Lecture_10

October 16, 2023

1 The Third Law of Thermodynamics

1.1 Classical

Let's conider the enthalpy and the Gibb's free energy again:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \tag{1}$$
$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T \tag{2}$$

If we perform a reaction in the lab (meaning it will be under constant temperature and pressure) we got the following information. First, change in enthalpy just becomes

$$\Delta H = \Delta Q$$

If $\Delta H < 0$, then heat is emitted from the system (exothermic reactions). If $\Delta H > 0$, then heat is absorbed into the system (endothermic reactions). For the Gibb's free energy, we found that under such conditions (constant T and P), $\mathrm{d}G \leq 0$ - that is, the system will always try to minimise the Gibbs energy in order to reach equilibrium. As such, if for the reaction $\Delta G < 0$, it can occur spontaneously!

So, for such a reaction we have that

$$G = H - T\,S$$

This means that as the temperature approaches 0, the Gibbs Free energy and the enthalpy approach each other. This was experimentally proven by Walter Nernst, who then postulated that the entropy should go as $\Delta S \to 0$ as $T \to 0$. This lead to the statement that

Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

1.2 Consequences

1.2.1 Heat Capacity

So how does the 3rd Law affect all of the things we've talked about so far? First, let's consider heat capacity. Given that

$$C = T\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial S}{\partial \ln T}\right) \to 0$$

as, when $T \to 0$, $\ln T \to \infty$ - so heat capacities go to 0 at 0 temperature!

1.2.2 Thermal Expansion

From Maxwell's equations, we have that

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

Since $S = S(T, P) \to 0$ as $T \to 0$ for all P, this implies that the left hand side of this equation also goes to 0. As such,

$$\lim_{T \to 0} \left(\frac{\partial V}{\partial T}\right)_P = 0$$

which also means that $\beta_P \to 0$. This means that thermal expansion stops.

With that, our discussion of the laws of classical thermodynamics comes to a close. Next, we're going to discuss statistical mechanics, and start looking at how we apply both classical and statistical thermodynamics to particular problems.

2 Equipartition of Energy

Before going further, we are going to discuss the equipartition theorem. To motivate our discussion, let's write down what the kinetic energy of a particle of mass m and moving a velocity v is

$$E_K = \frac{1}{2}mv^2.$$

Now, if we have a particle at the end of a spring, the potential energy of that particle when displaced by a distance x is

$$E_P = \frac{1}{2}kx^2$$

The total energy of a particle at the end of the spring is thus

$$E = E_K + E_P = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

As the particle oscillates back and forth, the energy within the system is constantly moving between kinetic energy and potential energy, while the total energy of the system remains constant. The interesting thing to note here is that both energy terms in this equation have a quadratic dependance on some variable (v^2 for kinetic, x^2 for potential).

Now let's imagine we have some system which is connected to a heat bath. The system is capable of extracting energy from the heat bath or transferring energy to it. What is the mean thermal energy of the system? The thermal energy must be stored as either kinetic energy or potential energy - how exactly is it distributed?

So, let's assume we can write the energy down as some quadratic function - that is, we could write

$$E = \alpha x^2$$

where α is some constant and x is some variable. The probability that the system would have a particular energy αx^2 would then be

$$P(x) = \frac{e^{-\beta \alpha x^2}}{\int_{-\infty}^{+\infty} e^{-\beta \alpha x^2}\,dx}$$

2

where the bottom term is an integral rather than the normal summation we see in Z because we're going to assume here that x can have non-integer values. The mean energy of the system is then

$$< E > = \int_{-\infty}^{+\infty} EP(x)\mathrm{d}x \tag{3}$$

$$< E > = \frac{\int_{-\infty}^{+\infty} \alpha x^2 e^{-\beta \alpha x^2}\mathrm{d}x}{\int_{-\infty}^{+\infty} e^{-\beta \alpha x^2}\mathrm{d}x} \tag{4}$$

$$< E > = \frac{1}{2\beta} \tag{5}$$

$$< E > = \frac{1}{2}k_\mathrm{B}T \tag{6}$$

This is a pretty significant result, as even though we've assumed an arbitrary function for the energy, the mean energy that we get out just depends on temperature! It is possible (but non-trivial) to extend this result to allow for the energy to be made up of multiple quadratics, say

$$E = \sum_{i=1}^{n} \alpha_i x_i^2$$

then the result becomes

$$< E >= \frac{n}{2}k_\mathrm{B}T$$

This is a very, very useful theorem. Each quadratic term that contributes to the total energy is called a mode, or degree of freedom of the system. Thus, we get the theorem for the equipartition of energy:

