be the atmospheric pressure on top of the lid plus the pressure due to the mass of the lid ($m_{lid}gA_{lid}$). When a vertical spring is displaced from the equilibrium, or the lid is displaced from the equilibrium position, the system will come back to equilibrium, *only because* there is a dissipation mechanism. How do we describe this situation thermodynamically? This is where the enthalpy comes in handy: in an adiabatic process ($\text{đ}Q = 0$) under constant external force, the enthalpy $H \equiv E - Jx$ is minimized on the way to the equilibrium. $\delta H = \delta E - J\delta x = \text{đ}Q + \text{đ}W - J\delta x = \text{đ}W - J\delta x \le 0$. The last inequality stems from the fact that some of the external work $J\delta x$ may be lost to heat in an irreversible process (due to friction at the spring support in the first example, or friction between lid and gas container in the second example, or any air resistance in both examples). Also note that this heat is assumed to dissipate outside the system, since we assume that the process for the system is adiabatic. How does this enthalpy minimization connect to our grand principle, the maximum entropy principle? It is simple: $dS_{tot} = dS + dS_R \ge \frac{\text{đ}Q}{T} + \frac{\text{đ}Q_R}{T_R} = \frac{\text{đ}Q_R}{T_R} \ge 0$, where $\text{đ}Q_R$ is the heat deposited by the irreversible process above. Here, the reservoir is everything outside our system (mass or gas). One can do a bit more: $\frac{\text{đ}Q_R}{T_R} = \frac{dE_R - J dx_R}{T_R} = \frac{-dE + J dx}{T_R} = \frac{-dH}{T_R}$. And so[3], $dS_{tot} \ge 0$ means $dH \le 0$. Enthalpy is often called a "heat function:" when J (e.g., $-P$) is held constant, $dH = dE - d(Jx) = T dS = \text{đ}Q$ for a reversible process. For the pressure-volume system, $H = E + PV$.

The above functions are the Legendre transforms of each other, mathematically speaking (it is similar to changing between the Lagrangian and the Hamiltonian in mechanics). So, the change of the thermodynamic potentials can be viewed as changing independent variables. Their definitions and the thermodynamic identities are listed here (assuming only one kind of mechanical work and also separating out the mechanical work from the chemical work, where only one kind of chemical species is assumed; the generalization to multiple kinds of chemical or mechanical work trivially requires a summation over the corresponding part). Note that the independent variables noted in the total differentials are correlated to when each thermodynamic potential is particularly useful and in which situation the corresponding thermodynamic potential is extremized towards the equilibrium.

Thermodynamic potentials and identities

$$dE = T\,dS + J\,dx + \mu\,dN \qquad \text{1st and 2nd laws} \tag{2.15}$$

$$dH = T\,dS - x\,dJ + \mu\,dN \qquad H = E - Jx \tag{2.16}$$

$$dF = -S\,dT + J\,dx + \mu\,dN \qquad F = E - TS \tag{2.17}$$

$$dG = -S\,dT - x\,dJ + \mu\,dN \qquad G = E - TS - Jx \tag{2.18}$$

$$d\Phi = -S\,dT + J\,dx - N\,d\mu \qquad \Phi = E - TS - \mu N \tag{2.19}$$

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[3] Note that, different from the case for F, G, or Φ, we have an inequality here: $dS_{tot} \ge -dH (\ge 0)$. Only if $dS = 0$, in addition to $\text{đ}Q = 0$, we will have the equality $dS_{tot} = -dH$, and, **only then, the entropy maximization will be completely equivalent to the enthalpy minimization**.

2.4 Some useful mathematical results

2.4.1 Gibbs-Duhem relation

Assuming the extensivity, we get

$$E(\lambda S, \lambda x, \lambda N) = \lambda E(S, x, N) \tag{2.20}$$

This would be the normal scaling behavior, valid in many cases but not always.

