Quiz 10

Answer the questions in the spaces provided. If you run out of room for an answer, continue on the back of the page.

Question:	1	Total
Points:	25	25
Score:		

Name: ______________________________

A general partition function Z for a Boltzmann distribution with discrete energy states is

$$Z = \sum_i \mathrm{e}^{-\beta E_i}$$

where $\beta = (k_B T)^{-1}$, E_i is the energy of microstate i, and the sum is over all possible microstates.

1. Consider a gas of N carbon monoxide (CO) molecules above a metallic surface. Treat each CO molecule as an independent, distinguishable two level system. Assume each CO molecule can exist in one of two energy states: free in the gas ($E_1 = 0$) and bound to the surface ($E_2 = -\epsilon$). Further assume there is a multiplicity of gas states γ_g and multiplicity of bound states γ_b available to each molecule, and that $\gamma_\mathrm{g} > \gamma_\mathrm{b} \gg N$.

   (a) (10 points) What is the partition function $q(T)$ for a single CO molecule in terms of ϵ, γ_g, γ_b, and $k_B T$?

   Solution:

$$q(T) = \gamma_\mathrm{g} \exp\left(-\frac{0}{k_B T}\right) + \gamma_\mathrm{b} \exp\left(-\frac{-\epsilon}{k_B T}\right)$$
$$q(T) = \gamma_\mathrm{g} + \gamma_\mathrm{b} \exp\left(\frac{\epsilon}{k_B T}\right)$$

   (b) (10 points) What is the partition function $Q(T)$ for N molecules of CO in terms of N, ϵ, γ_g, γ_b, and $k_B T$? Be sure to account for the indistinguishability of the CO molecules.

   Solution:

$$Q(T) = \frac{[q(T)]^N}{N!}$$
$$Q(T) = \frac{1}{N!}\left(\gamma_\mathrm{g} + \gamma_\mathrm{b} \exp\left(\frac{\epsilon}{k_B T}\right)\right)^N$$

   (c) (5 points) What is the average energy, $U = \langle E \rangle$ for N molecules of CO in terms of N, ϵ, γ_g, γ_b, and $k_B T$?

   Solution: For a single particle, the expected energy U_s is

$$U_s = 0 \cdot \frac{\gamma_\mathrm{g}}{q(T)} + (-\epsilon) \cdot \frac{\gamma_\mathrm{b} \exp\left(\frac{\epsilon}{k_B T}\right)}{q(T)}$$
$$= -\frac{\epsilon \gamma_\mathrm{b} \exp\left(\frac{\epsilon}{k_B T}\right)}{\gamma_\mathrm{g} + \gamma_\mathrm{b} \exp\left(\frac{\epsilon}{k_B T}\right)}$$

For the system of N particles,

$$U = \langle E \rangle = -\frac{N\epsilon\gamma_{\mathrm{b}} \exp\left(\frac{\epsilon}{k_B T}\right)}{\gamma_{\mathrm{g}} + \gamma_{\mathrm{b}} \exp\left(\frac{\epsilon}{k_B T}\right)}$$

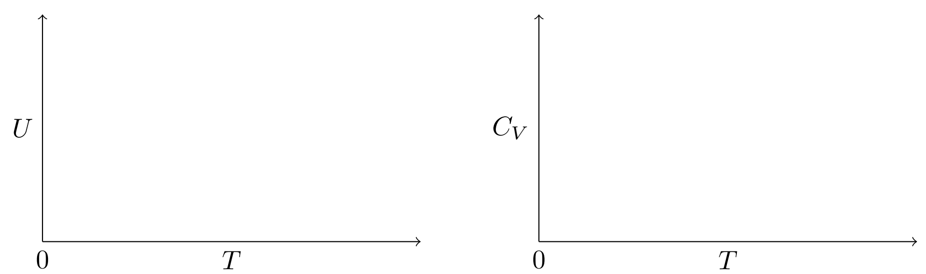
For fun, if you have time:

(d) What is the constant volume heat capacity, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ for N molecules of CO in terms of N, ϵ, γ_{g}, γ_{b}, and $k_B T$.

Solution:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{k_B T^2} \frac{N\epsilon^2 \gamma_{\mathrm{b}}\gamma_{\mathrm{g}} \exp\left(\frac{\epsilon}{k_B T}\right)}{\left(\gamma_{\mathrm{g}} + \gamma_{\mathrm{b}} \exp\left(\frac{\epsilon}{k_B T}\right)\right)^2}$$
$$= -\frac{\epsilon\gamma_{\mathrm{g}}}{k_B T^2} \frac{U(T)}{q(T)}$$

(e) Plot the energy $U(T)$ and constant volume heat capacity $C_V(T)$ as a function of temperature. Clearly indicate the high and low ($T = 0$) temperature limits.



Solution: