Recap   28 Feb

Ideal gases   in   canonical ensemble
$\hookrightarrow$ fix T, N

Energy levels depend on volume $V = L^3$

Partition functions for distinguishable vs. indis.

$$Z_D = (Z_1)^N = N! \, Z_I$$

$\hookrightarrow$ Same $\langle E \rangle_D = \langle E \rangle_I = \frac{3}{2} NT$

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

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

"Gibbs paradox"

Indis: Mixing reversible, $S_A' + S_B' = S_c = S_A + S_B$

Distin: Mixing irreversible, $S_A' + S_B' \geq S_c > S_A + S_B$

re-separate them. Due to the second law of thermodynamics, processes that produce an increase in entropy are irreversible.

[margin note: 25 Feb.]

[margin note: 28 Feb.]

4.4 Pressure, ideal gas law, and equations of state

Below Eq. 50 we emphasized that the ideal gas partition function depends on the volume of the gas, V, in addition to the fixed temperature T and conserved particle number N that always characterize systems governed by the canonical ensemble. Parameters like V that appear in the partition function are called **control parameters**, with the idea that they can (in principle) be controlled in experiments. Control parameters generally enter the partition function through the definition of the energies E_i for the micro-states ω_i. Another example is the magnetic field strength H for the spin systems we considered earlier.

Focusing on ideal gases for now, we see that all dependence on V drops out in our results for the average internal energy, Eq. 52. On the other hand, the entropies in Eq. 53 do depend on the volume. For both cases of distinguishable and indistinguishable particles, the entropy S depends on the same combination of volume and temperature: $V\lambda_{th}^{-3} \propto VT^{3/2}$. If we keep N fixed and consider using our experimental control to change the volume and the temperature of the system, the entropy will typically change as a consequence, unless the following relation is satisfied:

[margin note: $\lambda_{th} \propto \dfrac{1}{\sqrt{T}}$]

$$VT^{3/2} = \text{constant} \quad \Longrightarrow \quad S = \text{constant.}$$

Such **constant-entropy (or isentropic) processes** will be important in our upcoming analyses of thermodynamic cycles.[10] These cycles will involve making changes to control parameters, which is a topic we have already started to consider through the micro-canonical temperature (Eq. 22) and the canonical heat capacity (Eq. 36). The pressure of an ideal gas is similarly connected to a change in its volume, which we can motivate by thinking about squeezing an inflated balloon into a small box.

[margin note: $C_V = \dfrac{\partial \langle E \rangle}{\partial T}\Big|_V$]

[margin note: $\dfrac{1}{T} = \dfrac{\partial S}{\partial E}$]

The **pressure** is defined to be

$$P = -\frac{\partial}{\partial V} \langle E \rangle \Big|_S , \tag{55}$$

with constant entropy S. In words, the pressure is the isentropic response of the system's internal energy to a change in its volume.

In Unit 5 we will look in detail at processes that change some or all of the pressure, volume, temperature, or internal energy of an ideal gas, with N fixed. Although changing the temperature departs from the assumptions of the canonical ensemble, we will be able to understand such a process as a change from

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[10]The term *isentropic* is based on the Greek word ισος ("isos"), meaning "equal".

one canonical system (in thermodynamic equilibrium with a thermal reservoir that fixes the initial temperature T_0) into another (in thermodynamic equilibrium with a different thermal reservoir that fixes the final temperature T_f).

If we consider an isentropic process with N fixed, then the temperature and volume are related,

$$VT^{3/2} = c^{3/2} \qquad \longrightarrow \qquad T = cV^{-2/3}, \qquad \rightarrow S \text{ constant}$$

with c a constant. By inserting this into Eq. 52, we can relate the average internal energy to the volume,

$$\langle E \rangle = \frac{3}{2} NT = \frac{3c}{2} NV^{-2/3} \qquad \text{for constant entropy.}$$

Using this constant-entropy expression, what is the pressure for the ideal gas?

$$P = -\frac{\partial}{\partial V} \langle E \rangle \Big|_S = -\frac{3c}{2} N\left(\frac{-2}{3}\right) \frac{V^{-2/3}}{V} = \frac{N}{V}\left(cV^{-2/3}\right) = \frac{NT}{V}$$
$$\hookrightarrow T$$

You should find the **ideal gas law**,

$$PV = NT, \tag{56}$$

which is an example of an **equation of state**.

The "state" being referred to by this terminology is different from the micro-states that we have mostly discussed up until now. Whereas each micro-state is defined by detailed information about the microscopic degrees of freedom that constitute the system, this **thermodynamic state** or **macro-state** concerns only the large-scale (*macroscopic*) properties of the system, such as its pressure, volume, temperature, or internal energy. Equations of state are relations between these large-scale properties.