If the above is valid, then by taking the derivative and putting $\lambda = 1$, we get

$$\begin{aligned} E &= TS + Jx + \mu N & (2.21)\\ F &= Jx + \mu N & (2.22)\\ G &= \mu N & (2.23) \end{aligned}$$

By taking the derivative on E, and using the thermodynamic identity $dE = TdS + Jdx + \mu dN$, one concludes

$$SdT + xdJ + Nd\mu = 0 \tag{2.24}$$

This constraint on the variation on intensive coordinates is referred to as the Gibbs-Duhem relation.

2.4.2 Maxwell relations

Maxwell relations arise from the fact that $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$.

For instance,

$$dF = -SdT - PdV$$

So,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

is a Maxwell relation.

To make use of a Maxwell relation, if one encounters $\left(\frac{\partial A}{\partial B}\right)_C$, then one must look for a thermodynamic identify that involves $AdC + ...dB$ among those listed in page 9. As an example, if one counters $\left(\frac{\partial J}{\partial S}\right)_x$ then one has to look at the thermodynamic identity $dE = TdS + Jdx$ (assuming N is constant).

2.4.3 Euler's chain rule

Assume that x, y, z form a set of constrained variables

$$f(x, y, z) = 0$$

We assume that f is solvable for any variable x, y or z. These three variables can be any three thermodynamic variables, e.g., P, V, T, or S, E, T, etc.

1. For w, an arbitrary function of any two independent variables out of x, y, z,

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w = \left(\frac{\partial x}{\partial z}\right)_w \tag{2.25}$$

2.

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \tag{2.26}$$

3. Euler's chain rule.

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{2.27}$$

Proving these identities is left for your work.

2.5 Response functions

So, we now know various thermodynamics functions. How does one measure them? For instance, how does one measure S?

The answer is by measuring some response functions such as the heat capacity.

$$C_V = \left(\frac{đQ}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad \text{Heat capacity at constant volume} \tag{2.28}$$

$$C_P = \left(\frac{đQ}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{Heat capacity at constant pressure} \tag{2.29}$$

When the heat capacity is evaluated for a mole of molecules, or a gram of molecules, it is referred to as "specific heat."

Other response functions include

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{coefficient of thermal expansion} \tag{2.30}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{isothermal compressibility} \tag{2.31}$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \qquad \text{adiabatic compressibility} \tag{2.32}$$

With some algebra (using total differentials and Maxwell relations), one can get

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \tag{2.33}$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \tag{2.34}$$

Using Euler's chain rule, $\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -1$, and using $\left(\frac{\partial T}{\partial V}\right)_P = 1/\left(\frac{\partial V}{\partial T}\right)_P$, we get $\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$. Using Eqs. 2.30, 2.31, we get $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$. Using this in Eq. 2.33 and also doing similarly for Eq. 2.34, we get the equations for the entropy total differential in terms of measurable quantities only

$$TdS = C_V dT + \frac{\alpha T}{\kappa_T} dV \tag{2.35}$$

$$TdS = C_P dT - \alpha T V dP \tag{2.36}$$

From this, doing a little more calculation (which involves also using Maxwell relations), one can conclude

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{2.37}$$

One can also prove, starting from definitions of heat capacity, that

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \tag{2.38}$$

These are useful relations experimentally. Note also that the inverse of the compressibility is called the bulk modulus.

2.6 Stability

Recall that in Section 2.2, we derived a simple result that the temperature and the generalized forces equal in systems in equilibrium from the principle of the maximum entropy (thus, confirming the zeroth law and ensuring the self-consistency). However, to derive that result, we actually did not have to use the fact that the entropy is *maximum* at equilibrium. All we had to use was that the entropy was extremum ($\delta S = 0$)[4] at equilibrium.

Here, we consider the second order variation on S or other thermodynamic potentials to see what else we can learn by actually enforcing the maximum entropy condition. Before we start the new discussion, let us note the maximum entropy principle led to a slew of minimum principles in Section 2.2. It is slightly more interesting to use those minimum principles and so we shall do so here.

