Thermodynamics I

For an introduction to basic thermodynamics at the right level, see chapter 2 of Wang and Ricardo, volume 2. For more detail, see chapters 1–9, 19, and 20 of Blundell and Blundell. For interesting discussion, see chapters I-39 through I-43 of the Feynman lectures. There is a total of **79** points.

1   Ideal Gases and Heat Engines

Questions about ideal gas heat engines are straightforward. They were very common on the USAPhO a decade ago, though problems today tend to require a deeper understanding of thermodynamics. Nonetheless, it's fundamental material that you should know.

Idea 1

The ideal gas law comes in a few common forms,

$$PV = nRT = Nk_BT, \quad P = \frac{\rho RT}{\mu} = \frac{\rho k_BT}{m}.$$

Here, Avogadro's number is $N_A = N/n$, so that $R = N_Ak_B$, m is the mass of a gas molecule, and $\mu = N_Am$ is the molar mass. The first law of thermodynamics says

$$dU = dW + dQ, \quad dW = -P\,dV.$$

The heat capacity at constant volume is defined so that $dU = nC_V\,dT$ at constant volume. As a result, if we define $C_P = C_V + R$, we have

$$Q = \begin{cases} nC_V\Delta T & \text{at constant volume} \\ nC_P\Delta T & \text{at constant pressure} \end{cases} \qquad C_V = \begin{cases} 3R/2 & \text{monatomic} \\ 5R/2 & \text{diatomic} \\ 3R & \text{polyatomic} \end{cases}.$$

Using the first law, we can derive the results

$$W = -nRT\log\frac{V_f}{V_i} \text{ for isothermal expansion}$$

and

$$PV^\gamma = \text{constant for adiabatic expansion}, \quad \gamma = C_P/C_V,$$

both of which you should easily be able to rederive.

Idea 2

For a cyclic process that takes in heat Q_{in} from a hot reservoir at temperature T_H and outputs heat Q_{out} to a cold reservoir at temperature T_C, the work done is $W = Q_{\text{in}} - Q_{\text{out}}$, and the efficiency is

$$\eta = \frac{W}{Q_{\text{in}}} \leq 1 - \frac{T_C}{T_H}$$

where equality is achieved for reversible engines, such as the Carnot engine.

[**2**] **Problem 1.** Derive the Carnot efficiency using the fact that (a) the engine is reversible, so a complete cycle leaves the entropy of the universe unchanged, or (b) directly from idea 1.

> **Remark**
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> The most common mistake students make in this problem set is forgetting to account for the work done by the atmosphere.

[**3**] **Problem 2.** 🕓 USAPhO 2009, problem A4.

[**3**] **Problem 3.** 🕓 USAPhO 2011, problem A1.

If you want further practice, see USAPhO 1998 A1, 2008 A2, and 2010 A3. This kind of routine question should be easy. Some competitions try to make them harder by making the cycles more complicated (some truly crazy ones have been considered in the literature), but this is contrived and doesn't really require much insight. Instead, we'll move on to slightly subtler problems.

> **Example 1**
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> A cold room is initially at temperature T. The heater is turned on, raising the temperature to $T + \Delta T$. Assuming the thermal insulation is ideal, at most what fraction of the energy released by the heater stays in the room?

> **Solution**
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> As long as the room has any contact with the outside at all, air will leak out to set the pressure equal to atmospheric pressure. Its volume also stays the same, so by the ideal gas law, Nk_BT stays the same, but this is proportional to the internal energy of the air. Thus, at most 0% of the energy released by the heater stays in the room; the increase in average energy per molecule is exactly compensated by the decrease in the number of molecules. If there are thermal losses, the total internal energy of the air in the room actually decreases.

> **Example 2**
>
> A thermally isolated cylinder is divided into two compartments by a thermally conductive piston. Initially, the piston divides the cylinder into two compartments, A and B, of equal volume $V/2$ and temperature T_0. One mole of monatomic gas is in each compartment. An external agent slowly moves the piston to the side until the volumes are $V/3$ and $2V/3$. Throughout this process, the temperature remains uniform. What is the final temperature?

> **Solution**
>
> The tricky thing about this problem is that the pressures in the two compartments aren't equal; this is possible because the external agent is holding the piston. Instead, the temperatures

are made equal by heat conduction. The work done by the agent is

$$dW = -p_A \, dV_A - p_B \, dV_B = -RT \left(\frac{dV_A}{V_A} + \frac{dV_B}{V_B} \right).$$

On the other hand, this is also equal to the increase in energy,
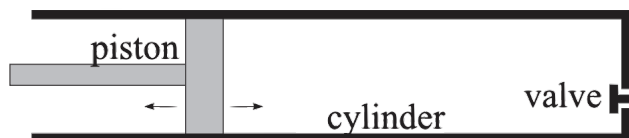
$$dW = dU = \frac{3}{2} nR \, dT = 3R \, dT.$$

Combining the two gives a differential equation,

$$3 \int \frac{dT}{T} = -\int \frac{dV_A}{V_A} - \int \frac{dV_B}{V_B}$$

which means the final temperature T_f obeys

$$3 \log \frac{T_F}{T_0} = -\log \frac{2}{3} - \log \frac{4}{3} = \log \frac{9}{8}, \quad T_F = \frac{3^{2/3}}{2} T_0.$$

[3] **Problem 4** (EstPhO 2002). In this problem we consider the combustion cycle of a car engine. Model the engine as a cylinder with a piston on the left and a valve on the right.