If the energy in a classical system is the sum of n quadratic modes, and the system is in contact with a heat reservoir at temperature T, the mean energy of the system is given by $nk_\mathrm{b}T/2$
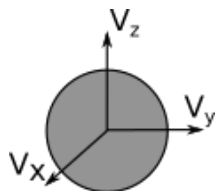
2.1 Applications

Translational motion in a monatomic gas: Imagine we have a particle which is able to move in all 3 directions. It has a velocity component associated with each direction, and as such, a kinetic energy associated with each direction. This gives

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

Summation of 3 quadratic modes, meaning the mean energy of the system

$$< E >= \frac{3}{2}k_\mathrm{B}T$$

Rotational motion in a diatomic gas: Imagine we have 2 particles bonded together with a rigid bond, such that the diatomic particle can then spin about 2 axes. This gives an additional 2 terms due to rotation about each axis which doesn't have a neat symmetry, giving
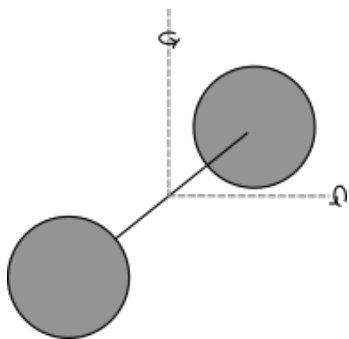
$$\frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}$$

This means the energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2}$$

and thus

$$<E> = \frac{5}{2}k_{\mathrm{B}}T$$

Vibrational energy in a diatomic gas: Now imagine that same gas, but where the bond is no longer rigid, but instead acts like a spring with spring constant k. This adds gives another 2 terms:
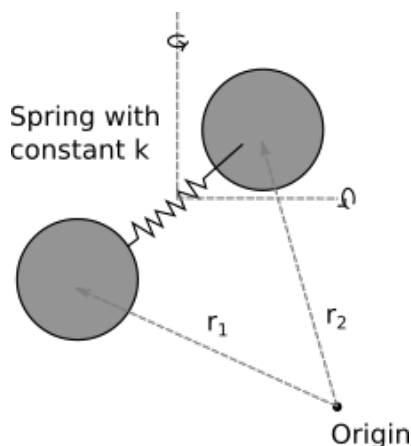
$$\frac{1}{2}\mu(\mathbf{r_1} - \mathbf{r_2})^2 + \frac{1}{2}k(|\mathbf{r_1} - \mathbf{r_2}| - l_0)^2$$

where k is an imagined spring constant, l_0 is the equilibrium molecular bond length, and μ is the reduced mass of the system. This means the total energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{1}{2}\mu(\mathbf{r_1} - \mathbf{r_2})^2 + \frac{1}{2}k(|\mathbf{r_1} - \mathbf{r_2}| - l_0)^2$$

and thus

$$<E> = \frac{7}{2}k_{\mathrm{B}}T$$

4

3 Revisiting the partition function

In this lecture, we are going to revisit the partition function which we discussed during the introductory part of the course, and figure out how it relates to the thermodynamic quantities which we introduced in classical thermal physics.

The partition function is defined as

$$Z = \sum_i \mathrm{e}^{-\beta E_i}$$

It looks pretty boring, but is a very powerful tool, as we'll shortly see. Typically, when solving a statistical mechanics issues, there are two steps.

1. Write down the partition function.
2. Follow the standard procedures needed to get the relevant quantity out of the partition function.

For this lecture, we are going to be focusing on the single particle partition function - that is, we will work out what Z is for a single particle. We'll generalise to many particles later.

3.1 Writing down the partition function

This is not too difficult a step, and is something you have encountered in your problem sets previously. Let's take a look at some explicit examples.

