

1. **A two-state system.** Remarkably, the decomposition between system and bath (as well as our counting tools with partition functions) work equally well in a quantum setting as in a classical setting. In fact, you may even prefer thinking about partition functions for quantum mechanical objects because an integral over all possible continuous classical microstates is replaced by a sum over quantized possibilities. In this problem, we consider the simplest quantized problem: a two-state system.

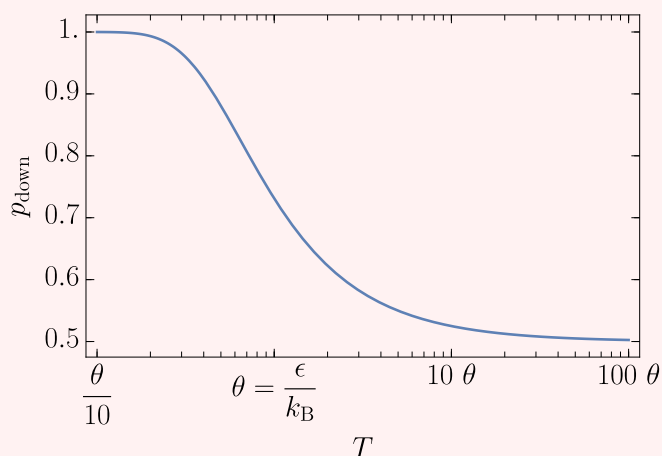
(i) In the presence of a magnetic field, a ^1H atom's nuclear spin can adopt one of two states that we call "up" or "down". We orient our field so that the nuclear spin aligns with the down state's nuclear spin. The magnetic field splits the energetic degeneracy of the up and down states, as described by the Zeeman effect. Let us call the ground state energy ϵ_0 and the excited state energy $\epsilon_0 + \epsilon$. The spin can switch between up and down states by exchanging energy with a thermal bath at temperature T . In terms of ϵ_0 , ϵ , T , and Boltzmann's constant k_B , what is the probability of the down state, p_{down} ? What is the probability of the up state, p_{up} ?

By the Boltzmann distribution, we know that $p(E) \propto e^{-\beta E}$, so we have

$$p_{\uparrow} = \frac{e^{-\beta(\epsilon_0 + \epsilon)}}{e^{-\beta(\epsilon_0)} + e^{-\beta(\epsilon_0 + \epsilon)}} = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}, \quad p_{\downarrow} = \frac{e^{-\beta\epsilon_0}}{e^{-\beta(\epsilon_0)} + e^{-\beta(\epsilon_0 + \epsilon)}} = \frac{1}{1 + e^{-\beta\epsilon}}.$$

Notice that ϵ_0 has dropped out of the probabilities—what's important is the relative difference between the energies, not the absolute energies themselves.

(ii) Plot the equilibrium probability of occupying the down (ground) state as a function of temperature. Label $\theta \equiv \epsilon/k_B$ on the x -axis. Discuss the low-temperature and high-temperature limits of p_{down} . What is the physical interpretation of θ ?



As $T \rightarrow 0$ and $\beta \rightarrow \infty$, $p_{\downarrow} \rightarrow 1$ —the thermal bath doesn't have enough energy to excite these protons into the higher-energy state. As $T \rightarrow \infty$ and $\beta \rightarrow 0$, $p_{\downarrow} \rightarrow 1/2$ —here, the thermal bath has so much energy that the minute energy difference between the two states is negligible, so the states are essentially degenerate and occupied with equal probability.

θ represents a transition temperature between these two regimes. Imprecisely, it is the temper-

ature at which a significant fraction of the protons can now access the higher-energy state.

