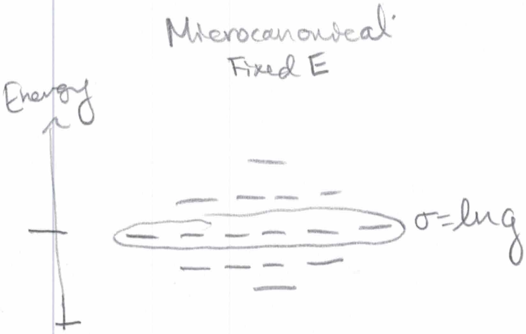
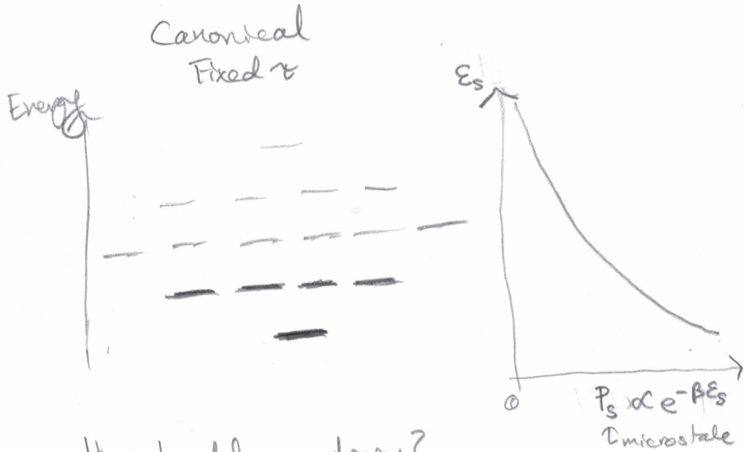
* Wrap up from last time: physical interpretation of heat capacity of paramagnet
* Continue understanding the meaning of entropy in a system @ fixed temperature





How to define entropy?

Last time: $\sigma(\tau) = \int d\tau\, C_v/\tau + \sigma(0)$

Microscopic alternative:

For g accessible microstates, $P_s = 1/g$ (Fundamental assumption!)

$\Rightarrow \sigma = \ln(1/P) = -\ln P$

For unequal probabilities, generalize to $\sigma = -\langle \ln P \rangle$ (1)

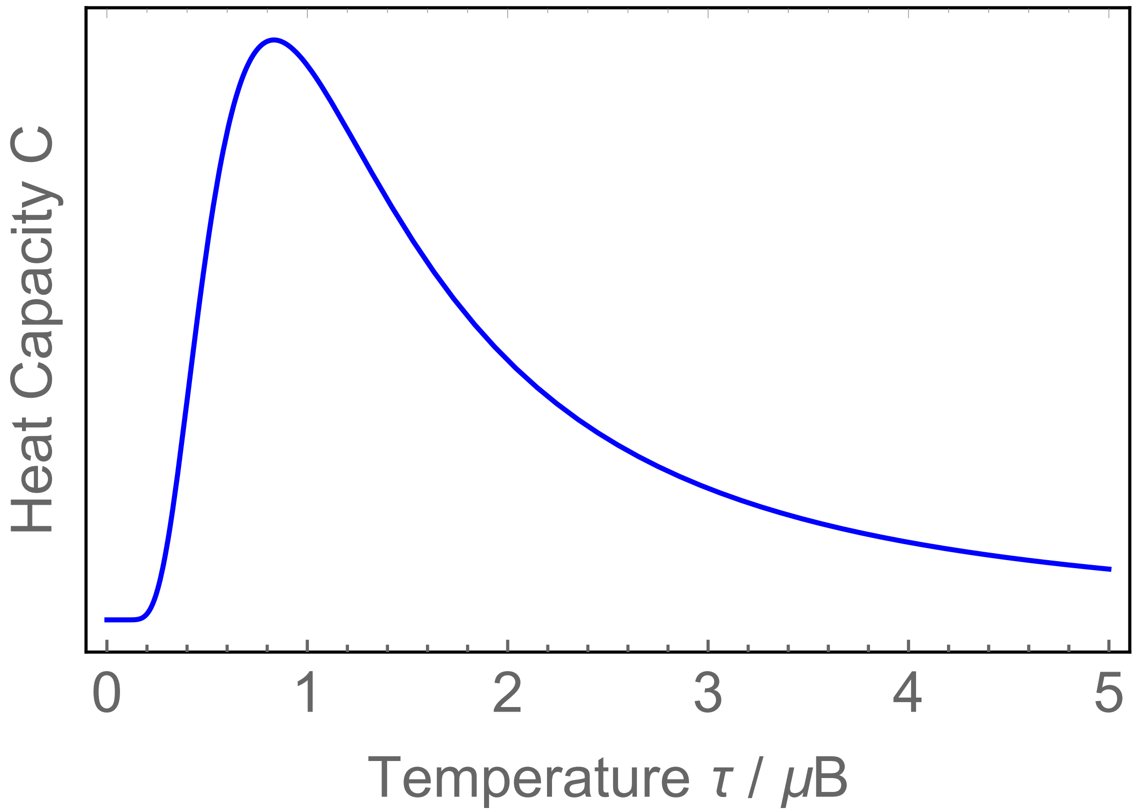
Ex 2. Use (1) to find σ in terms of Z, β and check result for consistency with result from last time.

