1 Simple Applications of Stat Mech

1.1 Gibbs Paradox

From the last lecture the Gibbs paradox $S > S' + S''$ is puzzling...

(indistinguishable) If the particles are identical we can keep track double counting with

$$Z_N = \frac{Z_1^N}{N!}$$

And from the log of the partition function

$$\begin{aligned} \ln Z_N &= N \ln Z_1 - \ln N! \quad \text{using} \quad \ln N! = N \ln N - N \\ &= N \ln Z_1 - N \ln N + N \end{aligned}$$

NOTE: This does not affect $\bar{E}, \bar{P}$ as they are still

$$\bar{E} = \frac{3}{2} NkT, \quad \bar{P} = \frac{NkT}{V}$$

The entropy is recaculated as

$$S = k(\ln Z + \beta E)$$

Using

$$Z_1 = \left(\frac{2m}{\hbar^2 \pi} \right)^{3/2} \beta^{-3/2} V$$

we have the entropy

$$S = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0 \right], \quad \sigma_0 = \sigma + 1 = \frac{3}{2} \ln \left(\frac{2\pi mk}{h^2} \right)^{3/2} + \frac{5}{2}$$

1.2 Equipartition Theorem

Using the Boltzmann function

Consider some systems described by generalized coordinates q_k, p_k with energies

$$E = E(q_1, \ldots, q_N, p_1, \ldots, p_N)$$

- Assumption 1: The total energy is additive

$$E = \epsilon_i(p_i) + E(q_1, \ldots, q_N, p_1, \ldots, \text{no } p_i, \ldots, p_N)$$

- Assumption 2: function ϵ_i is quasi-staic in p_i or usually the energy is quadratic i.e.

$$\epsilon_i(p_i) = b p_i^2$$

The average value of ϵ_i is

$$\begin{aligned} \overline{\epsilon_i} &= \frac{1}{Z} \int \epsilon_i e^{-\beta E} dq dp \\ &= \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_N)} \epsilon_i dq_1, \ldots, dp_N}{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_N)} dq_1, \ldots, dp_N} \end{aligned}$$

From the first assumption we know that the energy is additive so

$$\begin{aligned}\overline{\epsilon_i} &= \frac{\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\epsilon_i dp_i \cancel{\int e^{-\beta E'} dq_1,\ldots,dp_N}}{\int_{-\infty}^{\infty} e^{-\beta\epsilon_i} dp_i \cancel{\int e^{-\beta E'} dq_1,\ldots,dp_N}} \\ &= -\frac{\partial}{\partial\beta}\ln\left(\int e^{-\beta E} dp_i\right)\end{aligned}$$

Now using the second assumption the intgral becomes

$$\int e^{-\beta\epsilon_i} dp_i = \int e^{-\beta b p_i^2} dp_i$$

With a change of variables

$$y = \sqrt{\beta}p_i, \quad dy = \sqrt{\beta}dp_i$$

the integral becomes

$$= \frac{1}{\sqrt{\beta}}\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\frac{\pi}{\beta}}$$

which is independent of β so

$$\int e^{-\beta\epsilon_i} dp_i = C\beta^{-1/2}$$

where C is a constant. Thus

$$\overline{\epsilon_i} = -\frac{\partial}{\partial\beta}\ln\left(C\beta^{-1/2}\right) = \frac{1}{2\beta} = \frac{1}{2}kT$$

Worksheet

1. Use the equipartition theorem to determine the molar heat capacity at constant volume of a monoatomic gas: Given

$$\bar{\epsilon} = \frac{1}{2}kT \quad \text{for} \quad q_x, q_y, q_z \implies \bar{E} = \frac{3}{2}NkT$$

so the molar heat capacity is

$$c_V = \frac{\partial\bar{E}}{\partial T} = \frac{3}{2}Nk \implies c_p = \frac{c_V}{n} = \frac{3}{2}R, \quad R = \frac{N}{n}k = N_A k$$

2. A small particle undergoing Brownian motion in a liquid. The particle is in equilibrium with a bath at temp T. Use the equipartition theorem to determine the velocity dispersion

$$\begin{aligned}\bar{E}_x &= \frac{1}{2}m\overline{v_x}^2 = \frac{1}{2}kT \\ \implies \overline{v_x}^2 &= \frac{2\bar{E}_x}{m} = \frac{kT}{m}\end{aligned}$$

1.3 Specifc heat of solids

In 3D the energy is

$$E = \sum_{i=1}^{3N}\left[\frac{p_i^2}{2m} + \frac{1}{2}mk_i^2 q_i^2\right]$$

where we have three dimensions as well as a kinetic and potential dimension (6N degrees of freedom). From the equipartition theorem the average energy is

$$\bar{E} = 3N\left(\frac{1}{2}kT \cdot 2\right) = 3NkT$$

The molar heat capacity is roughly

$$c_p = \frac{c_V}{n} = \frac{3Nk}{n} = 3R$$

The molar heat capacity of a solids at $T = 300$ K are

$$c_p = \begin{cases} 25.35 \text{ J/mol K} & \text{Ag} \\ 22.75 \text{ J/mol K} & \text{S} \\ 25.39 \text{ J/mol K} & \text{Zn} \\ 24.20 \text{ J/mol K} & \text{Al} \\ 6.01 \text{ J/mol K} & \text{C} \end{cases}$$

Einstein's Solids: All atoms have the same spring constant $\omega = \sqrt{k/m}$ From the partition function, the average energy in 3D is

$$\bar{E} = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$