
LECTURE 24: CLASSICAL STATISTICAL PHYSICS
Friday, March 20, 2020

Recall that knowing $S(E, V, N)$ tells us basically everything about the system. Once you know (any) thermodynamic potential, “you win”. Notice we are back to using E for energy. Remember that we had a way to compute this:

$$S(E, V, N) = k_B \ln \left[\int \frac{d^{3N}p d^{3N}q}{h^{3N} N!} \delta(E - H(p, q)) \right]$$

This tells us everything about the system, but in general this integral is impossible (we were only able to do it for a very simple case, the ideal gas). Even if we wanted to approximate it using a Taylor expansion, we would get very frustrated with the δ -function.

Let’s go back to a canonical distribution of energy in a system connected to a reservoir separated by a diathermal wall. We can see that the total energy of the “universe” is just the sum of the system and the reservoir,

$$E_T = E + E_R$$

For such a system, we found that

$$P(E) = \frac{\Omega(E)\Omega_R(E_R)}{\Omega_T(E_T)}$$

Since we go by our maxim that the system goes to the state of maximal probability, we can just maximize the logarithm:

$$\ln P(E) = \ln \Omega(E) + \ln \Omega_R(E_T - E) - \ln \Omega_T(E_T)$$

Since the reservoir is large, we have $E \ll E_T$, so we can Taylor expand around it:

$$\ln P(E) = \ln \Omega(E) + \left[\ln \Omega_R(E_T) - \underbrace{\frac{\partial \ln \Omega_R(E_T)}{\partial E_T}}_{\frac{1}{k_B T_R} = \beta_R = \beta = \frac{1}{k_B T}} E + \mathcal{O}(E^2) \right] - \ln \Omega_T(E_T)$$

Notice that $\ln \Omega_R(E_T)$ and $\ln \Omega_T(E_T)$ don’t depend on E . We’ll put them into a new constant, $\ln Z$:

$$\ln P(E) = \ln \Omega(E) - \beta E - \ln Z$$

Now we can re-exponentiate to find

$$P(E) = \frac{1}{Z} \Omega(E) e^{-\beta E}$$

The one thing we don’t know in there is Z , but notice that $P(E)$ is a probability density, so it must be normalized. Therefore,

$$Z(T, V, N) = \int dE \Omega(E, V, N) e^{-\beta E}$$

If we want to give the proper terminology, $Z(T)$ is the “Laplace transform” of $\Omega(E)$.

Z is the “partition function”. It’s called Z after the German *Zustandssumme*, meaning “sum of states”.

Let’s do this derivation again, but in phase space. The probability of being in one particular microstate is

$$P(p, q) = \frac{\Omega_R(E_T - H(p, q))}{\Omega_T(E_T)}$$

$$\ln P(p, q) = \ln \Omega_R(E_T - H(p, q)) - \ln \Omega_T(E_T)$$

Again, if we recognize $H \ll E_T$, we can Taylor expand:

$$\ln P(p, q) = \ln \Omega_R(E_T) - \beta H(p, q) - \ln \Omega_T(E_T) + \dots = -\beta H(p, q) - \ln \tilde{Z}$$

Therefore,

$$P(p, q) = \frac{1}{\tilde{Z}} e^{-\beta H(p, q)}$$

and

$$\tilde{Z}(T, V, N) = \int d^{3N}p d^{3N}q e^{-\beta H(p, q)}$$

Notice this looks very similar to what we did before, but without any Ω functions. Notice also that there is a very obvious sum of states in \tilde{Z} in the form of an integral over all p and q . Asking the probability of finding a state with energy E is a different question than asking the probability of finding a particular state, since states can be degenerate.

Let's now link these two expressions.

$$\begin{aligned} Z(T, V, N) &= \int dE \underbrace{\Omega(E, V, N)}_{\int \frac{d^{3N}p d^{3N}q}{h^{3N}N!} \delta(E - H(p, q))} e^{-\beta E} \\ &= \int \frac{d^{3N}p d^{3N}q}{h^{3N}N!} \int dE \delta(E - H(p, q)) e^{-\beta E} \\ &= \frac{1}{h^{3N}N!} \int d^{3N}p d^{3N}q e^{-\beta H(p, q)} \\ &= \frac{1}{h^{3N}N!} \tilde{Z}(T, V, N) \end{aligned}$$

Therefore, we could write

$$P(p, q) = \frac{1}{Z h^{3N}N!} e^{-\beta H(p, q)}$$

and

$$Z(T, V, N) = \int \frac{d^{3N}p d^{3N}q}{h^{3N}N!} e^{-\beta H(p, q)}$$

This probability density on phase space is called the “canonical state”. These are probably the most important equations in classical statistical physics.