

Partition Functions

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1 Introduction

Partition functions are useful because it is easy to derive expectation values of parameters of the system from them. Below is a list of the major examples.

$$E = -\frac{\partial \ln(Z)}{\partial \beta}$$

$$p = kT \frac{\partial \ln(Z)}{\partial V}$$

$$S = k \ln(Z) - k\beta \frac{\partial \ln(Z)}{\partial \beta}$$

$$C_V = k\beta^2 \frac{\partial^2 \ln(Z)}{\partial \beta^2}$$

$$F = -kT \ln(Z)$$

$$\alpha = \frac{\partial \ln(Z)}{\partial N}$$

$$\mu_j = -kT \frac{\partial \ln(Z)}{\partial N_j}$$

You can see that every parameter can be expressed in terms of $\ln(Z)$ and this is the simplest expression for most parameters. Be careful when deriving the expression for pressure, it is not the derivative of E as is often the case.

$$p = -\left(\frac{\partial E}{\partial V}\right)_S \neq -\left(\frac{\partial E}{\partial V}\right)_{T,V,N}$$

We will derive these in a systematic way in this paper.

2 Boltzmann Factor and Partition Function

Consider a system A in thermal contact with a reservoir at temperature T with combined energy E_o . Let subscript r refer to the reservoir, o refer to the total system and no subscript refer to the system A .¹

$$P_j = \frac{\omega_r(E_o - E_j)}{\omega_o(E_o)}$$

$$= \frac{e^{S_r(E_o - E_j)/k}}{e^{S_o(E_o)/k}}$$

By expanding the entropy in powers of a small energy, the top exponent becomes

$$S_r(E_o - E_j) = S_r(E_o - E + E - E_j)$$

$$\cong S_r(E_o - E) + (E - E_j) \left. \frac{\partial S}{\partial E} \right|_{E_o - E = E_r}$$

$$= S_r(E_o - E) + (E - E_j)/T$$

And by the additivity of entropy the bottom exponent can be written as

$$S_o(E_o) = S(E) + S_o(E_o - E)$$

Therefore

$$P_j = \frac{e^{S_r(E_o - E)/k + (E - E_j)/kT}}{e^{S(E)/k + S_r(E_o - E)/k}}$$

$$= \frac{e^{(E - E_j)/kT}}{e^{S(E)/k}}$$

$$= e^{(E - TS)/kT} e^{-E_j/kT}$$

$$= e^{\beta F} e^{-\beta E_j}$$

So when we apply the normalization condition

$$\sum_j P_j = 1 \Rightarrow e^{\beta F} \sum_j e^{-\beta E_j} = 1$$

we see that the quantity defined by

$$Z \equiv \sum_j e^{-\beta E_j}$$

which we call the **partition function**, satisfies

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

The partition function is so named according to Wikipedia because “it encodes how the probabilities are partitioned among the different microstates,

¹This section is from Callen Page 350.

based on their individual energies.” The letter Z stands for Zustandssumme, which is German for “sum of states.” It is worth noting that the sum must be taken over all quantum states and not over all allowed energies since there may be degeneracies.

It is extremely important to understand that the whole partition function formalism is built on the assumption of a canonical ensemble, which means that the system is in contact with a thermal reservoir. Therefore, if you want to use the partition function at all, then you must be sure that your system is in contact with some kind of thermal reservoir, *unless* if the system remains in thermal equilibrium at a constant temperature. In that case the reservoir would have no effect and so it is not necessary. Thermal reservoirs come in many forms. For example electromagnetic radiation can act as a thermal reservoir, however usually thermal interactions occur via particle collisions.

3 Derived Quantities

Z is always a function of the complete set T, V, N , so you cannot determine these parameters from Z . You do not need to write the notation for keeping T, V , or N constant when taking derivatives of Z because these parameters are already assumed constant. Since these parameters are a complete set, no other parameters may be held constant or the system would be overdetermined. That is why we could not find the pressure by taking the volume derivative of energy – we could not hold entropy constant.

Of the four types of energy (E, F, G, H), the Helmholtz free energy F is the one that considers T and V as independent parameters. Note that all four consider N a constant parameter. Therefore only in terms of F can we create a fundamental relation with Z . This fundamental relation² is

$$Z \equiv \sum_r e^{-\beta E_r} = e^{-\beta F}$$

So what is the best way to remember all of the expressions for quantities derived from the partition function? Memorize this fundamental relation and how to use the Helmholtz free energy to derive the rest. Remember that $F = E - TS$ and start from the fundamental thermodynamic relation.

$$dE = TdS - pdV$$

$$dE = d(TS) - SdT - pdV$$

$$d(E - TS) = dF = -SdT - pdV$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{and} \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

²This is from Callen Pg 352

Let's starting deriving the relations. We automatically get

$$F = -kT \ln(Z)$$

Using the new partial derivatives,

$$S = k \frac{\partial(T \ln(Z))}{\partial T} = k \ln(Z) + kT \frac{\partial \ln(Z)}{\partial T} = k \ln(Z) + k\beta \frac{\partial \ln(Z)}{\partial \beta}$$

$$p = kT \frac{\partial \ln(Z)}{\partial V}$$

Now we can get μ_j from $\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T,V,N}$

$$\mu_j = -kT \frac{\partial \ln(Z)}{\partial N_j}$$

Then $\alpha = -\beta\mu$ so,

$$\alpha = \frac{\partial \ln(Z)}{\partial N}$$

We can even get the energy if we use some trickery.

