PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #3

February 4, 2026

Question 1: Entropy Change of an Ideal Gas

Problem: Compute the change of entropy as the volume of the box is doubled ($V \to 2V$), keeping N and E constant.

Solution:

We start with the Sackur-Tetrode equation for the entropy of a monoatomic ideal gas:

$$S = Nk_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{1}$$

Since N, E, and m are held constant, the term involving energy and mass is constant. Let's define $C = \frac{1}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2}$. The entropy can then be written as:

$$S(V) = Nk_B \left[\ln(V \cdot C) + \frac{5}{2} \right] \tag{2}$$

We want to find the change in entropy $\Delta S = S(2V) - S(V)$:

$$\begin{aligned} \Delta S &= Nk_B \left[\ln(2V \cdot C) + \frac{5}{2} \right] - Nk_B \left[\ln(V \cdot C) + \frac{5}{2} \right] \\ &= Nk_B \left[\ln(2V \cdot C) - \ln(V \cdot C) \right] \end{aligned}$$

Using the property of logarithms $\ln A - \ln B = \ln(A/B)$:

$$\begin{aligned} \Delta S &= Nk_B \ln \left(\frac{2V \cdot C}{V \cdot C} \right) \\ &= Nk_B \ln(2) \end{aligned}$$

Answer: The entropy increases by $Nk_B \ln 2$.

Question 2: Breakdown of the Sackur-Tetrode Equation

Problem Context: Helium gas ($m = 6.65 \times 10^{-27}$ kg) at room temperature ($T = 300$ K) and pressure ($P = 10^5$ Pa).

(a) Relationship between Energy and Temperature

We use the formal definition of temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial E} \tag{3}$$

From the Sackur-Tetrode equation, we isolate the terms depending on E:

$$S = Nk_B \ln\left(E^{3/2}\right) + \cdots = \frac{3}{2}Nk_B \ln E + \text{const} \tag{4}$$

Taking the derivative with respect to E:

$$\frac{\partial S}{\partial E} = \frac{3}{2}Nk_B \frac{d}{dE}(\ln E) = \frac{3}{2}\frac{Nk_B}{E} \tag{5}$$

Equating this to $1/T$:

$$\frac{1}{T} = \frac{3Nk_B}{2E} \implies E = \frac{3}{2}Nk_B T \tag{6}$$

(b) Entropy as a function of N, V, T

We substitute the result $E = \frac{3}{2}Nk_BT$ back into the original Sackur-Tetrode equation. The term inside the logarithm becomes:

$$\frac{V}{N}\left(\frac{4\pi m}{3Nh^2}E\right)^{3/2} = \frac{V}{N}\left(\frac{4\pi m}{3Nh^2}\cdot\frac{3}{2}Nk_BT\right)^{3/2} = \frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{7}$$

Thus, the entropy as a function of temperature is:

$$S(N,V,T) = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{8}$$

(c) Negative Entropy and Liquefaction

We are asked to find the temperature T where $S < 0$, assuming fixed density N/V calculated from room temperature conditions.

1. Calculate fixed density (V/N): Using the Ideal Gas Law $PV = Nk_BT$ at room temperature conditions:

$$\frac{V}{N} = \frac{k_B T_{room}}{P} = \frac{(1.38\times10^{-23}\,\text{J/K})(300\,\text{K})}{10^5\,\text{Pa}} = 4.14\times10^{-26}\,\text{m}^3 \tag{9}$$

2. Solve for T where S = 0: Setting $S = 0$ in the equation derived in part (b):

$$\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5}{2} = 0$$

$$\ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) = -2.5$$

$$\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = e^{-2.5} \approx 0.082$$

Isolating T:

$$T^{3/2} = \frac{e^{-2.5}}{(V/N)} \left(\frac{h^2}{2\pi m k_B} \right)^{3/2} \tag{10}$$

$$T = \left(\frac{e^{-2.5}}{V/N} \right)^{2/3} \frac{h^2}{2\pi m k_B} \tag{11}$$

Let's calculate the constant term $\frac{h^2}{2\pi m k_B}$:

$$\frac{h^2}{2\pi m k_B} = \frac{(6.626 \times 10^{-34})^2}{2\pi(6.65 \times 10^{-27})(1.38 \times 10^{-23})} \approx 7.6 \times 10^{-19}\,\text{K m}^2 \tag{12}$$

Now substituting the value for V/N:

$$\left(\frac{e^{-2.5}}{V/N} \right)^{2/3} = \left(\frac{0.082}{4.14 \times 10^{-26}} \right)^{2/3} = (1.98 \times 10^{24})^{2/3} \approx 1.58 \times 10^{16}\,\text{m}^{-2} \tag{13}$$

Multiplying these together:

$$T \approx (1.58 \times 10^{16})(7.6 \times 10^{-19}) \approx 0.012\,\text{K} \tag{14}$$

Conclusion: The Sackur-Tetrode equation predicts negative entropy at $T \approx 0.012$ K. Helium actually liquefies at $T \approx 4.2$ K.

Comparison: The temperature where the entropy formula becomes mathematically "absurd" (negative) is more than two orders of magnitude lower than the temperature where the physics of the ideal gas assumption actually breaks down (liquefaction). This implies that for all practical purposes where the gas remains a gas, the Sackur-Tetrode equation yields a valid positive entropy.