HH0060 Partition Function

Starting from the Boltzmann factor, $P(\varepsilon_s) \propto e^{-\varepsilon_s/\tau}$, it is convenient to introduce the partition function Z,

$$\boxed{Z = \sum_s e^{-\varepsilon_s/\tau}} \longrightarrow \boxed{P(\varepsilon_s) = \frac{1}{Z} e^{-\varepsilon_s/\tau}}$$

very very useful ☺

The average energy of the system can be computed from the partition function.

$$U = \langle \varepsilon \rangle = \sum_s \varepsilon_s P(\varepsilon_s) = \frac{1}{Z} \sum_s \varepsilon_s e^{-\varepsilon_s/\tau}$$

Compare both expressions.

Notice that $\frac{\partial Z}{\partial \tau} = \sum_s e^{-\varepsilon_s/\tau} \cdot (-\varepsilon_s)(-\frac{1}{\tau^2}) = \frac{1}{\tau^2} \sum_s \varepsilon_s e^{-\varepsilon_s/\tau}$

One obtains the very useful thermal identity,

$$\boxed{U = \tau^2 \frac{\partial \log Z}{\partial \tau}}$$

Let's apply these results to a binary spin.

⟨1⟩ A binary spin in thermal equilibrium

There are two states $\varepsilon_s = \pm mB = \pm \varepsilon$ for a binary spin. The partition function is rather simple,

$$Z = e^{\varepsilon/\tau} + e^{-\varepsilon/\tau} = 2\cosh(\varepsilon/\tau)$$

Taking derivative with respect to τ ⟶ average energy U

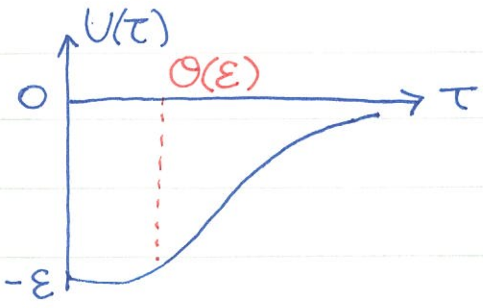
$$U = \tau^2 \frac{1}{Z} \frac{\partial Z}{\partial \tau} = \tau^2 \cdot \frac{1}{2\cosh(\varepsilon/\tau)} \cdot 2\sinh(\varepsilon/\tau) \cdot (-\frac{\varepsilon}{\tau^2})$$

$$\rightarrow \boxed{U = -\varepsilon \tanh(\varepsilon/\tau)}$$

$\tau \to 0$, $U \to -\varepsilon$ ✓

$\tau \to \infty$, $U \to 0$ ✓

Note that U is always negative



It shall be clear that $U \approx -\varepsilon$ for $\tau \ll \varepsilon$ where the ground state reigns. On the other hand, for $\tau \gg \varepsilon$, thermal fluctuations dominates and $U \approx \frac{1}{2}(-\varepsilon+\varepsilon) = 0$!

According to the first law $dU = \tau d\sigma - pdV + \mu dN$

At constant V, N,

$dU = \tau d\sigma$ $\longrightarrow$ Introduce the heat capacity C_V at const. V.

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

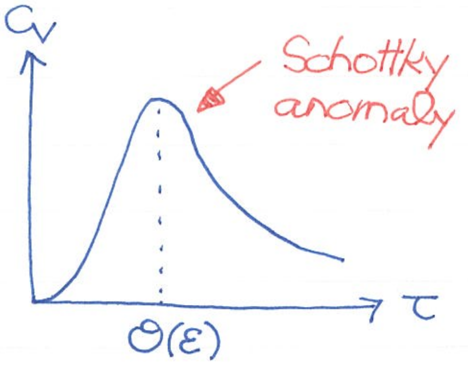
, note that $\tau d\sigma$ = infinitesmal heat.

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = -\varepsilon\, \mathrm{sech}^2(\varepsilon/\tau)\cdot\left(-\frac{\varepsilon}{\tau^2}\right) = \left(\frac{\varepsilon}{\tau}\right)^2 \frac{1}{\cosh^2(\varepsilon/\tau)}$$

For $\tau \ll \varepsilon$, $\cosh(\varepsilon/\tau) \approx \frac{1}{2} e^{\varepsilon/\tau}$, $C_V \approx \left(\frac{2\varepsilon}{\tau}\right)^2 e^{-2\varepsilon/\tau}$

The heat capacity is exponentially small at low temperatures. The exponential suppression arises from the energy gap $\Delta = 2\varepsilon$ in the binary spin system.

For $\tau \gg \varepsilon$, $\cosh(\varepsilon/\tau) \approx 1$, $C_V \approx \left(\frac{\varepsilon}{\tau}\right)^2$



The heat capacity is small for both high τ and low τ limits. But, there is a hump when $\tau \sim \varepsilon$. Why?