Heat Capacity

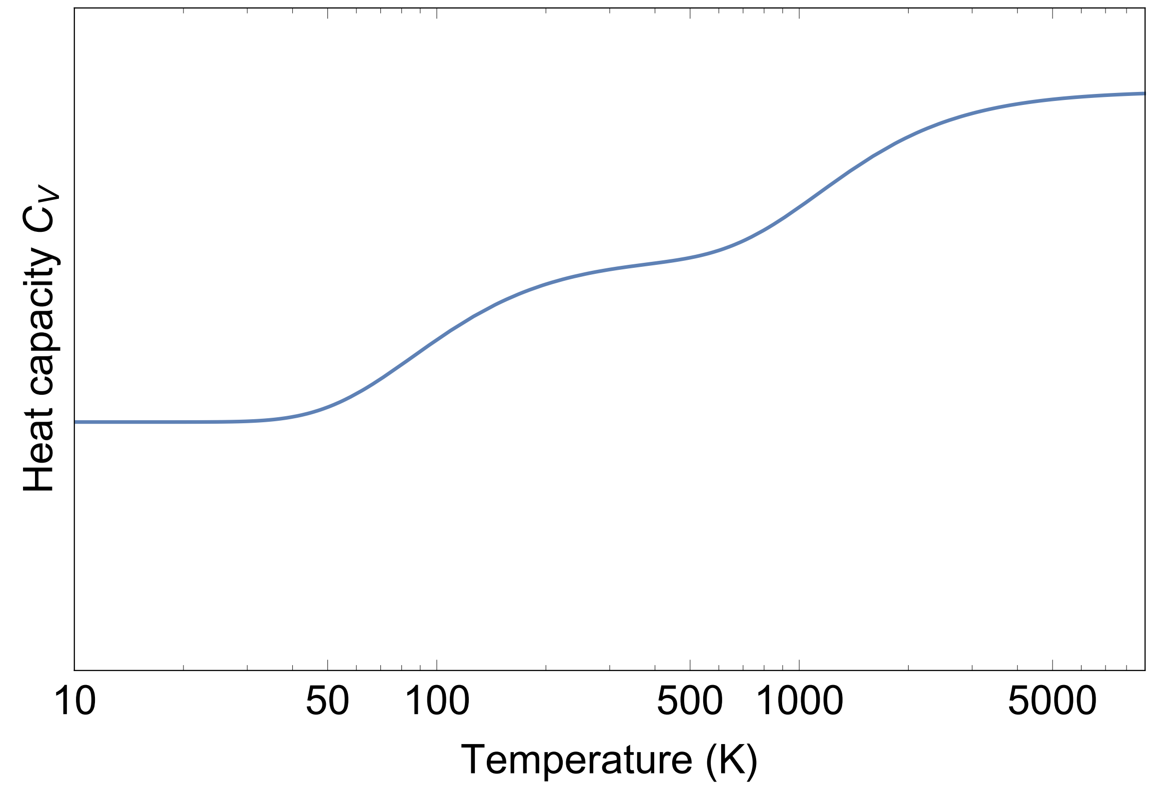
$$C = \frac{\partial E}{\partial \tau} = \tau \frac{\partial \sigma}{\partial \tau}$$

Note: this equality holds when external parameters (e.g., B, V) are held constant.

Paramagnet



Gas



c. 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?

