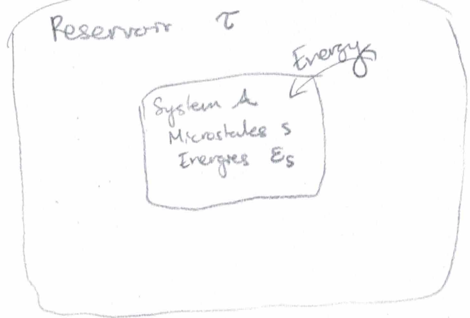
* Last time we began to examine a generic system in thermal equilibrium with a reservoir of temperature $\tau \longleftrightarrow$ inv. temp. $\beta \equiv \frac{1}{\tau} = \frac{d\sigma}{dE}$

* We showed that the relative probabilities of finding system in microstates s_1 (energy ε_1) and s_2 (energy ε_2) is:



$$\frac{P_1}{P_2} = e^{-\beta(\varepsilon_1 - \varepsilon_2)}, \quad \text{where } \beta = 1/\tau$$

$$= \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_2}} \longleftarrow \text{Boltzmann factor}$$

$\Rightarrow$ The probability of finding the system in state s is thus proportional to $e^{-\beta\varepsilon_s}$

$$P_s \propto e^{-\beta\varepsilon_s} = \underset{\uparrow \text{ unnormalized weight}}{W_s}$$

Ex. 1 Find the proportionality factor and use it to calculate $\langle E \rangle$

What is generally easier to measure than $\langle E \rangle$ is the heat capacity:

$$C_V = \left(\frac{\partial E}{\partial \tau}\right)_V$$

$\uparrow$ const. volume

(How much energy must we add to change the temperature by a fixed amount?)

* Measuring response function (heat capacity, magnetic susceptibility) is a common means of inferring microscopic properties of a material (e.g., magnetically ordered or not?)

* Today: what would you expect to measure if the material is well described by our simple model of non-interacting e^- spins

Name:

EXERCISE 3A: PARTITION FUNCTION

Objectives:

- Analyze a system in thermal equilibrium with a reservoir of known temperature. (Keywords: **canonical ensemble, partition function**.)
- Calculate the energy and **heat capacity** of a paramagnet vs. temperature.
- Derive and discuss the relationship between heat capacity and entropy.

Reading: Kittel & Kroemer, Ch. 3

Last time:

- We defined the temperature τ and inverse temperature $\beta \equiv 1/\tau = d\sigma/dE$.
- We derived the Boltzmann factor $e^{-\beta\varepsilon_s}$, where $\beta = 1/\tau$.

1. *Partition function.* Let X be a state function (e.g., magnetization; energy; volume or pressure of a gas) and X_s denote its value in a specific microstate s. Suppose that we know the *relative* probabilities of finding the system in different microstates, given by a set of weights w_s. How do we calculate the average value $\langle X \rangle$?

   a. The probability P_s of finding the system in microstate s is proportional to w_s, i.e., $P_s = w_s/Z$. What is the normalization factor Z?

   $P_s \propto w_s \Rightarrow P_s = w_s/Z$ proportionality factor

   Normalization: $1 = \sum_s P_s = \frac{1}{Z}\sum_s w_s \Rightarrow \boxed{Z = \frac{1}{\sum_s w_s}}$

   b. Write down a general expression for the average value $\langle X \rangle$ in terms of the weights w_s and Z.

   $\langle X \rangle = \sum_s P_s X_s = \frac{1}{Z}\sum_s w_s X_s$

   c. In the **canonical ensemble**, where the average is taken over identically prepared systems at **fixed temperature and particle number**, the quantity Z defined above is called the **partition function**. Write down explicit expressions for...

