PHY141 Lectures 22,23 notes

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6 Summary **39**

1 A system in contact with a thermal reservoir and the Boltzmann factor

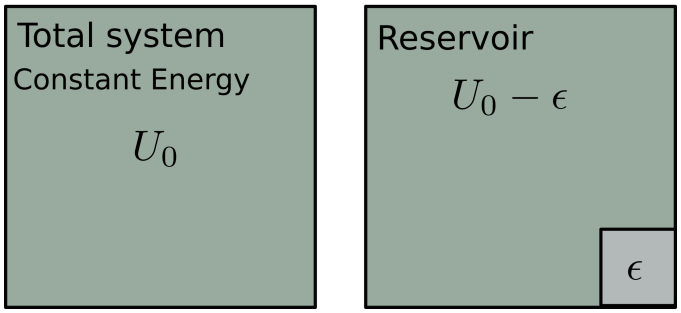

Figure 1: A thermal reservoir is much larger than a small subsystem that is in thermal contact with it. The total energy is conserved. The subsystem is in a particular state with energy ϵ. The total energy in the reservoir $U_{\mathcal{R}} = U_0 - \epsilon$. We assume the reservoir is large so $U_0 \gg \epsilon$. The reservoir is in equilibrium and has temperature T.

Suppose we have a small system $\mathcal{S}$ and it is contact with a big system which we call a thermal reservoir $\mathcal{R}$. What is the probability that the small system $\mathcal{S}$ is in a **particular** state with energy ϵ_s? The number of states accessible to $\mathcal{R} + \mathcal{S}$ is

$$g_{\mathcal{R}} \times 1 = g_{\mathcal{R}}$$

because we specify a specific state for $\mathcal{S}$. If the total energy is U_0 then the energy of the reservoir must be $U_{\mathcal{R}} = U_0 - \epsilon_s$.

The ratio of the probability for the system $\mathcal{S}$ to be in state with energy ϵ_1 compared to one with energy ϵ_2 depends on the ratio of the multiplicities of the reservoir

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g_{\mathcal{R}}(U_0 - \epsilon_1)}{g_{\mathcal{R}}(U_0 - \epsilon_2)}. \tag{1}$$

If the reservoir is large then these multiplicities are large. Recall that entropy $\sigma = \ln g$ or $g = e^{\sigma}$. We write the probability ratio in terms of the entropies

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp \sigma_{\mathcal{R}}(U_0 - \epsilon_1)}{\exp \sigma_{\mathcal{R}}(U_0 - \epsilon_2)} = \exp\left[\sigma_{\mathcal{R}}(U_0 - \epsilon_1) - \sigma_{\mathcal{R}}(U_0 - \epsilon_2)\right] \tag{2}$$

This depends on the change in reservoir entropy

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \exp \Delta\sigma_{\mathcal{R}} \tag{3}$$

with

$$\Delta\sigma_{\mathcal{R}} = \sigma_{\mathcal{R}}(U_0 - \epsilon_1) - \sigma_{\mathcal{R}}(U_0 - \epsilon_2). \tag{4}$$

If the reservoir is very large then the change in entropy of the reservoir is small. Furthermore $U_0 \gg \epsilon_1, \epsilon_2$. Recall a Taylor series

$$f(x_0 + \delta) = f(x_0) + f'(x_0)\delta + ...$$

Let's expand the entropy function

$$\sigma(U_0 - \epsilon) \approx \sigma(U_0) - \frac{d\sigma}{dU}\epsilon + ...$$

We recognize

$$\frac{d\sigma}{dU} = \frac{1}{k_B T}$$

Using this,

$$\sigma_{\mathcal{R}}(U_0 - \epsilon_1) \approx \sigma_{\mathcal{R}}(U_0) - \frac{\epsilon_1}{k_B T}$$
$$\sigma_{\mathcal{R}}(U_0 - \epsilon_2) \approx \sigma_{\mathcal{R}}(U_0) - \frac{\epsilon_2}{k_B T}$$

$$\begin{aligned} \Delta\sigma_{\mathcal{R}} &= \sigma_{\mathcal{R}}(U_0 - \epsilon_1) - \sigma_{\mathcal{R}}(U_0 - \epsilon_2) \\ &= -\frac{\epsilon_1}{k_B T} + \frac{\epsilon_2}{k_B T} \end{aligned} \tag{5}$$

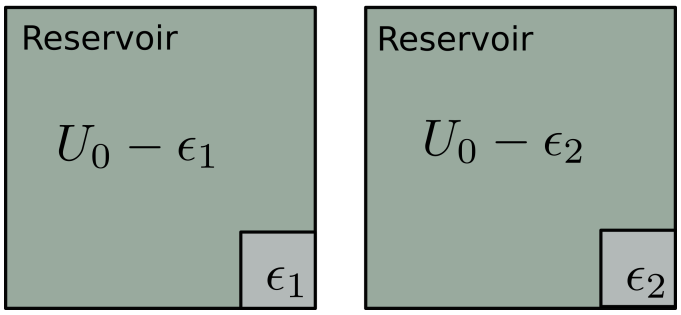

Figure 2: The probability that the subsystem $\mathcal{S}$ is in a particular state with energy ϵ_1 is compared to the probability that the subsystem $\mathcal{S}$ is in a particular state with energy ϵ_2. The total energy U_0 of thermal reservoir plus subsystem is constant.

We put this back into our equation for the probability ratio (equation 2)

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp(-\frac{\epsilon_1}{k_B T})}{\exp(-\frac{\epsilon_2}{k_B T})}. \tag{6}$$

The factor

$$e^{-\frac{\epsilon}{k_B T}}$$

is known as the **Boltzmann factor** and it is proportional to the probability that a system at temperature T is in a state with energy ϵ. This is true for any energy state.

When discussing a small system in contact with a thermal reservoir, the setting is sometimes called the **canonical ensemble**.

Let's look again at the form of the Boltzmann factor

$$e^{-\frac{\epsilon}{k_B T}}$$

If $\epsilon \gg k_B T$ then the Boltzmann factor is very small. That means that states with energies greater than $k_B T$ are unlikely. If $\epsilon \leq k_B T$ then the exponential factor is of order 1 and the energy state is likely to occur or be occupied.

Alternatively one can estimate what temperature is needed for a particular energy state to become probable.

Note that we have not been looking at the multiplicity of states in the small system $\mathcal{S}$, but rather have used the multiplicity of states for the reservoir $\mathcal{R}$. We could still calculate the entropy of our system $\mathcal{S}$, but not the way we did previously because its energy is not fixed. Its energy can vary because it is contact with the reservoir.

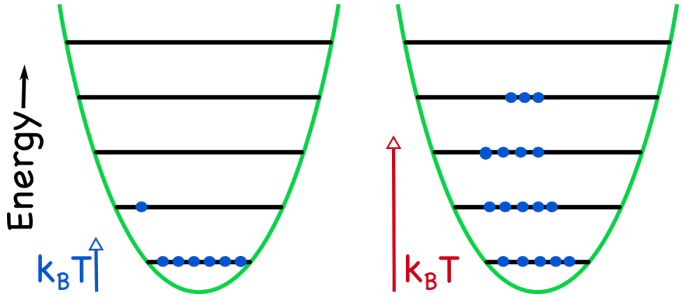

Figure 3: The probability that a system in contact with a thermal reservoir is found in a particular energy state depends on the Boltzmann factor.

1.1 The partition function

We consider a system $\mathcal{S}$ in contact with a thermal reservoir at temperature T. The probability that $\mathcal{S}$ is in state with energy ϵ_i depends on the Boltzmann factor

$$P(\epsilon_i) \propto e^{-\frac{\epsilon_i}{k_B T}}$$

We would like to find the constant of proportionality for the probability function.

The sum of the Boltzmann factors over all states of the system is known as the **partition function**

$$Z \equiv \sum_i e^{-\frac{\epsilon_i}{k_B T}} \tag{7}$$

Consider a function

$$P(\epsilon_i) = \frac{e^{-\frac{\epsilon_i}{k_B T}}}{Z} \tag{8}$$

This is proportional to the probability that the system is in state ϵ_i. If we sum over all possible states

$$\sum_i P(\epsilon_i) = \frac{\sum_i e^{-\frac{\epsilon_i}{k_B T}}}{Z} = \frac{Z}{Z} = 1$$

This means that P is normalized so the sum is 1. This means that equation 8 with Z defined as in equation 7 is in fact the probability function.

Many thermodynamic quantities are calculated using the probabilities given by equation 8.

What is the average energy of the system $\mathcal{S}$?

$$\bar{U} = \frac{\sum_i \epsilon_i P(\epsilon_i)}{\sum_i P(\epsilon_i)} = \sum_i \epsilon_i P(\epsilon_i) = \frac{1}{Z} \sum_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}}$$

What are the sizes of energy fluctuations? The variance

$$\sigma^2(U) = \sum_i (\epsilon_i - \bar{U})^2 P(\epsilon_i) = \frac{1}{Z} \sum_i (\epsilon_i - \bar{U})^2 e^{-\frac{\epsilon_i}{k_B T}}$$

1.2 Using the Boltzmann factor

Suppose we have a population of particles. Each particle can be in one of four energy levels $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3$. The particle population is in thermal equilibrium with a reservoir at temperature T.

