

16. Entropy of the ideal gas

Consider a classical ideal gas of particles of mass m . The Hamiltonian function is then given by

$$H = \frac{1}{2m} \sum_{i=1}^N p_i^2, \quad (1)$$

with p_i being the momentum of the i -th particle.

(a) Determine the phase space volume $\Sigma(E)$ with

$$\Sigma(E) = \frac{1}{h^{3N}} \int_{H(p,q) < E} d^{3N}q d^{3N}p, \quad (2)$$

and from this determine the following formula for the entropy S of the ideal gas

$$S = Nk_B \ln \left[V \left(\frac{E}{N} \right)^{3/2} \right] + \frac{3}{2} Nk_B \left[1 + \ln \left(\frac{4\pi m}{3h^2} \right) \right] \quad (3)$$

Hint: The surface of the $3N$ dimensional unit sphere is $2 \frac{\pi^{3N/2}}{\Gamma(3N/2)}$.

(4 points)

(b) Show that from the formula for entropy in Eq.(3) one can obtain the caloric equation of state $E = \frac{3}{2} k_B T$ and the thermal equation of state $pV = k_B N T$.

(2 points)

17. Gibbs paradox

We previously demonstrated that the entropy of an ideal gas was given by the formula

$$S = Nk_B \ln(V u^{3/2}) + Ns_0, \quad (4)$$

where $u = \frac{3}{2}k_B T$ and $s_0 = \frac{3k_B}{2} \left(1 + \ln \frac{4\pi m}{3h^2} \right)$. Considering two ideal gases, with N_1 and N_2 particles respectively, kept in two separate volumes V_1 and V_2 at the same temperature and same density.

- (a) Determine the difference in entropy of the combined system after the gases are allowed to mix in a joint volume $V = V_1 + V_2$, and show that this change of entropy is represented by

$$\frac{\Delta S}{k_B} = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2}, \quad (5)$$

which is the mixing entropy.

(1 point)

- (b) The Gibbs paradox arises when one considers the case of two identical ideal gases. Since the derivation of Eq. (5) is independent of the identity of the gases, joining the two systems would also lead to an increase of the entropy. This is a disastrous result since it implies that the entropy of a gas depends on its history, and therefore cannot be only a function of the thermodynamics state of the gas. Gibbs solved this paradox by postulating that the expression of $\Sigma(E)$, the number of states below the energy E is incomplete and should be divided by $N!$. Show that the entropy of the ideal gas then becomes

$$S = Nk_B \ln \left[\frac{V}{N} u^{3/2} \right] + \frac{3}{2} Nk_B \left[\frac{5}{3} + \ln \left(\frac{4\pi m}{3h^2} \right) \right]. \quad (6)$$

(1 point)

- (c) Work out the entropy of mixing for the case of different gases and then for identical gases and show that Eq. (6) solves the Gibbs paradox.

(1 point)

18. Symmetric and antisymmetric states of quantum particles

Let us consider a single particle with spin S confined in a one-dimensional box. The Hamiltonian operator \hat{H}_1 representing the particle then reads

$$\hat{H}_1 = \frac{\hat{p}^2}{2m} + V(\hat{x}), \quad (7)$$

where $V(x) = 0$ for $0 < x < L$ and $V(x) \rightarrow +\infty$ for any other case.

(a) Determine the eigenenergies and eigenvectors of \hat{H}_1 .

(1 Punkt)

(b) Considering now two uninteracting particles described by the joint Hamiltonian $\hat{H}_2 = \hat{H}_1 \otimes \mathbf{1} + \mathbf{1} \otimes \hat{H}_1$. Determine the form of the eigenvalues and eigenvectors when $S = 0$ (bosonic case). What is the ground state and its energy? Same question for the first excited state?

(1 Punkt)

(c) Considering now fermionic particles of spin $S = \frac{1}{2}$, determine the eigenvectors and corresponding eigenenergies. Which form take ground state and first excited state?

(1 Punkt)