Before we go on further, let us keep in mind that what we discuss here is a very natural thing. A system in stable equilibrium is resilient against perturbation. This principle, which we are familiar with from elementary mechanics (Hooke's law), must be valid in thermodynamic systems as well. In thermodynamics, this tendency of the equilibrium system to oppose any external change is generally known as the **Le Chatelier's principle**, which is quite useful in chemistry.

Now, in order to derive some useful results, let us pick one of the thermodynamic potentials (anything other than S will do). Just to be specific, pick the Gibbs free energy, $G = E - TS - Jx$. As we learned already in Section 2.3, when the system is in contact with a reservoir that keeps the system's temperature and pressure to be constant, then this Gibbs free energy can be re-written as $G = E - T_0 S - J_0 x$, where T_0 and J_0 are the temperature and the force of the reservoir. So, it is clear that when, e.g., S and x are varied in such a way that $\delta T = \delta J = 0$, G would be minimized. **But a fine but important point to realize is that the minimization principle means much more than this.** In fact, the minimization principle means the minimization of the following function

$$G = E - T_0 S - J_0 x \tag{2.39}$$

where T_0 and J_0 are the temperature and the generalized force, respectively, *of the reservoir* and E, S, x are the thermodynamic variables of the system, *free of the constraints,* $T = T_0$ *and* $x = x_0$.

To see that this is the case, all we have to do is to re-examine carefully what we actually proved in Section 2.3. [In the following expressions, and also anywhere in this section, any quantity with subscript R or 0 is the quantity for the reservoir.]

$dS_{tot} = dS + dS_R$, $dS_R = (dE_R - J_0 dx_R)/T_0 = (-dE + J_0 dx)/T_0$ and so $dS_{tot} = -dG/T_0$, where G is as given in Eq. 2.39. Therefore, $dS_{tot} \geq 0$ is equivalent to $dG \leq 0$.

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[4] Some words about notation. "d" is used when describing a change of an equilibrium variable (as in $dE = TdS - PdV$) while "δ" is used when describing a virtual change of an equilibrium variable, like in this section, or a non-equilibrium variation, like in Section 2.3.

What is important is that no where in this proof we have used the constraint that the system's temperature and force are equal to those of the reservoir. All we used is the maximum entropy principle and the (assumed) conservation principle (for E and x). Of course, the system's temperature and force will become those of the reservoir at equilibrium (Section 2.2). The point is that when a real system departs from the equilibrium it may do so freely of such constraints. The reservoir will try to re-establish those constraints. What is really nice is that since the maximum entropy principle is equivalent to the minimization of G, *all we need to think about* is the minimization of the Gibbs free energy *as written above*, Eq. 2.39, during this equilibration process!

Indeed, it is trivial to see that, to first order, we reproduce the results of Section 2.2. $\left(\frac{\partial G}{\partial S}\right)_x = 0$ means $\left(\frac{\partial E}{\partial S}\right)_x = T_0$, or $T = T_0$. Similarly, $\left(\frac{\partial G}{\partial x}\right)_S = 0$ means $J = J_0$. However, here we are concerned with the second derivatives. For the above Gibbs free energy to be minimum, we must have $\frac{\partial^2 G}{\partial S^2}\delta S^2 + 2\frac{\partial^2 G}{\partial S \partial x}\delta S \delta x + \frac{\partial^2 G}{\partial x^2}\delta x^2 \geq 0$ for any $\delta S, \delta x$. But notice that all relevant second derivatives are zero for the term $-T_0 S - J_0 x$. Thus, the condition remains unchanged if we replace G with E

$$\frac{\partial^2 E}{\partial S^2}\delta S^2 + 2\frac{\partial^2 E}{\partial S \partial x}\delta S \delta x + \frac{\partial^2 E}{\partial x^2}\delta x^2 \geq 0 \tag{2.40}$$