At $\tau \sim \mu B$ lots of spin configurations become accessible

→ Entropy can increase substantially

→ Favorable for energy to flow into system

→ Beyond $\tau \sim \mu B$, there are diminishing returns as $\tau \to \infty$, because Boltzmann factor $e^{-(\epsilon_\uparrow - \epsilon_\downarrow)/\tau}$ is already order unity

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

At low temperature, Boltzmann factor $e^{-\beta(\epsilon_\uparrow - \epsilon_\downarrow)}$ exponentially suppresses spin excitation ⇒ changes in temperature for $\tau \ll \mu B$ do little to change energy & entropy.

At high temperature...

Name:

EXERCISE 3B: ENTROPY AND HELMOLTZ FREE ENERGY

Objectives:

- Calculate the entropy in the canonical ensemble
- (~~Introduce~~ Review 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: $\langle E \rangle = -\frac{d \ln Z}{d\beta}$
- Partition function for the paramagnet: $Z = (e^{\beta\mu B} + e^{-\beta\mu B})^N$

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1. (From last time.) — See notes 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 ε_s, this expression for the entropy generalizes to

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

   a. Write down:

      i. ...the entropy σ in terms of the probabilities P_s.

      ii. ...the probability P_s in terms of β, ε_s, and the partition function Z.

$$\sigma = -\sum_s P_s \ln P_s$$

$$P_s = e^{-\beta\varepsilon_s}/Z$$

$$\sigma = -\sum_s \frac{1}{Z} e^{-\beta\varepsilon_s} \cdot \ln\left(e^{-\beta\varepsilon_s}/Z\right)$$

$$= -\frac{1}{Z}\sum_s e^{-\beta\varepsilon_s}\left(-\beta\varepsilon_s - \ln Z\right)$$

$$= +\frac{\beta}{Z}\sum_s \varepsilon_s e^{-\beta\varepsilon_s} + \frac{\ln Z}{Z}\cdot \overbrace{\sum_s e^{-\beta\varepsilon_s}}^{Z}$$

   b. Find an expression for σ that depends only on β and $\ln Z$.

(continuing from above)

We may recognize the first term as $\beta\langle E\rangle$, so

$$\sigma = \beta\langle E\rangle + \ln Z$$

$$\boxed{\sigma = -\beta\frac{\partial \ln Z}{\partial\beta} + \ln Z}$$

Both forms are useful.

(If we didn't recognize $\langle E\rangle$, can anyway rederive.)

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?

i. $C_V = \left(\frac{\partial E}{\partial \tau}\right)_V = -\frac{\partial}{\partial \tau}\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \beta}{\partial \tau}\frac{\partial^2 \ln Z}{\partial \beta^2}$

$= \frac{1}{\tau^2}\frac{\partial^2 \ln Z}{\partial \beta^2} = \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}$

ii. $C_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V = \tau \frac{\partial \beta}{\partial \tau}\cdot\frac{\partial \sigma}{\partial \beta} = -\frac{1}{\tau}\frac{\partial}{\partial \beta}\left(-\beta\frac{\partial \ln Z}{\partial \beta} + \ln Z\right)$

$= -\beta\left[-\frac{\partial \ln Z}{\partial \beta} - \beta\frac{\partial^2 \ln Z}{\partial \beta^2} + \frac{\partial \ln Z}{\partial \beta}\right]$

$= \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}$ ✓

d. Evaluate the entropy of the paramagnet as a function of temperature τ.

$Z = (e^{\beta\epsilon} + e^{-\beta\epsilon})^N$ $\qquad\qquad$ $\epsilon = \mu B$

$$\sigma = -\beta \frac{\partial \ln Z}{\partial \beta} + \ln Z$$

$$= -N\beta\epsilon \tanh(\beta\epsilon) + N\ln(\overbrace{e^{\beta\epsilon} + e^{-\beta\epsilon}}^{= 2\cosh(\beta\epsilon)})$$

$$= -\frac{N\mu B}{\tau} \tanh\left(\frac{\mu B}{\tau}\right) + N\ln\left[\cosh\left(\frac{\mu B}{\tau}\right)\right] + N\ln 2$$