Historically, equations of state were observed empirically and studied experimentally well before the mathematical development of statistical physics. In the 1660s, for instance, Robert Boyle experimented with changing the pressure of a gas while holding its temperature fixed, finding a special case of the ideal gas law,

$$PV = \text{constant} \qquad \text{for constant } N \text{ and } T,$$

which became known as "Boyle's law". (I include the quotation marks to acknowledge the limitations of assigning individuals full credit for advances arising from the work of broad scientific communities.)

Other equations of state reflecting different aspects of the ideal gas law were uncovered during the Industrial Revolution:

- $\dfrac{V}{T} = \text{constant}$ for constant N and P (1787, "Charles's law")

- $\dfrac{P}{T} = \text{constant}$ for constant N and V (1802, "Gay-Lussac's law")

- $\dfrac{V}{N} = \text{constant}$ for constant P and T (1812, "Avogadro's law") $\sim 10^{23}$

In the 1830s Émile Clapeyron combined these empirical results into the ideal gas law itself, which August Krönig and Rudolf Clausius independently derived on the basis of statistical physics in the 1850s. These historical data are useful to illustrate how progress in scientific and mathematical understanding went hand-in-hand with industrial developments, including the design of engines and related machines, which are connected to our next topic of thermodynamic cycles.

Unit 5: Thermodynamic cycles

5.1 Work, pressure and force

In the previous section we defined the pressure of a canonical ideal gas as the thermodynamic response of the internal energy to an isentropic change in the volume (Eq. 55). At the same time, we motivated this definition by thinking about 'squeezing' the system—exerting a force on it—which suggests a connection between pressure and force. Here we make this connection explicit by considering how the energy of an object changes when a force acts on it.

Let's begin by considering a single object at position $\vec{r} = (x, y, z)$, and suppose it is displaced by a vector $d\vec{r}$ due to a force $\vec{F}(\vec{r})$. The *work* done by this force is defined to be the resulting change in the energy of the object. Infinitesimally, $W = dE = \vec{F} \cdot d\vec{r}$, which generalizes to the line integral $W = \Delta E = \int \vec{F}(r) \cdot d\vec{r}$.

A famous example is an object falling due to the force of the Earth's gravity. That force is $\vec{F} = (0, 0, -mg)$, where m is the mass of the object, $g \approx 9.8 \text{ m/s}^2$ (metres per second per second) is the strength of gravity near the surface of the Earth, and the negative sign indicates that the gravitational force is directed downward. Suppose the object starts from rest, with initial kinetic energy $E_0 = 0$, and falls downward, parallel to $\vec{F}$, from a height h. Its final energy E_f upon hitting the ground comes from the work done by the Earth's gravity:

$$W = \int \vec{F}(r) \cdot d\vec{r} = -mg \int_h^0 dz = mgh > 0$$

$$E_f = E_0 + \Delta E = 0 + W = mgh = \frac{p_z^2}{2m} \qquad \longrightarrow \qquad p_z = -m\sqrt{2gh},$$

where $\vec{p} = (p_x, p_y, p_z)$ is the momentum introduced in Eq. 46.

Generalizing to $N \gg 1$ objects in a statistical system governed by the canonical ensemble, we define the **work** done by a force to be the resulting change in the system's average internal energy *due to that force*, $W = \Delta \langle E \rangle_{\text{force}}$. In practice, the volume is the control parameter that such a force will change.

This change in $\langle E \rangle$ due to a change in volume suggests that the work is related to the pressure defined by Eq. 55. We can formalize this relation by considering the setup shown below (from Schroeder's *Introduction to Thermal Physics*).
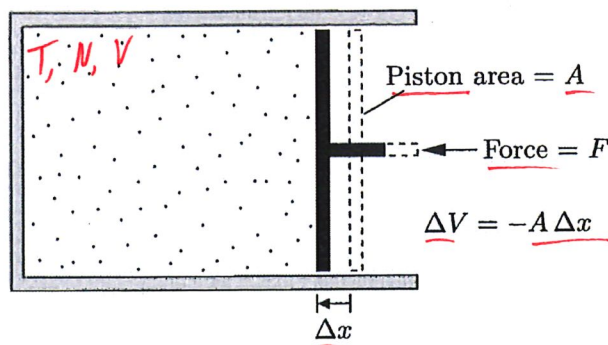
Here we have an ideal gas in a container of volume V, with one wall of that container being a piston that we can move by applying a force F. Let's demand that this process is isentropic—it does not change the entropy of the gas. The displacement Δx shown in the figure reduces the volume of the gas, by $\Delta V = -A\Delta x < 0$ 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

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

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,

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

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

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

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

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

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

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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,

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