Additional Problems in Thermodynamics

February 5, 2018

Problem 1 - Isothermal Expansion of Non-Ideal Gas

Statement

In discussion, we brought up two possible corrections to the ideal gas law. First, we observed that the particles have a weak attraction between them, so when they hit the walls of the container, their force is less than if they did not have any mutual attraction. The attractions are pairwise, so the corrections should be proportional to the density of attractions, N^2/V. Second, we observed that particles take up a non-zero effective volume. So the total volume accessible to the particles is less than the volume of the container. These corrections are parameterized by empirical constants a, b in the van der Waals equation of state:

$$\left(P + \frac{N^2}{V}a\right)(V - Nb) = Nk_BT \tag{1}$$

Suppose that a gas with known a, b is isothermally compressed at temperature T_0 from V_0 to $V_1 < V_0$. How much work is done on the gas?

Solution

To calculate the work, we can use

$$W = \int P(V)dV \tag{2}$$

Solving for P in Eq. 1,

$$P(V) = \frac{Nk_BT}{V - Nb} - \frac{N^2a}{V} \tag{3}$$

$$W = Nk_BT \ln\left(\frac{V_1 - Nb}{V_0 - Nb}\right) - N^2a \ln\left(\frac{V_1}{V_0}\right) \tag{4}$$

Problem 2 - First Law in Different Processes

Statement

Heat Q is added to a system of H_2. Suppose the heat is added (a) isothermally, (b) isochorically, or (c) isobarically. What is the change in the internal energy and the work done in each case? Assume that all temperatures involved are around room temperature.

Solution

For each part, we need to use the first law of thermodynamics (conservation of energy):

$$\Delta U = Q - W \tag{5}$$

(a) Isothermally means $\Delta T = 0$. Recall that the internal energy U is proportional to temperature. So $\Delta U = 0$ as well. Therefore $W = Q$ (using the sign convention that $W > 0$ when the system does work on the environment.

(b) Isochorically means that $\delta V = 0$. Looking at Eq. 2, if the volume never changes, the integral must be zero. Therefore $W = 0$ and so $\Delta U = Q$.

(c) Isobarically means that the pressure is constant. We can use the corresponding heat transfer equation to determine ΔT:

$$Q = mc_P \Delta T = NC_P \Delta T \tag{6}$$

We need to be a little careful with units. Since N is the number of molecules, not the number of moles, we want to use the extensive heat capacity. We need to count the number of degrees of freedom on H_2. At room temperature, the vibrational degrees of freedom are frozen out. So we effectively have 3 translational degrees of freedom and 2 rotational degrees of freedom. So by the equipartition theorem

$$C_V = \frac{5}{2}k_B \tag{7}$$

and since $C_P = C_V + k_B$:

$$C_P = \frac{7}{2}k_B \tag{8}$$

So

$$\Delta T = \frac{Q}{NC_p} = \frac{2}{7}\frac{Q}{Nk_B} \tag{9}$$

By the same reasoning,

$$U = \frac{5}{2}Nk_B T \tag{10}$$

so

$$\Delta U = \frac{5}{2}Nk_B \Delta T = \frac{5}{2}Nk_B \frac{2}{7}\frac{Q}{Nk_B} = \frac{5}{7}Q \tag{11}$$

Finally, using Eq. 5,

$$W = Q - \Delta U = \frac{2}{7}Q \tag{12}$$

Problem 3a - Getting Comfortable with Thermodynamic Cycles

So far we have looked at adding heat to a system, extracting work from a system, and general processes that involve a combination of heat and work. We can go further to now chain multiple processes together. An interesting case of chaining processes together is cycles–chains of processes where the state of the system at the end of the chain is the same as the state of the system at the start. In such cases, all state functions are zero. But there are plenty of quantites that are not state functions.

Let us begin with a simple process and get comfortable with the motions. N molecules of an ideal gas with heat capacity per molecule at constant volume $C_V = 3k_B$ is initially at pressure P_0 and temperature T_0 undergoes the following cycle:

1. Isobaric expansion to volume V_1.

2. Isochoric cooling to temperature T_1.

3. Isobaric compression to the original volume.

4. Isochoric heating to T_0.

Sketch the PV-diagram for this process. Calculate the total work extracted in the cycle. Indicate the graphical meaning of the total work on your diagram. Calculate the heat added in each step of the cycle. Check that the calculations agree with the first law of thermodynamics.