The steps of the process are as follows.

1. Gas entry: the piston moves from the rightmost position to the leftmost; fresh air comes in through the valve and fills the cylinder.

2. Pressure increase: the valve closes, and the piston quickly moves back to the rightmost position.

3. Work: fuel is injected in the cylinder and is ignited; you may model this process as occurring instantaneously. Then the gas starts expanding and pushes the piston to the leftmost position.

4. Gas disposal: the valve is opened. The piston is pushed to the right at constant pressure until it reaches its rightmost position, and the process then repeats.

Neglect friction and heat conduction, suppose the number of fuel molecules is negligible compared to the number of air molecules, and treat air as a diatomic ideal gas. Let k be the ratio of the maximum and minimum volumes of the cylinder. Draw the cycle on a PV diagram and find its efficiency.

[3] **Problem 5** (IZhO 2022). A quasistatic process is carried out with one mole of an ideal monatomic gas, as a result of which its initial volume $V_0 = 1 \, \text{m}^3$ increases four times, and the initial pressure $P_0 = 10^5 \, \text{Pa}$ decreases two times. For each small section of the quasistatic process, the ratio of work to the change in internal energy is the same. Find the total work done by the gas in this process.

[3] **Problem 6.** ⟳ USAPhO 2018, problem A3.

2   Dynamic Ideal Gases

Idea 3

Problems involving ideal gases can be mechanics questions. For example, the first law of thermodynamics becomes conservation of energy, where the energy includes the internal energy of the gas in addition to the usual kinetic and potential energy. You may also have to use the principles of hydrostatic equilibrium and Bernoulli's principle from **M7**.

Example 3

A space station is a large cylinder of radius R_0 filled with air molecules of mass m. The cylinder spins about its axis at an angular velocity ω, and the air rotates along with it. If the temperature T is constant inside the station, what is the ratio of the air pressure at the center of the station to the pressure at the rim?

Solution

If we work in a frame rotating with the space station, this is a fluid statics problem. By considering force balance on a thin parcel of air of radial thickness dr and area A, we have

$$A\,dP = \rho g_{\text{eff}} A\,dr$$

where $g_{\text{eff}} = \omega^2 r$ is the centrifugal acceleration. Applying the ideal gas law,

$$\frac{dP}{P} = \frac{m g_{\text{eff}}}{k_B T}\,dr$$

which integrates to give

$$\frac{P(r=0)}{P(r=R_0)} = e^{-m\omega^2 r^2/2k_B T}.$$

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[5] **Problem 7.** In this problem we'll make a simple model for the atmosphere.

(a) Assume the atmosphere to be an ideal gas at constant temperature T in mechanical equilibrium, with gas molecules of mass m. Show that the pressure depends on height as

$$P(h) = P_0\,e^{-mgh/k_B T}$$

by demanding that small parcels of gas be in mechanical equilibrium.

(b) The assumption of constant temperature is not very accurate. Sunlight warms air near the ground, causing large parcels of it to slowly rise; simultaneously other parcels of air slowly fall. This results in a well-mixed atmosphere and, since heat conduction in air is poor, the rising and falling processes are approximately adiabatic, not isothermal. Assuming the air molecules are diatomic with mass m, show that the temperature varies linearly with height. Does the atmosphere get colder or hotter with increasing height?

(c) Estimate the rate of temperature change with height numerically; is your result reasonable?

(d) Now ignoring the mixing effect of the sun, argue that an atmosphere with a temperature gradient or larger or smaller magnitude than the result you found in part (c) will be unstable or stable against spontaneous convection, respectively. (Hint: see idea 4.)

(e) ⋆ More generally, one might wonder how the total energy of the atmosphere, summed over all molecules, is divided into kinetic (i.e. thermal) and potential (i.e. gravitational) energy. Show that for *any* configuration in mechanical equilibrium (i.e. not necessarily adiabatic or isothermal), $E_{\text{grav}}/E_{\text{kin}}$ has the same value, and find this value.

When "thermal inversion" occurs, the temperature gradient has the opposite sign to the natural one you found in part (b), causing the atmosphere to be very stable against convection. Such events can cause very high air pollution in cities, since the pollutants can't escape. For more about atmospheric physics, see chapter 37 of Blundell.

[**3**] **Problem 8.** 🕐 USAPhO 1997, problem B2.

