

Introduction to Statistical Physics

Lecture notes for the Master course

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**Johann Wolfgang Goethe University ,
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PART III: Boltzmann distribution and Helmholtz Free Energy

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In previous lectures:

- The average value, or mean value of a function $f(s)$ taken over a probability distribution $P(s)$ is

$$\langle f \rangle = \sum_s f(s) P(s) \quad (0.1)$$

- Using the example of system made of spins. When we bring together two systems S_1 and S_2 , the multiplicity of the combined system which contain $N = N_1 + N_2$ spins, for a spin excess $2s$ can be written in terms of the multiplicities of the individual systems as

$$g(N, s) = \sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1) \quad (0.2)$$

or if we relate the multiplicity to the energies, like

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1) \quad (0.3)$$

where $U = U_1 + U_2$, and the sum over U_1 goes over all values $U_1 \leq U$.

- We have seen via examples that when two systems are in thermal contact, the values of s_1 and s_2 (or U_1 and U_2) that are more probable (occur most often) are will be very close to the values of s_1 and s_2 (or U_1 and U_2) that make the product of the individual multiplicities $g_1 g_2$ maximum. Departures from those values are very weird. Therefore, in equilibrium one expect that the approach

$$g(N, U) \sim \text{Largest}_{U_1} (g_1(N_1, U_1) g_2(N_2, U - U_1)) \quad (0.4)$$

will be enough to describe the properties of the total system in the equilibrium.

- In order to deduce what are the values of U_1 and U_2 that make $g_1(N_1, U_1) g_2(N_2, U - U_1)$ maximum, we ask $g(N, U)$ (following the approach given in (0.4)) to be an extremum, *i. e.* $dg = 0$. (In fact a maximum. We distribute the total energy U between the individual systems in such way that the number of accessible states is maximum). The result is that

$$\frac{1}{g_1} \left(\frac{\partial g_1}{\partial U_1} \right)_{N_1} = \frac{1}{g_2} \left(\frac{\partial g_2}{\partial U_2} \right)_{N_2} \quad (0.5)$$

which we can rewrite as

$$\left(\frac{\partial \log(g_1)}{\partial U_1} \right)_{N_1} = \left(\frac{\partial \log(g_2)}{\partial U_2} \right)_{N_2} \quad (0.6)$$

By comparison with thermodynamics we that we can define the *fundamental entropy* σ and the *fundamental temperature* as

$$\sigma(N, U) := \log[g(N, U)] \quad (0.7)$$

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{N, V} \quad (0.8)$$

which are linked to the thermodynamic entropy and temperature by the *Boltzmann constant* $k_B = 1.381 \times 10^{-23} \text{ J/K}$, namely:

$$S = k_B \sigma \quad (0.9)$$

$$T = k_B \tau \quad (0.10)$$

- The entropy measures the number of microstates (quantum states) accessible to a system.
- Basic assumption: A closed system might be in any of these microstates. The microstates are either accessible or inaccessible to the system, and the system can be with equal chances in any of the accessible states.
- When we bring two systems into contact we expect the total energy to be constant, but to redistribute between the systems in such way that the entropy is maximum. This maximum is attained when the temperature for one system is equal to the temperature for the second system.
- Notation issue: when we say

$$\left(\frac{\partial f}{\partial x} \right)_y \quad (0.11)$$

it means that $f = f(x, y)$ and that y is kept constant when we perform the differentiation of $f(x, y)$ respect x . Namely,

$$\left(\frac{\partial f}{\partial x} \right)_y = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x, y)}{\Delta x} \quad (0.12)$$

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1 What we will learn in this Lecture

- The *NVT* systems: those that are allowed to interchange energy with the environment but that maintain constant the number of particles N , the volume V and the temperature..
- We will see that to determine the probability of a *NVT system* to have a certain energy, the only thing we need to know from the environment is its temperature, nothing more is needed.
- There is a key-magnitude from which to derive all the thermodynamics for NVT systems, i.e. the *partition function*, namely

$$Z(\tau) = \sum_s e^{-\epsilon_s/\tau} \quad (1.1)$$

where \sum_s means sum over all microstates. The probability of finding the system in a state given by energy ϵ_s is

$$P(\epsilon_s) = \frac{e^{-\epsilon_s/\tau}}{Z(\tau)} \quad (1.2)$$

- Thus, given that the partition function $Z(\tau)$ of our NVT system is known, we will see that the *internal energy* U , and the *free energy of Helmholtz* are given by:

$$U(\tau) \equiv \langle \epsilon \rangle \equiv \langle H \rangle = \tau^2 \frac{\partial \ln[Z(\tau)]}{\partial \tau} = - \frac{\partial \ln[Z(\beta)]}{\partial \beta} \quad (1.3)$$

$$F(\tau) \equiv A(\tau) = -\tau \ln[Z(\tau)] \quad (1.4)$$

where $\beta \equiv -1/\tau$. We will get insight about the meaning of F .