Suppose an experimental measurements gives us the ratio of numbers of particles in the third and first energy states. The ratio of numbers of particles is the same as the ratio of Boltzmann factors. We have a measurement of

$$\frac{p(3)}{p(1)} = e^{\frac{-(\epsilon_3 - \epsilon_1)}{k_B T}}$$

If we know $\epsilon_3 - \epsilon_1$ then we can solve for the temperature T.

$$T = \frac{1}{k_B} \frac{\epsilon_1 - \epsilon_3}{\ln(p(3)/p(1))}$$

Suppose the 4 energy levels are in the form $\epsilon_n = \left(\frac{1}{2} + n\right) \epsilon_0$. The partition function is

$$\begin{aligned} Z &= e^{-\frac{\epsilon_0}{2k_B T}} + e^{-\frac{3\epsilon_0}{2k_B T}} + e^{-\frac{5\epsilon_0}{2k_B T}} + e^{-\frac{7\epsilon_0}{2k_B T}} \\ &= e^{-\frac{\epsilon_0}{2k_B T}} \left(1 + e^{-\frac{\epsilon_0}{k_B T}} + e^{-\frac{2\epsilon_0}{k_B T}} + e^{-\frac{3\epsilon_0}{k_B T}}\right) \end{aligned}$$

With

$$x = e^{-\frac{\epsilon_0}{k_B T}},$$

the partition function is

$$Z = \sqrt{x} \left(1 + x + x^2 + x^3\right).$$

If we also know the energy ϵ_0, then we can compute x and Z. Notice the geometric form for Z that sometimes makes it possible to more easily calculate and manipulate the partition function. From the ratio of numbers of particles in any two states it is possible to find T and x (assuming that we know the energy levels). Once you know x you know the partition

function Z and this lets you calculate the fraction of particles in any of the 4 states.

$$P(1) = \frac{1}{Z} e^{-\frac{\epsilon_0}{2k_B T}} = \frac{\sqrt{x}}{Z}$$
$$P(2) = \frac{x^{\frac{3}{2}}}{Z}$$
$$P(3) = \frac{x^{\frac{5}{2}}}{Z}$$
$$P(4) = \frac{x^{\frac{7}{2}}}{Z}.$$

2 The Maxwell-Boltzmann velocity distribution

Using the Boltzmann factor, we find the distribution of particle velocities in a gas of non-interacting monoatomic particles. The gas is at temperature T.

For a non-relativistic particle the kinetic energy of the particle is

$$\epsilon_{v_x,v_y,v_z} = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2)$$

Using the Boltzmann factor, the probability that a particle has velocity v_x, v_y, v_z is

$$\begin{aligned} P(\mathbf{v}) &\propto \exp\left(-\frac{\epsilon_{v_x,v_y,v_z}}{k_B T}\right) \\ &\propto \exp\left(-\frac{m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)\right) \end{aligned} \tag{9}$$

The normalization can be found using the partition function or by direct integration over volume in velocity space. We notice that this looks like a Gaussian or normal probability distribution $p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/(2\sigma^2)}$ for each velocity component but with dispersion or variance $\sigma^2 = k_B T/m$ in each velocity component.

Including normalization, the Gaussian with a single direction velocity component gives probability distribution

$$P(v_x)dv_x = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_x^2}{2k_B T}}\ dv_x. \tag{10}$$

Taking into account all three directions the probably distribution

$$P(\mathbf{v})dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z. \tag{11}$$

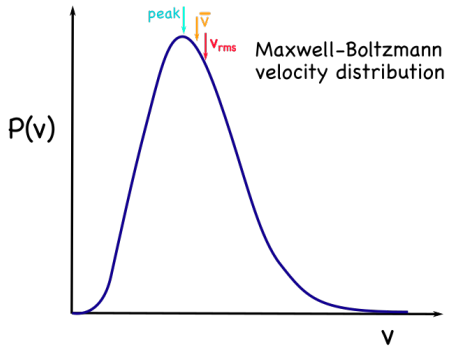

Figure 4: The shape of the Maxwell-Boltzmann velocity distribution as a function of speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. The probability $P(v) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$. The velocity dispersion gives $\sqrt{\langle v^2 \rangle} = v_{\rm rms} = \sqrt{3k_B T/m}$.

The volume element in velocity space can be written in terms of the speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$

$$dv_x dv_y dv_z = 4\pi v^2 dv$$

giving a probability distribution for the speed

$$P(v)dv = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv. \tag{12}$$

When we refer to the **rms** (root mean squared) velocity we mean the square root of the average value of v^2 which is the average value of $v_x^2 + v_y^2 + v_z^2$. The average value of v^2 (which we can write $\bar{v^2}$ or $\langle v^2 \rangle$ is also called the *velocity dispersion*,

$$\langle v^2 \rangle = \int dv\ v^2 P(v) = \int dv_x dv_y dv_z\ (v_x^2 + v_y^2 + v_z^2) P(\mathbf{v}). \tag{13}$$

Each component can be integrated separately and each one should give the same number which is the variance of the Gaussian distribution.

$$\langle v_x^2 \rangle = \langle v_x^2 \rangle = \langle v_x^2 \rangle = \frac{k_B T}{m}$$

The rms velocity

$$v_{\rm rms} = \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle} = \sqrt{\frac{3k_B T}{m}}. \tag{14}$$

Integrating over the Maxwell-Boltzmann velocity distribution gives average kinetic energy

$$\bar{E} = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{\rm rms}^2 = \frac{3}{2} k_B T. \tag{15}$$

Notice that the rms velocity $v_{\rm rms}$ depends on temperature T.

The heat capacity per molecule is still

$$\frac{dE}{dT} = \frac{3}{2}k_B \tag{16}$$

reflecting the three degrees of freedom for motion in three directions.

Note that $\sqrt{\langle v^2 \rangle}$ is not necessarily the same thing as the mean speed $\langle v \rangle$ and this is not necessarily the same thing as the velocity of the peak of the Maxwell-Boltzmann velocity distribution. The peak velocity would be where $\frac{dP(v)}{dv} = 0$.

2.1 Consequences of the Maxwell-Boltzmann distribution

2.1.1 Equipartition

High mass molecules and low mass molecules both obey the Maxwell-Boltzmann distribution.

$$\frac{1}{2}m_i v_{\rm rms,i}^2 = \frac{3}{2}k_B T$$

where each type of molecule labelled with index i. The rms velocity of the molecule

$$v_{\rm rms,i} \propto m_i^{-\frac{1}{2}}.$$

This is known as **equipartition of energy** as each type of molecule has a similar average kinetic energy.

Low mass particles like Helium (4 amu) move faster than higher mass molecules like oxygen (O^2; 32 amu).

2.1.2 Jeans escape

The Maxwell-Boltzmann distribution has a high velocity tail. Particles above the Earth's escape velocity can leave the Earth's atmosphere. Low mass molecules like hydrogen and helium are more likely to escape. The escape rate depends on the ratio of the rms velocity and the escape velocity. The process is known as Jeans escape and is important over long periods of time for early atmospheric evolution. If some molecules are ionized, the mass of their constituents is lower and more likely to escape. So chemical processes in the upper atmosphere can also cause atmospheric escape.

2.1.3 Brownian motion and diffusion

Larger molecules move more slowly than smaller ones. The diffusion or mixing rate of small molecules is faster than the diffusion or mixing rate of larger molecules.

2.1.4 The sound speed

Information travels through a gas approximately at the rms velocity set by the mean molecular weight of the molecules in the gas. The sound speed is similar to the rms velocity, $v_s \sim \sqrt{\frac{k_B T}{\bar{m}}}$ where $\bar{m}$ is the average mass of a particle. The sound speed depends on temperature and mean molecular mass. The sound speed is lower at lower temperature. The sound speed is higher in air mixed with Helium than in regular air which is mostly nitrogen.

2.1.5 Evaporation and sublimation

Some atoms can have energies high enough to overcome bonds of their neighbors and escape the solid or liquid phase. This is called sublimation (if escaping the solid) or evaporation (if escaping the liquid).

3 A particle in a box and the ideal gas

An **ideal gas** is comprised of N non-interacting monotonic particles (not molecules) in a box.

To quantize energy we use the particle's deBroglie wavelength and assume that an integer number of deBroglie wavelengths fit in the box. We count the number of energy states for a single particle in the box. We assume that the box is thermal contact with a reservoir. We use the Boltzmann factor to compute the partition function at temperature T for a single particle in a box. The mean energy of this particle as a function of temperature is computed from the partition function. We compute the heat capacity from the mean energy of a single particle by taking the derivative w.r.t to temperature.

The entropy of a particle in a box is computed using the multiplicity of states at a particular energy. We use a similar calculation to compute the entropy of N particles in a box. These two expressions will be used to derive the ideal gas law.

3.1 A particle in a box

We consider a mass m in a cubic box of length L. The volume is $V = L^3$. The particle's deBroglie wavelength must fit nicely within the box. The deBroglie wavelength

$$\lambda_{\text{deBroglie}} = \frac{h}{p}$$

where p is its momentum. Because integer numbers of wavelengths must fit within the box, the particle's momentum and energy are quantized.

