

Prob 15. Find the classical partition function for an ideal-gas mixture, without the consideration of particle indistinguishability. There are two types of molecules: N_1 molecules with molecular mass m_1 and N_2 molecules with molecular mass m_2 . The system occupies a volume V and is maintained at temperature T . Obtain an expression for the system entropy.

$$\begin{aligned} Z &= \int d\vec{r}_1 d\vec{p}_1 \prod_{i=1}^{N_1} \exp(-\beta \frac{p_i^2}{2m_i}) = \int d\vec{r}_1 d\vec{p}_1 d\vec{r}_{N_2} d\vec{p}_{N_2} \prod_{i=1}^{N_1} \exp(-\beta \frac{p_i^2}{2m_i}) \prod_{j=1}^{N_2} \exp(-\beta \frac{p_j^2}{2m_j}) \\ &= \int d\vec{r}_1 d\vec{p}_1 \prod_{i=1}^{N_1} \exp(-\beta \frac{p_i^2}{2m_i}) \cdot \int d\vec{r}_{N_2} d\vec{p}_{N_2} \prod_{j=1}^{N_2} \exp(-\beta \frac{p_j^2}{2m_j}) \\ &= V^{N_1} \cdot \left(\frac{2m_1 \pi}{\beta} \right)^{3N_1/2} \cdot V^{N_2} \cdot \left(\frac{2m_2 \pi}{\beta} \right)^{3N_2/2} = \left(V \cdot \left(\frac{2\pi}{\beta} \right)^{\frac{3}{2}} \right)^{N_1+N_2} \cdot m_1^{3N_1/2} \cdot m_2^{3N_2/2} \end{aligned}$$

where $\beta = (k_B T)^{-1}$

$$F = -k_B T \ln Z = -k_B T \left[(N_1 + N_2) \ln \left(V \cdot (2\pi k_B T)^{3/2} \right) + \frac{3N_1}{2} \ln m_1 + \frac{3N_2}{2} \ln m_2 \right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V, N_1, N_2} = \frac{3}{2} N_1 k_B (1 + \ln(2\pi m_1 k_B T)) + N_1 k_B \ln V + \frac{3}{2} N_2 k_B (1 + \ln(2\pi m_2 k_B T)) + N_2 k_B \ln V$$

Prob 16. Mixing of Two Ideal Gases. Consider a system that contains a partition wall in the middle. The two sides have equal volumes $V/2$. The left side of the system contains N_1 ideal gas particles with mass m_1 , and the right contains N_2 particles with mass m_2 .

(a) Using the results from previous problems, find the total entropy S_a .

For a system with only one kind of ideal gas, from Prob 15, we know that the entropy is $S = \frac{3}{2} N k_B (1 + \ln(2\pi m k_B T)) + N k_B \ln V$.

where N is the # of particles, m is the molecular mass,

V is the volume the gas occupies. (Set $N_1=N, N_2=0$)

$$\begin{aligned} \text{So the total entropy } S_a &= S_1 + S_2 = \frac{3}{2} N_1 k_B (1 + \ln(2\pi m_1 k_B T)) + N_1 k_B \ln \frac{V}{2} \\ &\quad + \frac{3}{2} N_2 k_B (1 + \ln(2\pi m_2 k_B T)) + N_2 k_B \ln \frac{V}{2} \end{aligned}$$

(b) Now assume that the partition wall has been removed and we have waited long enough that the mixture system has reached thermodynamical equi. Calculate the entropy of the mixture S_b .

From Prob. 15, we know that the entropy of the mixture is

$$S_b = \frac{3}{2}N_1 k_B (1 + \ln(2\pi m_1 k_B T)) + N_1 k_B \ln V + \frac{3}{2}N_2 k_B (1 + \ln(2\pi m_2 k_B T)) + N_2 k_B \ln V$$

(c) Now define the entropy of mixing, $\Delta S = S_a - S_b$, what conclusion would you draw?

$$\Delta S = S_a - S_b = N_1 k_B (\ln \frac{V}{2} - \ln V) + N_2 k_B (\ln \frac{V}{2} - \ln V) = (N_1 + N_2) k_B \ln \frac{1}{2} < 0$$

Thus the process decrease the total entropy! There must be something wrong with the classical calculation.

Prob. 17 The Gibbs Paradox Consider a system that contains a partition wall.

Now consider the situation when the two gases are identical, i.e., $N_1 = N_2 = N$, $m_1 = m_2 = m$.

(a) Write down the entropy S_{before} before the partition wall is removed.

$$S_{\text{before}} = 3N k_B (1 + \ln(2\pi m k_B T)) + 2N k_B \ln \frac{V}{2}$$

(b) Write down the entropy S_{after} after the partition wall is slowly moved.

"Slowly moved" means that the system is at equi. all the time.

$$S_{\text{after}} = 3N k_B (1 + \ln(2\pi m k_B T)) + 2N k_B \ln V$$

(c) Find the entropy difference $\Delta S = S_{\text{before}} - S_{\text{after}}$, which is non-zero. However, removing (or replacing) the partition wall doesn't alter the microscopic behavior of the gas. From thermodynamics, we should expect $\Delta S = 0$. Historically, failure to appreciate the significance of the identity of the particles led to the above inconsistency called the Gibbs Para-

$$\Delta S = S_{\text{before}} - S_{\text{after}} = 2N k_B (\ln \frac{V}{2} - \ln V) = 2N k_B \ln \frac{1}{2} \neq 0.$$

Prob. 18. Consider a semi-classical ideal gas that obeys the Boltzmann distribution.

The partition function can be written as $Z_N = z_1^N / N!$, where $N! \approx (N/e)^N$ accounts for

the indistinguishability of the particles and z_1 is the single-particle partition function.

Calculate the entropy of the system, and compare with the result from a previous prob.

From the previous questions, we know that the entropy without the $N!$ correction is

$$S_0 = \frac{3}{2} N k_B (\ln (2\pi m k_B T) + 1) + N k_B \ln V \quad \text{where } N \text{ is the \# of particles, } m \text{ is molecular mass and } V \text{ is the volume occupied.}$$

Now introduce the $N!$ correction, $Z = z_0 / N!$, $F = F_0 + k_B T \ln N! \approx F_0 + k_B T N (\ln N - 1)$

$$S = -\partial F / \partial T = S_0 - k_B N (\ln N - 1)$$

$-k_B N (\ln N - 1)$ shows the difference between the classical & semi-classical calculation.

Prob 19. Use the expression found in Prob. 18 for the entropy and redo the Gibbs' Paradox Problem.

$$S'_\text{before} = S_\text{before} - k_B N (\ln N - 1) - k_B N (\ln N - 1) = S_\text{before} - 2 k_B N (\ln N - 1)$$

$$S'_\text{after} = S_\text{after} - k_B \cdot (2N) (\ln 2N - 1)$$

$$\begin{aligned} \Delta S' &= S'_\text{before} - S'_\text{after} = \Delta S - 2 k_B N (\ln N - 1) - 2 k_B N (\ln 2N - 1) \\ &= 2 N k_B \ln \frac{1}{2} - 2 N k_B (\ln N - \ln 2N) \\ &= 2 N k_B \ln \frac{1}{2} - 2 N k_B \ln \frac{1}{2} = 0 \end{aligned}$$