- On the way, we will learn that the thermodynamic *pressure* P and the *heat capacity at constant volume* C_V are given by the following relations

$$C_V \equiv \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_V = \left(\frac{\partial U}{\partial \tau} \right)_{N,V} = \frac{1}{\tau^2} (\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2) \quad (1.5)$$

$$P \equiv \langle p \rangle = - \left(\frac{\partial U}{\partial V} \right)_\sigma = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U \quad (1.6)$$

and that the following relations hold

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V \quad (1.7)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_\tau \quad (1.8)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V} \right)_\tau \quad (1.9)$$

- Let's start

2 NVT systems

2.1 motivation

Until now we have dealt with closed systems, such that the energy of the system E , the number of particles N , the volume V , and the temperature T are kept constant. Those systems are many times far from the typical situations one would like to study.

In a first approach we will allow the system to exchange energy with a much bigger system (*the reservoir* aka *the environment*) which is supposed to be so big that the exchanges of energy with our system do not change the temperature of the reservoir.

Thus, in this case we want to study, energy can enter or escape our system but N , V and T are constant. An experimental realization close to this ideal case (neglecting metal expansion or contraction) would be for instance a certain amount of gas contained inside a cube made of iron in the middle of our room.

A key question is how much information we need to know about the environment to describe the system. A second question is what tools will allow me to predict the thermodynamics of my system (the value of the macroscopic observable, for instance P, C_V, \dots) given my knowledge about the microstates and their energy.

2.2 The Boltzmann Factor

Let's consider a total system \mathcal{T} composed of the reservoir \mathcal{R} and the system of our interest \mathcal{S} . We assume \mathcal{T} to be a closed system.

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We can ask ourselves: what is the probability of finding our system \mathcal{S} in microstates such that their energy is ϵ_s ? Let's denote such probability by $P(s)$, as we know from previous lessons, the probability must be related to the multiplicity

$$P(\epsilon_s) \sim g_{\mathcal{T}}(U_{\mathcal{T}}) = g_{\mathcal{R}}(U_{\mathcal{T}} - \epsilon_s) g_{\mathcal{S}} \quad (2.1)$$

for simplicity let's assume that there is only one microstate in \mathcal{S} that leads to energy ϵ_s , i.e.

$g_{\mathcal{S}} = 1$, therefore

$$P(\epsilon_s) \sim g_{\mathcal{R}}(U_{\mathcal{S}} - \epsilon_s) = \exp(\ln[g_{\mathcal{R}}(U_{\mathcal{S}} - \epsilon_s)]) \quad (2.2)$$

$$= \exp(\sigma(U_{\mathcal{S}} - \epsilon_s)) \rightarrow \text{Taylor expansion} \rightarrow = \quad (2.3)$$

$$= \exp(\sigma(U_{\mathcal{S}}) - \sigma'(U_{\mathcal{S}}) \epsilon_s \pm \dots) \quad (2.4)$$

$$\approx \exp(\sigma(U_{\mathcal{S}}) - \sigma'(U_{\mathcal{R}}) \epsilon_s \pm \dots) \quad (2.5)$$

$$= \exp(\sigma(U_{\mathcal{S}}) - \left(\frac{1}{\tau}\right) \epsilon_s \pm \dots) \quad (2.6)$$

$$= \exp(\sigma(U_{\mathcal{S}})) \exp(-\epsilon_s/\tau) \quad (2.7)$$

where τ is the temperature of the reservoir. Thus given that $\exp(\sigma(U_{\mathcal{S}})) = cte$ we have

$$P(\epsilon_s) \sim \exp(-\epsilon_s/\tau), \quad (2.8)$$

i.e. the probability of finding a system in a particular microstate s in a NVT system is proportional to the so-called *Boltzmann factor* $\exp(-\epsilon_s/\tau)$, and all what we need to know about the environment \mathcal{R} is its temperature τ (that in equilibrium must coincide with that of our system \mathcal{S}).