$$E = F + TS = F - \frac{1}{k\beta} \frac{\partial F}{\partial T} = F + \beta \frac{\partial F}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta} = -\frac{\partial \ln(Z)}{\partial \beta}$$

And finally the heat capacity at constant volume comes from $C_V = \left(\frac{\partial E}{\partial T} \right)_V$.

$$C_V = k\beta^2 \frac{\partial^2 \ln(Z)}{\partial \beta^2}$$

4 Probability Explanation

Let's look at this from another angle. The partition function formalism works because it produces the probabilities of states to make an expectation value summation.³

$$P_j = C e^{-\beta E_j} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Z}$$

$$\begin{aligned} \bar{E} &= \sum_j P_j E_j = \sum_j \frac{e^{-\beta E_j}}{Z} E_j = \frac{1}{Z} \sum_j e^{-\beta E_j} E_j \\ &= \frac{1}{Z} \sum_j -\frac{\partial}{\partial \beta} (e^{-\beta E_j}) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln(Z)}{\partial \beta} \end{aligned}$$

Similarly for E^2 ,

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

³This section taken from Reif Pg 212

This can be rewritten as

$$\overline{E^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 = -\frac{\partial \overline{E}}{\partial \beta} + \overline{E}^2$$

Therefore the fluctuation in energy is

$$(\overline{\Delta E})^2 = \overline{E^2} - \overline{E}^2 = -\frac{\partial \overline{E}}{\partial \beta} = \frac{\partial^2 \ln(Z)}{\partial \beta^2}$$

5 General Parameter

If the microstate energies all depend on a parameter λ by

$$E_r = E_r^{(0)} + \lambda A$$

where $E_r^{(0)}$ does not depend on λ , then the expectation value of A is

$$\begin{aligned} \overline{A} &= \frac{1}{Z} \sum_r A e^{-\beta(E_r^{(0)} + \lambda A)} \\ &= \frac{1}{Z} \sum_r -\frac{1}{\beta} \frac{\partial}{\partial \lambda} e^{-\beta(E_r^{(0)} + \lambda A)} \\ &= -kT \frac{\partial \ln(Z)}{\partial \lambda} \end{aligned}$$

You can also be really tricky and use this to find the expectation values of quantities that are not in the Hamiltonian by artificially adding them in and setting $\lambda \rightarrow 0$ at the end. ⁴

6 Momentum Integral Approximation

Since momentum is found in every Hamiltonian that refers to a particle, it is very common that you have to sum over momentum states in a partition function. The reason that the sum is not infinite is because momentum is always quantized inside any container. In thermodynamics we always have a volume V , which tells us the size of our container. We want to approximate the sum over momentum states with an integral, which will be much easier to handle. However, in order to derive the integral, we will have to assume the container is a cubical box. As it turns out, the result is independent of the shape of the container, even though the only evidence I have is an equation from classical thermodynamics.

$$p = \hbar k = \hbar \sqrt{\left(\frac{\pi n_x}{L}\right)^2 + \left(\frac{\pi n_y}{L}\right)^2 + \left(\frac{\pi n_z}{L}\right)^2}$$

⁴This section came from Wikipedia's article: Partition Function

$$= \frac{\hbar\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

So the partition function for the simple Hamiltonian $H = p^2/2m$ is

$$\begin{aligned} Z &= \sum_j e^{-\beta E_j} = \sum_j e^{-\beta p_j^2/2m} \\ &= \left[\sum_j e^{-\beta \hbar^2 \pi^2 (n_x)_j^2 / 2mL^2} \right]^3 \\ &= \left[\int_0^\infty e^{-\beta \hbar^2 \pi^2 n_x^2 / 2mL^2} dn_x \right]^3 \\ &= \left[\int_0^\infty e^{-\beta p_x^2 / 2m} d\left(\frac{L}{\hbar\pi} p_x\right) \right]^3 \\ &= \frac{V}{\pi^3 \hbar^3} \left[\int_0^\infty e^{-\beta p_x^2 / 2m} dp_x \right]^3 \\ &= \frac{V}{2\pi^3} \frac{1}{\hbar^3} \int_{-\infty}^\infty e^{-\beta(p_x^2 + p_y^2 + p_z^2) / 2m} dp_x dp_y dp_z \end{aligned}$$

In the last line the momentum takes on its classical meaning as the components of the momentum vector, whereas before it was a positive quantity based on the quantum wave function.

This result is true for arbitrary shaped containers because the classical expression for the partition function is ⁵

$$Z = \frac{1}{h^3} \int e^{-\beta H} dx dy dz dp_x dp_y dp_z$$

7 Grand Canonical Partition Function

- Microcanonical Ensemble - ensemble of isolated systems, can be used to derive the expression for entropy
- Canonical Ensemble - ensemble of systems that can exchange thermal energy with a reservoir, can be used to derive the Boltzmann factor and the partition function formalism
- Grand Canonical Ensemble - ensemble of systems that can exchange both thermal energy and particles with a reservoir

8 Quantum Statistics

I think that you are supposed to use the same expression for the partition function when dealing with quantum statistics.

⁵This is Callen (16.68) or Reif 7.12)