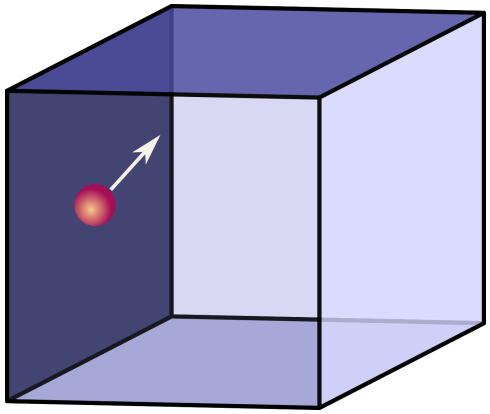

Figure 5: A particle in a cubic box. The particle's kinetic energy and momentum are quantized.

The momentum and energy are quantized with three **positive integer quantum numbers** n_x, n_y, n_z which tell us how many deBroglie wavelengths fit in each side of the box,

$$\begin{aligned} L \approx & n_x \lambda_x \\ L \approx & n_y \lambda_y \\ L \approx & n_z \lambda_z. \end{aligned}$$

This gives

$$p_x \approx \frac{h}{\lambda_x} \approx \frac{h n_x}{L}$$

The kinetic energy for motions in x alone is

$$\frac{1}{2} m v_x^2 \approx \frac{p_x^2}{2m} \approx \frac{1}{2m} \frac{h^2 n_x^2}{L^2}$$

The kinetic energy of the particle is $K = p^2/(2m)$ which takes values

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right) \tag{17}$$

Here I have restored factors of π for the quantum problem of a particle in a cubic potential well.

3.2 The partition function for a particle in a box

We assume that our particle in the box is in thermal equilibrium with a **reservoir** at temperature T.

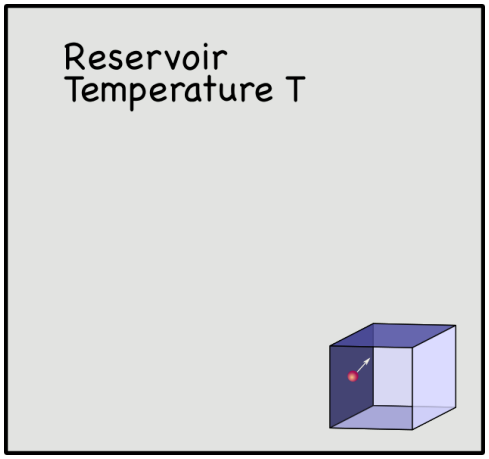

Figure 6: A particle in a cubic box. We assume the box is in thermal equilibrium with a thermal reservoir at temperature T.

We use the energy in equation 17 and the Boltzmann factor to find the partition function for a single particle in a box,

$$\begin{aligned} Z &= \sum_{n_x,n_y,n_z} e^{-\beta\epsilon_{n_x,n_y,n_z}} \\ &= \sum_{n_x,n_y,n_z} e^{-\alpha^2(n_x^2+n_y^2+n_z^2)} \end{aligned}$$

where n_x, n_y, n_z are integer quantum numbers. Here the inverse temperature

$$\beta \equiv \frac{1}{k_B T}$$

and the constant

$$\alpha^2 = \beta \frac{\hbar^2}{2m} \frac{\pi^2}{L^2}$$

We can approximate the sum in the partition function with integrals

$$\begin{aligned} Z &\approx \int_0^\infty e^{-\alpha^2 n_x^2} dn_x \int_0^\infty e^{-\alpha^2 n_y^2} dn_y \int_0^\infty e^{-\alpha^2 n_z^2} dn_z \\ &\approx \left(\int_{n_x=0}^\infty e^{-\alpha^2 n_x^2} dn_x \right)^3 \end{aligned}$$

The definite integral

$$\int_0^\infty e^{-\alpha^2 x^2} dx = \frac{1}{\alpha} \int_0^\infty e^{-y^2} dy$$
$$= \frac{1}{\alpha} \frac{\sqrt{\pi}}{2}.$$

Using this handy integral, our partition function is

$$Z \approx \left(\frac{\pi^{\frac{1}{2}}}{2\alpha} \right)^3 = \frac{\pi^{3/2}}{8} \left(\beta \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \right)^{-\frac{3}{2}}$$
$$= \left(k_B T \frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} L^3 \tag{18}$$

We have succeeded in computing the partition function for a single particle in a box!

Notice that the 3/2 power came from having three degrees of freedom. Notice that Z depends on volume.

3.3 The mean energy of the particle in the box

We now compute the mean energy of this one particle in a box that is in contact with a thermal reservoir at temperature T.

The mean energy of a system in contact with a thermal reservoir is

$$\bar{E} = \sum_i \epsilon_i P(\epsilon_i)$$

where the probabilities are given by the Boltzmann factor. This can be written in terms of a derivative of the partition function.

With inverse temperature $\beta = 1/(k_B T)$

$$Z = \sum_i e^{-\beta \epsilon_i}$$
$$\frac{dZ}{d\beta} = \sum_i -\epsilon_i e^{-\beta \epsilon_i}$$
$$-\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{d \ln Z}{d\beta} = \frac{1}{Z} \sum_i \epsilon_i e^{-\beta \epsilon_i}$$
$$= \bar{E}$$

It is useful to remember that the average energy can be computed from the partition function

$$\bar{E} = -\frac{1}{Z} \frac{dZ}{d\beta}. \tag{19}$$

The partition function for the particle in the box, equation 18, we rewrite in the form

$$Z = a\beta^{-\frac{3}{2}} \qquad \text{with} \qquad a = \left(\frac{m}{2\pi\hbar^2}\right)^{\frac{3}{2}} L^3.$$

We use this and equation 19 to compute the average energy

$$\begin{aligned} \frac{dZ}{d\beta} &= -\frac{3}{2} a\beta^{-\frac{5}{2}} \\ \bar{E} &= -\frac{1}{Z}\frac{dZ}{d\beta} = \frac{3}{2}\beta^{-1} \\ &= \frac{3}{2} k_B T. \end{aligned} \tag{20}$$

The important thing in this calculation is the exponent! The factor a drops out.

The quantity $\bar{E}$ is the mean energy for a single particle in a box with 3 degrees of freedom in its kinetic energy. For N non-interacting particles in the same 3D box we can multiply by N giving total mean energy

$$U = \frac{3}{2} N k_B T. \tag{21}$$

3.4 Heat capacity

The heat capacity can be defined as

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V. \tag{22}$$

The heat capacity of the single particle in the box (that is in contact with a thermal reservoir) can be computed from the mean energy with

$$U = \frac{3}{2} k_B T$$

giving

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} k_B.$$

This is the specific heat capacity per particle in an ideal gas.

3.5 Entropy of a particle in a box

We start with a particle in a box that has a constant energy ϵ. What is the multiplicity of states that have this energy?

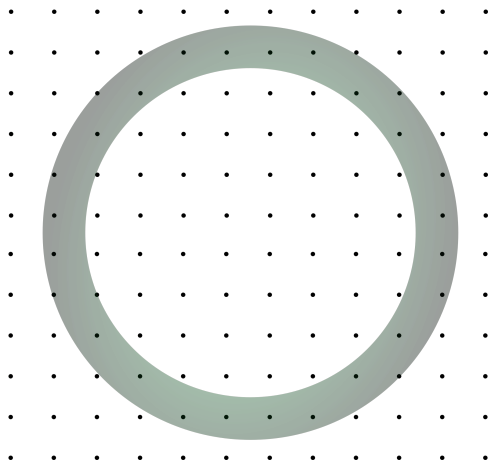

Figure 7: Counting states. Here we count the number of states in an annulus of thickness 1. The area of the annulus is $A = 2\pi R\, dR$ where R is the radius of the annulus and dR is the thickness of the annulus. The number of states within the annulus is proportional to $2\pi R$.

The energy as a function of three integer quantum numbers is (Equation 17)

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

The energy depends on $R = \sqrt{n_x^2 + n_y^2 + n_z^2}$ which is the radius of a shell in three dimensional space spanned by integers n_x, n_y, n_z. The number of states can be approximated as the volume of a shell with thickness 1 or

$$4\pi R^2 dR = 4\pi(n_x^2 + n_y^2 + n_z^2) = g(\epsilon_{n_x,n_y,n_z}) \tag{23}$$

with $dR = 1$. Why are we using $dR = 1$? Up to a constant of proportionality, the multiplicity of states is independent of the width of the the shell.

We can rewrite the quadratic sum of quantum numbers in terms of the energy

$$\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{2m}{\hbar^2}\left(\frac{L}{\pi}\right)^2 \epsilon_{n_x,n_y,n_z}$$

This and equation 23 gives multiplicity of states

$$g(\epsilon, L) \approx 4\pi \frac{2m}{\hbar^2}\left(\frac{L}{\pi}\right)^2 \epsilon \tag{24}$$

and entropy (from the natural logarithm of the multiplicity)

$$\sigma(\epsilon, L) = \text{constant} + 2\ln L + \ln \epsilon \tag{25}$$

It will be useful to rewrite the length in terms of the volume, $L = V^{\frac{1}{3}}$, and energy $U = \epsilon$ giving

$$\sigma(U, V) = \text{constant} + \frac{2}{3} \ln V + \ln U. \tag{26}$$

Notice that the entropy depends on volume!