2.3 The partition Function

We have said that the partition function is proportional to the Boltzmann factor $P(\epsilon_s) \sim \exp(-\epsilon_s/\tau)$, but to get the probability itself we need to normalise the previous expression by a certain normalisation factor that we call $Z(\tau)$ to highlight that it depends on the temperature τ . This normalisation factor is known as *the partition function*, it is defined as

$$Z(\tau) = \sum_s e^{-\epsilon_s/\tau} \quad (2.9)$$

the sum of the Boltzmann factors of all microstates.

The partition function, allow us to get the normalised probability,

$$P(\epsilon_s) = \frac{\exp(-\epsilon_s/\tau)}{Z(\tau)} \quad (2.10)$$

but in addition, it is a key expression to get the thermodynamics of the NVT systems as we will show know with some examples.

2.3.1 The averaged energy of a system at temperature τ

The *internal energy* U (that should coincide with the averaged energy of the system) can be written as

$$U \equiv \langle \epsilon \rangle \equiv \langle H \rangle = \sum_s \epsilon_s P(s) = \sum_s \epsilon_s \frac{\exp(-\epsilon_s/\tau)}{Z(\tau)} \quad (2.11)$$

where H is usually used to refer to the *Hamiltonian of the system* (\rightarrow expand explanation about H). The previous expression can be written using the parameter differentiation as (Z is constant at fixed τ , and $\beta = 1/\tau$)

$$U = \frac{1}{Z(\tau)} \sum_s \left(\frac{-\partial}{\partial \beta} \right) e^{-\beta \epsilon_s} \quad (2.12)$$

$$= \rightarrow \beta \text{ does not depend on } s \rightarrow = \frac{1}{Z(\tau)} \left(\frac{-\partial}{\partial \beta} \right) \sum_s e^{-\beta \epsilon_s} \quad (2.13)$$

where $\sum_s e^{-\beta \epsilon_s}$ is by definition the partition function, and therefore

$$U = \frac{1}{Z(\tau)} \left(\frac{-\partial \tau}{\partial \beta} \frac{\partial}{\partial \tau} \right) Z(\tau) \quad (2.14)$$

using that

$$\left(\frac{\partial \tau}{\partial \beta} \right) = \frac{-1}{\beta^2} = -\tau^2 \quad (2.15)$$

we get

$$U = \frac{\tau^2}{Z(\tau)} \left(\frac{\partial Z(\tau)}{\partial \tau} \right) \quad (2.16)$$

which can be rewritten as

$$U(\tau) = \tau^2 \frac{\partial \ln[Z(\tau)]}{\partial \tau} = -\frac{\partial \ln[Z(\beta)]}{\partial \beta} \quad (2.17)$$

2.3.2 An example: the two-level system

Let's suppose we have a system \mathcal{S} in which there are only two possible states s_0 and s_1 with energies $\epsilon_0 = 0$ and $\epsilon_1 = \epsilon$. What is the averaged energy of this system at temperature τ ?

Fist, we calculate the partition function of the system:

$$Z(\tau) = \sum_s e^{-\epsilon_s/\tau} = 1 + e^{-\epsilon/\tau} \quad (2.18)$$

now we use that

$$U(\tau) = \tau^2 \frac{\partial \ln[Z(\tau)]}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \ln[1 + e^{-\epsilon/\tau}] \quad (2.19)$$

$$= \tau^2 \frac{\left(\frac{\epsilon}{\tau^2}\right) e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} = \epsilon \frac{e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} \quad (2.20)$$

$$= \epsilon \frac{1}{1 + e^{+\epsilon/\tau}} \quad (2.21)$$

In figure XXXXXXXXXX you can see a plot of $U(\tau)$ as a function of τ . Observe the behaviour for $\tau \rightarrow 0$ and $\tau \rightarrow \infty$, in this last case $U \rightarrow \epsilon/2 \neq \epsilon$ because at high temperature one expect the two levels to be equally populated (i.e. we can find the system with the same probability in state s_0 or in the state s_1).

2.3.3 Heat Capacity and the Fluctuation-response theorem

We have got that the average energy of a system is a function that depends on the temperature of the system

$$U \equiv \langle U \rangle = \tau^2 \frac{\partial \ln[Z(\tau)]}{\partial \tau}. \quad (2.22)$$

In thermodynamics it is usual to define the change of the average energy of a system U due to a change of temperature as the heat capacity C . The heat capacity is used, as we will see later, in several situations to characterise the behaviour of the system. The value of C is expected to be dependent on the nature of the change, for instance we can change T at fixed N and V and we speak of the isochoric heat capacity C_V , or alternatively we could fix N and P , and we speak of the isobaric heat capacity C_P , in general $C_V \neq C_P$.