From the definition,

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

For a binary spin, we know $\sigma(0) = \log(g(\tau=0)) = 0$.

$$\boxed{\sigma(\tau) = \int_0^\tau \frac{C_V}{\tau'} d\tau'}$$

Introduce the dimensionless variable $x = \tau/\varepsilon$ $\longrightarrow$ $C_V = \frac{1}{x^2}\frac{1}{\cosh^2(1/x)}$

$$\sigma(\tau) = \int_0^{\tau/\varepsilon} \frac{C_V}{x} dx = \int_0^{\tau/\varepsilon} \frac{1}{x^3}\frac{1}{\cosh^2(1/x)} dx$$

look up the integral table.

$$= \log\left[\cosh\left(\frac{1}{x}\right)\right] - \frac{1}{x}\tanh(1/x) - [-\log 2]$$

OK, OK, I lied.... I used Mathematica for integrals ☺

It is rather nice that the entropy $\sigma(\tau)$ obtained this way is identical to Shannon entropy,

$$\sigma_I \equiv \sum_s -P_s \log P_s = \langle -\log P \rangle \qquad P_s = \frac{1}{Z} e^{-\varepsilon_s/\tau}$$

$$= \langle \log Z + \varepsilon/\tau \rangle \Longrightarrow \boxed{\sigma_I = \log Z + U/\tau}$$

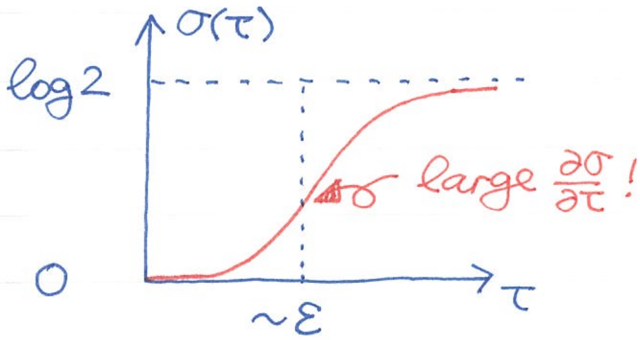
entropy for Boltzmann distribution.

We already calculate Z and U before,

$$\boxed{\sigma_I = \log\left[2\cosh(\varepsilon/\tau)\right] - \left(\frac{\varepsilon}{\tau}\right)\tanh\left(\frac{\varepsilon}{\tau}\right)}$$

$\sigma_I = \sigma$

$$= \log\left[\cosh\left(\frac{1}{x}\right)\right] - \frac{1}{x}\tanh\left(\frac{1}{x}\right) + \log 2 = \sigma(\tau)$$

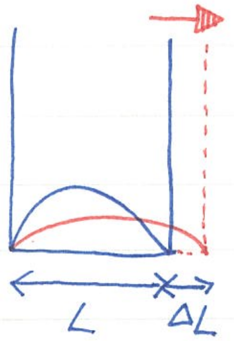


- For $\tau \ll \varepsilon$, $P(-\varepsilon) = 1$, $P(\varepsilon) \approx 0$, the entropy is almost 0.
- For $\tau \gg \varepsilon$, $P(-\varepsilon) \approx P(\varepsilon) \approx \frac{1}{2}$, the entropy is almost $\log 2$

Thus, in both low temp. and high temp. limits, the entropy does not change much. It means that heat capacity C_V is small in both limits.

Only around $\tau \sim \varepsilon$, entropy increases significantly, leading to the Schottky anomaly in C_V.

② Pressure: Consider a particle in a 1D box. The energy is



$$\varepsilon_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \propto \frac{1}{L^2}$$

Changing L gives rise to energy change,

$$\Delta\varepsilon_n = \frac{\partial \varepsilon_n}{\partial L} \cdot \Delta L \xrightarrow{3D} \frac{\partial \varepsilon_n}{\partial V} \Delta V, \quad \Delta V = A \Delta L$$

Assume the probability distribution does not change during volume expansion (constant σ). The average energy of the system also changes,

$$\Delta U = \langle \Delta \varepsilon \rangle = \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle \Delta V.$$ For positive pressure, $\frac{\partial \varepsilon_n}{\partial V} < 0$

and vice versa. Thus, we define pressure p as

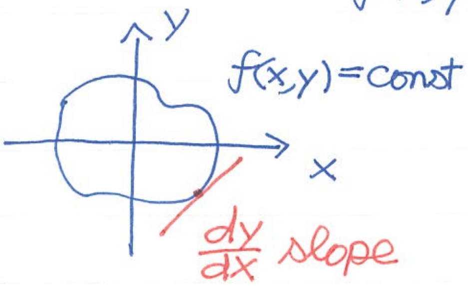
$$p \equiv -\left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle = -\sum_n P_n \frac{\partial \varepsilon_n}{\partial V} = -\frac{\partial}{\partial V} \sum_n P_n \varepsilon_n = -\left(\frac{\partial U}{\partial V}\right)_\sigma$$

const. entropy.

Finally, we obtain the important relation $\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_\sigma}$ Now, we would like to show another expression for p.

review.

$$f(x,y) = \text{const} \longrightarrow df = 0, \quad \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 0$$



Thus, $\frac{dy}{dx} = -\frac{\partial f/\partial x}{\partial f/\partial y}$ simple

Here comes the key!

$$\frac{dy}{dx} = \left(\frac{\partial y}{\partial x}\right)_f$$

This is the proper notation!

Now make the following replacement, $f \to \sigma$, $x \to V$, $y \to U$

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -\frac{(\partial \sigma/\partial V)_U}{(\partial \sigma/\partial U)_V}$$ note that $\left(\frac{\partial \sigma}{\partial U}\right)_V = \frac{1}{\tau}$ and $\left(\frac{\partial U}{\partial V}\right)_\sigma = -p$

We arrive at a non-trivial expression $\boxed{p = \tau \left(\frac{\partial \sigma}{\partial V}\right)_U}$

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