Statistical Mechanics

Worksheet 2

April 27, 2023

Entropy of the ideal gas

We will calculate the Entropy S of an ideal gas. Let us consider constant number of particles N, so the result will be a function of T and V.

For these considerations, the first law of the thermodynamics can be written using the entropy differential

$$dU = TdS - PdV$$

1. Using the equation of state, the equipartition theorem and the last equation to write the diferential of entropy dS as a function of T and V.
2. Integrate this equation, using as reference state T_0, V_0 and S_0.
3. Change the final variables V, T to P, T and discuss the dependence of S with the thermodynamic parameters.

Entropy can be understood under different frameworks. Right now we just developed the classical thermodynamics involved. We will work more on this important concept further on.

Cycles with non Ideal Gases

A thermodynamic cycle implies that after a series of transformations, the initial and final state are the same. Given the first law, this implies that the change on the internal energy over all the cycle is null

$$\oint dU = 0 \tag{1}$$

Therefore, if the cycle produces any kind of work, it was *transformed* from an amount of heat coming from an external source.

Let us study in particular the Carnot cycle

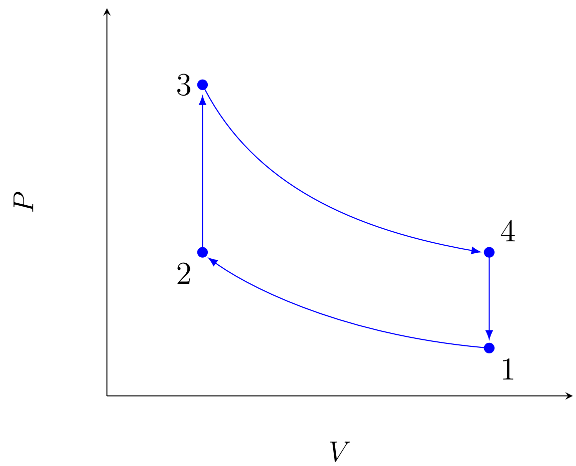

Figure 1: Carnot cycle

Consider now a non ideal gas model. The Van der Waals gas is defined by the equation of state,

$$\left(P + \frac{a}{V^2}\right)(V - b) = Nk_BT, , \tag{2}$$

where a and b measure the average attraction between particles and the volume exclusion respectively. We want to show that the efficiency of the cycle goes as

$$\eta = 1 + \frac{T_{\text{cold}}}{T_{\text{hot}}} \tag{3}$$

This can be done following several steps:

1. We need the adiabatic curve. To do so, compute the derivative $\frac{\partial V}{\partial T}\big|_S$.

   Hint Find a change of variables from (V, T) to (S, T) so the relationship between volume and temperature for an adiabatic process becomes clear.

2. Substituting T in 2 and show that for an adiabatic process

$$(V - Na)^{5/3}\left(P + a\frac{N^2}{V^2}\right) = \text{constant} \tag{4}$$

3. Calculate the work done on the gas, the heat absorbed by the gas, and the change in the internal energy of the gas.

   Hint Do it independently for all the 4 parts of the cycle.

4. Now we can calculate the efficiency

$$\eta = \frac{W}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{5}$$

Equations of state

The equation of state constrains the form of internal energy as in the following examples.

1. Starting from $dU = TdS - PdV$, show that the equation of state $PV = Nk_BT$ in fact implies that U can only depend on T.

2. What is the most general equation of state consistent with an internal energy that depends only on temperature?.

3. Show that for a van der Waals gas C_V is a function of temperature alone.

Photon gas Carnot cycle

The aim of this problem is to obtain the black-body radiation relation, $U(T, V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.

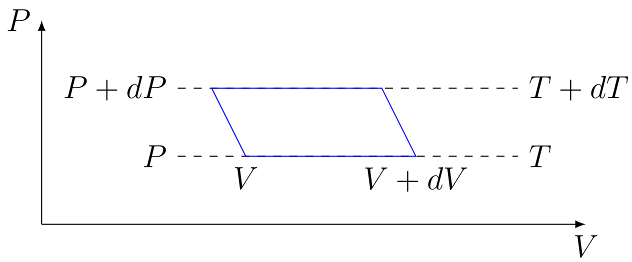

Figure 2: Photon gas Carnot cycle

1. Express the work done, W, in the above cycle, in terms of dV and dP.

2. Express the heat absorbed, Q, in expanding the gas along an isotherm, in terms of P, dV, and an appropriate derivative of $U(T, V)$.

3. Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.

4. Observations indicate that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^4 / 45(\hbar c)^3$ is a constant. Use this information to obtain $U(T, V)$, assuming $U(0, V) = 0$.

5. Find the relation describing the adiabatic paths in the above cycle.