(iii) Using your expressions for p_{up} and p_{down} , calculate the expected energy $\langle E \rangle$ in terms of ϵ_0 , ϵ , k_B and T .

$$\langle E \rangle = E_{\uparrow}P_{\uparrow} + E_{\downarrow}P_{\downarrow} = \epsilon_0 + \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}\epsilon.$$

(iv) An alternative way to compute the expected energy is to compute

$$\langle E \rangle = -\frac{\partial \ln Q(\beta)}{\partial \beta},$$

where $Q(\beta) = \sum_{\nu} e^{-\beta E(\nu)}$ is the canonical partition function and $\beta = 1/(k_B T)$. If this expression does not look familiar, look back through your old homeworks and find where you showed that it is true. The sum over ν includes all the microstates, but for the two-state spin system there are only two. Give an explicit form for $Q(\beta)$ then differentiate to confirm your answer to (iii).

In this two-state system, we simply have $Q = e^{-\beta\epsilon_0} + e^{-\beta(\epsilon_0+\epsilon)}$. Differentiating yields

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial \beta}(-\beta\epsilon_0 + \ln(1 + e^{-\beta\epsilon})) = \epsilon_0 + \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}\epsilon.$$

(v) Now assume there are N independent (non-interacting) spins. Compute $Q(\beta, N)$ for the N -spin system in terms of the 1-spin partition function $Q(\beta)$ that you found in the previous part. Use $Q(\beta, N)$ to compute $\langle E \rangle$ for the N -spin system. How does it differ from your answer in (iv)?

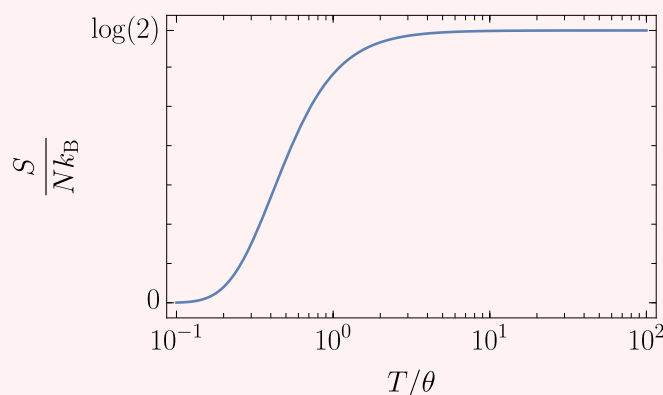
Because the spins are independent, we have $Q(\beta, N) = Q(\beta)^N$. Hence differentiating yields

$$\langle E \rangle = -\frac{\partial \ln Q(\beta, N)}{\partial \beta} = -N \frac{\partial \ln Q(\beta)}{\partial \beta} = N \langle E_{\text{one spin}} \rangle.$$

(vi) Recall that our study of statistical mechanics started by asserting that there is a function $S = k_B \ln \Omega$. It would usually be awkward to directly count the number of states Ω , so we would like to sometimes be able to compute S another way. We have shown that in the thermodynamic limit, $-\beta A = \ln Q(\beta, N)$, where $A = \langle E \rangle - TS$ is the Helmholtz free energy. Use your answers to (e) to compute S as a function of N , k_B , ϵ , and T . Plot $S/(Nk_B)$ as a function of T/θ . Briefly comment on the low-temperature and high-temperature limits (i.e., what are the limits and can they be simply explained on physical grounds?).

Rearranging the given equations yields

$$\begin{aligned}\frac{S}{k_B} &= \beta(\langle E \rangle - A) = \beta\langle E \rangle + \ln Q(\beta, N) \\ &= \beta N \left(\epsilon_0 + \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \epsilon \right) - \beta N \epsilon_0 + N \ln(1 + e^{-\beta\epsilon}) \\ &= N \left[\frac{\beta\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} + \ln(1 + e^{-\beta\epsilon}) \right].\end{aligned}$$



As $T \rightarrow 0$ and $\beta \rightarrow \infty$, we have $S \rightarrow 0$. This is sensible: at low temperatures, all the protons will be in the lowest-energy state, and there exists only one such microstate of this type. As $T \rightarrow \infty$ and $\beta \rightarrow 0$, we have $S \rightarrow Nk_B \ln 2$. This too is sensible, based on our analysis of p_\downarrow in (b). In this high-temperature limit, each proton has equal probability of being in either one of the two states, so there are 2^N microstates in all.

