

- **D: Adiabatic Compression from volume V_4 to volume V_1 .** During this process, the temperature of the gas increases from T_c back to T_h . Analogously to step B, we find the work done on this leg to be:

$$W_D = -\Delta U = -\frac{f}{2}Nk(T_h - T_c) < 0.$$

The gas does work on the piston.

The total work done in one cycle of the Carnot Engine's operation is the sum $W_A + W_B + W_C + W_D$. After a bit of algebra, you can find

$$W_T = -Nk \left[T_h \log \left(\frac{V_2}{V_1} \right) + T_c \log \left(\frac{V_4}{V_3} \right) \right]$$

. Now the adiabatic relations appropriate for steps B and D are:

$$\begin{aligned} T_h V_2^{\gamma-1} &= T_c V_3^{\gamma-1} \\ T_c V_4^{\gamma-1} &= T_h V_1^{\gamma-1} \end{aligned}$$

These imply the relation $(V_1/V_2) = (V_4/V_3)$ which allows us to simplify the total work expression:

$$W_T = -Nk \log \left(\frac{V_2}{V_1} \right) (T_h - T_c) < 0.$$

The gas does work on the piston!

14 Free Energy and Thermodynamic Potentials

Notes not available.

15 Boltzmann Factor and the Partition Function

Ω is too hard to calculate for all but a handful of systems. I'm sure there are others for which one can straightforwardly find Ω , but I only know of the ones we've worked with: the ideal gas, the two-state paramagnet, the isolated H-atom, and the quantum harmonic oscillator. So, if we didn't have another approach to statistical mechanics, we would have no fundamental insights into most systems. We would only be able to operate at the "chemistry level" of measuring enthalpies and extrapolating entropies and specific heats. etc. As physicists, we'd like to be able to calculate S from first principles for all systems. Fortunately there is an alternative to starting with the multiplicity function. It is the *partition function*.

Question: What is the probability of finding a system in a given macrostate when the system is in thermal equilibrium with a reservoir at temperature T and total energy U_0 ?

Answer: One of the most difficult derivations in physics. However, we can heuristically arrive at the correct answer: For concreteness, take the system to be an atom with discrete energy states E_n . Let $P(E_1)$ be the probability that the atom is in state E_1 , and $P(E_2)$ be the probability that the atom is in state E_2 . Now, $P(E_1)/P(E_2) = \Omega_1/\Omega_2$. Since, $S = k \log \Omega$, we have $\Omega_n = \exp(S_n/k)$. The entropy of the atom is the entropy of the reservoir S_R at energy $U_0 - E_n$. The ratio of probabilities is then

$$\frac{P(E_1)}{P(E_2)} = \frac{e^{S_R(U_0-E_1)/k}}{e^{S_R(U_0-E_2)/k}} = \frac{e^{S_R^{(1)}/k}}{e^{S_R^{(2)}/k}}$$

If the reservoir's temperature is constant, as the atom exchanges small amounts of heat with it, then $dS_R = -dU/T$, so we have the important result that the ratio of probabilities of the atom being in the states E_1 and E_2 is

$$\frac{P(E_1)}{P(E_2)} = e^{-(E_1-E_2)/kT}$$

What about the absolute probability of the atom being in state E_1 . Clearly the *relative* probability is $e^{-E_1/kT}$, so to find the absolute probability of being in that state, I'd want to normalize by the sum of all the relative probabilities:

$$P(E_1) = \frac{e^{-E_1/kT}}{\sum_n e^{-E_n/kT}}$$

Definitions: The relative probability $e^{-E_n/kT}$ is called the *Boltzmann Factor*. The sum over all relative probabilities is called the *Partition Function*, Z . The probability of a system being in state E_n is then

$$P(E_n) = \frac{1}{Z} e^{-E_n/kT}$$

Average Values: For a function $f(x)$ with probability distribution $P(x)$, the average value of the function, $\langle f \rangle$ will be given by

$$\langle f \rangle = \sum_n f(x_n) P(x_n) = \frac{1}{Z} \sum_n f(x_n) e^{-\beta E_n}$$

where $\beta \equiv 1/kT$.