Remark

A Foehn is a hot, dry wind that comes down from a mountain range. This occurs in three steps. First, warm air rises adiabatically up the opposite side of the mountain range. As the air rises, it cools, causing the water vapor to condense and fall as rain. The now dry air then falls adiabatically down the mountain range. Since the heat capacity is now lower, the falling air heats up more than the rising air cooled down, becoming hot and dry at the bottom.

Idea 4

Consider an ideal gas in a container. In simple heat engine problems, we assume the gas stays in equilibrium, meaning that it has a single, well-defined pressure and temperature throughout. But in almost all real-world applications, there will be some deviations from equilibrium.

For example, suppose you started to heat the bottom of the container. Then the gas would no longer be in thermal equilibrium, because it doesn't have a uniform temperature, and if the heating is sufficiently sudden, it wouldn't be in mechanical equilibrium, because it wouldn't have a uniform pressure either. For a human-scale container, mechanical equilibrium is usually reestablished quickly, by a readjustment of the density. Thermal equilibrium is reestablished on a longer timescale, as energy spreads out through heat transfer.

In this simple example, we were able to talk about the temperature of individual parts of the gas, even though the gas as a whole wasn't in thermal equilibrium. That's because each piece of the gas is in thermal equilibrium with itself, so temperature can be defined locally. In more violent situations, even that might not be possible.

In general, conservation laws are quite useful for nonequilibrium problems, because following the detailed dynamics may be impossible.

> **Example 4**
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> A thermally insulated chamber contains a vacuum; it is connected to the outside by a small valve. The valve is opened until the air inside the chamber reaches atmospheric pressure, then closed. The temperature of the air outside the chamber is T_0. Treating the air as diatomic, what is the temperature T of the air inside the chamber?

> **Solution**
>
> Let the chamber have a volume V, and let the atmospheric pressure be p_0. As our system, consider the set of all air that eventually makes it inside the chamber, and suppose this air has volume V_0 before it enters the chamber. The work done on this air by the entire rest of the atmosphere, as it enters the chamber, is $p_0 V_0$. The final internal energy of the air is
>
> $$ E = \frac{5}{2}nRT_0 + p_0 V_0 = \frac{7}{2}nRT_0. $$
>
> On the other hand, we also have $E = nC_V T = (5/2)nRT$, which gives
>
> $$ T = \frac{7}{5}T_0. $$
>
> At that point, the flow stops because the pressure is equalized, even though the temperature isn't. This is an example of mechanical equilibrium being attained before thermal equilibrium. (In the long run, the temperature will equality too, by heat transfer through the walls.)
>
> Where does the extra thermal energy of the gas come from? As we just said, it's from the air behind it pushing it into the chamber. But on a slightly deeper level, the energy is ultimately gravitational: the entire atmosphere shrinks down toward the Earth a bit once the volume V_0 of air is removed from it, and this decrease in gravitational potential energy is exactly the same as the increase in thermal energy of this system.

[2] **Problem 9.** Consider two cylinders A and B of equal volume V, connected by a thin valve. The cylinders are thermally insulated from the environment, but conduct heat well between each other. Cylinder A is equipped with a piston that can compress the gas inside. Initially, the valve is sealed, cylinder A contains an ideal monatomic gas at temperature T, and cylinder B contains a vacuum.

Now suppose the valve is opened, and the piston is slowly pushed inward so that the pressure in cylinder A remains constant, until it cannot go any further. What is the final temperature of the gas, and what is the final volume of cylinder A?

[4] **Problem 10.** Consider a cylinder of gas with cross-sectional area A and volume V. Assume all surfaces are frictionless and thermally insulating. A piston of mass m is placed snugly on top, and the entire setup is inside an atmosphere with pressure P_{atm}.

(a) First suppose the system is in equilibrium, so that the pressure of the gas inside is $P_{\text{atm}} + mg/A$. The piston is then given a slight downward displacement. Find the frequency of small oscillations by assuming the ideal gas law always holds for the gas as a whole. This setup is known as the Ruchardt experiment, and can be used to determine γ.

(b) Under what circumstances is the result of part (a) a good approximation?

(c) Now suppose that instead, the piston is initially suspended from a thread carrying tension mg, so that the pressure of the gas is just P_{atm}. Suddenly, the thread is cut. The piston falls down the cylinder and bounces up and down several times before eventually coming to rest. Explain why the equation $PV^\gamma = \text{const}$ cannot be used to determine the final state.

(d) Assuming the final downward displacement of the piston is d, find the net work done on the gas, assuming that *all* of the energy dissipated goes into the gas.

(e) Find d and the final temperature of the gas, assuming the gas is monatomic.