2. **A harmonic oscillator.** Consider a one-dimensional quantum harmonic oscillator, which has equally spaced discrete energy levels: $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots$. We assume the harmonic oscillator is in contact with a large thermal bath at temperature T .

(i) As in Problem 2, the canonical partition function is $Q(\beta) = \sum_\nu e^{-\beta E(\nu)}$, but now ν has more than two possibilities. In fact, there is an infinite number of possibilities. Use the fact that energy levels are equally spaced to compute the partition function in terms of \hbar, ω, k_B , and T . [Hint: a geometric series can be summed exactly. Also, you can leave your answers in terms of exponential functions, but you may find future parts of this problem to be easier if you simplify things in terms of the hyperbolic cosecant function.]

The canonical partition function is given by $Q = \sum_{n=0}^{\infty} e^{-\beta E_n}$, where $E_n = \hbar\omega \left(\frac{1}{2} + n\right)$ is the energy of the n^{th} level. We recognize that this sum is a geometric series.

$$Q = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega} \right)^n = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}.$$

I asked for this as a function of T , not β , which is simple enough:

$$Q(T) = \frac{\exp\left(-\frac{\hbar\omega}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} = \frac{1}{2} \operatorname{csch}\left(\frac{\hbar\omega}{2k_B T}\right).$$

You might not have recognized that the expression could be rewritten compactly in terms of the hyperbolic cosecant, which is fine. I've chosen to write it this way since it makes the differentiation that much simpler. But you could get to all the right answers if you leave everything in terms of the exponentials.

(ii) By differentiating Q appropriately, determine the average energy $\langle E \rangle$, which should also be a function of T .

Notice that $\ln Q$ is a cumulant generating function, so

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_B T}\right).$$

Or in terms of the exponentials, this would be:

$$\langle E \rangle = \frac{\hbar\omega \left(\exp\left(\frac{\hbar\omega}{2k_B T}\right) + \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \right)}{2 \left(\exp\left(\frac{\hbar\omega}{2k_B T}\right) - \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \right)}$$

It's always a good idea to check that the limiting behavior agrees with what you'd expect. When T approaches 0, you get $\langle E \rangle \rightarrow \hbar\omega/2$, the ground state energy. That's good! And when T approaches, ∞ , the average energy also diverges.

(iii) A common experiment is to measure how much energy must be put into a system to increase the temperature, the so-called heat capacity. In other words, the heat capacity measures the rate of energy increase with increasing temperature:

$$C = \frac{\partial \langle E \rangle}{\partial T}.$$

By writing $\langle E \rangle$ in terms of a derivative of $\ln Q$, demonstrate that C is related to a second derivative of $\ln Q$. Use this observation to compute both the typical size of the energy fluctuations $\langle \delta E^2 \rangle$ and the heat capacity C . Both of these quantities should be functions of the temperature.

The relationship between heat capacity and energy fluctuations is given by:

$$C = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{\partial^2 \ln q}{\partial \beta^2} \left(-\frac{1}{k_B T^2} \right) = \frac{\langle \delta E^2 \rangle}{k_B T^2}$$

Since we have the partition function q , we can take the two derivatives with respect to β to explicitly compute the energy fluctuations.

$$\langle \delta E^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln \left(\frac{1}{2} \operatorname{csch} \left(\frac{\hbar\omega\beta}{2} \right) \right) = \frac{(\hbar\omega)^2}{4} \operatorname{csch}^2 \left(\frac{\hbar\omega}{2k_B T} \right).$$

You may have done this in terms of all of the exponentials, in which case you'd have arrived at

$$\langle \delta E^2 \rangle = \left(\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{2k_B T}\right) - \exp\left(-\frac{\hbar\omega}{2k_B T}\right)} \right)^2.$$

The heat capacity C is just $k_B T^2$ times this result for $\langle \delta E^2 \rangle$.