Both C_V and C_P are examples of what are called *response functions*, i.e. somehow they tell us about how the system evolves when we change some parameter of the system. Let's focus on the isochoric heat capacity, which can be defined as

$$C_V \equiv \left(\frac{\partial U}{\partial \tau} \right)_{N,V} \quad (2.23)$$

with a little bit of algebra (see below) it is possible to show that

$$C_V = \frac{1}{\tau^2} (\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2) \quad (2.24)$$

where $(\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2)$ is the variance of the energy of the system, sometimes written σ_ϵ^2 (do not confuse it with the fundamental entropy σ !).

Equation (2.24) is known as the *fluctuation-response-theorem* which is very important because links the fluctuations of the energy with a macroscopic observable.

One can get now might be a little bit confuse : from eq (2.24) one can infer that the fluctuations of the energy increase with the size of the system (because C_V is an extensive property which depends on the size of the system). How is that possible if we were speaking in previous lessons about the fact that the distribution of the energies is very peaked around the maximum of the distribution. Was that not true?

Everything is ok. The explanation is the following: C_V is extensive, therefore should depend on the number of particles in the system $C_V \sim N$, and thus from eq. (2.24) we get $\sqrt{(\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2)} = \sigma_\epsilon \sim N^{1/2}$. Indeed the fluctuations are bigger when we increase the size of the system, but the relative fluctuations tend to zero, namely

$$\frac{\sigma_\epsilon}{N} \sim \frac{N^{1/2}}{N} \sim \frac{1}{\sqrt{N}} \quad (2.25)$$

that goes to zero in the limit $N \rightarrow \infty$.

Let's now proof eq (2.24)

$$C_V \equiv \left(\frac{\partial U}{\partial \tau} \right)_{N,V} = \frac{\partial \beta}{\partial \tau} \frac{\partial}{\partial \beta} \langle U \rangle \quad (2.26)$$

$$= -\tau^{-2} \left(\frac{\partial}{\partial \beta} \frac{\sum_s \epsilon_s e^{-\beta \epsilon_s}}{\sum_s e^{-\beta \epsilon_s}} \right) \quad (2.27)$$

let's apply now the rule

$$\left(\frac{f}{g}\right)' = \frac{f'g - fg'}{g^2} \quad (2.28)$$

and we get

$$C_V = -\tau^{-2} \frac{(\sum_s (-\epsilon_s^2) e^{-\beta\epsilon_s}) (\sum_s e^{-\beta\epsilon_s}) - (\sum_s \epsilon_s e^{-\beta\epsilon_s}) (\sum_s (-\epsilon_s) e^{-\beta\epsilon_s})}{(\sum_s e^{-\beta\epsilon_s})^2} \quad (2.29)$$

$$= -\tau^{-2} \left(\frac{-\sum_s \epsilon_s^2 e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}} - \left(\frac{\sum_s \epsilon_s e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}} \right)^2 \right) \quad (2.30)$$

$$= -\tau^{-2} (-\langle \epsilon^2 \rangle + (\langle \epsilon \rangle)^2) \quad (2.31)$$

$$= \tau^{-2} (\langle \epsilon^2 \rangle - (\langle \epsilon \rangle)^2) = \tau^{-2} \sigma_\epsilon^2 \quad (2.32)$$

2.3.4 Pressure

Let's consider now we perform a *reversible process* that consist on changing in a reversible way the volume of a container. See figure ZZZZZZZZZZZZ

A *reversible process* is a process in which during the changes the system is always infinitesimally close to equilibrium conditions. Then, if we reverse the process, we are sure that we go back to the initial state.