3.6 Entropy of N particles in a box

The previous calculation makes it easier to compute the entropy of N particles in a box.

We consider a box with a constant volume but now we put N non-interacting particles in it. The total kinetic energy is fixed.

For each particle we have three quantum numbers. The total energy as a function of 3N integer quantum numbers is (extending Equation 17)

$$\begin{aligned} \epsilon_{3N} &= \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \sum_{i=1}^{N} (n_{xi}^2 + n_{yi}^2 + n_{zi}^2) \\ &= \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \left(\sum_{j=1}^{3N} n_j^2\right). \end{aligned} \tag{27}$$

To estimate the multiplicity of states at a single energy we need to find the surface area of a sphere in 3N dimensions with radius

$$\begin{aligned} R &= \sqrt{\sum_{j=1}^{3N} n_j^2} \\ &= \left(\epsilon_{3N} \frac{2m}{\hbar^2} \left(\frac{L}{\pi}\right)^2\right)^{\frac{1}{2}} \\ &= \left(\epsilon_{3N} \frac{2m}{\hbar^2 \pi^2}\right)^{\frac{1}{2}} V^{\frac{1}{3}} \end{aligned} \tag{28}$$

On the second line I use equation 27. On the last line I related volume to the length of the box with $V = L^3$.

The area of the sphere in 3N dimensions gives us the volume in a shell of thickness 1 in 3N dimensions and this gives us the number of states at a fixed energy.

The volume of a sphere in N dimensions is $V \sim R^N$. The area of the shell with radius R in N dimensions is $dV/dR = NR^{N-1}$.

Here we have a sphere in $3N$ dimensions and the area of the shell with radius R in $3N$ dimensions is $\propto R^{3N-1}$.

Using a width for the shell of 1, the multiplicity of states depends on the volume in the shell of width 1

$$g(\epsilon) \sim R^{3N-1}$$

with energy ϵ a function of R. Subbing in for the radius R with equation 28, the multiplicity of states

$$g(\epsilon, V, N) \propto V^{\frac{3N-1}{3}} \epsilon^{\frac{3N-1}{2}}. \tag{29}$$

With $N = 1$ this is consistent with what we found in the previous section. We compute the entropy from the multiplicity

$$\sigma(\epsilon, V, N) = \ln g(\epsilon, N, V)$$
$$\sigma(\epsilon, V, N) \sim N \ln V + \frac{3}{2} N \ln \epsilon + \text{constant}$$

where for large N we approximate $3N-1$ as $3N$ and we have ignored constants that might be irrelevant at large N. As we computed the entropy for a box with constant volume and energy

$$\sigma(U, V, N) \approx N \ln V + \frac{3}{2} N \ln U + \text{constant} \tag{30}$$

with total energy $U = \epsilon$.

This implies that entropy is larger for a larger volume box at larger energy and with more particles, as we might expect.

4 Pressure and the ideal gas law

Using the Maxwell Boltzmann distribution we associated $\frac{3}{2} k_B T$ with the kinetic energy of a particle or particles in a box that is in contact with a thermal reservoir at temperature T. This also gives the mean velocity v of particles in the box. The pressure is the rate that momentum from collisions is transferred to a wall of the box. This depends on the number of particles in the box. Each collision gives mv momentum to a wall but the rate of collisions per unit area is set by nv where n is the number density $n = N/V$ or the number of atoms per unit volume. The number of collisions per unit time on a wall of area A is

$$\frac{\text{collisions}}{\text{time}} = nvA$$

The momentum change in each collision $\Delta p \sim mv$. The rate momentum is imparted to the wall of area A

$$\frac{dp}{dt} = \frac{\text{collisions}}{\text{time}} \times mv \sim nvA \times mv = nmv^2 A$$

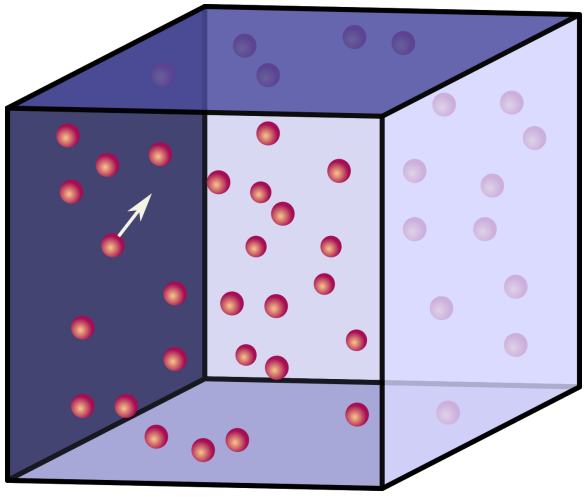

Figure 8: A box containing N particles.

The rate of change of momentum is the force, $F = \frac{dp}{dt}$. The force per unit area

$$\frac{F}{A} = \frac{1}{A}\frac{dp}{dt} \sim nmv^2.$$

Using the relation between kinetic energy and temperature, the rate of change of momentum per unit area transferred to the wall is

$$nmv^2 \sim nk_BT.$$

The rate of change of momentum per unit area is the same as force per unit area or pressure. We expect pressure

$$p \sim nk_BT. \tag{31}$$

4.1 Pressure and PdV work

We consider a small system $\mathcal{S}$, that is contact with a thermal reservoir but now $\mathcal{S}$ can vary in volume. We decrease the volume slowly with an external force from V to $V - \Delta V$. If we do this slowly enough the system can stay in the same quantum states, but because the volume varies, the energy of these states can slowly vary.

$$U(V - \Delta V) = U(V) - \frac{\partial U}{\partial V}\Delta V....$$

$$\Delta U = -\frac{\partial U}{\partial V}\Delta V$$

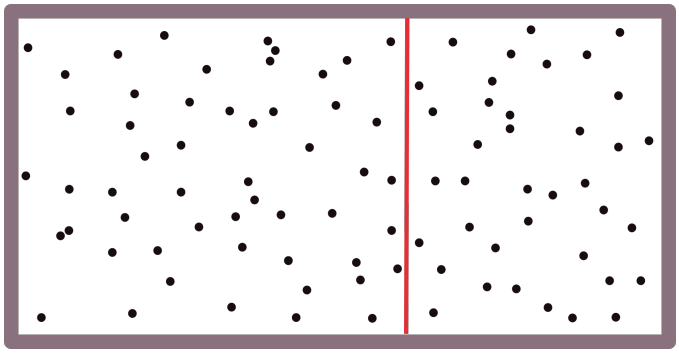

Figure 9: Two systems that are separated by a barrier. Previously we discussed two systems, each with constant volume and numbers of particles but allowed the two systems to exchange heat. We could allow the two systems to exchange particles and we could allow the barrier to move so that the volumes vary.

The work done to change the energy is $\frac{\partial U}{\partial V}\Delta V$.

Why does slowly changing the volume of a gas container change the energy?

Consider a gas container (a piston) that has cross sectional area A and length h giving volume Ah. We make the system smaller by pushing on it to reduce h while maintaining area A. We push the piston in. The change in volume $dV = Adh$. The pressure is a force per unit area so we are pushing with a force $F = pA$. The work is force times distance or

$$W = pAdh = pdV$$

giving a change in energy $dU = -pdV$. This implies that pressure

$$p = -\frac{dU}{dV}.$$

It is natural to associate pressure with

$$p = -\left(\frac{\partial U}{\partial V}\right)_{\sigma} \tag{32}$$

We have added a subscript σ to signify that we did not change the entropy while varying the volume.

4.2 Another way to describe pressure

Above, we have kept the entropy fixed because we needed to change the pressure slowly to maintain the same quantum states.

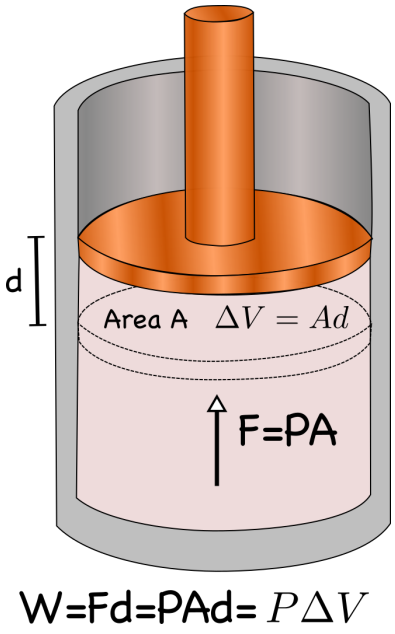

Figure 10: PdV work done on a piston by a gas. The gas is heated, and the piston moves upward by a distance d. The difference in volume is $\Delta V Ad$ where A is the cross sectional area. The work done by the gas is $W = Fd = P\Delta V$. Here P is the pressure.

