PHYS 301
Thermodynamics and Statistical Mechanics

Problems #7
Wednesday, 03/04/2026

Question 1.

For a general gas molecule, the total partition function is the product of the translational (Z_{trans}), rotational (Z_{rot}), vibrational (Z_{vib}), and electronic degeneracy (Z_e) partition functions.

$$Z_{1\,\text{molecule}} = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} Z_e. \tag{1}$$

Here, we will take $Z_e = 1$ for simplicity. We have seen many times that $Z_{\text{trans}} = V/\lambda_Q^3$. In class, we also saw that the rotational partition function is

$$Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta j(j+1)\epsilon} \approx \frac{k_{\text{B}} T}{\epsilon} \quad \text{for} \quad k_{\text{B}} T \gg \epsilon, \tag{2}$$

where ϵ is the rotational energy constant, and where we have assumed the molecule to have no particular symmetry. For vibrations, the energy levels are those of a quantum harmonic oscillator with natural frequency ω

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega. \tag{3}$$

We have actually computed this partition function in the context of the Einstein solid. It is

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta \left(n + \frac{1}{2} \right) \hbar \omega} = \frac{e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega/2}} = \frac{1}{2 \sinh \left(\beta \hbar \omega/2 \right)}. \tag{4}$$

For a gas of N indistinguishable molecules, the partition function is then

$$Z_{N\,\text{molecules}} = \frac{(Z_{1\,\text{molecule}})^N}{N!} \tag{5}$$

(a) In the high-temperature limit ($k_{\text{B}} T \gg \epsilon, \hbar \omega$), compute the average energy $\langle E \rangle$ for a gas of N molecules in volume V at temperature T.

(b) Compute the heat capacity C_V in the high-temperature limit.

(c) Now repeat the calculation of $\langle E \rangle$ and C_V in the low-temperature limit ($k_{\text{B}} T \ll \epsilon, \hbar \omega$). Is the answer larger or smaller than at high temperature? Why?

(d) Assuming that $\hbar \omega \gg \epsilon$, sketch the function $C_V/(N k_{\text{B}})$ for this gas as a function of temperature.