3.1.1 The two level system

Let the energy of a system be $\pm\epsilon/2$. The partition function for such a system is thus

$$Z = \mathrm{e}^{\beta\epsilon/2} + \mathrm{e}^{-\beta\epsilon/2} = 2\cosh\left(\frac{\beta\epsilon}{2}\right)$$

3.1.2 The simple harmonic oscillator

Let the energy of a system be $(n+1/2)\hbar\omega$, where $\hbar = h/(2\pi)$ and n can go up to infinity. The partition function for such a system is thus

$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{\beta(n+1/2)\hbar\omega} = \mathrm{e}^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty}\mathrm{e}^{-\beta n\hbar\omega} = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}$$

where we've used the result for an infinite geometric progression of

$$a\sum_{n=0}^{\infty} r^n = \frac{a}{1-r}$$

where a is a constant to simplify the expression.

3.2 Deriving useful quantities from the partition function

Ok, now that we can write down what the partition function, let's see what we can derive from it.

3.2.1 The internal energy (U)

As discussed in previous lectures, the internal energy of a system is given by

$$U = \sum_i P_i E_i$$

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Given that $Z = \sum_i e^{-\beta E_i}$, then $\frac{dZ}{d\beta} = -\sum_i E_i e^{-\beta E_i}$. This leaves us with

$$U = -\frac{1}{Z}\frac{dZ}{d\beta} = -\frac{d\ln Z}{d\beta}$$

as we've seen previously. It can also sometimes be useful to rewrite this in terms of temperature. Using

$$\beta = \frac{1}{k_B T} \rightarrow \frac{d\beta}{dT} = -\frac{1}{k_B T^2}$$

gives

$$U = k_B T^2 \frac{d\ln Z}{dT}$$

3.2.2 Heat Capacities

Recalling that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

we get

$$C_V = 2k_B T \frac{d\ln Z}{dT} + k_B T^2 \frac{d^2 \ln Z}{dT^2}$$

3.2.3 Entropy (S)

The probability of a state being in some energy j is given by

$$P(E_j) = \frac{e^{-\beta E_j}}{Z}$$

Taking the log gives

$$\ln P(E_j) = -\beta E_j - \ln(Z)$$

If we now recall our statistical definition of entropy, which was

$$S = -k_B \sum_i P_i \ln P_i$$

(see Lecture 6) then we get

$$S = k_B \sum_i P_i[\beta E_i + \ln(Z)] = k_B \beta \sum_i P_i E_i + \ln(Z) \sum_i P_i]$$

We can now substitute $U = \sum_i P_i E_i$ and $\sum_i P_i E_i = 1.0$ to get

$$S = k_B[\beta U + \ln(Z)]$$

which in terms of temperature works out as

$$S = \frac{U}{T} + k_B \ln(Z)$$

3.2.4 The Helmholtz Free Energy (F)

The Helmholtz Free Energy is given by

$$F = U - TS$$

Using the above substituion for S then leads to

$$F = -k_{\mathrm{B}}T \ln(Z)$$

or, in terms of Z is

$$Z = \mathrm{e}^{-\beta F}$$

The Helmholtz Free Energy turns out to be very useful in deriving pretty much everything else we've defined over the last 4 weeks. For example, we can get the entropy by recalling that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

(again, Lecture 6) which gives

$$S = k_{\mathrm{B}} \ln(Z) + k_{\mathrm{B}}T \left(\frac{\partial \ln(Z)}{\partial T}\right)_V$$

which is the same as the above expression if we use the relation between U and $\frac{\mathrm{d}\ln Z}{\mathrm{d}T}$ derived earlier.

