- **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, $< f >$ will be given by

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

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:

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

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 $< U >= U$ 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: $U(kT >> \hbar\omega) \approx kT$. **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 $\partial Z/\partial\beta = -\sum_s E(s)e^{-\beta E(s)} = -Z < U >$. The handy result is then:

$$< U >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

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 $-\mu B$? $P(-\mu B) = (1/Z)e^{\beta\mu B} = (1 + e^{-2\beta\mu B})^{-1}$

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

Hydrogen Atom: The energy levels in the hydrogen atom are given by $E_n = -K/n^2$ where $K = 13.6$ eV is the Rydberg constant. The full quantum state of the hydrogen atom is determined by the set of quantum number (n, l, m) where $n = 1, 2, 3, \ldots$ is the principle quantum number, $l = 0, 1, 2, \ldots, n-1$ is the orbital angular momentum quantum number, and $m = -l, -l+1, \ldots, l$ is the spin quantum number. For each value of n there are n^2 pairs of allowed (l, m) so, we say the energy level degeneracy in the hydrogen atom is $g(n) = n^2$. For degenerate systems, each quantum state contributes to the partition function according to

$$Z = \sum_s g(s)e^{-\beta E(s)}$$

For the hydrogen atom, we have $Z = \sum_n n^2 e^{+\beta K/n^2}$. It is easy to show that this sum does not converge. The explanation is a bit subtle, but can be understood in the following two ways.

Practical explanation: The difference between ionization energy and the energy of the hydrogen atom in the nth state is $13.6/n^2$ eV. This energy difference is tiny for $n > 10$ or so. A hydrogen atom in the $n = 10$ state is going to be ionized by thermal fluctuations at most relevant temperatures. So, from a practical perspective, the hydrogen partition function need not include terms past $n = 10$ or so.

More subtle explanation: The radius of the nth hydrogen orbit scales as n^2. Beyond $n = 10^3$ or so, the radius of the hydrogen atom, $r_n = n^2 a_0$ ($a_0 = 0.5 \times 10^{-10} m$) approaches macroscopic size. At $n = 10^4$, the hydrogen atom is a centimeter in diameter. The correspondence principle requires that quantum laws of motion give way to classical laws of motion so that it is not valid to carry out the partition sum over the energy levels $E_n = -K/n^2$ into the classical regime.

Rotation of Diatomic Molecules The text considers the rotational partition function Z_{rot} for diatomic molecules. First consider molecules with distinguishable (different) atoms such as CO, HCl, etc. Rotational energies for these systems are given by $E(j) = j(j+1)\epsilon$ where$j = 0, 1, 2, \ldots$ is the rotational quantum number and ϵ is a constant with units of energy. The degeneracy of these levels is $g(j) = 2j+1$. The partition function for a rotational system is thus

$$Z_{\text{rot}} = \sum_{j=0} (2j+1)e^{-\beta\epsilon j(j+1)}.$$

When the rotational energy level spacing is much smaller than the thermal energy scale kT, we can replace the sum above with an integral by treating the rotational quantum number j as a continuous variable:

$$Z_{\text{rot}} \approx \int_0^\infty (2j+1)e^{-\beta\epsilon j(j+1)}dj.$$

A variable substitution $x \equiv j(j+1)\epsilon\beta$ yields

$$Z_{\text{rot}} \approx \frac{1}{\epsilon\beta}\int_0^\infty e^{-x}dx = \frac{kT}{\epsilon}$$

for $kT >> \epsilon$. Average rotational energies are easily obtained in this high temperature limit:

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = 1/\beta = kT$$

for $kT >> \epsilon$.

If the atoms are identical, rotations of π produce identical states so the partition function over counts by a factor of 2, and the correct high temperature rotational partition function for diatomic molecules like H_2 and O_2 is $Z_{\text{rot}} = kT/2\epsilon$.

Equipartition

Here we show that the equipartition theorem comes directly out of the partition function for a free particle. The equipartition theorem tells us that each degree of freedom that appears quadratically in the total energy of a particle in thermal equilibrium with its environment contributes an average energy $kT/2$ to the particle's total average energy.

The free particle of mass m has the classical energy $E = p^2/2m$. The partition function is

$$Z_f = \frac{1}{h^3}\int d^3\vec{r}\int d^3\vec{p}e^{-\beta p^2/2m}. \tag{74}$$

The spatial part is easily integrated to get the (arbitrary) total volume, V. What remains is a product of three Gaussian integrals:

$$\begin{aligned} Z_f = \frac{V}{h^3}\left(\int dpe^{-\beta p^2/2m}\right)^3 &= V\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 \\ &= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \\ &= \frac{V}{V_Q}, \end{aligned}$$

where V_Q is the "quantum volume" $(h^2/2\pi mkT)^{3/2}$. The free particle partition function is expressed as the ratio of the physical (arbitrary) volume to a volume that can be interpreted as the box with dimensions equal to the deBroglie wavelength of the particle.