[3] **Problem 11** (Russia 2008). A cylinder with a metal bottom and insulating walls is underneath a thin massive metal piston located at a height h, which is much smaller than the cylinder diameter. A resistor of resistance r is placed inside and connected to an electric circuit with an emf $\mathcal{E}$.
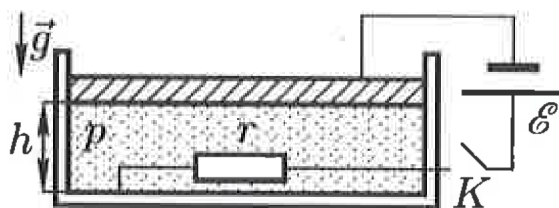
The circuit is connected to the piston and cylinder bottom with light flexible wires. Initially, the switch is open, the cylinder is filled with helium at a pressure $p \gg \epsilon_0 \mathcal{E}/h^2$, which you can treat as a monatomic ideal gas with a dielectric constant of 1. The system is thermally insulated, placed in vacuum, and at thermal and mechanical equilibrium. Then the switch K is closed. Find the height H of the piston after a long time.

[4] **Problem 12** (Grad). A long, cylindrical tank of length L and radius R is placed on a carriage that can slide without friction on rails. The mass of the empty tank and carriage is M. Initially, the tank is filled with an ideal gas of total mass $m \ll M$ at pressure P_0 and temperature T_0. The left end of the tank is heated to a fixed temperature T_1, while the right end of the tank has its temperature fixed at T_0, where $T_1 - T_0 \ll T_0$.

In this problem, you need only work to first order in $(T_1 - T_0)/T_0$. Suppose that the temperatures have been maintained for long enough for the gas to enter a steady state.

(a) Argue that the temperature $T(x)$ of the gas in the tank is a linear function of position.

(b) Find the density of the gas in the tank as a function of position.

(c) Find the distance the carriage has moved.

(d) In order for the carriage to have moved, a horizontal force had to have acted on it. Where did this force come from?

[4] **Problem 13.** ⏱ APhO 2010, problem 3B. A mathematically tough problem on a collapsing bubble.

[5] **Problem 14.** ⏱ IPhO 2010, problem 2. A neat, tricky problem about how chimneys work.

3   Statistical Mechanics

There are fundamentally two approaches to describing systems of many interacting particles: bottom-up and top-down. In the top-down approach of thermodynamics, we try to roughly describe the behavior of the whole system in terms of a few macroscopically measurable observables, such as pressure and temperature, and hope this is enough information to extract what we want. In the bottom-up approach, we start by analyzing the behavior of individual molecules, governed by Newtonian mechanics. Of course, we can't do this exactly, but it turns out to be possible to make probabilistic statements about individual molecules. This is the approach of statistical mechanics.

Idea 5: Boltzmann Distribution

The probability distribution for the states of a particle in a system of temperature T is proportional to $e^{-E/k_B T}$. Specifically:

- For quantum systems, where the energy levels are discrete, the probability of being in a state n with energy E_n is proportional to $e^{-E_n/k_B T}$.

- For a single classical particle, the state is instead specified by (x, p), the position and the momentum, and the probability density in this space, called phase space, is proportional to $e^{-E(x,p)/k_B T}$.

It isn't possible to derive the Boltzmann distribution from anything we've already covered, but you'll see in **T2** how it emerges from a simpler postulate.

Example 5: Isothermal Atmosphere

Do problem 7 using statistical mechanics.

Solution

The energy is
$$E(h, p) = mgh + \frac{p^2}{2m}$$
and the probability distribution for heights is found by integrating over momenta,
$$p(h) \propto \int dp\, e^{-E(h,p)/k_B T} = e^{-mgh/k_B T} \int dp\, e^{-p^2/2m}.$$

However, this integral is simply a constant, so we just get
$$p(h) \propto e^{-mgh/k_B T}.$$

Since the particles are assumed independent (since we have an ideal gas), the probability for a particle to be at a point is proportional to the density of gas at that point. We see the density falls exponentially with height, so by the ideal gas law, the pressure does too.

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[1] **Problem 15.** Do example 3 using statistical mechanics.

[3] **Problem 16.** Some basic computations for ideal gases.

(a) For an ideal gas in a box, show that the probability distribution of speeds obeys

$$p(v) \propto v^2 e^{-mv^2/2k_B T}$$

at any point in the box, regardless of the shape of the box.

(b) Compute the most probable speed, i.e. the location of the peak of this probability distribution.

(c) Show that the average kinetic energy is $\langle mv^2/2 \rangle = 3k_B T/2$. This is a special case of the equipartition theorem, shown below. (Hint: you will have to do a somewhat tricky integral. See the example below and the examples in **P1** for guidance.)

Idea 6: Equipartition Theorem

Suppose some degree of freedom in phase space contributes to the energy by a power law,

$$E \propto p^n \text{ or } H \propto x^n.$$

Then in thermal equilibrium, there is an average energy of $k_B T/n$ in this degree of freedom. The proof of this is just a straightforward generalization of the reasoning in problem 16(c). Note that the proof of the equipartition theorem is entirely classical, i.e. it holds when a system is adequately described by classical mechanics.

Here are a few important examples of the equipartition theorem.

