"[The Boltzmann distribution] is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived." —Richard Feynman

1. **The climb up.** In class we presented a reasonable but less than rigorous derivation of the Boltzmann distribution,

$$P(\nu) \propto e^{-\beta E(\nu)},$$

for microstates ν of a system that can exchange energy with a very large bath. This result was obtained from the fundamental relationship

$$P(\nu) \propto \Omega_{\mathrm{B}}(E_{\mathrm{T}} - E(\nu))$$

through a Taylor expansion of $\ln \Omega_{\mathrm{B}}$, where E_{T} denotes the total energy shared by system and bath, and $\Omega_{\mathrm{B}}(E_{\mathrm{B}})$ is the number of bath microstates with energy E_{B}. Here you will develop this argument a little more carefully (and perhaps a little more convincingly—you may have wondered, for example, why we were Taylor expanding $\ln \Omega_{\mathrm{B}}$ and not Ω_{B}).

We will assume that Ω_{B} has a large deviation form,

$$\Omega_{\mathrm{B}} = [\omega_{\mathrm{B}}(\epsilon_{\mathrm{B}})]^{N_{\mathrm{B}}},$$

where N_{B} is the number of molecules in the bath, $\epsilon_{\mathrm{B}} \equiv E_{\mathrm{B}}/N_{\mathrm{B}}$ is the corresponding energy per molecule, and $\omega_{\mathrm{B}}(\epsilon_{\mathrm{B}})$ is a smooth function that does not depend on the size of the bath. As in lecture the dependence of Ω_{B} on E_{B} will be used to define a property β of the bath:

$$\beta \equiv \left(\frac{\partial \ln \Omega_{\mathrm{B}}}{\partial E_{\mathrm{B}}} \right)_{N_{\mathrm{B}}, V_{\mathrm{B}}}$$

(i) Show that β is insensitive to the extent of the bath. In particular, relate β to ω_{B} and derivatives of ω_{B} with respect to ϵ_{B}. Explain why this relationship indicates independence of the bath's size. (Since we saw in lecture that this β is an inverse temperature, it should be pleasing that it doesn't depend on bath size. When I say to put a test tube in a 25° C water bath, I shouldn't have to specify if the bath is 1 liter or 2 liters in volume. Assuming the volume of the bath is very big compared to the system, I should be able to specify β alone.)

(ii) Show that

$$\left(\frac{\partial \Omega_{\mathrm{B}}}{\partial E_{\mathrm{B}}} \right)_{N_{\mathrm{B}}, V_{\mathrm{B}}} = \beta \Omega_{\mathrm{B}}$$

(iii) Show that

$$\left(\frac{\partial^2 \Omega_{\mathrm{B}}}{\partial E_{\mathrm{B}}^2} \right)_{N_{\mathrm{B}}, V_{\mathrm{B}}} = \beta^2 \Omega_{\mathrm{B}} + c.$$

Identify the quantity c and explain why it can be neglected in the limit $N_{\mathrm{B}} \to \infty$.

(iv) Calculate

$$\left(\frac{\partial^n \Omega_{\mathrm{B}}}{\partial E_{\mathrm{B}}^n} \right)_{N_{\mathrm{B}}, V_{\mathrm{B}}}$$

for arbitrary (integer) n. Do not include any terms that are negligible in the limit $N_B \to \infty$.

(v) Consider the Taylor expansion

$$
\begin{aligned}
\Omega_B(E_T - E) &= \Omega_B(E_T) - E\left(\frac{\partial \Omega_B}{\partial E_B}\right)_{N_B, V_B} + \frac{1}{2}E^2\left(\frac{\partial^2 \Omega_B}{\partial E_B^2}\right)_{N_B, V_B} + \dots \\
&= \sum_{n=0}^{\infty} \frac{1}{n!}(-E)^n\left(\frac{\partial^n \Omega_B}{\partial E_B^n}\right)_{N_B, V_B},
\end{aligned}
$$

where all partial derivatives are implicitly evaluated at $E = 0$.

Combining your results together with this expansion, show that the relationship

$$
\Omega_B(E_T - E(\nu)) \propto e^{-\beta E(\nu)}
$$

is exact in the limit $N_B \to \infty$ of an infinitely large bath.

2. **The slide down.** Remarkably, the decomposition between system and bath (as well as our counting tools with cumulant generating functions) work equally well in a quantum setting as a classical setting. Consider a one-dimensional quantum harmonic oscillator, which has equally spaced discrete energy levels: $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega \dots$. (Warning: this ω has nothing to do with what we were calling ω in Problem 1, but the notation is reasonably standard in both cases. I'm sticking with it despite the possibility for confusion.) We assume the harmonic oscillator is in contact with a large thermal bath at temperature T.

(i) We have seen that the cumulant generating function for fluctuations in a variable X takes the form $Z(\beta) = \langle e^{-\beta X}\rangle$, where $Z(\beta)$ can also be viewed as the normalization constant of the probability distribution with $P(X) \propto e^{-\beta X}$. The Boltzmann distribution physically gives us such an exponentially biased probability distribution—we expect to measure the various quantized energies with $P(E) \propto e^{-\beta E}$. Out of convention, let us use q to denote the moment generating function for the energy fluctuations (the canonical partition function). Find q as a function of T. [Hint: a geometric series can be summed exactly.]

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

(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.

(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 cumulant generating functions change when you incorporate multiple *independent* components.]

(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!