Defining x_i as the generalized displacement that *includes* temperature and number of particles, this condition that we just found can be written simply as $\sum_{i,j} \frac{\partial^2 E}{\partial x_i \partial x_j}\delta x_i \delta x_j \geq 0$. Then, noting that $\frac{\partial E}{\partial x_i} = J_i$, we get that $\sum_j \frac{\partial^2 E}{\partial x_i \partial x_j}\delta x_j = \delta J_i$. Using this, then we get

$$\sum_{i,j} \delta x_i \, \delta J_i \geq 0 \tag{2.41}$$

Or, explicitly separating out the entropy term and the number term, while denoting only the mechanical work by x (of which we assume that there is only one),

$$\delta S \, \delta T + \delta x \, \delta J + \delta N \, \delta \mu \geq 0 \tag{2.42}$$

This is then the general condition for the stability.

What can we learn from these considerations? One way to see that is going back to Eq. 2.40. For this positive definite quadratic form to be valid, we see that the matrix

$$\begin{bmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial x} \\ \frac{\partial^2 E}{\partial S \partial x} & \frac{\partial^2 E}{\partial x^2} \end{bmatrix} \tag{2.43}$$

must be positive definite. This necessarily means that $\left(\frac{\partial^2 E}{\partial S^2}\right)_x > 0$ and $\left(\frac{\partial^2 E}{\partial x^2}\right)_S > 0$. The first implies that $\left(\frac{\partial T}{\partial S}\right)_x > 0$. Therefore, $\left(\frac{\partial S}{\partial T}\right)_x > 0$. Or, the heat capacity

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x \geq 0 \qquad \text{for any } x \tag{2.44}$$

The second implies that $\left(\frac{\partial J}{\partial x}\right)_S > 0$. This means that the adiabatic compressibility

$$\kappa_S \equiv \frac{1}{x}\left(\frac{\partial x}{\partial J}\right)_S \geq 0 \qquad \text{for any } x \tag{2.45}$$

In general, Eqs. 2.41, 2.42 are useful, as they can be used in any combination of the thermodynamic variables. For instance, one might ask – how about $\left(\frac{\partial S}{\partial T}\right)_J$? To consider that, one can take J and T as two independent variables (while, of course, keeping N fixed). Then, we can plug in Eq. 2.42 two equations, $\delta x = \left(\frac{\partial x}{\partial J}\right)_T \delta J + \left(\frac{\partial x}{\partial T}\right)_J \delta T$ and $\delta S = \left(\frac{\partial S}{\partial J}\right)_T \delta J + \left(\frac{\partial S}{\partial T}\right)_J \delta T$, to get

$$\left(\frac{\partial S}{\partial T}\right)_J \delta T^2 + \left[\left(\frac{\partial x}{\partial T}\right)_J + \left(\frac{\partial S}{\partial J}\right)_T\right]\delta T \delta J + \left(\frac{\partial x}{\partial J}\right)_T \delta J^2 \geq 0 \tag{2.46}$$

$$\left(\frac{\partial S}{\partial T}\right)_J \delta T^2 + 2\left(\frac{\partial S}{\partial J}\right)_T \delta T \delta J + \left(\frac{\partial x}{\partial J}\right)_T \delta J^2 \geq 0 \tag{2.47}$$

where the $\delta T \delta J$ term has been simplified using the Maxwell relation $\left(\frac{\partial S}{\partial J}\right)_T = \left(\frac{\partial x}{\partial T}\right)_J$. The above equation implies, necessarily, that constant "force" specific heat

$$C_J \equiv T\left(\frac{\partial S}{\partial T}\right)_J \geq 0 \qquad \text{for any } J \tag{2.48}$$

and the isothermal compressibility

$$\kappa_T \equiv \frac{1}{x}\left(\frac{\partial x}{\partial J}\right)_T \geq 0 \qquad \text{for any } x \tag{2.49}$$

Note that we have used only necessary conditions here. To extract more conditions we can impose the condition that the determinant of the matrix corresponding to the quadratic form is positive (or zero).

These results are examples of the Le Chatelier principle. Why? For instance, if the heat capacity is positive, it means that as the system absorbs heat, its temperature goes up. That means it has a more tendency to give out heat, opposing the change.