$\tanh x \xrightarrow{x\to 0} 0$

$\xrightarrow{x\to\infty} 1$

$\cosh x \xrightarrow{x\to 0} 1$

$\xrightarrow{x\to\infty} e^x/2$

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

$\tau \gg \mu B \Leftrightarrow \beta\epsilon \ll 1 \Rightarrow \sigma \approx 0 + N\ln(1) + N\ln 2 = N\ln 2$

$\therefore$ All microstates accessible

$\tau \ll \mu B \Leftrightarrow \beta\epsilon \gg 1 \Rightarrow \sigma \approx -N\beta\epsilon + N\beta\epsilon \to 0$

only unique ground state $\downarrow\downarrow\downarrow\downarrow\downarrow$ $\downarrow B$ is accessible

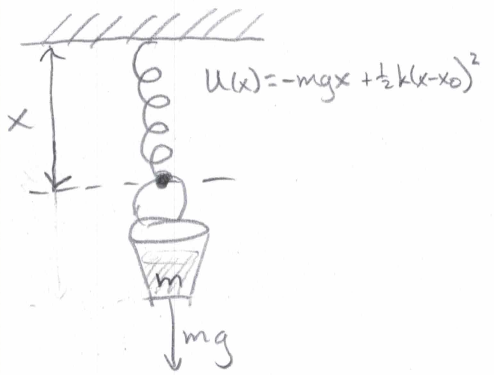
f. Hopefully your result is consistent with the **Third Law of Thermodynamics**: the entropy approaches a constant value as the temperature approaches zero. Under what circumstances would the entropy approach a *nonzero* constant?

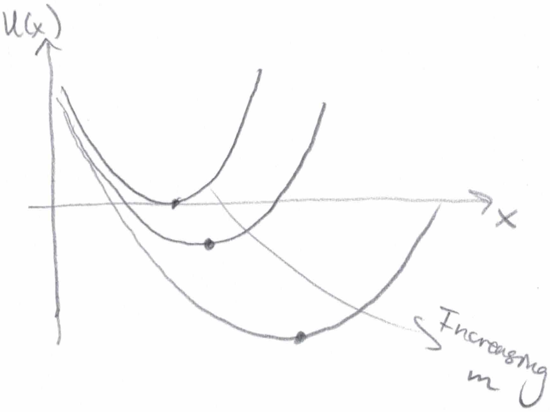
✓ Consistent

Nonzero const. if more than one degenerate ground state,

e.g. $\uparrow\uparrow\uparrow\uparrow\uparrow$, $\downarrow\downarrow\downarrow\downarrow\downarrow$ (ferromagnet)

Ex. 3 Thermal vs. mechanical equilibrium





Minimizing U(x) tells us equilibrium position as external parameter (e.g., m) is varied.

Ex 3. Similar concept for finding macrostate of a system in thermal equilibrium with a reservoir.

Claim: $F(N, \tau, \underbrace{\vec{x}}_{\text{external parameters}}) \equiv E - \tau\sigma$ (Helmholtz free energy), is minimized in thermal equilibrium.

Specifically — minimizing F of the system maximizes total entropy of the system & reservoir.

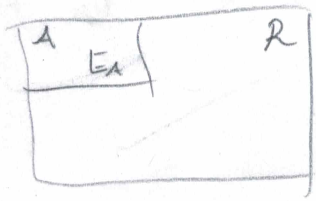
Example (paramagnet) & proof.

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 τ.



$$dF_A = dE_A - \tau d\sigma_A - \sigma \cancel{d\tau_A}^{\to 0}$$

$$= dE_A - \underbrace{\frac{dE_A}{d\sigma_A} \cdot d\sigma_A}_{dE_A} = 0$$

$\therefore$ F_A extremized in thermal equilibrium

b. Find F in terms of Z.

