Here we have an ideal gas in a container of volume V, with one wall of that container being a piston that we can move by applying a force F. Let's demand that this process is isentropic—it does not change the entropy of the gas. The displacement Δx shown in the figure reduces the volume of the gas, by $\Delta V = -A\Delta x < 0$ where A is the surface area of the piston. Since the force F is parallel to the piston's displacement Δx, it does positive work $W = F\Delta x > 0$. Therefore the internal energy of the gas increases by $\Delta\langle E\rangle = W$, at the same time as its volume decreases isentropically, so from Eq. 55 we have

$$P = -\frac{\partial}{\partial V}\langle E\rangle\bigg|_S = -\frac{W}{\Delta V} = \frac{F\Delta x}{A\Delta x} = \frac{F}{A}. \tag{57}$$

This identifies the pressure of an ideal gas in a container as the force per unit area that the gas exerts on the container wall, reassuringly consistent with our everyday experiences.

Rearranging the expressions above, we can obtain an expression for the work *put into* the gas by its surroundings — that is, by the external force applied to move the piston and change the volume. Still assuming an isentropic process, this input work must match the increase in the gas's average internal energy,

$$W = \Delta\langle E\rangle = -P\Delta V \qquad \text{for constant entropy.} \qquad d\langle E\rangle = W + more$$

If the entropy is allowed to change, this relation between work and pressure will still hold. However, as we will see in the next section, the non-constant entropy will introduce an additional change in the average internal energy unrelated to a force, leading to $W \neq \Delta\langle E\rangle$ and leaving only the relation

$$W = -P\Delta V = -P dV \qquad \text{more generally.} \tag{58}$$

Later we will be interested in using the gas as a thermodynamic engine that *does work on* its surroundings. This removes energy from the gas, corresponding to a negative $W < 0$, and we will need to be careful to keep track of the negative signs and their physical meaning.

Of course, as we change the volume of the gas, the pressure itself may change as described by the gas's equation of state—such as the ideal gas law, Eq. 56. Recall that we are fixing the particle number N in order to work with the canonical ensemble. With the equation of state providing an expression $P(V)$ for the pressure as a function of the volume, Eq. 58 generalizes to

$P = \frac{NT}{V}$

$$W = -\int_{V_0}^{V_f} P(V)\, dV. \tag{59}$$

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5.2   Heat and entropy

Now let's switch things up by changing the temperature T of an ideal gas while keeping its volume V and particle number N constant. Since the volume is constant, Eq. 59 indicates that no work is done, $W = 0$. Even so, from Eq. 52 we have $\langle E\rangle = \frac{3}{2}NT$ and can see that the average internal energy still changes,

$$d\langle E\rangle = \frac{3}{2}N dT. \tag{60}$$

$$S_D = \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{th}^3}\right)$$

$$S_f = \frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

In order to remain consistent with our discussion in the previous section, we should expect a change in the entropy to accompany this change in the internal energy that occurs with no work done. Indeed, for both cases of distinguishable and indistinguishable particles, the temperature dependence of the entropy in Eq. 53 is the same:

$$S = N \log\left(\lambda_{th}^{-3}\right) + T\text{-independent} = N \log\left(T^{3/2}\right) + T\text{-independent}.$$

What is the change in entropy that results from changing the temperature by dT?

$$dS = d\left(\frac{3}{2}N\log T\right) = \frac{3}{2}N\frac{dT}{T} = \frac{d\langle E\rangle}{T}$$

Looking back to Eq. 60, you should find $d\langle E\rangle = TdS$, which leads us to another important definition.

The **heat** added to or removed from a statistical system is defined to be

$$Q = T\,dS, \tag{61}$$

and corresponds to the change in the average internal energy of the system when the volume and particle number are kept constant.

As for the work W considered in the previous section, we can generalize this infinitesimal definition to

$$Q = \int_{S_0}^{S_f} T(S)\,dS, \tag{62}$$

with $Q = \Delta\langle E\rangle$ when the volume is constant. Here we assume it will be possible to invert the usual canonical relation that expresses the entropy as a function of the temperature, $S(T)$. (Some textbooks refer to infinitesimal heat and work as "dQ" and "dW", but this is easy to misread as a 'change' in heat or work, while the heat and work are themselves changes in the internal energy.)