- A mass on a spring in one dimension has

$$E = \frac{p^2}{2m} + \frac{kx^2}{2}.$$

  This involves two degrees of freedom in phase space, each with $n = 2$, so the average energy is $2(k_B T/2) = k_B T$.

- In problem 7 you considered a system with a linear potential energy, $E(h) = mgh$. This is a degree of freedom with $n = 1$, and accordingly, the average potential energy of each molecule is $k_B T$.

- An atom in a solid can be thought of as attached to its neighbors by springs. Since the atom is in three dimensions, this yields three copies of the first example, and hence an average thermal energy of $3k_B T$. This implies that the specific heat per atom in a solid is $3k_B$ (or equivalently $3R$ per mole), which is called the Dulong–Petit law.

Incidentally, because systems in thermal equilibrium are also in long-term mechanical equilibrium, the virial theorem from **M6** applies, and tells us the ratio between the average kinetic and potential energy; of course, it matches the result of the equipartition theorem. You'll investigate some more key examples in the problems below.

Example 6

A free particle in one dimension, $H = p^2/2m$, has energy levels $E_n = n^2 E_0$ for $n = 0, 1, 2, \ldots$, as we will show in **X1**. Show that the average energy at high temperatures is consistent with the equipartition theorem.

Solution

The probability of being in energy level n is proportional to $e^{-n^2 E_0/k_B T}$. Therefore, by normalizing the probability distribution, the probability itself is

$$p_n = \frac{e^{-n^2 E_0/k_B T}}{\sum_{m=0}^{\infty} e^{-m^2 E_0/k_B T}}.$$

Therefore, the average value of the energy is

$$\langle E \rangle = \sum_{n=0}^{\infty} n^2 E_0 \, p_n = \frac{\sum_{n=0}^{\infty} n^2 E_0 e^{-n^2 E_0/k_B T}}{\sum_{n=0}^{\infty} e^{-n^2 E_0/k_B T}}.$$

At high temperatures, this quantum result should reduce to the classical result of the equipartition theorem. Note that at such temperatures, the typical values of n will be very high. Therefore, we can treat the sums over n as continuous integrals,

$$\langle E \rangle \approx \frac{\int_0^{\infty} dn \, n^2 E_0 e^{-n^2 E_0/k_B T}}{\int_0^{\infty} dn \, e^{-n^2 E_0/k_B T}} = \frac{\int_0^{\infty} x^2 e^{-x^2} \, dx}{\int_0^{\infty} e^{-x^2} \, dx} k_B T$$

where we switched to the dimensionless variable $x = \sqrt{n^2 E_0/k_B T}$. Evaluating either of these integrals is tricky, but we can relate them using integration by parts,

$$\int_0^{\infty} x^2 e^{-x^2} \, dx = \int_0^{\infty} (2xe^{-x^2} \, dx) \frac{x}{2} = \frac{1}{2} \int_0^{\infty} e^{-x^2} \, dx.$$

Therefore, the ratio of integrals is $1/2$, giving an average energy of $k_B T/2$ as expected.

[**3**] **Problem 17.** The energy of a photon is $E = pc$.

(a) Treating the photon classically, compute the average energy of a photon moving in one dimension, assuming it obeys the Boltzmann distribution with temperature T. Check that the result obeys the equipartition theorem.

(b) Generalize this result to three dimensions to compute γ for a 3D photon gas.

[**3**] **Problem 18.** A one-dimensional quantum harmonic oscillator has energy levels $E_n = nE_0$ for $n \geq 0$, as you will show in **X1**.

(a) Compute the average energy of the system at temperature T.

(b) Show that at high temperatures, the average energy obeys the equipartition theorem.

(c) Show that the energy at low temperatures is instead exponentially suppressed. This is why some modes are said to "freeze out", so they do not contribute to C_V.

The phenomenon of "freezing out" was one of the greatest puzzles of classical physics in the 19th century, though nobody anticipated the resolution would be as strange as quantum mechanics.

[**3**] **Problem 19.** The Boltzmann distribution can be normalized to a probability distribution by dividing by the so-called partition function $Z = \sum_n e^{-E_n/k_B T}$.

(a) For a quantum harmonic oscillator, compute the probability of occupancy of the ground state (i.e. the lowest energy state) at temperature T.

(b) Do the same for the hydrogen atom, where $E_n = -E_0/n^2$ for $n \geq 1$. You should get a rather strange answer. Does it make physical sense?

[**3**] **Problem 20.** To model paramagnetism, consider a set of N independent magnetic dipoles in a vertical magnetic field B and temperature T. Each dipole has two possible quantum states, spin up and spin down, with energies $\boldsymbol{\mu} \cdot \mathbf{B}$ and magnetic dipole moment $\mu_z = \pm e\hbar/2m$.

(a) Defining the magnetization M as the total magnetic moment, find the average magnetization of the magnet as a function of T.

(b) Show that $M \propto 1/T$ in the limit of high T. This result is called Curie's law.

Remark

In principle, all of our results about statistical mechanics can be derived by following the microscopic dynamics, e.g. the collisions of atoms with each other for a gas. It's just very hard to do so in practice.

However, you can still get a bit of insight in simple cases. For example, consider a one-dimensional ideal gas in a uniform gravitational field, $E = p^2/2m + mgh$. Since the kinetic energy is a quadratic degree of freedom, and the potential energy is a linear degree of freedom, the average potential energy must be twice the average kinetic energy. Furthermore, this should be true no matter how rarely collisions happen; less frequent collisions simply mean it takes longer to get to thermal equilibrium, without changing what that equilibrium is.

Therefore, we have the concrete, classical mechanical prediction that a mass bouncing elastically on the ground, suffering no collisions at all, will have an average potential energy equal to twice its average kinetic energy, which you can verify directly from Newton's laws.

Here's a more subtle puzzle. In our analysis of the isothermal atmosphere, we found that the distribution of speeds is the same everywhere. But if you look at any one particle, it will clearly pick up speed as it falls down. How is this self-consistent? Wouldn't this tend to increase the temperature at lower heights?

Again, it's easiest to think about this situation in the limit of a very thin gas, where collisions are rare. Indeed, each particle that starts at the top of the atmosphere will pick up a lot of speed as it falls down. But why are there any particles at the top at all? Because at

the bottom of the atmosphere, which is much more dense, particles occasionally get a lot of energy through collisions, which propels them to the top. In equilibrium, the particles going down *do* arrive at the bottom with unusually high speed, but they're balanced out by the unusually fast particles going the other way. Keeping track of the details here can be quite complex, especially when collisions are frequent, but miraculously the Boltzmann distribution takes care of it all for us!

4   Kinetic Theory

Idea 7

Kinetic theory is the branch of statistical mechanics that focuses on the motion of individual molecules in a gas. It can get quite mathematically involved, since one must consider the effects of molecular collisions, which is why the subject is usually reserved for graduate school. However, in some simple situations, collisions can be neglected, effectively making the molecules independent.

Example 7: Ideal Gas Law

Derive the ideal gas law using kinetic theory.

Solution

Without loss of generality, we consider a cubical container of gas of side length L and N gas molecules. Consider the pressure exerted on a wall aligned with the yz plane. A given gas molecule will hit this wall with period $2L/v_x$, transferring a momentum of $2p_x$. Then the pressure on the wall is

$$P = \frac{F}{A} = \frac{1}{L^2} \frac{N \langle p_x v_x \rangle}{L}.$$

This can be written as

$$P = \frac{N}{V} \langle p_x v_x \rangle = \frac{N}{V} \frac{\langle \mathbf{p} \cdot \mathbf{v} \rangle}{3} = \frac{N}{3V} \langle m v^2 \rangle = \frac{N k_B T}{V}$$

where we used rotational symmetry and the equipartition theorem.

Of course, this calculation was doable because we neglected interactions between different gas molecules. However, this doesn't matter as much as one might think. We assumed molecules can cross the whole container without colliding, but if they do, the derivation still basically works because they just transfer their momentum to another molecule. As long as the molecules are moving freely most of the time, the answer above is approximately right.

In **T2**, we'll see how an attractive interaction can lower the pressure. When the gas gets very dense, the effect can be drastic. In **T3**, we'll see how it can make the gas condense into a liquid.

[**2**] **Problem 21.** Use kinetic theory to find the pressure of a photon gas (i.e. an ideal gas of massless particles, which satisfy $E = pc$) in terms of its total internal energy U and volume V. Use this result to find γ for a photon gas, where γ is defined so that PV^γ is constant in an adiabatic process.

Example 8

An astronaut of mass M stranded in outer space makes a primitive rocket as follows. They take a piece of dry ice of mass $m \ll M$ and molar mass μ and put it in a long, thin glass held at temperature T. The dry ice sublimates, and the astronaut points the opening of the glass in the opposite of the direction they want to go. Estimate, within an order of magnitude, how fast the astronaut is going after all the dry ice is gone.

Solution

Let m' be the mass of a molecule of dry ice. By the equipartition theorem, the molecules have speed

$$v \sim \sqrt{\frac{kT}{m'}} = \sqrt{\frac{NkT}{Nm'}} = \sqrt{\frac{RT}{\mu}}.$$

The molecules exit the glass traveling more or less in the same direction, so by momentum conservation the final speed of the astronaut is on the order of

$$\frac{m}{M} v = \frac{m}{M}\sqrt{\frac{RT}{\mu}}.$$

We have implicitly assumed that the glass is long enough that the molecules get into thermal equilibrium with the glass before they leave it. For a short glass, the answer would instead depend on the typical speeds of molecules at the moment they sublimate.

Example 9

A container of volume V is filled with a gas of uniform temperature T, and placed in a vacuum. If a small hole is punched in the container and gas slowly leaks out, how does the temperature in the container change over time?

Solution

The mean free path λ is the average distance a gas molecule moves before it hits another one. Let d be the width of the hole. There are two important limiting cases.

