

Statistical Mechanics

Worksheet 1

April 20, 2023

Maxwell's Velocity Distribution

Let us use several considerations to build the velocity distribution on a gas. One of the first considerations is to think that the gas is the same in all directions. Therefore it is called to be *isotropic*. In a practical sense, the distribution of velocities $f(\mathbf{v})$ depends exclusively on the norm of the vector $v = |\mathbf{v}|$, or equivalently $v^2 = |\mathbf{v}|^2$. Hence, the probability density of finding a particle with velocity $|\mathbf{v}|$ has a dependence like,

$$f(\mathbf{v}) = f(v^2) = f(v_x^2 + v_y^2 + v_z^2). \quad (1)$$

In principle, it is fair also to assume that there is no correlation among the velocities in different directions (v_x , v_y and v_z are independent), then

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)f(v_y^2)f(v_z^2). \quad (2)$$

The mathematical function fulfilling this equation is an exponential.

$$f(\mathbf{v}^2) = C \exp(-a\mathbf{v}^2) \quad (3)$$

Notice that for $a > 0$ this is a Gaussian function.

Let us find the full expression.

1. Probability distributions have to be normalized. Calculate a relationship between a and C after integrating [3](#)

Hint To do that, consider the limits for v_x , v_y and v_z along the whole real axis $(-\infty, \infty)$.

Hint Notice that the integral of Gaussians is well defined in the whole real axis.

2. Taking the relation between of the kinetic energy and the temperature

$$k_B T = \langle K \rangle \quad (4)$$

Find that

$$a = \frac{-m}{2k_B T} \quad (5a)$$

$$C = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \quad (5b)$$

Hint Using the fact that to calculate averages from continuous probability distributions

$$\langle A(x) \rangle = \int dx A(x) P(x) \quad (6)$$

with $P(x)$ the probability distribution of x , and $A(x)$ any observable.

Hint Make use of the $\Gamma(z)$ function,

$$\Gamma(z) = \int_0^\infty dx e^{-x} x^{z-1}. \quad (7)$$

where the *Gamma*(z)-function¹ is the generalization of the factorial on the complex plane such that $\Gamma(z+1) = z\Gamma(z)$, and some well known values as $\Gamma(3/2) = 1/2$ and $\Gamma(1/2) = \sqrt{\pi}/2$.

Expansion/Compression of Gases

An adiabatic process is defined as one where no heat either enters nor leaves the system. Consider a reversible adiabatic process for the following

Let us consider three different thermodynamical paths to go from (P_1, V_1) to (P_2, V_2) Isobaric expansion followed by an isochoric decrease in pressure C_1 . An isochoric decrease in pressure followed by an isobaric expansion C_2 . An adiabatic expansion C_3 .

The three paths are showed in red, blue and purple in the following figure

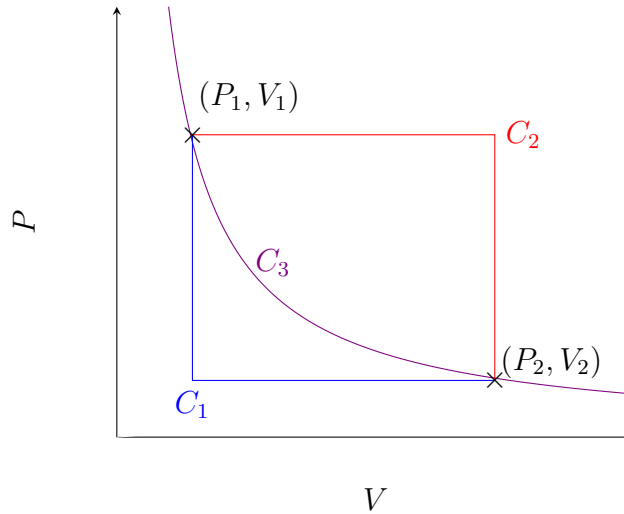


Figure 1: Representation of the different processes paths.

Evaluate the differences on internal energies, heat and work among the paths. Why does the internal energy has a different behaviour than the other two quantities? **Hint** Take the differences on internal energy dU for the three paths and compare them. Repeat the same with work and heat and try to justify the differences.

¹The $\Gamma(z)$ -function is going to be very useful for calculating certain integrals in future worksheets.

Exact and inexact differentials

Consider the following differential

$$\mathbf{F} \cdot d\mathbf{x} = (x^2 - y)dx + xdy \quad (8)$$

Is it exact?.

Calculate

$$\int_{C_i} \mathbf{F} \cdot d\mathbf{x} \quad (9)$$

with C_i are the contours from $(1, 1)$ to $(2, 2)$ in figure 2. If it is not an exact differential, what is the integrating factor? Determine the original function.

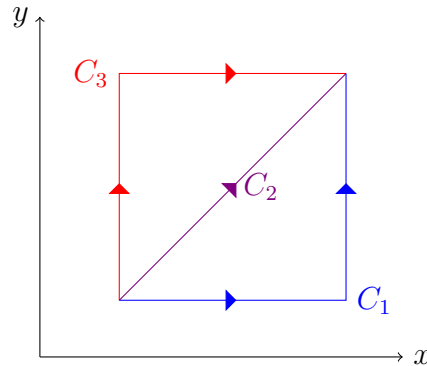


Figure 2: Representation of the integration contours.

Equipartition Theorem

One of the most useful and important theorems in physics is the *Equipartition Theorem*. The equipartition of the energy states

- Every degree of freedom contributes $\frac{1}{2}k_B T$ to the average energy.

Diatomic Ideal Gas

Consider an ideal gas such that every particle is made out of two *atoms* (like those in the ideal gas) at a fixed distance (see 3).



Figure 3: Representation of a single particle of a: Monoatomic (left) and diatomic (right) ideal gases

1. Write the contributions to the energy of every degree of freedom for a monoatomic and a diatomic ideal gas.

Hint Consider arbitrarily x , y and z , and choose around which axis you include the rotational degrees of freedom. **Hint** Notice that there are symmetries in both systems. In the diatomic

case, not all the rotations are important, reason this and justify the number of degrees of freedom.

2. Discuss the ratio/difference of energies of a monoatomic and a diatomic ideal gases at the same temperature. **Hint** Use the equipartition theorem to find the
3. Using the first law of thermodynamics to write the heat capacities C_V and C_P for both a monoatomic and diatomic ideal gases, and show that $\gamma = C_P/C_V$ goes

$$\gamma_{\text{Monoatomic}} = \frac{5}{3} \quad (10a)$$

$$\gamma_{\text{Diatomic}} = \frac{7}{5} \quad (10b)$$

Hint Use the *Mayer's relation* $C_P - C_V = R$ with R the gas constant $R = N_A k_B$ with N_A the avogadro's number and k_B The Boltzmann constant.

Isothermal expansion

Apply the first principle of thermodynamics, and do the energy balance (heat, work, internal energy) of the reversible and irreversible isothermal compression/expansion described in Example 1.3 of Greiner