Also like the work, the heat Q is positive when energy is added to the system to increase $\langle E\rangle$, and negative when energy is removed. Recalling that the canonical ensemble involves placing the system in thermal contact with a large external thermal reservoir, we can recognize that this energy is not being created or destroyed, but is instead flowing back and forth between the system and the reservoir. When considering heat, we will also demand that no *entropy* is created or destroyed — a positive dS will indicate entropy flowing into the system from the reservoir, while a negative change reflects entropy moving from the system to the reservoir. Because the total entropy of the system plus its reservoir is constant,

these processes are reversible, making it possible for the system to return to its starting macro-state.[11]

We have already considered isentropic processes with $dS = 0$, for example in the definition of pressure in Eq. 55. With our assumption of reversibility, the definition of heat provides a new perspective on such processes:

$Q = T \, dS$

> We define an **adiabatic process** to be a change in the control parameters of a system that occurs without transferring heat, $Q = 0$. When this process is reversible, Eq. 61 guarantees that it also does not change the system's entropy.

Since the canonical ensemble requires thermal contact between the system and its surroundings, the practical way to avoid heat exchange is to change the control parameters quickly. That is, **adiabatic processes are fast** enough that the system does not have time to exchange heat (and hence entropy) with its surroundings. The opposite extreme would be a process slow enough that any and all possible heat exchange can be completed while it is underway. Based on our work in Section 2.4, we can see that such heat exchange will keep the system's temperature equal to the temperature of its surroundings. Taking that surrounding temperature to be constant, we reach the conclusion that **constant-temperature (or isothermal) processes are slow**. Real processes generally exist in between these two extremes, usually closer to the adiabatic limit.

5.3 Thermodynamic cycles

Now we can generalize our considerations in the previous two sections to address simultaneous changes in the temperature T and the volume V of an ideal gas, still with fixed particle number N. We are used to working with the internal energy $\langle E \rangle (T, V)$ and entropy $S(T, V)$ as functions of the temperature and volume. Inverting the latter relation allows us to instead express the temperature $T(S, V)$ as a function of the entropy and volume, which carries through to the internal energy $\langle E \rangle = \frac{3}{2} NT$,

$$\langle E \rangle (T, V) \;\rightarrow\; \langle E \rangle (S, V).$$

Expanding the internal energy to first order in a multi-variable Taylor expansion, we have

$\left(\frac{1}{T}\right)^{-1}$

$-P$

$$\langle E \rangle (S, V) \approx \langle E \rangle (S_0, V_0) + (S - S_0) \left. \frac{\partial \langle E \rangle}{\partial S} \right|_V + (V - V_0) \left. \frac{\partial \langle E \rangle}{\partial V} \right|_S.$$

This approximation becomes exact in the limit of infinitesimal changes

$$\langle E \rangle (S, V) - \langle E \rangle (S_0, V_0) \rightarrow d\langle E \rangle \qquad S - S_0 \rightarrow dS \qquad V - V_0 \rightarrow dV.$$

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[11] In the case of irreversible processes, there must be sources of entropy creation. Adding these to the heat, Eq. 61 generalizes to the "Clausius inequality" $Q < T \, dS$.

At the same time, we can recognize the temperature from Eq. 22 and the (negative) pressure from Eq. 55, to obtain

$$d\langle E \rangle = T\,dS - P\,dV = Q + W. \tag{63}$$

This is a generalized form of the **first law of thermodynamics**: Any change in the internal energy of a statistical system must be matched by (either or both) heat exchange with its surroundings or work done by or on those surroundings.

We now have all the concepts and **key equations** needed to consider a variety of ways to manipulate an ideal gas in a container:

- Eq. 52 for the internal energy: $\langle E \rangle = \frac{3}{2}NT$

- Eq. 53 for the condition of constant entropy: $VT^{3/2} = \text{constant}$

- Eq. 56 for the equation of state (ideal gas law): $PV = NT$

- Eq. 63 for the first law of thermodynamics: $d\langle E \rangle = T\,dS - P\,dV = Q + W$

As examples of manipulations we can carry out by changing the system's control parameters, the piston we considered in Section 5.1 allows us to compress or expand the gas. This change in volume could be fast to keep the entropy constant (adiabatic), or slow to keep the temperature constant (isothermal). Alternately, we can clamp the piston in place to keep the volume constant, and add heat to the gas to increase its temperature — according to the ideal gas law, this will also increase the pressure of the gas. Or we can add heat while keeping the pressure constant by applying a constant force to the piston. The ideal gas law then implies the volume will increase, pushing out the piston — which could be used as a way for the system to do work on its surroundings.

It's possible to carry out a sequence of such manipulations that cause the system to end up in the same thermodynamic (macro-)state in which it started, with the same pressure, volume, temperature and internal energy. This sequence can then be repeated over and over again, always returning to the same starting point. Such a repeatable process is known as a **thermodynamic cycle**. As we will see in the next section, such cycles can make use of heat to have the system do work on its surroundings (providing an *engine*), or make use of work to remove heat from the system (providing a *refrigerator*), among other applications.

