Name:



**EXERCISE 3B: ENTROPY AND HELMOLTZ FREE ENERGY**

*Objectives:*

- Calculate the entropy in the canonical ensemble
- Introduce the **Third Law of Thermodynamics**
- Define the **Helmholtz free energy**
- Show that the Helmholtz free energy is minimized in the canonical ensemble

*Reading:* Kittel & Kroemer, Ch. 3

*Last time,* we defined/derived:

- Heat capacity (at constant volume): $C_V \equiv \left(\frac{\partial E}{\partial \tau}\right)_V$
- Average energy in the canonical ensemble: $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$
- Partition function for the paramagnet: $Z = (e^{\beta \mu B} + e^{-\beta \mu B})^N$

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1. (From last time.)
   a. Physically, how do you interpret the peak in the heat capacity of the paramagnet? If you increased the magnetic field $B$, which way would you expect the peak to shift?

   b. How do you explain the limiting behavior of the paramagnet's heat capacity at low and high temperature?

2. *Entropy in the canonical ensemble.* For a system that is equally likely to be found in any of $g$ accessible energy states (e.g., in the microcanonical ensemble), the probability of occupying each state is $P = 1/g$, corresponding to an entropy $\sigma = -\ln P$. In the canonical ensemble, where the probability $P_s$ of finding the system in a state $s$ depends on its energy $\varepsilon_s$, this expression for the entropy generalizes to

$$\sigma = -\langle \ln P \rangle. \tag{1}$$

   a. Write down:
      i. ...the entropy $\sigma$ in terms of the probabilities $P_s$.
      ii. ...the probability $P_s$ in terms of $\beta$, $\varepsilon_s$, and the partition function $Z$.

   b. Find an expression for $\sigma$ that depends only on $\beta$ and $\ln Z$.

c. Check your expression for the entropy by evaluating the heat capacity from…
   i. $C_V = \left(\frac{\partial E}{\partial \tau}\right)_V$
   ii. $C_V = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V$

   Do the two results agree?

d. Evaluate the entropy of the paramagnet as a function of temperature $\tau$.

e. Explain the high- and low-temperature limits of your result from part d.

f. Hopefully your result is consistent with the **Third Law of Thermodynamics**: the entropy approaches a constant value as the temperature approaches zero. Under what circumstances would the entropy approach a *nonzero* constant?

3. *Helmholtz Free Energy.*
The relationship between energy, entropy, and temperature in the canonical ensemble can be summarized in the form:

$$E - \tau\sigma = F(N, \tau, \mathbf{x}), \tag{2}$$

where $F$ depends on the partition function $Z(N, \mathbf{x})$, and thus also on any external parameters $\mathbf{x}$ (e.g., magnetic field, volume) that influence the partition function.

a. The Helmholtz free energy quantifies a compromise between lowering the energy $E_{\mathcal{A}}$ and increasing the entropy $\sigma_{\mathcal{A}}$ in a system $\mathcal{A}$ coupled to a thermal reservoir. Show that in thermal equilibrium, the system configuration is such as to extremize the Helmholtz free energy $F_{\mathcal{A}}$. Do this by evaluating the change $dF_{\mathcal{A}}$ in free energy associated with an infinitesimal change in the system's configuration, involving energy transfer $dE_{\mathcal{A}}$ from the reservoir and a change $d\sigma_{\mathcal{A}}$ in the system's entropy at constant temperature $\tau$.

b. Find $F$ in terms of $Z$.

c. As a concrete example, sketch the Helmholtz free energy $F$ as a function of magnetization $M$ for a paramagnet in a magnetic field $B$ at two different temperatures $\tau_2 > \tau_1 > 0$. (. . . continued on next page . . . )

i. First, separately sketch the **energy** $E$ and **entropy** $\sigma$ vs. magnetization $M$. *Hint:* you have previously shown that at fixed magnetization (i.e., in the microcanonical ensemble) the entropy is given by

$$\sigma = -\left(\frac{N}{2} + \frac{M}{2\mu}\right) \ln\left(\frac{1}{2} + \frac{M}{2\mu N}\right) - \left(\frac{N}{2} - \frac{M}{2\mu}\right) \ln\left(\frac{1}{2} - \frac{M}{2\mu N}\right). \qquad (3)$$

To make your sketch as accurate as possible, you may find it helpful to evaluate $d\sigma/dM$ at $M = \pm N\mu$.

ii. Sketch $E - \tau_i \sigma$ vs. $M$ for three different temperatures $\tau_3 > \tau_2 > \tau_1 > 0$ on a single plot. Mark the magnetizations $M(\tau_i)$ that minimize the Helmholtz free energy.

iii. Based on your sketches, what happens to the magnetization as $\tau \to 0$? as $\tau \to \infty$? Is the behavior consistent with your expectations?

d. Verify that minimizing the Helmholtz free energy maximizes the total entropy $\sigma_{\mathcal{A}+\mathcal{R}}$ of the system and reservoir.

i. Write down the multiplicity $g_{\mathcal{A}+\mathcal{R}}(E)$ of states of the composite system that have energy $E$ in system $\mathcal{A}$. Express $g_{\mathcal{A}+\mathcal{R}}(E)$ in terms of the multiplicity $g_{\mathcal{A}}(E)$ of states of $\mathcal{A}$ at energy $E$, a Boltzmann factor, and an overall constant $C$ that is independent of $E$.

ii. Express the total entropy $\sigma_{\mathcal{A}+\mathcal{R}}$ in terms of the temperature $\tau$ and the energy $E_{(\mathcal{A})}$ and entropy $\sigma_{(\mathcal{A})}$ of $\mathcal{A}$. (We will ordinarily omit the subscript $\mathcal{A}$.)

iii. Find the infinitesimal change $d\sigma_{\mathcal{A}+\mathcal{R}}$ in entropy of $\mathcal{A}+\mathcal{R}$ associated with an infinitesimal transfer of energy $dE$ from the reservoir $\mathcal{R}$ to system $\mathcal{A}$ at fixed temperature.

iv. Express $d\sigma_{\mathcal{A}+\mathcal{R}}$ in terms of the corresponding change $dF$ in free energy.

v. Based on your expression in iv., explain why the most probable energy $\hat{E}$ of the system $\mathcal{A}$ is that which minimizes the Helmholtz free energy.