Solution
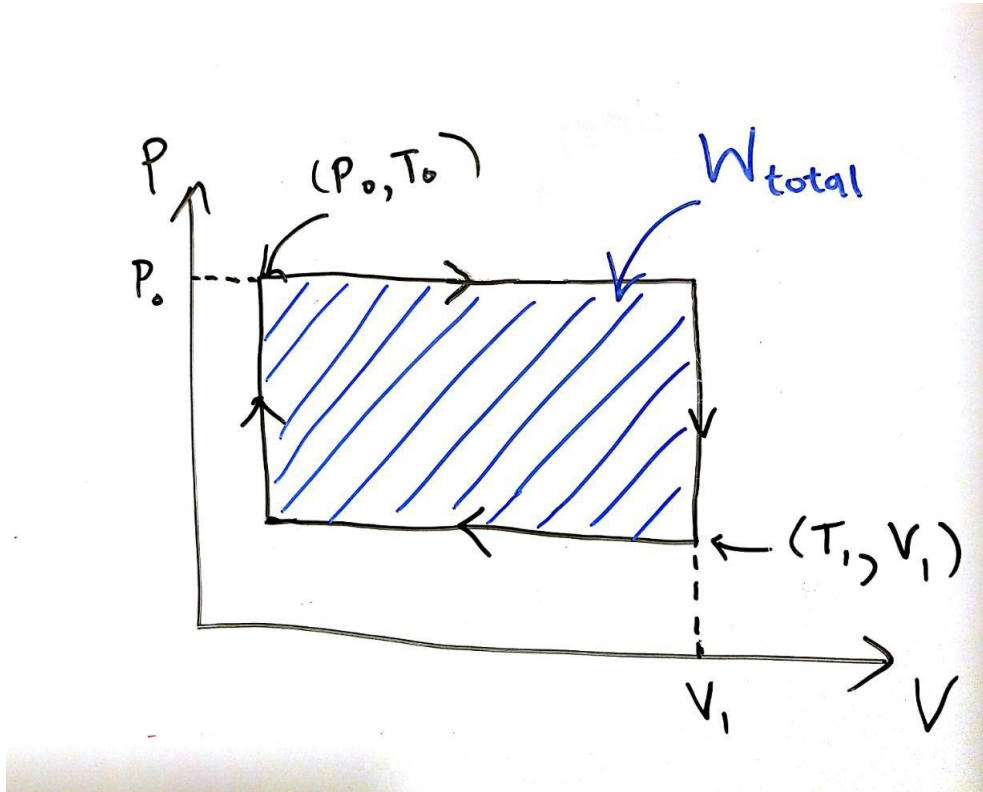
The work done in step 1, henceforth denoted W_1 is given by Eq. 2:

$$V_0 = \frac{Nk_BT_0}{P_0} \tag{13}$$

$$W_1 = P_0 \int dV = P_0(V_1 - V_0) = P_0\left(V_1 - \frac{Nk_BT_0}{P_0}\right) \tag{14}$$

Since the second step is isochoric, the work done in this step $W_2 = 0$. The pressure at the end of this step is given by

$$P_1 = \frac{Nk_BT_1}{V_1} \tag{15}$$

The work in the third step is then

$$W_3 = P_1 \int dV = \frac{Nk_BT_1}{V_1}(V_0 - V_1) = \frac{Nk_BT_1}{V_1}\left(\frac{Nk_BT_0}{P_0} - V_1\right) \tag{16}$$

Since the fourth step is isochoric, the work done in this step $W_4 = 0$. Adding these four pieces together,

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$$W_{\text{total}} = P_0 \left(V_1 - \frac{Nk_BT_0}{P_0} \right) + \frac{Nk_BT_1}{V_1} \left(\frac{Nk_BT_0}{P_0} - V_1 \right) = \left(P_0 - \frac{Nk_BT_1}{V_1} \right) \left(V_1 - \frac{Nk_BT_0}{P_0} \right) \qquad (17)$$

The total heat exchange in one cycle will be $Q_{\text{total}} = W_{\text{total}}$ by the first law. To calculate the heat in each step, though, we need to know the temperature at the beginning and end of each process. We can then use $Q = NC_V\Delta T$ and $Q = NC_P\Delta T$ for each step. At the end of step 1, the volume of the gas is V_1 and its pressure is P_0. Therefore, the change in temperature during step 1 is

$$\Delta T = \frac{P_0V_1}{Nk_B} - T_0 \qquad (18)$$

This step occurs isobarically, so

$$Q_1 = NC_P\Delta T = N(3k_B + k_B) \left(\frac{P_0V_1}{Nk_B} - T_0 \right) = 4Nk_B \left(\frac{P_0V_1}{Nk_B} - T_0 \right) \qquad (19)$$