We showed: $\sigma = \beta\langle E\rangle + \ln Z$

$\Rightarrow$ $\boxed{F = E - \tau\sigma = E - E - \tau \ln Z = \tau \ln Z}$

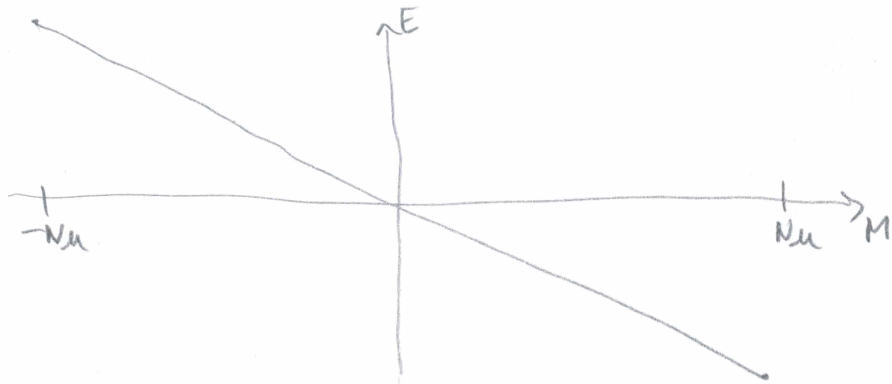
c. As a concrete example, sketch the Helmholtz free energy F as a function of magnetization M for a paramagnet in a magnetic field B at two different temperatures $\tau_2 > \tau_1 > 0$. (... continued on next page ...)

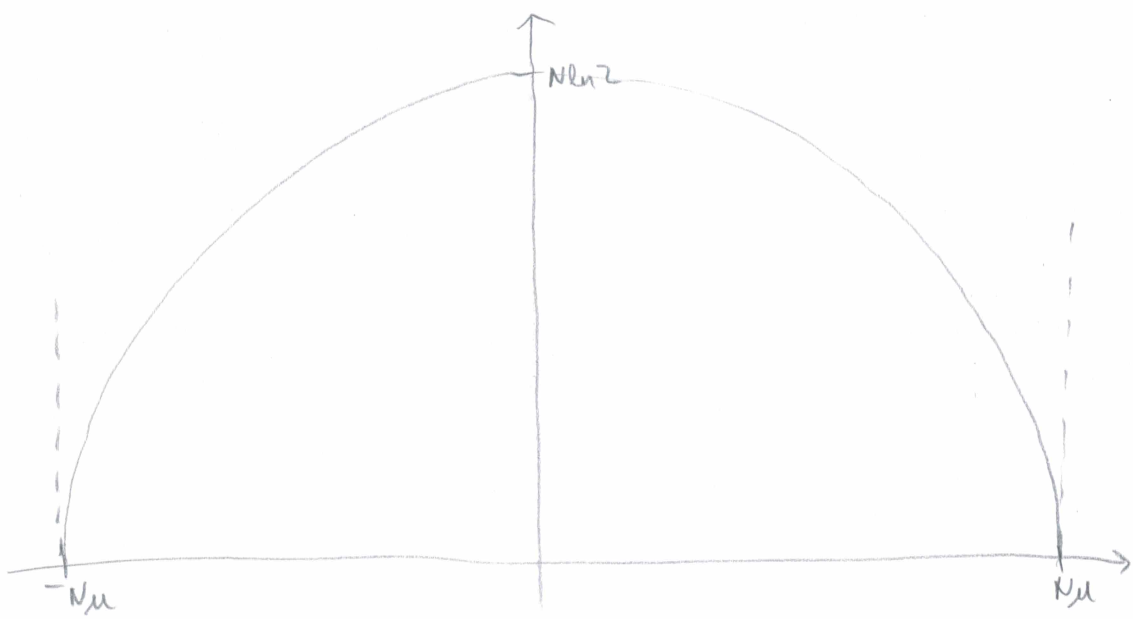
Name:

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

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

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





See details on next page.

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

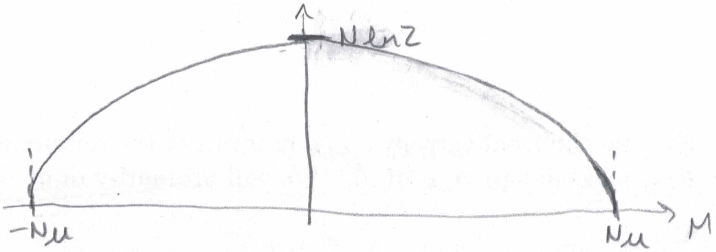
σ symmetric under $M \leftrightarrow -M$; at $M=0$, $\sigma = -N\ln(1/2) = N\ln 2$