It is often useful to have additional ways to find key variables. For two systems in both thermal contact and that can exchange volume (there is a moveable partition between them) the entropy is a function of volume and energy

$$\sigma(U, V)$$

Small changes

$$d\sigma(U,V) = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV$$

Assume that we select changes that keep the total entropy (or temperature) unchanged. We denote these changes as

$$dU_\sigma \qquad \text{and} \qquad dV_\sigma.$$

Then

$$\begin{aligned} 0 &= \left(\frac{\partial \sigma}{\partial U}\right)_V dU_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U dV_\sigma \\ 0 &= \left(\frac{\partial \sigma}{\partial U}\right)_V \frac{dU_\sigma}{dV_\sigma} + \left(\frac{\partial \sigma}{\partial V}\right)_U \\ 0 &= \left(\frac{\partial \sigma}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U \end{aligned}$$

Our definition of temperature

$$\frac{1}{k_B T} = \left(\frac{\partial \sigma}{\partial U}\right)_V$$

We insert this into our previous relation

$$0 = \frac{1}{k_B T}\left(\frac{\partial U}{\partial V}\right)_\sigma + \left(\frac{\partial \sigma}{\partial V}\right)_U$$

We rewrite this as

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -k_B T \left(\frac{\partial \sigma}{\partial V}\right)_U$$

Previously we found pressure

$$p = -\left(\frac{\partial U}{\partial V}\right)_\sigma$$

This gives us a new relation for pressure

$$p = k_B T \left(\frac{\partial \sigma}{\partial V}\right)_U \tag{33}$$

Why does this make sense? Keeping energy fixed but reducing the volume is like squeezing a bunch of fast moving particles into a smaller space. They bounce more frequently against the container walls giving a higher pressure.

4.3 The ideal gas law

The ideal gas law is a relation between the number of molecules N, pressure p, volume V and temperature T. Energy is missing.

Using equation 33 for pressure

$$p = k_B T \left(\frac{\partial \sigma}{\partial V} \right)_U \tag{34}$$

and equation 30 for the entropy of N particles in a box

$$\sigma(U, V) \approx N \ln V + \frac{3}{2} N \ln U + \text{constant} \tag{35}$$

$$\left(\frac{\partial \sigma}{\partial V} \right)_U = \frac{N}{V}$$

and giving

$$p = k_B T \frac{N}{V} \tag{36}$$

which we recognize as the ideal gas law

$$PV = N k_B T. \tag{37}$$

Using number of particles per unit volume $n = N/V$ equation 36 is equivalent to equation 31 which we rewrite here

$$p = n k_B T. \tag{38}$$

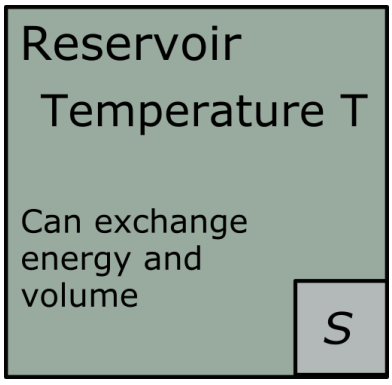

Figure 11: A system $\mathcal{S}$ can exchange volume and energy with reservoir that has temperature T. The system change in energy is the sum of heat and work $dU = TdS - pdV$.

4.4 Thermodynamic identity. PdV and TdS. Work and Heat.

We allow a system $\mathcal{S}$ to exchange both volume and energy with a reservoir, as shown in Figure 11. This gives $\sigma(U, V)$.

$$d\sigma(U,V) = \left(\frac{\partial\sigma}{\partial U}\right)_V dU + \left(\frac{\partial\sigma}{\partial V}\right)_U dV$$

Using our definition for temperature and our new expression for pressure (Equation 33 which is $p = k_B T \frac{\partial\sigma}{\partial V}$)

$$d\sigma(U,V) = \frac{1}{k_B T} dU + \frac{p}{k_B T} dV$$

We can write this as

$$\begin{aligned} dU &= k_B T d\sigma(U,V) - pdV \\ &= TdS - pdV \end{aligned}$$

using conventional entropy $S = k_B\sigma$.

For a system that is in contact with a thermal reservoir but is allowed to vary in volume, the change in its energy

$$dU = TdS - pdV \tag{39}$$

where the TdS term can be called *heat* and the pdV term can be called *work*. This is the work done **on** the system.

4.5 Beyond ideal: Specific heat of a diatonic molecular gas

In previous sections we have discussed an ideal gas where the particles do not interact. Each particle has only kinetic energy. In this section we again require that particles do not interact, but we relax the requirement that energy is only in the form of kinetic energy. We consider a gas comprised of diatonic molecules. Diatonic molecules have vibration and rotational energy states as well as different possible kinetic energy states.

For a diatonic molecule there are only two rotational degrees of freedom. This is because only two axes of rotation are perpendicular to the line connecting the two atoms. Rotation around the axis connecting the two atoms does not give any energy. Relevant is the moment of inertia of the molecule as the rotational energy levels depend on it. Rotational spectra are often described in terms of a rotational constant that is in units of inverse length. The rotation constant for a diatonic molecule is

$$B = \frac{h}{8\pi^2 cI}$$

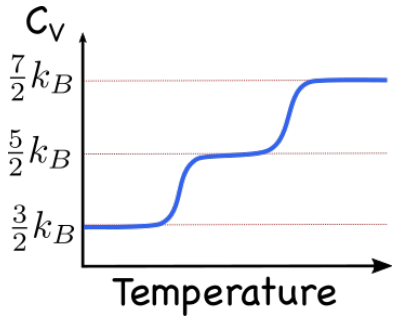

Figure 12: As the temperature increases, energy quanta can be put in degrees of freedom that require more energy for excitation. The heat capacity depends on the number of degrees of freedom. A monotonic ideal gas has 3 translational degrees of freedom and the heat capacity per molecule $C_V = \frac{3}{2}k_BT$. A diatonic molecular gas would also have two rotational degrees of freedom. When the temperature is high enough to excite rotational degrees of freedom, the heat capacity per molecule $C_V = \frac{5}{2}k_BT$. Even though there is a single degree of freedom in vibrational motion for a diatonic molecule, equipartition between kinetic and potential energy gives k_BT for vibrations instead of half of this. When the temperature is high enough to populate vibrational modes the heat capacity per molecule $C_V = \frac{7}{2}k_BT$.

with c the speed of light, h is Planck's constant and I is the moment of inertia. The energy of transitions are related to the rotational constant

$$E_J = hcBJ(J+1)$$

where J is an integer quantum number. The moment of inertia for a diatonic molecule is

$$I = \mu d^2$$

where reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$ and m_1, m_2 are the atom masses and d is a mean distance between the two atoms. We compare k_BT to E_J. With

$$k_BT \gtrsim hcB \tag{40}$$

rotational states should be excited.

For a diatonic molecule there is only one degree of freedom for vibrations as there is only one way to stretch the molecule. However the total energy is a sum of potential energy and kinetic energy terms. Equipartition is similar to the virial theorem and both terms have about the same mean energy. The relevant energy is $\hbar\omega$ where $\omega = \sqrt{k/\mu}$, with μ the reduced mass and k the spring constant representing the inter-atomic force. With

$$k_BT \gtrsim \hbar\omega, \tag{41}$$

vibrational states should be excited.

4.6 Beyond ideal: The mean free path

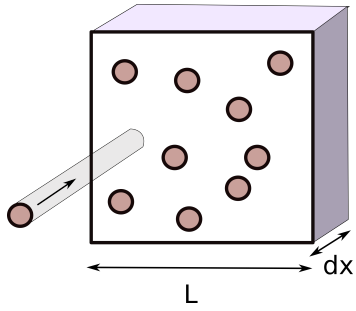

Figure 13: A particle moving in the x direction passes through the box. The probability that the particle collides with a particle in the box depends on the fraction of area filled by the particles in the box.

Interactions such as collisions between particles are ignored when approximating a gas as an ideal gas. To estimate the role of pairwise interactions, we estimate the rate that a particle collides with another particle. The **mean free path** is the typical distance travelled by a particle between collisions.

Consider a distribution of particles with number density n (number per unit volume). We consider an area A and a volume

$$V = A\ dx$$

where dx is a small distance. The number of particles in that volume is

$$N = nA\ dx.$$

Suppose the particles are molecules with size d. The cross sectional area of a molecule $\sigma_A \sim d^2$. Looking at our volume face on, the area filled by molecules in our volume is

$$A_{filled} = \sigma_A N = \sigma_A nA\ dx.$$

The fraction of area filled is

$$f_A = \frac{A_{filled}}{A} = \frac{\sigma_A N}{A} = n\sigma_A\ dx.$$

The probability that a single molecule moving in the dx direction and passing through this volume depends on the fraction of area filled by molecules. $P = f_A$. The probability per unit time that a molecule moving at velocity $v = dx/dt$ hits another molecule is

$$f_A/dt = n\sigma_A\ dx/dt = nv\sigma_A.$$

This is the same thing as the collision rate.

In other words, for a single molecule, the rate of collisions (the number of collisions per unit time)

$$\frac{dc}{dt} \sim n v_{\rm rms} \sigma_A \tag{42}$$

where σ_A is a cross sectional area and is similar to d^2 where d is a size scale of the molecule, and we have used the typical velocity of a molecule $v_{\rm rms}$.