Example: Quantum Harmonic Oscillator: Recall that the microscopic energy of an individual QHO is given by $E_n = \frac{1}{2}\hbar\omega + n\hbar\omega$. The partition function for this system is then

$$Z_{QHO} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}.$$

Let's define $x \equiv \beta\hbar\omega$, so that

$$Z = e^{-x/2} \sum_{n=0}^{\infty} e^{-nx}$$

. That sum should look familiar. It can be shown that it has the closed form expression

$$\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}}.$$

. Making use of the observation that $\sinh x \equiv (e^x - e^{-x})/2$, we find

$$Z = \frac{1}{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

The temperature dependence of the total energy can be found using the relation for the average or expectation value of a function:

$$\begin{aligned} Z \langle U \rangle &= \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar\omega e^{-\beta(n+\frac{1}{2})\hbar\omega} \\ &= \left[\sum_{n=0}^{\infty} n\hbar\omega e^{-\beta n\hbar\omega} + \sum_{n=0}^{\infty} \frac{1}{2} \hbar\omega e^{-\beta n\hbar\omega} \right] e^{-\beta\hbar\omega/2} \\ &= \frac{x}{2\beta} e^{-x/2} \left[2 \sum_{n=0}^{\infty} n e^{-nx} + \sum_{n=0}^{\infty} e^{-nx} \right] \\ &= \frac{x}{2\beta} e^{-x/2} \left[\frac{1 + e^{-x}}{(1 - e^{-x})^2} \right]. \end{aligned}$$

In the last step, I used the following useful trick:

$$\begin{aligned} \frac{d}{dx} \sum_{n=0}^{\infty} e^{-nx} &= - \sum_{n=0}^{\infty} n e^{-nx} \\ \Rightarrow \sum_{n=0}^{\infty} n e^{-nx} &= - \frac{d}{dx} \frac{1}{1 - e^{-x}} = \frac{1}{(1 - e^{-x})^2} \end{aligned}$$

Dividing by Z , we find the total internal energy $\langle U \rangle = U$ to be

$$U_{QHO} = \frac{\hbar\omega}{2} \frac{e^{\beta\hbar\omega} + 1}{e^{\beta\hbar\omega} - 1}$$

High Temperature Approximation At high temperature $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega + O(\beta\hbar\omega)^2$. Applying this expansion to the numerator and denominator, we find that the high temperature behavior of the total internal

energy U is linear in T : $U(kT \gg \hbar\omega) \approx kT$. **Heat Capacity of the QHO** To calculate the heat capacity of an Einstein Solid consisting of N QHO's, we follow the prescription $C_V = (\partial U / \partial T)_V$:

$$\begin{aligned} C_V = \left(\frac{\partial U}{\partial T} \right)_V &= \frac{\partial \beta}{\partial T} \left(\frac{\partial U}{\partial \beta} \right)_V \\ &= -Nk\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_V \\ &= -Nk\beta^2 (\hbar\omega)^2 \left[\frac{-e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \right] \\ &= Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \end{aligned}$$

You should verify that the low temperature behavior of the heat capacity is

$$C_V \propto \frac{1}{T^2} e^{-\hbar\omega/kT}.$$

A Useful Relation For any system with microscopic energy spectrum $E(s)$ there is a useful relation for calculating the total energy U . Notice that $\partial Z / \partial \beta = -\sum_s E(s) e^{-\beta E(s)} = -Z \langle U \rangle$. The handy result is then:

$$\langle U \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Another Example: Two-state paramagnet For a two-state paramagnet with microscopic energy spectrum given by $E(s) = (-\mu B, +\mu B)$, the partition function is:

$$Z = \sum_s e^{\beta E(s)} = e^{\beta\mu B} + e^{-\beta\mu B} = 2 \cosh(\beta\mu B).$$

Using the relation for U above, we find the temperature dependence of the total energy to be:

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\mu B \tanh(\beta\mu B)$$

The magnetization is $M = -U/B = \mu \tanh(\beta\mu B)$. What is the probability of the paramagnet being in the energy state $-\mu B$? $P(-\mu B) = (1/Z) e^{\beta\mu B} =$

These results are the same as we found earlier using the much more calculation-intensive process based on the multiplicity function Ω .