

Statistical Mechanics

Worksheet 2

April 27th, 2023

1 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 differential 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.

2 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

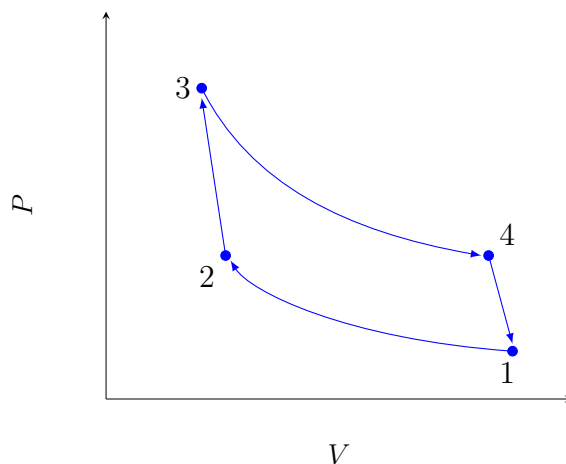


Figure 1: Carnot cycle

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

$$\left(P + \frac{a}{V^2}\right)(V - b) = Nk_B T, \quad (2)$$

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

$$\eta = 1 + \frac{T_{\text{cold}}}{T_{\text{hot}}} \quad (3)$$

This can be done following several steps:

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

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

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

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

$$\eta = \frac{W}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \quad (5)$$

3 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 $PV = Nk_B T$ 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.

4 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.

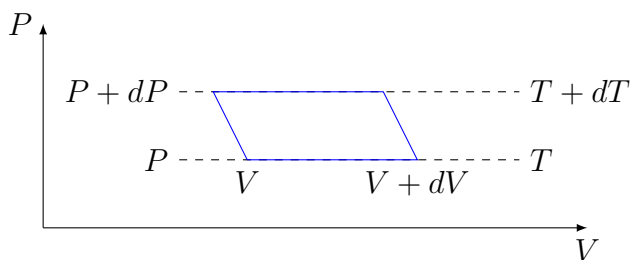


Figure 2: Photon gas Carnot cycle

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.