The **average time between collisions** is

$$\tau = \frac{1}{dc/dt} = \frac{1}{n v_{\rm rms} \sigma_A}. \tag{43}$$

The distance travelled between collisions or **mean free path** is

$$l_{\rm mfp} \sim v_{\rm rms} \tau \sim \frac{1}{n \sigma_A}. \tag{44}$$

The ideal gas law is $p = n k_B T$ so $n = p/(k_B T)$ giving

$$l_{\rm mfp} \sim \frac{k_B T}{p \sigma_A}$$

5 Some Thermodynamics

Heat and work are two different forms of energy transfer. Heat is the transfer of energy into a system by thermal contact with a reservoir. Work is the transfer of energy into a system by a change in external parameters. These parameters can include volume, electric field or gravitational potential.

A mechanism for converting heat into work is a heat engine. A combustion engine is such an engine. Electrical energy can be generated from heat with a generator.

A fundamental difference between heat and work is in the entropy. The energy transfer dU from a reservoir to a system via thermal contact at temperature T involves $dS = dU/T$. We refer to this energy transfer as heat.

Work is energy transferred via changing external parameters such as volume. For example the position of a piston. No entropy is transferred.

The total energy of system plus reservoir remains fixed. However the total entropy may not be fixed. If we restrict ourselves to reversible changes, then the total entropy of interacting systems remains constant.

For a reversible process, the heat received by the system

$$dQ = T dS = k_B T d\sigma$$

If dU is its energy change then

$$dU = dW + dQ$$

where dW is the work done on the system. For $dU = T dS$ we have pure heat. For $dU = dW$ we have pure work.

5.1 Heat Engines, Refrigerators and Heat pumps – Converting Heat into Work or Work into Heat Flow

Heat engines convert heat into work. There is a limit to their efficiency because entropy overall must remain constant or increase. Work can be completely converted to heat but heat cannot be completely converted into work.

Refrigerators are heat engines in reverse. They use work to move heat from low temperature (inside) to a higher temperature (outside).

Air conditioners are refrigerators that cool the inside of a room.

A heat pump is similar to a refrigerator. Work is used to move heat from low temperature (outside) to a higher temperature (inside).

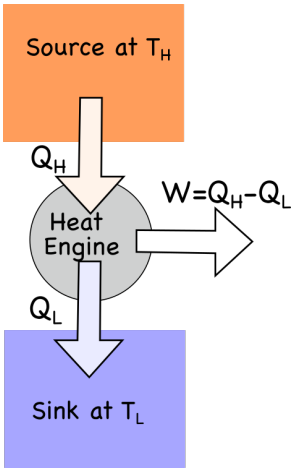

Figure 14: A heat engine. There are two thermal reservoirs, a hotter one and a colder one. The engine uses the heat to do work.

5.2 Efficiency of a Heat Engine

Figure 14 shows an energy flow diagram. The engine absorbs heat Q_H at a higher or hotter temperature T_H. The engine emits heat Q_L at a lower temperature T_L. Both T_L and T_H are thermal reservoirs. The work done by the engine is W (or M in Figure 14.

The efficiency of the engine

$$\epsilon \equiv \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_H} \tag{45}$$

The heat absorbed from the hot reservoir is how much energy is being used, so it is like a cost in the efficiency ratio.

What is the maximum efficiency of a heat engine?

The engine periodically returns to its initial state, with the same energy. This means the total energy absorbed is equal to the sum of that emitted into the cold reservoir and that done as work,

$$Q_H = Q_L + W$$

Inserting this into our equation for efficiency (equation 45)

$$\epsilon = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \tag{46}$$

The efficiency cannot be greater than 1 and it is only equal to 1 if there is no heat emitted into the cold reservoir ($\epsilon = 1$ if $Q_L = 0$).

To find the maximum efficiency, we need to consider the second law of thermodynamics. The total entropy of engine plus reservoirs must not decrease. The entropy absorbed by the engine is $\Delta S_{\text{abs}} = \frac{Q_H}{T_H}$. The entropy emitted by the engine is $\Delta S_{\text{emit}} = \frac{Q_L}{T_L}$. Entropy could increase in the reservoir but it cannot keep decreasing. This means that

$$\frac{Q_L}{T_L} \geq \frac{Q_H}{T_H}. \tag{47}$$

More (or equal) entropy must be emitted by the engine than is absorbed by the engine in each cycle. We can write this as

$$\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H}. \tag{48}$$

Subtracting we find

$$1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H}.$$

We insert this into equation 46 for the efficiency of the engine

$$\epsilon \leq 1 - \frac{T_L}{T_H} \tag{49}$$

The temperature ratio of the reservoirs places a limit on the efficiency of the engine. The maximum efficiency

$$\epsilon_{max} \equiv 1 - \frac{T_L}{T_H} \tag{50}$$

A larger temperature ratio increases the maximum possible efficiency.

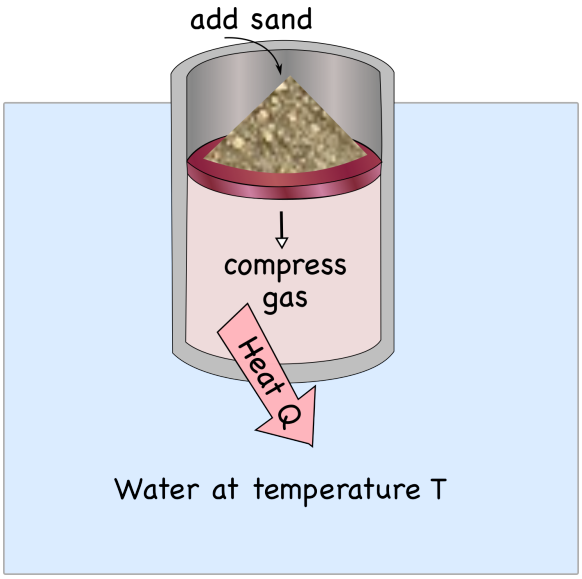

Figure 15: Operations on an enclosed gas that is contact with a thermal reservoir. Because the temperature is fixed, the total energy is fixed, however work is done on the gas and heat is transferred to the reservoir.

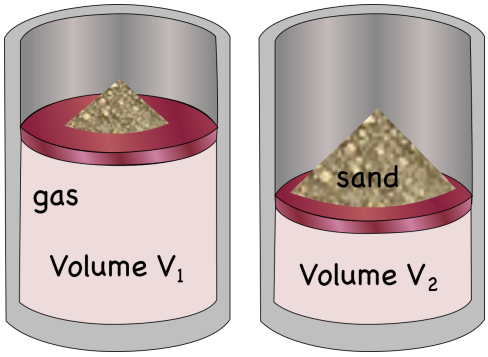

Figure 16: PdV work done on an enclosed gas with a piston. Sand is slowly added on top of the piston and the gas is compressed. If the piston is not in thermal contact with a reservoir and the sand is added slowly, the compression is adiabatic. When adiabatic there is no heat transferred from the system and the change in energy is equal to the work done on the system; $dU = -PdV$.

5.3 Trajectories on PV plots

Below I introduce some terms commonly used when discussing operations on an ideal gas that has a fixed number of atoms or molecules. Relevant is energy change $dU = TdS - PdV$ with $-PdV$ corresponding to work W and TdS corresponding to heat Q.

Work done **on** the system is $W = -PdV$.
Work done **by** the system is $W = PdV$.
Heat transferred **to** the system is $Q = TdS$.

- **Reversible**: Slowly enough to stay nearly in equilibrium. An operation that is not reversible is free expansion into a vacuum. Often paths on a PV plot are assumed to be slow enough to be reversible. For reversible changes, the total entropy of system plus external systems is constant.
- **Isothermal**: At constant temperature. For an ideal gas, this implies no energy change as $U \propto k_B T$.
- **Isochoric**: At constant volume. No PdV work is done, but heat can be transferred.
- **Isobaric**: At constant pressure. Changes in volume involve PdV work.
- **Isentropic**: At constant entropy.
- **Adiabatic**: Without exchanging heat. The energy is not fixed as work can be done on the gas. Reversible and adiabatic is equivalent to isentropic. When a transition is described as adiabatic, it is often assumed that it is isentropic.

For slow changes, the work done **by** the ideal gas is $\int PdV$ and this corresponds to area integrated under a curve on a plot where P is the y axis and V is the x axis.

The work done by the system on a horizontal or isobaric path on Figure 17 is $W = P\Delta V$.

Vertical or isochoric paths on Figure 17 keep V constant so no work is done. However heat is transferred to the gas. Because $dU = TdS - PdV$, the heat $Q = \int TdS$ is equal to the energy change ΔU.

For isothermal variations on an ideal gas $dU = Q - W = 0$, and heat equals work; $Q = W$.