16 Maxwell Speed Distribution

The Maxwell distribution describes the relative probabilities for particle velocities in a gas. The text derives the distribution function $D(v)$ which defines the relative probability of finding a molecule in the gas with a particular speed v. Important points about $D(v)$:

- The actual value of $D(v)$ at any point has no particular meaning. "Its purpose in life is to be integrated" in the sense that a the absolute probability of finding a molecule in the gas with speed between v_1 and v_2 is

$$P(v_1...v_2) = \int_{v_1}^{v_2} D(v)dv \tag{75}$$

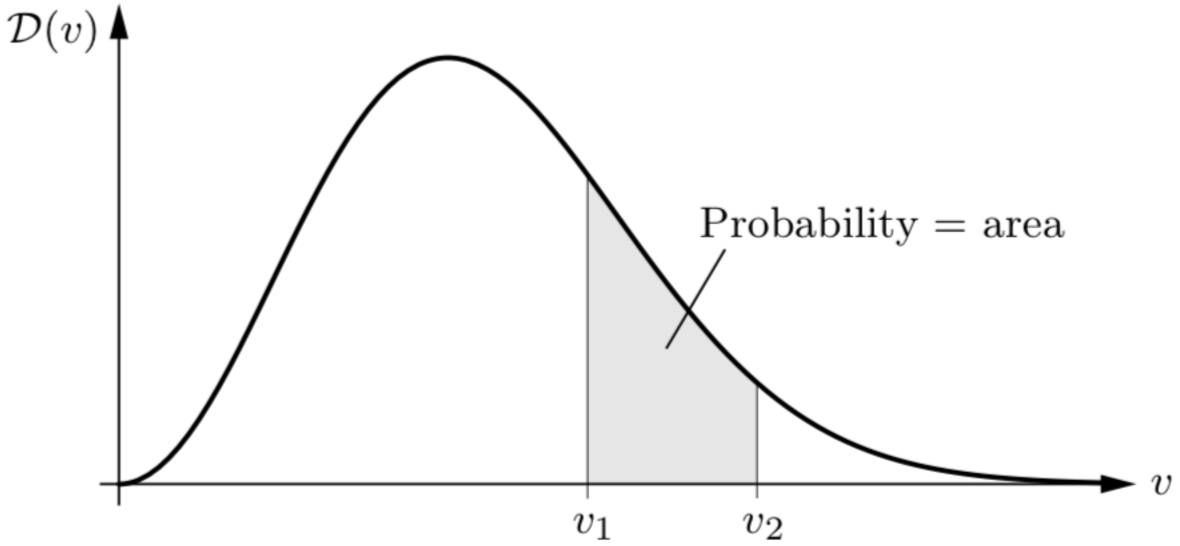

Figure 7: **Maxwell Distribution** $D(v)$

- The derivation of $D(v)$ in the text for a gas of particles with mass m in three dimensions results in

$$D(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}. \tag{76}$$

There are three important quantities that can be obtained from the Maxwell Distribution:

1. The most probable speed (obtained by maximizing $D(v)$): $v_{max} = \sqrt{2kT/m}$.
2. The average speed, obtained from $\bar{v} = \int vD(v)dv = \sqrt{8kT/\pi m}$.
3. The root-mean-square speed, obtained from $\sqrt{\bar{v^2}} = \sqrt{\int v^2 D(v)dv} = \sqrt{3kT/m}$.

Notice that the absolute probability of finding a molecule in the gas with a specific speed is identically zero. It only makes sense to talk about finding a molecule with a speed within a range of speeds bounded by v_1 and $v_2 \neq v_1$.

Example: Atmospheric helium. We can easily calculate the rms-speeds of helium atoms in the troposphere. The mass of a helium atom is 4 amu = $6.68 \times 10^{-27} kg$. The temperature of the troposphere ranges between 17° and -50°.

- What is the rms speed of helium at the top of the troposphere? Answer: $v_{rms} = \sqrt{3kT/m} = 1264$ m/s.
- What fraction of helium atoms at the top of the troposphere have speeds greater than the escape speed for the earth (11.2 km/s)? Answer: The probability of finding a helium atom with speeds greater than 1264 m/s is

$$P(v > 1.12 \times 10^4 m/s) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_{1.12\times 10^4 m/s}^{\infty} v^2 e^{-mv^2/2kT}.$$

It's convenient to use the variable transformation $x = v\sqrt{m/2kT} = v/v_{max}$ (note $v_{max} = \sqrt{2/3}v_{rms}$):

$$4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^{3/2} \int_{x_{min}}^{\infty} x^2 e^{-x^2} dx = \frac{4}{\sqrt{\pi}} \int_{x_{min}}^{\infty} x^2 e^{-x^2} dx,$$

where the lower limit is the value of x when $v = 1.12 \times 10^4$ m/s: $x_{min} = 10.85$. We find

$$P(v > 1.12 \times 10^4 m/s) \approx 0.00619$$

or about 0.62% of the helium molecules in lower atmosphere have speeds sufficient to escape.

Of course, the mean free path in the lower atmosphere is quite small which further limits the probability of escaping entirely from the earth. A better place to do these calculations is in the exosphere where atoms with sufficient speeds are unlikely to collide with anything and so will escape if their speeds exceed escape speed. You should redo this calculation for the exosphere where the average temperature is around 1800K.