If $\lambda \ll d$, then molecules can't make it out of the hole without undergoing many collisions. Thus, if the gas has some average flow velocity, its molecules will be carried along with it. We can thus treat the gas like a continuous fluid, and the logic of example 4 applies. The gas inside the container does $P\,dV$ work on the gas exiting and hence loses energy. Thus, the remaining gas cools down, so the temperature of the container decreases over time. (Doing this problem quantitatively requires the analogue of Bernoulli's principle for gases, which we derive in **T3**.)

> If $d \ll \lambda$, then molecules fly out of the hole without encountering any others at all; this is the regime of "effusion". Therefore, we shouldn't think in terms of an average gas pressure or flow velocity, but rather just consider each molecule on its own. An individual molecule has a greater chance of escaping through the hole if it's moving faster. Thus, the molecules that come out will on average be higher energy than the ones that stay in the container. So just as in the opposite limit, the remaining gas cools down. (This limit is treated quantitatively in problem 2.24 of Wang and Ricardo, volume 2.)

Remark

The previous example implies that a gas of uniform temperature can turn into a hot gas and a cold gas without needing any external work, which seems to directly contradict the second law of thermodynamics! To phrase it another way, you can use the free temperature difference to run a heat engine, which seemingly allows perpetual motion.

Of course, the resolution is that the total entropy of the gas is still going up. The kinetic energy is getting less spread out, but the positions of the atoms are getting more spread out, since some can now be outside the container. Thus, the "perpetual motion" only works as long as the gas is still leaking out of the container; it stops once the density becomes uniform. The lesson here is that, while most setups extract work from a temperature difference, more generally you can extract it from any potential increase in entropy; in this case, it comes from an initial difference in densities.

[**2**] **Problem 22** (Kalda). Natural uranium consists of mainly two isotopes, ^{238}U and ^{235}U, and the relative concentration of the latter is 0.7%. Uranium is enriched by a multi-stage process, where at each stage, evaporated UF_6 is led through a porous wall. The porous wall is a thin film with microscopic holes, much smaller than the mean free path of the molecules, but larger than the dimension of the molecules. How many stages are needed to increase the ^{235}U content to 1.4%? The molar mass of fluoride is $19\,\mathrm{g/mol}$.

[**2**] **Problem 23** (Grad). A small vessel with a tiny hole of diameter d is placed inside a chamber, where the pressure is so low that the mean free path is $\lambda \gg d$. The temperature of the gas in the chamber is T_0, and the pressure is P_0. The temperature in the vessel is kept at a constant $T_1 = 4T_0$.
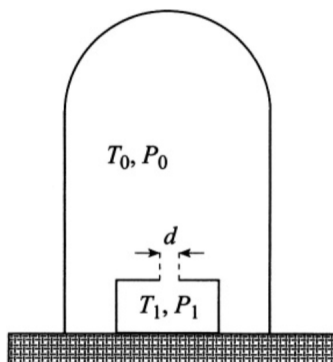
What is the pressure inside the vessel when steady state is reached?

[**5**] **Problem 24.** In this problem, we consider a simple kinetic theory model for "transport" in a sparse gas. Two parallel plates are at a distance L from each other. The space between the plates is filled with a gas of density ρ, with molecule of mass m. Assume that the gas density is low enough to neglect collisions between gas molecules, and that all radiation effects can be neglected.

(a) Suppose the two plates are held at temperatures $T + \Delta T$ and T, where $\Delta T \ll T$. Assume that when gas molecules bounce from a plate, they instantly obtain the plate's temperature. Estimate the heat flux per area P/A (in units of W/m^2) between the plates. (This determines the thermal conductivity, to be defined in **T2**.)

(b) Suppose the top plate moves with a transverse speed $v_\parallel$ parallel to itself, while the bottom plate is still, and $mv_\parallel^2 \ll T$. Assume that when gas molecules bounce from a plate, they obtain that plate's transverse speed. Estimate the force per area F/A on each plate. (This determines the viscosity, as defined in **M7**.)

Both the thermal conductivity and viscosity are associated with the transport of conserved quantities (energy and transverse momentum, respectively) through the gas. Now, above we have neglected collisions entirely, which is unrealistic for most gases unless they are extremely sparse. However, it's possible to get some rough estimates for what happens in the presence of collisions.

(c) Let σ be the cross-sectional area of a gas molecule. Estimate the mean free path d of a gas molecule.

(d) Our previous analysis held when $L \ll d$. Now suppose, more realistically, that $L \gg d$. Estimate P/A and F/A in the steady state. (Hint: consider a set of imaginary planes that are spaced by a distance d, and consider the heat/momentum flow between pairs of adjacent planes; for such pairs, collisions can be neglected.)

(e) Suppose a gas molecule begins at the top plate, and both plates have temperature T. Again assuming that $L \gg d$, estimate the typical time it takes before the gas molecule hits the bottom plate. (Hint: model the position of the particle as a sum of random steps, and recall the facts about variance in **P2**.)

