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

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

- Assumption 1: The total energy is additive

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

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

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

The average value of ϵ_i is

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

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

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

To find the heat capacity:

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

so

$$\begin{aligned} c_V &= 3N\hbar\omega\left(-\frac{1}{(e^{\beta\hbar\omega} - 1)^2} e^{\beta\hbar\omega}\hbar\omega\right)\left(\frac{1}{kT^2}\right) \\ &= 3Nk\frac{\hbar^2\omega^2}{T^2}\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \end{aligned}$$

Einstein was smart and defined an "Einstein temperature" $\Theta_E \equiv \hbar\omega/k$ and using

$$\beta = \frac{1}{kT} \implies \beta\hbar\omega = \frac{\hbar\omega}{kT} = \frac{\Theta_E}{T}$$

so the heat capacity is (using $Nk = nR$)

$$c_V = 3nR\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}$$

Temperature limits

- High T limit: $\Theta_E \ll T$

  Using the approximation $e^x \approx 1 + x$ for $x \ll 1$ we have

  $$c_V = 3nR\left(\frac{\Theta_E}{T}\right)^2 \frac{1 + \Theta_E/T}{(\Theta_E/T)^2} = 3nR\left(1 + \frac{\Theta_E}{T}\right) = 3nR$$

  For most solids $\Theta_E \approx 300$ K, but for Carbon $\Theta_E \approx 1300$ K—since the frequency of $\omega = \sqrt{k/m}$ is high for low molecular weight.

- For a low temperature limit $\Theta_E \gg T$ and $\Theta_E/T \gg 1$ so

  $$c_V \to 3nR\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T} \to 0 \quad \text{as} \quad T \to 0$$

1.4 Maxwell velocity distribution

The average velocity of a distribution of particles in a box is

$$\bar{\mathbf{v}} = 0$$

For a simple molecule in a gas

$$\epsilon = \frac{p^2}{2m} + \epsilon_{\text{int}}$$

where we can ignore this constant internal energy due to rotation and vibration of a molecule. The probablity should also be proportional to the boltzmann factor

$$P(\mathbf{r}, \mathbf{p})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p} \propto e^{-\beta\frac{p^2}{2m}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{p}$$

Since $\mathbf{v} = \mathbf{p}/m$ we have

$$\begin{aligned} f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} \equiv \quad & \text{mean \# of molecules in} \\ & \mathbf{r} \to \mathbf{r} + \mathrm{d}\mathbf{r} \text{ and } \mathbf{v} \to \mathbf{v} + \mathrm{d}\mathbf{v} \\ & \propto e^{-\beta\frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} \end{aligned}$$

So we get

$$f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} = Ce^{-\beta\frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

where C is the normalization factor taken from integrating over all space

$$N = \int_{\mathbf{r}}\int_{\mathbf{v}} f(\mathbf{r},\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

This function only depends on velocity because it does not matter where the particle is inside the box to get the velocity distribution so

$$\begin{aligned} N &= \int_{\mathbf{r}} \mathrm{d}^3\mathbf{r} \int_{\mathbf{v}} f(\mathbf{v})\,\mathrm{d}^3\mathbf{v} \\ &= VC \iiint_{-\infty}^{\infty} e^{-\beta\frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{v} \quad v = \sqrt{v_x^2 + v_y^2 + v_z^2}, \quad \mathrm{d}^3\mathbf{v} = \mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \end{aligned}$$

and using the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

we get the normalization factor

$$N = VC\left(\frac{2\pi}{\beta m}\right)^{3/2}$$

or

$$C = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2}$$

Now that we are equipped with the normalization factor we can find the *Maxwell velocity distribution*

$$f(\mathbf{v})\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v} = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta\frac{mv^2}{2}}\,\mathrm{d}^3\mathbf{r}\,\mathrm{d}^3\mathbf{v}$$

Worksheet

1. IN a laser absorption experiment

$$\begin{aligned} V f(\mathbf{v})\,\mathrm{d}v_x &= \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta\frac{mv_x^2}{2}}\,\mathrm{d}v_x \int e^{-\beta\frac{mv^2}{2}}\,\mathrm{d}v_y\,\mathrm{d}v_z \\ &= N\left(\frac{\beta m}{2\pi}\right)^{3/2} \frac{2\pi}{\beta m} e^{-\beta\frac{mv_x^2}{2}}\,\mathrm{d}v_x \\ g(\mathbf{v})\,\mathrm{d}v_x &= N\left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\beta\frac{mv_x^2}{2}}\,\mathrm{d}v_x \end{aligned}$$

Maxwell velocity distribution cont'd