Note that while the above "proof" seems solid, it does not exclude real systems that are exceptions. For instance, there do exist negative heat capacity systems (e.g. in a certain star) – such a system is intrinsically unstable and cannot be brought into equilibrium by contacting with a reservoir. I.e., the very first assumption of the thermodynamic equilibrium is broken for such a system, and such a system cannot be considered extensive.

Lastly, note that the notion of compressibility is often extended to the N, μ variables too. From the above, we would conclude that the "chemical compressibility"

$\frac{1}{N}\frac{\partial N}{\partial \mu} \geq 0$. Note that $\frac{\partial N}{\partial \mu}$ is generally proportional to the density of states at the chemical potential μ. For this reason, some exotic materials whose (many body) density of states vanish at the chemical potential (like one dimensional Luttinger liquids or electrons in graphene) are sometimes referred to as an incompressible fluid.

2.7 The third law

Nernst postulated that the entropy of all systems tends to zero as the temperature goes to absolute zero.

$$S(T \to 0, X) \to 0 \tag{2.50}$$

Here, X is taken to be a thermodynamic variable, other than the temperature. There can be more than one X's, but here, for simplicity, we write down only one.

This law is generally alright, as long as it is not broken by an exotic state, which may have a significant residual entropy at absolute zero. For instance, in a "spin ice" compound, the residual entropy can be truly finite[5] ($O(N)$), and, if this phase persists to zero temperature, then the third law must then be stated as

$$S(T \to 0, X) \to \text{constant} \tag{2.51}$$

The third law, in either form, has the following consequences.

1. The heat capacity $C_X \equiv T\ \partial S/\partial T|_X \to 0$ as $T \to 0$.

   Proof: $S(T,X) - S(0,X) = \int_0^T dT' \frac{C_X(T')}{T'}$, and the integral diverges as $T \to 0$ unless $C_X(T) \to 0$ as $T \to 0$. The integral must vanish by the third law.

2. $\lim_{T\to 0} \left.\frac{\partial S}{\partial X}\right|_T = 0$ (as long as the constant is independent of X in the second form).

3. Thermal expansion coefficient $\alpha_J \equiv \frac{1}{x}\left.\frac{\partial x}{\partial T}\right|_J \to 0$ as $T \to 0$.

   Proof: By Maxwell's relation, $\left.\frac{\partial x}{\partial T}\right|_J = \left.\frac{\partial S}{\partial J}\right|_T \to 0$ by 2. So, assuming that x is finite, $\alpha_J \to 0$.

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[5] Keep in mind that, in the macroscopic limit, "0" means "vanishingly smaller than N." That is, $S = 0$ actually means $\lim_{N\to\infty} \frac{S}{N} = 0$.

4. The zero temperature cannot be reached in any finite steps using a thermodynamic method.

   Proof: Let us assume that by adjusting a thermodynamic variable X from X_1 to X_2, we can cool the system from T_1 to T_2. $S(T_1, X_1) - S(0, X_1) = \int_0^{T_1} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_1}$. $S(T_2, X_2) - S(0, X_2) = \int_0^{T_2} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_2}$. Subtracting the first equation from the second, while using the third law, we get $S(T_2, X_2) - S(T_1, X_1) = \int_0^{T_2} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_2} - \int_0^{T_1} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_1}$. It is physically clear (and consistent with the known cooling techniques) that the cooling will be the most effective if the cooling process is adiabatic (since any surrounding element will tend to heat the system) and reversible (since an irreversible process will make the final entropy higher, leading to a higher final temperature). Under these two conditions, we have $S(T_2, X_2) - S(T_1, X_1) = 0$. And, thus, we get $\int_0^{T_2} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_2} = \int_0^{T_1} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_1}$. Now, assume that $T_2 = 0$. We have, then, $\int_0^{T_1} dT' \left.\frac{C_X(T')}{T'}\right|_{X=X_1} = 0$. This is an impossibility since the specific heat is normally positive (Eqs. 2.44,2.48). QED.