i. The **partition function** Z as a function of inverse temperature β and energies ε_s of the microstates s

$$W_s = e^{-\beta\varepsilon_s} \Rightarrow Z = \sum_s e^{-\beta\varepsilon_s}$$

ii. The average value $\langle X \rangle$ in terms of β and Z

$$\langle X \rangle = \frac{1}{Z}\sum_s X_s e^{-\beta\varepsilon_s}$$

d. Derive the following general relation between the expectation value of the energy and the partition function $Z = \sum_s e^{-\beta\varepsilon_s}$:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}. \tag{1}$$

$$\langle E \rangle = \frac{1}{Z}\sum_s \varepsilon_s e^{-\beta\varepsilon_s}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_s e^{-\beta\varepsilon_s}$$

$$= -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$

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

2. *Energy and heat capacity of the paramagnet.* The **heat capacity** of a system at constant volume is

$$C_V \equiv \left(\frac{\partial E}{\partial \tau}\right)_V . \tag{2}$$

would matter e.g. for a gas: are we keeping p or V fixed?

Calculate the energy E and heat capacity C_V of a paramagnet of N spins of magnetic moment μ in a magnetic field B at temperature τ. (Here, the volume plays no role.)

a. Show that the partition function for the paramagnet can be written in the form $Z = (a+b)^N$, where a and b depend on the energies $\pm\epsilon \equiv \pm\mu B$ of the two spin states and the inverse temperature $\beta = 1/(k_B T)$. What are a and b?

$\epsilon_\uparrow \equiv \epsilon$

$\epsilon_\downarrow \equiv -\epsilon$

Concept: $Z = \left(e^{-\beta\epsilon_\uparrow} + e^{-\beta\epsilon_\downarrow}\right)^N$

2^N terms of form $e^{-\beta(N_\uparrow\epsilon_\uparrow + N_\downarrow\epsilon_\downarrow)}$ with $N_\uparrow + N_\downarrow = N$

More formally: microstates $(\epsilon_1, \ldots, \epsilon_N) \equiv s$, $\epsilon_j = \pm\epsilon$ $\Leftarrow$ $\boxed{\text{Start here}}$

$$Z = \sum_{\epsilon_1=\pm\epsilon}\sum_{\epsilon_2}\cdots\sum_{\epsilon_N} e^{-\beta\sum_j \epsilon_j} \quad (2^N \text{ terms})$$

$$= \sum_{\epsilon_1}\sum_{\epsilon_2}\cdots\sum_{\epsilon_N} e^{-\beta\epsilon_1} e^{-\beta\epsilon_2}\cdots e^{-\beta\epsilon_N}$$

$$= \left(\sum_{\mu_1} e^{-\beta\epsilon_1}\right)\left(\sum_{\mu_2} e^{-\beta\epsilon_2}\right)\cdots\left(\sum_{\mu_N} e^{-\beta\epsilon_N}\right)$$

$$\sum_{\epsilon_j} e^{-\beta\epsilon_j} = e^{-\beta\epsilon} + e^{+\beta\epsilon}$$

$$\therefore Z = \prod_{j=1}^{N}\left(e^{-\beta\epsilon} + e^{\beta\epsilon}\right) = \left(e^{-\beta\epsilon} + e^{\beta\epsilon}\right)^N$$

b. How else might you write out the partition function of the paramagnet? Why is the form in a. more convenient?

$$\sum_{N_\uparrow=0}^{N}\binom{N}{N_\uparrow} e^{-\beta\epsilon(N_\uparrow - N_\downarrow)} = \sum_{N_\uparrow=0}^{N}\binom{N}{N_\uparrow} e^{-\beta\epsilon(2N_\uparrow - N)}$$

Much more convenient to work with the simple algebraic form in (a) (e.g., to take $\partial \ln Z/\partial\beta$) than to deal with unevaluated sum over $N_\uparrow$.

c. Use Eq. 1 to evaluate the energy $E(B, \tau)$ of the paramagnet.