(iv) Now imagine that the quantum harmonic oscillator is actually a three-dimensional harmonic oscillator but that the oscillations in the x , y , and z dimensions are independent. Then the single three-dimensional harmonic oscillator will behave like three one-dimensional harmonic oscillators. What will be the new values of $\langle E \rangle$, $\langle \delta E^2 \rangle$, and C for the three-dimensional oscillator. [Hint: Don't compute more than you have to! Think about how the partition functions change when you incorporate multiple *independent* components.]

The new cumulant generating function for energy will simply be $3 \ln q$, with one factor of $\ln q$ coming from each degree of freedom. As a result, the first two cumulants, $\langle E \rangle$ and $\langle \delta E^2 \rangle$, both increase by a factor of 3. Since C equals the second cumulant time $k_B T^2$, it will also increase by a factor of 3.

$$\begin{aligned}\langle E \rangle &= \frac{3\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_B T}\right) \\ \langle \delta E^2 \rangle &= \frac{3(\hbar\omega)^2}{4} \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_B T}\right) \\ C &= \frac{3k_B T^2 (\hbar\omega)^2}{4} \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_B T}\right)\end{aligned}$$

(v) Repeat your logic from (iv) to determine C for N three-dimensional harmonic oscillators. Einstein considered this as a model for vibrations of the positions of N atoms around their equilibrium positions in a crystal. At that time, measurements of heat capacity in macroscopic materials could be handled in the lab even if the single-atom vibrations could not be directly measured. By detecting how C varied with temperature T , Einstein argued that one could infer microscopic information about the nature of the vibrations. Pretty cool!

The same logic applies, but now 3 becomes $3N$.

$$\begin{aligned}\langle E \rangle &= \frac{3N\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2k_B T}\right) \\ \langle \delta E^2 \rangle &= \frac{3N(\hbar\omega)^2}{4} \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_B T}\right) \\ C &= \frac{3Nk_B T^2 (\hbar\omega)^2}{4} \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_B T}\right)\end{aligned}$$

3. **Practice connecting partition functions to thermodynamic potentials.** Consider an isothermal-isobaric ensemble of microstates in which both energy and volume are allowed to fluctuate but the number of particles N is fixed.

(i) Following our development of the canonical ensemble in lecture, determine the probability distribution $P(\nu)$ and partition function $\zeta(\beta, \beta p, N)$ for this ensemble.

Now we let the system exchange energy and volume with the surroundings:

$$E_T = E(\nu) + E_B(\nu_B) \quad \text{and} \quad V_T = V(\nu) + V_B(\nu_B).$$

The probability of microstate ν is thus determined from the multiplicity of the bath:

$$P(\nu) \propto \Omega_B(E_T - E(\nu), V_T - V(\nu)).$$

By Taylor expanding $\ln P(\nu)$ for small $E(\nu)$ and small $V(\nu)$, we get

$$\ln P(\nu) = \text{const} - E \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B} - V \left(\frac{\partial \ln \Omega_B}{\partial V_B} \right)_{E_B, N_B} = \text{const} - \beta E - \beta p V.$$

Hence

$$P(\nu) \propto e^{-\beta E(\nu) - \beta p V(\nu)}.$$

This distribution is normalized by the partition function

$$\zeta(\beta, \beta p, N) = \sum_{\nu} e^{-\beta E(\nu) - \beta p V(\nu)}.$$

(ii) By grouping together microstates with the same volume, the isothermal-isobaric partition function can be written in the form

$$\zeta = \sum_V (\dots) \tag{1}$$

Identify the summand that belongs in this expression.