The change in energy of a system in a state s due to the change in volume ΔV can be written via the following Taylor expansion

$$\epsilon_s(V - \Delta V) = \epsilon_s(V) - \frac{d\epsilon_s}{dV} \Delta V + \dots \quad (2.33)$$

$$\epsilon_s(V - \Delta V) - \epsilon_s(V) = -\frac{d\epsilon_s}{dV} \Delta V \quad (2.34)$$

From mechanics we know that when we apply a pressure p_s isotropically over a system, and the change in volume is ΔV , the mechanical work needed to do this is $W = p_s \Delta V$. If the system does not have any other way of changing its internal energy. Then $\Delta U_s = W = p_s \Delta V$. (\rightarrow expand explanation). Thus, by comparing $\Delta U_s = P \Delta V$ with eq. (2.34), we identify the pressure acting onto a system in a state s as

$$p_s \equiv -\frac{d\epsilon_s}{dV}. \quad (2.35)$$

Nonetheless, we are interested in the thermodynamic pressure P , that which should coincide with the averaged pressure over all possible states of the system $P = \langle p_s \rangle$. The value of P can be derived as follows

$$P \equiv \langle p_s \rangle = \sum_s p_s P(s) = \quad (2.36)$$

$$= \sum_s -\frac{d\epsilon_s}{dV} \frac{e^{-\epsilon_s/\tau}}{Z(\tau)}. \quad (2.37)$$

Taking into account that neither $e^{-\epsilon_s/\tau}$ nor $Z(\tau)$ depend on the volume, we can introduce it into the derivative. Thus the thermodynamic pressure is

$$P \equiv \langle p \rangle = - \left(\frac{\partial U}{\partial V} \right)_{\sigma, N} \quad (2.38)$$

notice the differentiation at constant entropy due to the reversible nature of the compression we have assumed. This means than before applying the differentiation one should have an expression of U as a function of $U(\sigma, V, \dots)$. [More details in appendix D of the Thermal Physics by Kittel-Kroemer)].

Sometimes can be easier to calculate the pressure via other relations than eq. (2.38), an alternative expression for the pressure can be derived as follows:

Let's assume that the fundamental entropy σ can be written as a function of the averaged energy of the system U and the volume V , i.e. $\sigma = \sigma(U, V)$. Therefore from thermodynamics (or from mathematics) we know that it's differential can be written as

$$d\sigma(U, V) = \left(\frac{\partial \sigma}{\partial U} \right)_V dU + \left(\frac{\partial \sigma}{\partial V} \right)_U dV \quad (2.39)$$

Let's now assume a process that changes the volume and the averaged energy of the system in such way that the change in entropy is zero, i.e a reversible process, which means $d\sigma(U, V) = 0$. Then, from eq. (2.39) and the fact that

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_V \quad (2.40)$$

we get

$$\left(\frac{\partial U}{\partial V} \right)_\sigma = -\tau \left(\frac{\partial \sigma}{\partial V} \right)_U \quad (2.41)$$

and using the first expression we have got for the pressure we see that we can also write the pressure as

$$P \equiv \langle p \rangle = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U \quad (2.42)$$

Using this last result it is possible to get one of the usual *thermodynamic identities* $dU = \tau d\sigma - p dV$. Let's substitute eq. (2.42) into eq. (2.39) then we get

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV \quad (2.43)$$

which can be rewritten as

$$\tau d\sigma = dU + p dV \quad (2.44)$$

that leads to the afford mentioned thermodynamic identity $dU = \tau d\sigma - p dV$.

2.3.5 Considerations about the Helmholtz free energy

From thermodynamics we know that one of the key *thermodynamic potentials* is the *Helmholtz free energy*, usually denoted with F or A depending on the books. This function is usually defined as

$$F \equiv U - \tau \sigma \quad (2.45)$$

This function is very interesting for several reasons: in the classical mechanics (where neither τ or σ are considered, or said in another way, all is supposed to happen at constant entropy) the energy plays the main role. When entropy enters into consideration, an NVT system should reach a compromise between minimising the energy as far as possible but maximising the entropy also as far as possible. The function F weights such two contributions and it will be a extremum (in fact a minimum) when the system is in equilibrium. This can be shown easily, assume we have again our system \mathcal{S} and our reservoir (environment) \mathcal{R} , then an infinitesimal reversible transfer from \mathcal{R} to \mathcal{S} at constant temperature can be written as

$$dF_{\mathcal{S}} = dU_{\mathcal{S}} - \tau d\sigma_{\mathcal{S}}. \quad (2.46)$$

We already know that

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_V \quad (2.47)$$

therefore $dU = \tau d\sigma$ at constant volume, which implies $dF = 0$. This proves it its an extremum.