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[N \ln(e^{-\beta\epsilon} + e^{\beta\epsilon})\right]$$

$$= \frac{+N\epsilon e^{-\beta\epsilon} - N\epsilon e^{\beta\epsilon}}{e^{-\beta\epsilon} + e^{\beta\epsilon}} = -N\epsilon \cdot \frac{e^{\beta\epsilon} - e^{-\beta\epsilon}}{e^{\beta\epsilon} + e^{-\beta\epsilon}}$$

$$= -N\epsilon \tanh(\beta\epsilon)$$

$$\therefore \quad \boxed{E = -N\mu B \tanh\left(\frac{\mu B}{\tau}\right)}$$

Note: we will stop explicitly writing $\langle \cdot \rangle$. By E we mean $\langle E \rangle$, and fluctuations about mean are small in thermodynamic limit.

d. Calculate the heat capacity C_V from the energy.

Useful relation: $\frac{d}{dx}\tanh(x) = \text{sech}^2(x)$, where $\text{sech}\, x = \frac{2}{e^x + e^{-x}}$

Check: $$\frac{d}{dx}\left(\frac{e^x - e^{-x}}{e^x + e^{-x}}\right) = \frac{(e^x + e^{-x})^2 - (e^x - e^{-x})^2}{(e^x + e^{-x})^2} = \frac{4}{(e^x + e^{-x})^2}$$

Thus: $$\frac{\partial E}{\partial \tau} = -N\mu B\, \text{sech}^2\left(\frac{\mu B}{\tau}\right)\left(\frac{-\mu B}{\tau^2}\right)$$

$$\boxed{C_V = \frac{N(\mu B)^2}{\tau^2}\, \text{sech}^2\left(\frac{\mu B}{\tau}\right)}$$

e. Sketch the heat capacity as a function of temperature. To this end, first determine the limiting behavior of the heat capacity . . .

i. . . . for $\tau \ll \mu B$

$$\operatorname{sech}(x) \xrightarrow[x\to\infty]{} \frac{2}{e^x} = 2e^{-x}$$

$$\Rightarrow C_V \longrightarrow 4N\left(\frac{\mu B}{\tau}\right)^2 e^{-2\mu B/\tau}$$ exponentially suppressed as $\tau \to 0$

ii. . . . for $\tau \gg \mu B$

$$\operatorname{sech}(x) \xrightarrow[x\to 0]{} \frac{2}{2} = 1$$

$$\Rightarrow C_V \longrightarrow N\left(\frac{\mu B}{\tau}\right)^2$$

iii. Based on the analysis above, sketch $C_V(\tau)$.

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3. The heat capacity can alternatively be defined in terms of the temperature and entropy, without explicit reference to the energy.

   a. Derive a general expression for C_V in terms of σ and τ.
   Hint: Start by writing C_V/τ in terms of Eq. 2 and the definition of temperature.

$$\frac{C_V}{\tau} = \left(\frac{\partial E}{\partial \tau}\right)_V \cdot \frac{d\sigma}{dE} = \left(\frac{\partial \sigma}{\partial \tau}\right)_V$$

$$\Rightarrow C_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$$

   b. Suppose that you have measured the heat capacity of a solid as a function of temperature. Is this enough information to deduce the entropy $\sigma(\tau)$? Why or why not?

$$\frac{C_V}{\tau} = \frac{\partial \sigma}{\partial \tau}\Big|_V$$

$$\Rightarrow \sigma(\tau) - \sigma(0) = \int_0^{\tau'} d\tau' \, \frac{C_V}{\tau'}$$

$$\sigma(\tau) = \sigma(0) + \int_0^{\tau'} d\tau' \, C_V/\tau'$$

do we know $\sigma(0)$?

Third Law of thermodynamics: Entropy approaches a constant as temperature approaches zero.

E.g. unique ground state: $\downarrow\downarrow\downarrow\downarrow\downarrow$ $\Rightarrow \sigma \to 0$ as $\tau \to 0$

Few degenerate ground states: $\downarrow\downarrow\downarrow\downarrow\downarrow, \uparrow\uparrow\uparrow\uparrow\uparrow$ $\Rightarrow \sigma \to \ln 2$
Ferromagnet

By constant, we mean entropy does not depend on N. **(Hence $\sigma(0)$ is negligibly small in the thermodynamic limit.)**

(Violations of 3rd law? Possibly spin glasses w/ exponentially many degenerate ground states.)

Parts c-d (page 7) will be completed next class.