$$\begin{aligned} \zeta(\beta, \beta p, N) &= \sum_{\nu} e^{-\beta E(\nu) - \beta p V(\nu)} \\ &= \sum_V e^{-\beta p V} \sum_{\nu \text{ with } V(\nu)=V} e^{-\beta E(\nu)} \\ &= \sum_V e^{-\beta p V} Q(N, V, \beta) \end{aligned}$$

(iii) For a macroscopic system, the sum in Eq. (1) is overwhelmingly dominated by the contribution from a single value V^* of the volume. Exploiting this fact, determine a relationship between $\ln \zeta$ and basic thermodynamic quantities. Could your answer have been easily anticipated? Explain.

$$\begin{aligned}
\ln \zeta(\beta, \beta p, N) &= \ln \sum_V e^{-\beta p V} Q(N, V, \beta) \\
&\approx \ln e^{-\beta p V^*} Q(N, V^*, \beta) \\
&= -\beta p V^* + \ln Q(N, V^*, \beta) \\
&= -\beta p V^* - \beta A(N, V^*, \beta) \\
&= -\beta(p V^* + A(N, V^*, \beta)) \\
&= -\beta G(\beta, \beta p, N),
\end{aligned}$$

where we have used $\ln Q(N, V, \beta) = -\beta A(N, V, \beta)$. Notice that the log of the partition function ζ is $-\beta$ times the free energy for the ensemble, in this case the Gibbs free energy since we are holding p, T , and N fixed. The pattern is general, so the result could be anticipated.

(iv) Compute the derivative $(\partial \ln \zeta / \partial(\beta p))_{\beta, N}$. Using this result, verify the relationship you determined in part (iii).

$$\begin{aligned}
\left(\frac{\partial \ln \zeta}{\partial(\beta p)} \right)_{\beta, N} &= \frac{\partial}{\partial(\beta p)} \ln \left[\sum_V Q(N, V, \beta) e^{-\beta p V} \right] \\
&= -\frac{1}{\zeta} \sum_{\nu} V(\nu) e^{-\beta p V(\nu) - \beta E(\nu)} \\
&= -\langle V \rangle.
\end{aligned}$$

Note that $dG = V dp - S dT + \mu dN$, so

$$V = \left(\frac{\partial G}{\partial p} \right)_{T, N} = -k_B T \left(\frac{\partial \ln \zeta}{\partial p} \right)_{T, N} = -k_B T (-\beta \langle V \rangle) = \langle V \rangle.$$

Hence the equality in (iii) is consistent.

(v) Compute the derivative $(\partial^2 \ln \zeta / \partial(\beta p)^2)_{\beta, N}$. Using this result, derive a relationship between mean square volume fluctuations $\langle \delta V^2 \rangle$ (where $\delta V = V - \langle V \rangle$) and the isothermal compressibility $\kappa_T = -V^{-1}(\partial V / \partial p)_{T, N}$.

First note that

$$\left(\frac{\partial^2 \ln \zeta}{\partial(\beta p)^2} \right)_{\beta, N} = \langle \delta V^2 \rangle$$

because $\ln \zeta$ is a cumulant generating function for V . Like we did for studying heat capacity, we can relate this second derivative to a “susceptibility” that records how susceptible the mean is to change in response to a change in the intensive variable. In this case that susceptibility is the isothermal compressibility, which records by how much the volume changes in response to

a change in pressure.

$$\langle \delta V^2 \rangle = \frac{\partial}{\partial \beta p} \left(\frac{\partial \ln \zeta}{\partial (\beta p)} \right)_{\beta, N} = - \left(\frac{\partial}{\partial \beta p} \langle V \rangle \right)_{\beta, N} = -k_B T \left(\frac{\partial \langle V \rangle}{\partial p} \right)_{\beta, N} = k_B T V \kappa_T.$$

Thus

$$\kappa_T = \frac{\beta}{V} \langle \delta V^2 \rangle.$$