17 Partition Functions and Free Energy

A quick review of the four thermodynamic potentials:

- Total Internal Energy U is the energy of the thermal motions and internal states of the system.
- Enthalpy $H = U + PV$ is the energy recovered when you annihilate a system of volume V and total internal energy U. The extra bit of energy PV comes from the work done by the collapsing atmosphere at pressure P as it fills the space once occupied by the system.
- Helmholtz Free Energy $F = U - TS$ is the total work you can extract when you annihilate a system with total internal energy U in an environment at temperature T. The free energy is less than the internal energy of the system because you need to dump some heat, equal to TS into the environment in order to get rid of the system's entropy. So F is the *available* or *free* energy.
- Gibbs Free Energy $G = H - TS$ is the work you can extract when you annihilate a system with total internal energy U in an environment at temperature T and constant pressure P.

See Ch. 5 for applications of these potentials. H and G are mostly useful when treating chemical reactions in an atmosphere at constant temperature and pressure. The Helmholtz free energy F is mostly used for atomic physics problems and other applications in which an atmosphere is not present or is not important to the dynamics of the problem.

Here we'll connect the Free Energy F to the partition function and derive some relations that will allow us to use F to compute the thermodynamic properties of an arbitrary system.

In analogy with the derivation of the Boltzmann Factor and the partition function, the text argues (not quite derives) the relationship between Z and F:

$$F = -kT \ln Z$$

The thermodynamic properties are obtained from the following relations: $S = -(\partial F/\partial T)|_{V,N}$, $P = -(\partial F/\partial V)|_{T,N}$, $\mu = -(\partial F/\partial N)|_{T,V}$. You should be able to compute the entropy for the QHO from this approach (Prob. 6.42). It's also worth reviewing the Carnot Cycle. We derived the total work done in a Carnot cycle and it's straightforward to show that the change in the free energy ΔF around the Carnot cycle is related to the work done in the cycle according to $W_T \leq \Delta F$. This result shows that F is indeed the maximum work obtainable in a process in which the final temperatures and volumes are the same as the initial temperatures and volumes.

18 Partition Functions for Composite System

For N indistinguishable particles, the partition function for the system is

$$Z = \frac{1}{N!} Z_1^N$$

where Z_1 is the partition function for a single particle in the system. If we specialize to consider the system to be an ideal gas of indistinguishable molecules and allow these molecules to have energy in translational, rotational, and internal modes, we can write the single particle partition function as

$$Z_1 = e^{-\beta E_T}.$$

Here, E_T, the total energy might be written as $E_T = E_{trans} + E_{rot} + E_{vib} + E_{electronic} + E_{nuclear}$ where each successive energy is much larger than the previous term:

$$E_{trans} < E_{rot} < E_{vib} << E_{electronic} << E_{nuclear}.$$

Let's label the non-translational energy states as internal energies:

$$E_{int} = E_{rot} + E_{vib} + E_{electronic} + E_{nuclear}.$$

We then have

$$Z_1 = e^{-\beta E_{trans}} e^{-\beta E_{int}} = Z_{trans} Z_{int}.$$

We could further break down $Z_{int} = Z_{rot} Z_{vib} Z_{electronic} Z_{nuclear}$. In practice, because the electronic and nuclear energies are so high, the exponential terms for these energies are all close to 1, so the partition functions $Z_{electronic} Z_{nuclear} \approx 1$.

Back to Z_{trans}: The book computes this partition function for a molecule in a volume V and finds $Z_{trans} = V/v_Q$ where v_Q is the "quantum volume" and is

$$v_Q = \left(\frac{h}{\sqrt{2\pi m}} \right)^3 \beta^{3/2}.$$

We then have

$$Z_N = \frac{1}{N!} \left(\frac{V Z_{int}}{v_Q} \right)^N.$$

There is no need to specify Z_{int} yet. We can go quite far without referencing a specific internal energy distribution. To compute the thermodynamic properties of the system, we use our usual tricks:

$$U = -\frac{\partial \ln Z}{\partial \beta} = U_{int} + \frac{3}{2} NkT.$$

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} Nk + \frac{\partial U_{int}}{\partial T}.$$

The Free energy is similarly straightforward:

$$F = -kT \ln Z = -NkT[\ln V - \ln N - \ln v_Q + 1] - NkT \ln Z_{int}.$$

The last term in the expression for F can be summarized as $F_{int} = -NkT \ln Z_{int}$. The pressure $P = -(\partial P/\partial V)|_{T,N} = NkT/V$. Only the entropy and the chemical potential depend on the internal energies:

$$S = -\left(\frac{\partial F}{\partial T} \right) |_{V,N} = Nk \left[\ln \left(\frac{V}{N v_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{int}}{\partial T}$$

and

$$\mu = \left(\frac{\partial F}{\partial N} \right) |_{T,V} = -kT \ln \left(\frac{V Z_{int}}{N v_Q} \right).$$