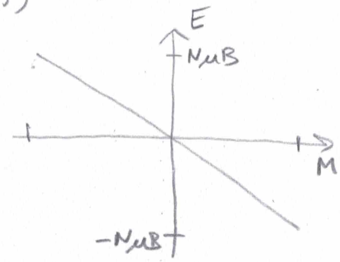
$$\text{At } M = -N\mu + \xi,\ \sigma = -\left(\tfrac{N}{2} - \tfrac{N}{2} + \tfrac{\xi}{2\mu}\right)\ln\left(\tfrac{1}{2} - \tfrac{1}{2} + \tfrac{\xi}{2\mu N}\right) - \left(\tfrac{N}{2} + \tfrac{N}{2} - \tfrac{\xi}{2\mu}\right)\ln\left(\tfrac{1}{2} + \tfrac{1}{2} - \tfrac{\xi}{2\mu N}\right)$$

$$= -\frac{\xi}{2\mu}\ln\left(\frac{\xi}{2\mu N}\right) - \left(N - \frac{\xi}{2\mu}\right)\ln\left(1 - \frac{\xi}{2\mu N}\right) \xrightarrow{0} \text{as } \xi \to 0 \ ✓$$

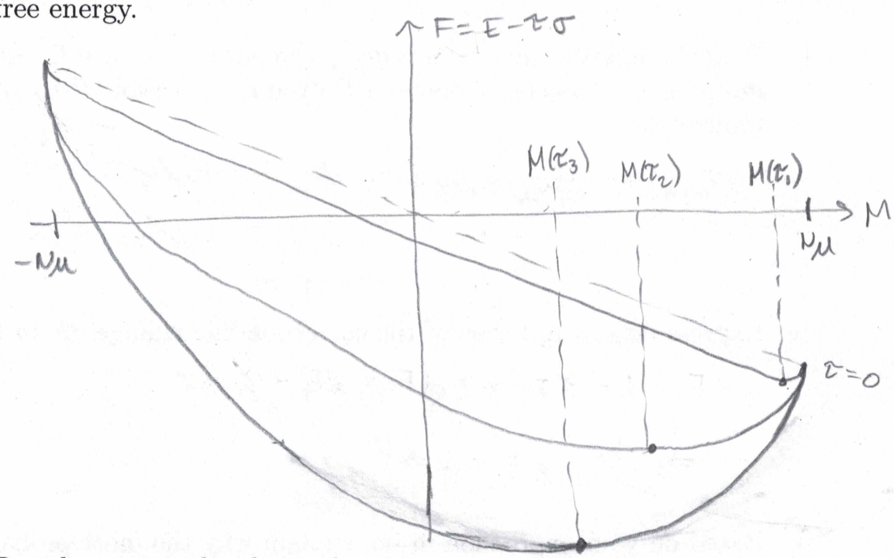
$$\approx -\frac{\xi}{2\mu}\ln\left(\frac{\xi}{2\mu N}\right) + \frac{\xi}{2\mu} + O(\xi^2)$$

$$\therefore \left.\frac{d\sigma}{dM}\right|_{M=-N\mu} = \left.\frac{d\sigma}{d\xi}\right|_{\xi=0} = -\frac{1}{2\mu}\ln\left(\frac{\xi}{2\mu N}\right) \cancel{- \frac{\xi}{2\mu}\cdot\frac{1}{\xi}} \cancel{+ \frac{1}{2\mu}} + O(\xi) \longrightarrow \infty$$





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?

$M \to N\mu$ as $\tau \to 0$: Low entropy but large $\frac{d\sigma}{dM} \propto \frac{d\sigma}{dE} = \frac{1}{\tau}$ ✓

$M \to 0$ as $\tau \to \infty$: $N_\uparrow = N_\downarrow$ maximizes entropy ✓
(E negligible at high τ)

Name:

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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.

$$g_{A+R}(E) = g_A(E)\, g_R(E_{tot} - E) = g_A(E) \cdot C e^{-\beta E}$$

Here, we have used $\underbrace{\frac{g_R(E_{tot}-E)}{g_R(E_{tot})}}_{C \longrightarrow} = e^{\sigma(E_{tot}-E) - \sigma(E_{tot})} = e^{-\beta E}$

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

$$\sigma_{A+R} = \sigma_A(E) + \ln C - \beta E$$

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.

$$d\sigma_{A+R} = d\sigma_A - \beta dE = d\sigma_A - dE/\tau$$

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

$$F = E - \tau\sigma \Rightarrow dF = dE - \tau d\sigma$$

$$\Rightarrow d\sigma_{A+R} = -\tau dF$$

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.

Total entropy of system+reservoir is maximized when Helmoltz free energy of system A is minimized.