3.2.5 Pressure

From Lecture 7 we have that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_{\mathrm{B}}T \left(\frac{\partial \ln(Z)}{\partial V}\right)_T$$

3.2.6 Enthalpy

This lets us write down the enthalpy as

$$H = U + PV = k_{\mathrm{B}}T^2 \frac{\mathrm{d}\ln Z}{\mathrm{d}T} + k_{\mathrm{B}}TV \left(\frac{\partial \ln(Z)}{\partial V}\right)_T$$

3.2.7 Gibbs Free Energy

$$G = F + PV = -k_{\mathrm{B}}T \ln(Z) + k_{\mathrm{B}}TV \left(\frac{\partial \ln(Z)}{\partial V}\right)_T$$

4 Working through an example

Let's take the 2 level system which was described earlier. This system has a partition function of

$$Z = 2 \cosh\left(\frac{\beta \epsilon}{2}\right)$$

The internal energy of the system is

$$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = -\frac{\epsilon}{2}\tanh\left(\frac{\beta\epsilon}{2}\right)$$

The heat capacity of the system is given by

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_V = k_{\mathrm{B}}\left(\frac{\beta\epsilon}{2}\right)^2 \operatorname{sech}^2\left(\frac{\beta\epsilon}{2}\right)$$
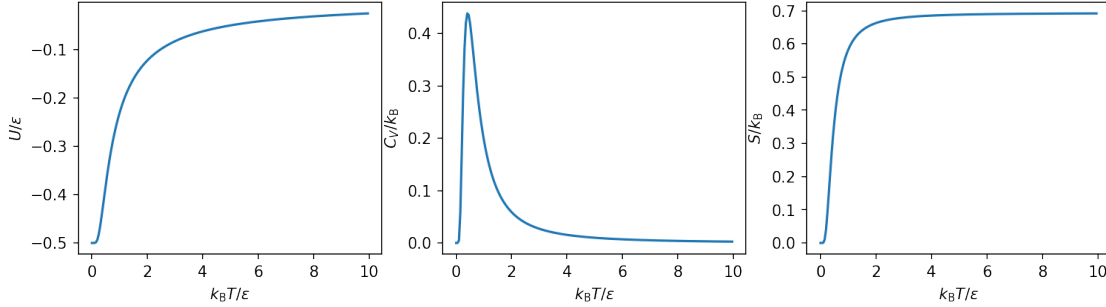
The Helholtz Free energy is

$$F = -k_{\mathrm{B}}T\ln Z = -k_{\mathrm{B}}T\ln\left[2\cosh\left(\frac{\beta\epsilon}{2}\right)\right]$$

and so the entropy is

$$S = \frac{U - F}{T} = -\frac{\epsilon}{2T}\tanh\left(\frac{\beta\epsilon}{2}\right) + k_{\mathrm{B}}\ln\left[2\cosh\left(\frac{\beta\epsilon}{2}\right)\right]$$

Let's now look at what each of these functions are doing.

These plots are very instructive. Let's consider 2 distinct temperature regimes and see what the plots tell us: ### $T \to 0$ As the temperature drops to 0, the internal energy converges to $-\epsilon/2$. That is, the system settles into the ground state. The heat capacity and the entropy converge to 0, as they should in accordance with the third law.

4.0.1 $T \to \infty$

As the temperature goes to $infinity$, the internal energy converges to 0. This is because at these high temperatures, the probabilities that either state is populated are both 0.5, and the internal energy is $U = \sum_i P_i E_i = -0.5\frac{\epsilon}{2} + 0.5\frac{\epsilon}{2} = 0$. The heat capacity goes to 0. This can be understood by considering the fact that adding any energy to the system as this stage does not affect which state the system is likely to be in.

The heat capacity does have a maximum - that is, there is a temperature at which adding more energy substantially changes the proability of the internal energy changing.

This example demonstrates the big picture behind statistical mechanics. You write down Z, derive the relevant quantities, and then examine how those quantities behave for various temperatures. However, writing Z down isn't always easy - there are only a handful of systems that we are explicitly able to solve for the discrete energy levels.

4.1 Combining Partition Functions

Let's now consider a system where the energy has various **independent** contributions, where the contributions are distinguishable. For example, imagine the energy is given by

$$E_{i,j} = E_i^{(a)} + E_j^{(b)}$$

The partition function for such a combination would be

$$Z = \sum_i \sum_j e^{-\beta(E_i^{(a)} + E_j^{(b)})} = \sum_i e^{-\beta E_i^{(a)}} \sum_j e^{-\beta E_j^{(b)}} = Z_a Z_b$$

so in this case, the partition functions of the independent contributions multiply. It is simple to generalise this to N **independent** contributions, in which case we get

$$Z = \prod_{i=1}^{N} Z_i$$