Now we want to proof it is a minimum. The total energy is $U_{\mathcal{T}} = U_{\mathcal{S}} + U_{\mathcal{R}}$, on the other hand the total entropy is $\sigma_{\mathcal{T}} = \sigma_{\mathcal{S}} + \sigma_{\mathcal{R}}$ because it is an extensive property. Therefore

$$\sigma_{\mathcal{T}} = \sigma_{\mathcal{S}} + \sigma_{\mathcal{R}} = \sigma_{\mathcal{S}}(U_{\mathcal{S}}) + \sigma_{\mathcal{R}}(U_{\mathcal{T}} - U_{\mathcal{S}}) \Rightarrow Taylor \rightarrow \quad (2.48)$$

$$\sigma_{\mathcal{R}}(U_{\mathcal{T}}) - U_{\mathcal{S}} \left(\frac{\partial \sigma_{\mathcal{R}}}{\partial U_{\mathcal{R}}} \right)_{V,N} + \sigma_{\mathcal{S}}(U_{\mathcal{S}}) \quad (2.49)$$

and again,

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{V,N} \quad (2.50)$$

and thus we have that

$$\sigma_{\mathcal{T}} = \sigma_{\mathcal{R}}(U_{\mathcal{T}}) - \frac{F_{\mathcal{S}}}{\tau} \quad (2.51)$$

where $F_{\mathcal{S}}$ is the free energy of our system. We know that $\sigma_{\mathcal{R}}(U_{\mathcal{T}})$ must be a constant because the whole energy $U_{\mathcal{T}}$ is a constant. In equilibrium, things go in such way that $\sigma_{\mathcal{T}}$ must be a maximum, so the only way this can happen is if in equilibrium $F_{\mathcal{S}}$ is a minimum. If we depart from the equilibrium situation in a NVT system, and increase in F should be observed.

2.3.6 Differential relations involving the Helmholtz free energy F

Given the definition of the Helmholtz free energy

$$F \equiv U - \tau \sigma \quad (2.52)$$

from thermodynamics (or from mathematics) we know that the differential of F can be expressed as

$$dF = dU - \tau d\sigma - d\tau \sigma \quad (2.53)$$

using that $\tau d\sigma = dU + pdV$ (derived before) we can write dF as

$$dF = -\sigma d\tau - p dV \quad (2.54)$$

From this thermodynamic identity we can get the following results when we consider either V or τ (only one at the same time) to be constant, namely

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V \quad (2.55)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_\tau \quad (2.56)$$

which are used in many situations. In fact, once F is known for a given system, all the remaining thermodynamic expressions can be obtained. Now the question is like in the case of the energy, how can I obtain F from my knowledge about the microscopic system? We will see this in the next section.

Know before finish with the differential relations involving F , notice that if we compare the following two expressions for the pressure

$$P = - \left(\frac{\partial F}{\partial V} \right)_\tau \quad (2.57)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_\sigma \quad (2.58)$$

and we remember that by definition $F \equiv U - \tau\sigma$ then it is possible to rewrite the pressure in two terms

$$P = - \left(\frac{\partial U}{\partial V} \right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V} \right)_\tau \quad (2.59)$$

the energy pressure (dominant in most solids where the entropy contribution is small respect the energetic contribution) and the entropy pressure (dominant in gases and elastic polymers, where the reverse happens).

Notice that just thinking that by analogy with classical mechanics, in a NVT it is enough to consider the pressure to be given by

$$P = \frac{\partial U}{\partial V} \quad (2.60)$$

can be very misleading and far from the correct values of P .

2.3.7 How to compute Helmholtz free energy F from our microscopic knowledge of the system

All previous expressions we have been deriving for F are very nice, but it was almost pure thermodynamic considerations that we have used. I would like to compute F in the same way I know how to compute U from my knowledge of the microscopics of the system. This can be accomplished by using the partition function (remember, the keystone of the statistical mechanics for NVT systems).

It is possible to show that

$$F(\tau) = -\tau \ln[Z(\tau)] \quad (2.61)$$

where $Z(\tau)$ is the partition function of our system. This comes from the fact that $F \equiv U - \tau\sigma$ can be written using that

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V \quad (2.62)$$

as the following partial differential equation

$$F = U + \tau \left(\frac{\partial F}{\partial \tau} \right)_V \quad (2.63)$$

from which eq. (2.61) is the only acceptable solution. It is possible to show the uniqueness of the solution and that the addition of a constant to eq. (2.61) must be zero if we want the entropy to reduce to what one expects in the limit $\tau \rightarrow 0$ ([See Kittel for more info]).

Therefore, once we know the partition function $Z(\tau)$ for our NVT system, then we can compute F , U , and derive whatever other macroscopic magnitude of use in thermodynamics like σ , P , C_V , etc ...

That's the power of statistical mechanics

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