Thanks to the key equations above, we can specify the full macro-state for an ideal gas solely in terms of the pressure P and the volume V. With fixed N, the ideal gas law fixes the temperature $T = \frac{PV}{N}$, which then determines the internal energy $\langle E \rangle \propto NT$. This makes it convenient to represent the system's macro-state as a point in a **pressure–volume (or PV) diagram** — a graph with the volume on the horizontal axis and the pressure on the vertical axis. The manipulations discussed above correspond to lines in PV diagrams. In the case of a thermodynamic cycle, the lines must meet up to form a closed path for the system to go around as the cycle is repeated.

As a first example, the figure below shows the PV diagram for a (slow) isothermal expansion of the gas.
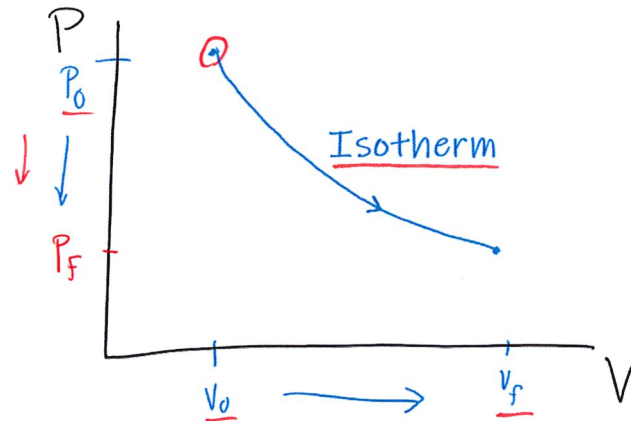
The line in a PV diagram for an isothermal process is known as an *isotherm*. As the volume expands from V_0 to V_f, the temperature (and therefore PV) is constant. What is the change in pressure $\Delta P = P_f - P_0$ in terms of P_0, V_0 and V_f? What would it mean if two isotherms were to cross in a PV diagram?

$$P_0 V_0 = V_f P_f \quad \rightarrow \quad P_f = P_0 \left(\frac{V_0}{V_f} \right) < P_0$$

$$\Delta P = P_0 \left(\frac{V_0}{V_f} - 1 \right) < 0$$

Crossing $\rightarrow$ $T = \frac{PV}{N}$ same $\rightarrow$ same isotherm

Similarly, we can consider the PV diagram below for a (fast) adiabatic compression of the gas.
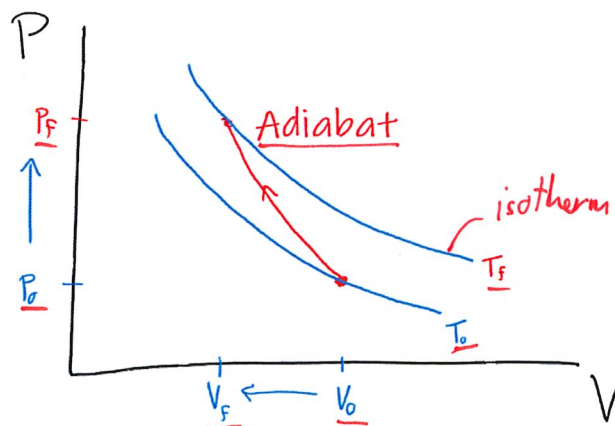
$$Q = T \, dS$$

In this case both the pressure and temperature change, while the entropy (and therefore $VT^{3/2}$) is constant. What are ΔP and the change in the temperature $\Delta T = T_f - T_0$ in terms of P_0, V_0, V_f and the fixed number of particles N?

$$V_o T_o^{3/2} = V_F T_f^{3/2} \longrightarrow T_F = T_o \left(\frac{V_o}{V_F} \right)^{2/3}$$

$$\Delta T = T_o \left[\left(\frac{V_o}{V_F} \right)^{2/3} - 1 \right] = \frac{P_o V_o}{N} \left[\left(\frac{V_o}{V_F} \right)^{2/3} - 1 \right] > 0$$

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5.4 The Carnot cycle

A famous thermodynamic cycle was proposed by Sadi Carnot in 1824, and laid the groundwork for subsequent development of engines and refrigerators later in the nineteenth century. The key idea is to propose that the ideal gas in its container can exchange energy with either of *two* different thermal reservoirs: a 'hot' reservoir with temperature T_H and a 'cold' reservoir with temperature T_L. The Carnot cycle consists of four stages, which are first shown below in the form of a PV diagram, then illustrated in a sketch (adapted from Schroeder's *Introduction to Thermal Physics*) that provides a more concrete picture of the physical processes, and finally summarized in words.