For a clear discussion of the ideas of this problem, see sections 7.3 and 7.4 of The Art of Insight.

[**5**] **Problem 25.** ⟲ EuPhO 2017, problem 2. A nice problem using many of the above ideas.

> **Example 10**
>
> A box of mass M contains an ideal gas consisting of many particles, with total mass M_g. Find $\langle V_x^2 \rangle$, the average mean-square velocity of the box along the x-axis.

> **Solution**
>
> This problem illustrates how kinetic theory can get very subtle, even when we don't have to keep track of the detailed collision dynamics. First, note that if each gas molecule has mass m, then each one has $\langle v_x^2 \rangle = k_B T/m$ by equipartition. Now there are two simple arguments that give different answers.
>
> 1. If we apply equipartition of energy to the box itself, we get $\langle V_x^2 \rangle = k_B T/M$.

2. The total momentum of the box and gas together is zero, so

$$MV_x = -m\sum_{i=1}^{N} v_{x,i}.$$

On the other hand, by the rules of error propagation introduced in **P1**,

$$\left\langle \left(m\sum_{i=1}^{N} v_{x,i} \right)^2 \right\rangle = m^2\, N\, \frac{k_B T}{m} = k_B T M_g$$

which implies

$$\langle V_x^2 \rangle = \frac{M_g}{M^2} k_B T.$$

What's going on? It actually turns out that both of these arguments are wrong in general, but each one is correct in different limiting cases.

The problem with the first argument is that the derivation of equipartition of energy assumes that each degree of freedom is independent of the others, i.e. it ignores the fact that when the box picks up momentum, the gas must have a compensating opposite total momentum. The problem with the second argument is that it assumes the velocities of the molecules are independent of each other, which might not be true.

Note that the energy and momentum of the box are related by $E = P^2/2M$. Now, if the box is heavy, $M \gg M_g$, it can store lots of momentum even when it has very little energy, and conversely when it has a decent amount of energy it must have an enormous momentum. The latter implies that the first argument fails. But the second argument works, because the box serves as a "sink" for momentum. For example, the gas molecules could all be moving to the right, and that would be easily compensated by the box moving slightly to the left.

If the box is light, $M \ll M_g$, then it can have lots of energy even having negligible momentum. In this case, the first argument works, because the box doesn't ever have enough momentum to substantially affect the gas's behavior. But the second argument fails, because if the box can't carry much momentum, then the gas molecules' momenta must almost entirely cancel out among themselves, meaning that they are not independent.

The general solution can be found with a simple trick. The problem with the equipartition argument is essentially that we treat the box velocity V_x as independent of the center of mass velocity of the gas, $\overline{v}_x$. We can therefore switch to the variables

$$v_{\mathrm{CM}} = \frac{M_g \overline{v}_x + M V_x}{M_g + M}, \quad v_{x,\mathrm{rel}} = V_x - \overline{v}_x.$$

These two new variables are independent, because the momentum conservation constraint just says the former is always equal to zero. Thus, we can safely apply equipartition of energy to v_{rel}. Recalling the reduced mass idea from **M6**, we have

$$E \supset \frac{1}{2}\mu v_{x,\mathrm{rel}}^2, \quad \mu = \frac{M M_g}{M + M_g}.$$

By equipartition we have
$$\langle v_{x,\text{rel}}^2 \rangle = \frac{k_B T}{\mu}$$

and by momentum conservation we conclude

$$\langle V_x^2 \rangle = \left(\frac{M_g}{M + M_g} \right)^2 \langle v_{x,\text{rel}}^2 \rangle = \frac{k_B T}{M} \frac{M_g}{M + M_g}$$

which reduces to the two answers found above in the appropriate limits. This problem turns out to be relevant to astrophysics, where it is a toy model for the dynamics of a supermassive black hole in a galaxy. For a complete analysis which starts from the postulates of kinetic theory, see this paper.

Remark

Above, we discussed the distinction between "bottom-up" and "top-down" approaches, but there are also bridges between the subjects. For example, suppose you had a large volume of gas, where the mean free path is much smaller than the container's size. Here, the gas can come into equilibrium *locally*, at which point we may describe its state with a temperature field $T(\mathbf{x}, t)$, along with other fields, such as pressure, density, and velocity. This leads to the subject of hydrodynamics, which can be derived from kinetic theory. We started on this subject in **M7**, but there we neglected any thermal properties; we will return to it in **T3**.

On the other hand, suppose an entire macroscopic system is already in thermal equilibrium. The system is homogeneous, so there's no need for hydrodynamics, but it can still be difficult to infer the macroscopic behavior of the system. For example, if you had water molecules at a given temperature and pressure, it's still hard to calculate what phase they're in! In physics, our best tool for this kind of problem is the renormalization group, which bridges the gap by considering a series of "coarse-graining" operations that gradually zoom out. This is a deep subject, typically reserved for graduate courses.