5.4 Adiabatic variation of an ideal gas and the adiabatic index

We consider a parcel of gas that is not allowed to exchange heat with its surroundings. This can happen if the gas parcel cannot radiate efficiently and heat conduction to its surroundings is slow compared to variations in pressure and density. It can do work on its

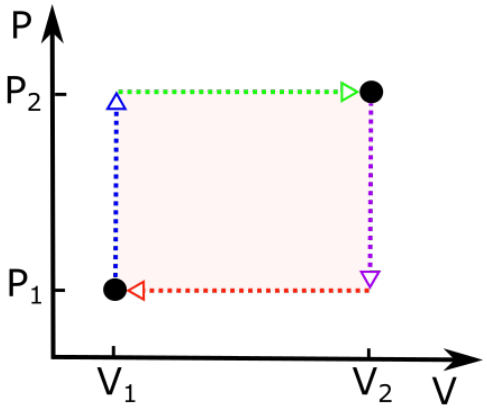

Figure 17: The state of an ideal gas is given by a point on a pressure vs volume or PV diagram. We assume that the number of gas particles is fixed. Because of the ideal gas law, the temperature and energy are uniquely determined by P and V. Because $PV = Nk_BT$, temperature and energy is lowest on the lower left and highest on the upper right. We take V_1, P_1 to be the lower left point and V_2, P_2 to be the upper right point. The work done by the system going from V_1, P_1 to V_1, P_2 (lower left to upper left point, following the blue line) is zero. The work done by the system ($W = \int P\, dV$) going from V_1, P_2 to V_2, P_2 (from lower left point to upper left on the blue line and then to upper right point on the green line) is $P_2(V_2 - V_1)$. The work done by the system going around a loop counter-clockwise is the same as the area within the loop, $W = (V_2 - V_1)(P_2 - P_1)$. After going around the look the energy U is the same as it was originally. In other words $\Delta U = 0$ around the loop. This means that the total heat transferred to the system $Q = W$ is the same as that done by the system.

surroundings and its surrounding can do work on it. So its energy is not fixed. The change in energy is equal to the work done on the system.

$$dU = -PdV$$

If we have an ideal monotonic gas we use

$$U = \frac{3}{2}Nk_BT$$

where N is the number of molecules in the parcel.

$$dU = -PdV$$
$$\frac{3}{2}Nk_Bd T = -PdV$$

We divide both sides of the equation by $Nk_BT = PV$.

$$\begin{aligned}\frac{3}{2}Nk_BdT &= -PdV \\ \frac{3}{2}\frac{dT}{T} &= -\frac{dV}{V} \\ \frac{3}{2}d\ln T &= -d\ln V\end{aligned}$$

We integrate

$$\begin{aligned}\frac{3}{2}\ln T &= -\ln V + \text{constant} \\ \ln T &= -\frac{2}{3}\ln V + \text{constant} \\ T &\propto V^{-\frac{2}{3}} \\ PV &\propto V^{-\frac{2}{3}} \\ PV^{\frac{5}{3}} &= \text{constant}\end{aligned}$$

This is often written

$$PV^{\gamma} = \text{constant} \tag{51}$$

with $\gamma = 5/3$ called the **adiabatic index**. **The value $\gamma = 5/3$ is for a monotonic ideal gas.**

For a diatonic gas the index would be 7/5 or 9/7 instead of 5/3 because of extra degrees of freedom that increase the energy. We can redo the above calculation with energy $U = \frac{n}{2}Nk_BT$ for n degrees of freedom to find the adiabatic index

$$\gamma = \frac{2}{n} + 1 = \frac{2+n}{n}. \tag{52}$$

Sound waves are nearly adiabatic so the adiabatic index γ appears in the speed of sound,

$$c_s = \sqrt{\gamma\frac{P}{\rho}}.$$

5.5 Isothermal compression

We consider isothermal compression from P_1, V_1 to P_2, V_2 at constant temperature T and with a volume decrease so $V_2 < V_1$. The idea gas law $PV = Nk_BT$. The work done on the

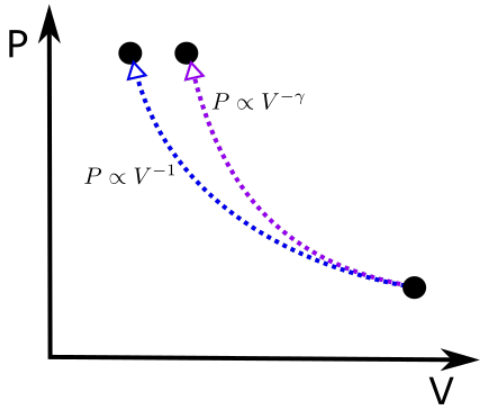

Figure 18: Isothermal variation has $P \propto 1/V$ whereas adiabatic variation (the steeper curve) has $P \propto V^{-\gamma}$. Because the total energy depends depends on $k_B T \propto PV$, the isothermal curves are also constant energy curves. Adiabatic curves are curves where no heat is transferred but energy is not constant. In both cases work done on the system $W = -\int P(V)dV$ and is minus the area integrated under the curve.

system during compression

$$\begin{aligned} W_{isothermal} &= -\int_{V_1}^{V_2} P(V)dV = -\int_{V_1}^{V_2} \frac{Nk_BT}{V}dV \\ &= -Nk_BT \ln V\Big|_{V_1}^{V_2} \\ &= -Nk_BT \ln \frac{V_2}{V_1} \end{aligned} \tag{53}$$

Because $PV = Nk_BT$, and temperature T is constant, we can write Nk_BT in terms of P_1V_1 or P_2V_2,

$$W_{isothermal} = -V_1P_1 \ln \frac{V_2}{V_1} = -V_2P_2 \ln \frac{V_2}{V_1}. \tag{54}$$

5.6 Adiabatic compression and work

We consider adiabatic compression from P_1, V_1 to P_2, V_2 and with a volume decrease so $V_2 < V_1$. We assume $PV^\gamma = K$ with K a constant. The work done on the system during

compression

$$\begin{aligned} W_{adiabatic} &= -\int_{V_1}^{V_2} P(V)dV = -\int_{V_1}^{V_2} KV^{-\gamma}dV \\ &= \frac{K}{\gamma-1}V^{-\gamma+1}\Big|_{V_1}^{V_2} = \frac{K}{\gamma-1}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right] \\ &= \frac{1}{\gamma-1}(P_2V_2 - P_1V_1) \end{aligned} \tag{55}$$

Adiabatic means no heat exchange, $Q = 0$, so $dU = -PdV$ along the path. That means we can compute the work done on the system from the change in energy. Energy

$$U = \frac{n}{2}Nk_BT$$

depends on the degrees of freedom, n, Equation 52 relates adiabatic index γ to $n/2$ with

$$\frac{n}{2} = \frac{1}{\gamma-1}.$$

This gives $U = \frac{1}{\gamma-1}Nk_BT$ and

$$\Delta U = \frac{1}{\gamma-1}Nk_B\Delta T. \tag{56}$$

Using the ideal gas law $Nk_B\Delta T = \Delta(PV)$ we find

$$\Delta U = \frac{1}{\gamma-1}\Delta(PV) \tag{57}$$

which is equivalent to what we found by integrating PdV work (equation 55)! We have shown that integrating PdV work for an adiabatic path is equivalent to computing the energy change from the endpoints. This is because adiabatic means that no heat is transferred along the path, and because $dU = Q + W$, that means the total energy change is equal to the total work done on the system.

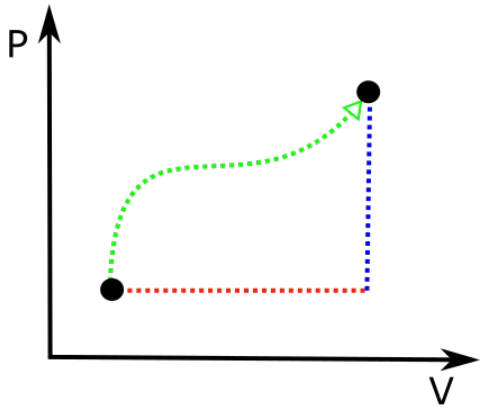

Figure 19: On a curved path (the green one), the work done on the system can be computed from $W = -\int PdV$ along the path. If you know the energy change from the points at the ends of the path, you can determine the heat transferred along the same path using $dU = Q + W$.

5.7 The Carnot Cycle

The Carnot cycle is an idealized description of a heat engine. It achieves theoretically the maximum efficiency possible.

In the Carnot cycle a gas is expanded and compressed in four stages. The stages alternate in whether they are isothermal or isentropic.

During the isentropic stages, work is done but there is no heat transferred.

During the isothermal stages, the energy is fixed, so heat transferred is equal to the work done.

After going around a loop (a single 4 stage cycle) the total energy change is zero. This is equal to the total heat transferred in a cycle plus the total work done by the gas in a cycle.

The total work done by the gas is the area enclosed by the loop in a PV diagram.

The ratio of heat transferred on one stage to total work done in the cycle is called the Carnot efficiency.

The Carnot cycle and efficiency give a limit on what could in principle be achieved rather than what is in fact achieved by real systems. Real systems are less efficient because they do not have well defined constant temperature reservoirs and heating and cooling processes are not perfectly reversible.