The second step is isochoric cooling to temperature T_1, so

$$Q_2 = NC_V\Delta T = 3Nk_B \left(T_1 - \frac{P_0V_1}{Nk_B} \right) \qquad (20)$$

The change in temperature in the third step is given by

$$\Delta T = \frac{1}{Nk_B} \left(\frac{Nk_BT_1}{V_1} \right) \left(\frac{Nk_BT_0}{P_0} \right) - T_1 \qquad (21)$$

So

$$Q_3 = NC_P\Delta T = 4Nk_B \left(\frac{Nk_BT_1T_0}{P_0V_1} - T_1 \right) \qquad (22)$$

Finally, the heat in the fourth step is

$$Q_4 = NC_V\Delta T = 3Nk_B \left(T_0 - \frac{Nk_BT_1T_0}{P_0V_1} \right) \qquad (23)$$

So if we have done everything correctly, $Q_1 + Q_2 + Q_3 + Q_4 = W$:

$$Q_{\text{total}} = P_0V_1 - Nk_BT_1 + \frac{N^2k_B^2T_0T_1}{P_0V_1} - Nk_BT_0 \qquad (24)$$

If you expand Eq. 17, you can see that it indeed will expand to Q_{total} above!

Problem 3b - Brayton Cycle

Statement

For this thermodynamic cycle, we will use N molecules of an ideal monoatomic gas at around room temperature. The Brayton cycle is composed of four steps as depicted below:
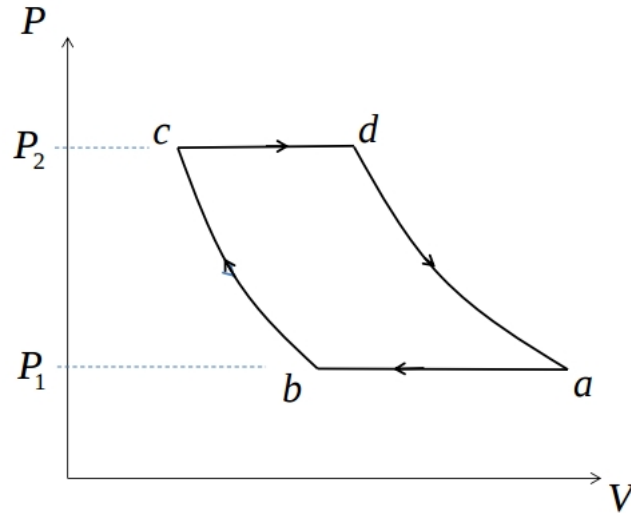
1. Process cd is isobaric expansion at pressure P_2

2. Process da is adiabatic expansion

3. Process ab is isobaric compression at pressure P_1

4. Process bc is adiabatic compression

In terms of the values given above and fundamental constants, find the ratio of the volume at state c to the volume at state b. Also find the ratio of the volume at state a to the volume at state d. Now suppose that the volume at state d is known to be V_0. Find the work done in the process da. Comment on the physical meaning of the sign of the work. *Hints:* Recall that for an adiabatic process, $Q = 0$ and PV^γ is a constant, where $\gamma = C_P/C_V$, the "adiabatic coefficient" which in general differs between gases.

Solution

Let V_a, V_b, V_c, V_d be the volumes of the gas at points a,b,c, and d, respectively. First, we want to find V_c/V_b. Since the process bc is adiabatic, PV^γ is constant. Since the gas is monoatomic,

$$C_V = \frac{3}{2}k_B \tag{25}$$

so

$$\gamma = \frac{C_P}{C_V} = \frac{3/2 + 1}{3/2} = \frac{5}{3} \tag{26}$$

This means that

$$P_1 V_b^\gamma = P_2 V_c^\gamma \tag{27}$$

So

$$\boxed{\frac{V_c}{V_b} = \left(\frac{P_1}{P_2}\right)^{3/5}} \tag{28}$$

Similarly,

$$P_2 V_d^\gamma = P_1 V_a^\gamma \tag{29}$$

$$\boxed{\frac{V_a}{V_d} = \left(\frac{P_2}{P_1}\right)^{3/5}} \tag{30}$$

To find the work along the process da, we use the definition of work in Eq. 2. But we need to write pressure as a function of volume. Luckily we have a simple way to do that for an adiabatic process. First, the end points of my process occur at V_d and V_a, where

$$V_a = \left(\frac{P_2}{P_1}\right)^{3/5} V_d \tag{31}$$

Second, the condition that PV^γ is constant holds everywhere during an adiabatic process. This means that if we know what that constant is at any point during the process, we know what it is for every point. In this case, we know the pressure and volume at the beginning, so