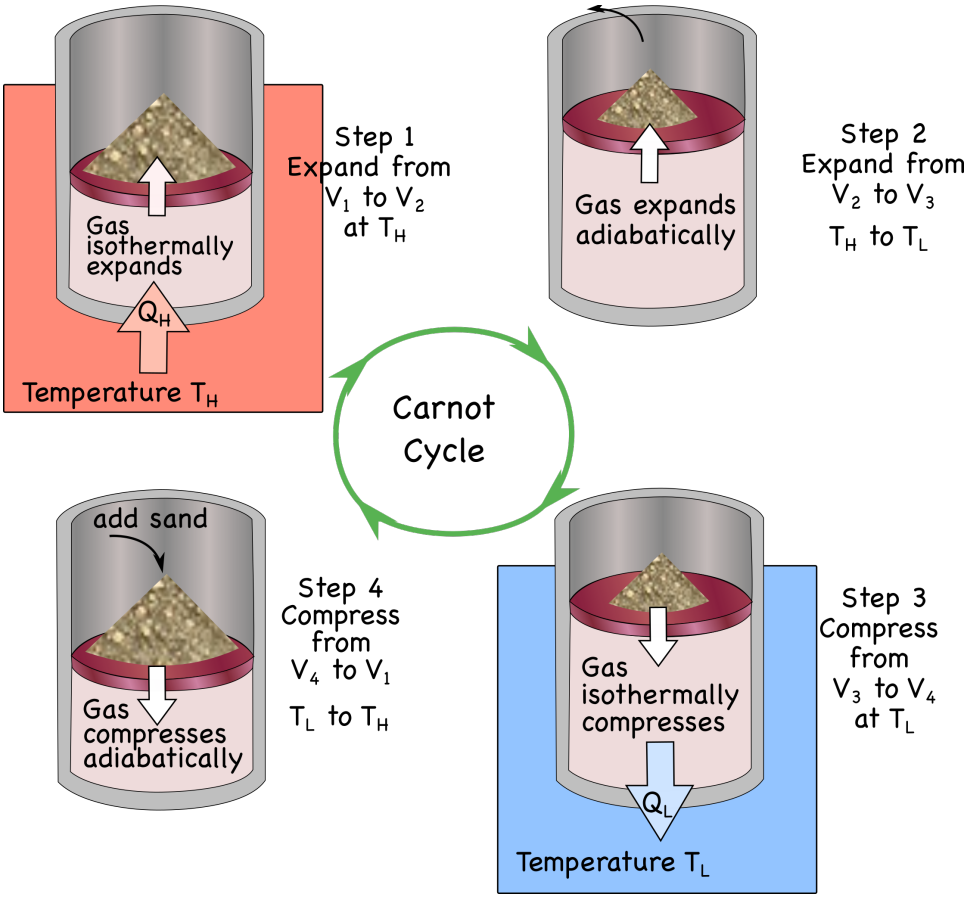

Figure 20: Steps of a Carnot cycle. Step 1 and Step 3 are isothermal, whereas Step 2 and Step 4 are adiabatic.

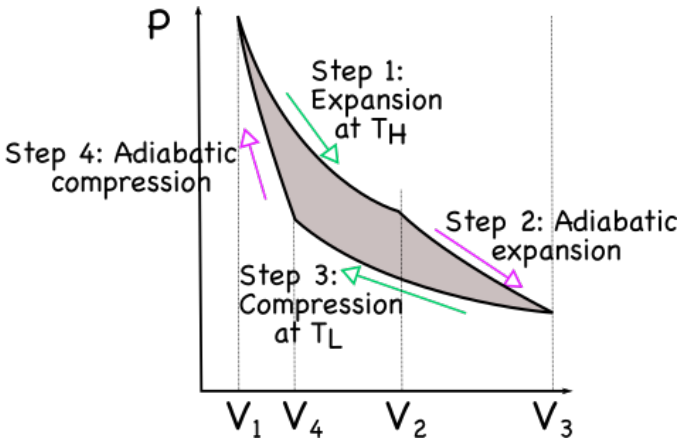

Figure 21: Steps of a Carnot cycle in an ideal gas on a PV diagram. The total work done by the system is the integral of the area enclosed by the loop.

The steps of a Carnot cycle.

1. Isothermal expansion. The engine stays at a constant temperature T_H. Heat is transferred reversibly from the hot reservoir. The heat transferred to the engine is Q_H. (An increase in volume at constant temperature increases entropy). The entropy increase of the engine is $\Delta S_1 = Q_H/T_H$. The energy change of the engine is 0, the work done by the engine is equal to the heat.

2. Adiabatic expansion. (Isentropic reversible expansion). There is no heat transfer. Entropy remains the same. However the change in energy is equal to the work done on the engine $dU = -\int PdV$. The gas cools to T_L.

3. Isothermal compression. The engine stays at a constant temperature T_L. Heat is transferred from the engine to the thermal reservoir. The entropy change of the engine is $\Delta S_2 = Q_L/T_L$. There is no energy change but the work is again equal to the heat.

4. Adiabatic compression. The gas increases in temperature back to T_H. There is no heat transfer. Entropy remains the same. The change in energy is equal to the work done on the engine.

The work done by the gas is the integral of PdV around the loop in P, V space.

$$W = \oint PdV = \oint (TdS - dU) = \oint TdS \tag{58}$$

The last step follows because after going about a loop in PV space, there is no energy change. To find the work done by the engine we need only compute the area of a loop in

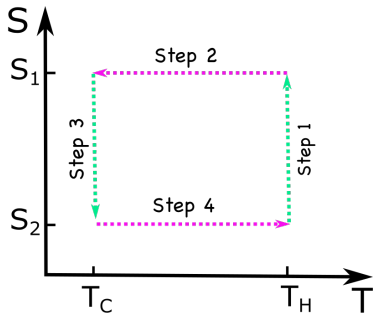

Figure 22: Another view of a Carnot cycle but in entropy vs temperature space. Temperature is proportional to energy. Vertical paths are isothermal. Horizontal paths are adiabatic (isentropic). Because $dS = 0$ on the horizontal paths, the heat transfer is equal to the work along them. The area in S, T space is equivalent to the area enclosed in P, V space. The work done by the system is equal to the area in either space.

S, T space

$$W = (T_H - T_L)(S_1 - S_2) \tag{59}$$

where S_1 is the entropy on the top of the loop in S, T space.

Because variations are done adiabatically the entropy changes during the isothermal stages are equal.

$$|\Delta S_1| = \frac{Q_H}{T_H} = |\Delta S_2| = \frac{Q_L}{T_L}. \tag{60}$$

Using equation 59 and the definition for the efficiency of a heat engine (equation 45)

$$\begin{aligned} \epsilon &= \frac{W}{Q_H} \\ &= \frac{(T_H - T_L)(S_1 - S_2)}{Q_H} \end{aligned} \tag{61}$$

We now use equation 60 for $S_1 - S_2$

$$\begin{aligned} \epsilon &= \frac{(T_H - T_L)}{Q_H}\frac{Q_H}{T_H} \\ &= 1 - \frac{T_L}{T_H}. \end{aligned} \tag{62}$$

This is equal to the maximum efficiency possible (equation 50). The Carnot cycle is an example of an ideal heat engine that achieves the maximum efficiency.

6 Summary

For a small system in contact with a thermal reservoir at temperature T, the probability that the system is in a particular state with energy ϵ_i is given by

$$P(\epsilon_i) = \frac{1}{Z} e^{-\frac{\epsilon_i}{k_B T}}$$

where Z is the partition function,

$$Z = \sum_i e^{-\frac{\epsilon_i}{k_B T}}$$

The factor $e^{-\frac{\epsilon_i}{k_B T}}$ is called the Boltzmann factor.

The average energy can be computed from the partition function

$$\bar{E} = -\frac{1}{Z}\frac{dZ}{d\beta}$$

where $\beta = 1/(k_B T)$.

For a Maxwell-Boltzmann velocity distribution (and good for a particle in a box or an ideal gas)

$$\bar{E} = \frac{1}{2} m \bar{v}^2 = \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T$$

Equipartition: the mean kinetic energy of each type molecule in a gas is about the same.

For a closed system that can vary in volume and is in contact with a thermal reservoir, a reversible change in energy in the system

$$dU = TdS - pdV$$

where the $Q = TdS$ term can be called *heat* and the $W = -pdV$ term can be called *work*. The number of particles in our closed system remains fixed. Here the heat is that transferred into the system and the work is that done on the system.

The specific heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The specific heat capacity per particle is $\frac{3}{2} k_B T$ for a monotonic gas.

The ideal gas law

$$PV = N k_B T$$

It may be useful to write N in terms of moles times Avogadro's number. We can keep the variables in MKS units if pressure P is in Pa (Pascal), volume V is in m^{-3}, k_B is in J/K,

N is the number of particles and temperature T is in Kelvin. If you are doing chemistry you are probably not going to be using these units!

Adiabatic variations (isentropic + reversible) in an ideal gas obey $PV^\gamma =$ constant where γ is the adiabatic index. Here the number of particles we are considering remains fixed.

For a monotonic ideal gas the adiabatic index $\gamma = 5/3$. For a monotonic ideal gas the specific heat capacity $C_V = \frac{3}{2}Nk_B$ and the total internal energy $U = \frac{3}{2}Nk_BT$. Here we have N particles in our system.

The relation between the adiabatic index and degrees of freedom n is $\frac{1}{\gamma-1} = \frac{n}{2}$.

Efficiency ϵ of a heat engine depends on the ratio of work W done by the engine divided by heat Q_H transferred from the hotter reservoir during a complete cycle

$$\epsilon = \frac{W}{Q_H} \leq 1 - \frac{T_L}{T_H}$$

The maximum efficiency depends on the temperatures of cold and hot reservoirs T_L, T_H.