$$P(V) = \left(\frac{V_d}{V}\right)^{5/3} P_2 \tag{32}$$

Now we can assemble the pieces:

$$W = \int P(V)dV = P_2 V_d^{5/3} \int_{V_d}^{V_a} V^{-5/3}dV = -\frac{3}{2}P_2 V_d^{5/3} V^{-2/3}\Big|_{V_d}^{V_a} \tag{33}$$

$$= -\frac{3}{2}P_2 V_d^{5/3}\left(\left(\frac{P_2}{P_1}\right)^{-2/5} V_d^{-2/3} - V_d^{-2/3}\right) = \boxed{\frac{3}{2}P_2 V_d\left(\left(1 - \frac{P_1}{P_2}\right)^{2/5}\right)} \tag{34}$$

The work is positive because the gas is expanding without gaining heat, so it is losing energy to the environment.

Problem 3c - Stirling Cycle

Statement

For this thermodynamic cycle, we will use N molecules of an ideal diatomic gas at around room temperature. The Stirling cycle is composed of four steps as well:
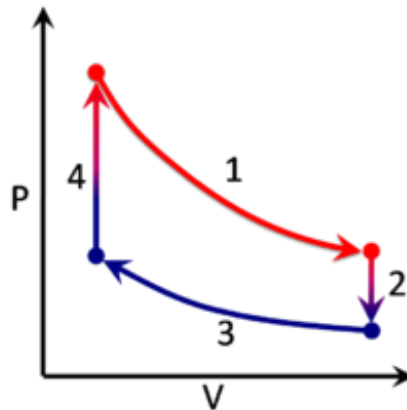
The steps correspond to

1. Isothermal expansion starting at a known pressure P_1 and volume V_1

2. Isochoric cooling ending at a known pressure P_2 and volume V_2

3. Isothermal compression

4. Isochoric heating

Calculate the step-wise work extracted and total work and heat added in each step.

Solution

The work in the two isochoric legs is zero. The work in an isothermal leg is given by calculating Eq. 2. For the work in process 1, W_1, we need to express the temperature of the process in terms of the given quantities:

$$T_1 = \frac{P_1 V_1}{N k_B} \tag{35}$$

$$PV = N k_B T_1 \tag{36}$$

$$W_1 = \int P(V) dV = \int_{V_1}^{V_2} \frac{N k_B T_1}{V} dV = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right) \tag{37}$$

Likewise, for W_3:

$$W_3 = \int P(V) dV = \int_{V_2}^{V_1} \frac{N k_B T_2}{V} dV = P_2 V_2 \ln\left(\frac{V_1}{V_2}\right) \tag{38}$$

So the total work is then

$$W_{\text{total}} = \ln\left(\frac{V_2}{V_1}\right)(P_1 V_1 - P_2 V_2) \tag{39}$$

To find the heat added in step 1, we use the first law Eq. 5. Remember that since step 1 is isothermal, $\Delta U = 0$, so $Q_1 = W_1$.

$$Q_1 = W_1 = P_1 V_1 \ln\left(\frac{V_2}{V_1}\right) \tag{40}$$

and by the same reasoning

$$Q_3 = \int_{V_2}^{V_1} \frac{N k_B T_2}{V} dV = P_2 V_2 \ln\left(\frac{V_1}{V_2}\right) \tag{41}$$

The heat along the isochoric legs can be calculated using the heat capacity C_V for a diatomic gas, $5 k_B / 2$:

$$Q_2 = \frac{5}{2} N k_B (T_2 - T_1) = \frac{5}{2}(P_2 V_2 - P_1 V_1) \tag{42}$$

and

$$Q_4 = \frac{5}{2} N k_B (T_1 - T_2) = \frac{5}{2}(P_1 V_1 - P_2 V_2) \tag{43}$$

Other Cycles and Remarks

Naturally there are other cycles that can be constructed, and two major ones I have omitted are the Carnot cycle and the Otto cycle. I have omitted them because they are covered in the textbook. In discussion, I mentioned that we can represent a system in PV space or TS space, where S is the entropy of the system. In PV space, isobaric and isochoric processes are represented by lines perpendicular to the axes. When the cycle is composed of only isobaric and isochoric processes, such as in Problem 3a, the cycle forms a rectangle in PV space and the total work extracted is just the area of the rectangle. In TS space, isothermal and adiabatic processes are represented by lines perpendicular to the axes. When the cycle is composed of only isothermal and adiabatic processes, such as the Carnot cycle, the cycle forms a rectangle in TS space and the total heat added is just the area of the rectangle.