6.2 Average Values

For <u>any</u> statistical treatment, the average of a variable is the probability that value i occurs summed over all possibilities.

For example, the probability for $S_z = \hbar/2$ is 0.7 and the probability for $S_z = -\hbar/2$ is 0.3

$\Rightarrow \quad \bar{S}_z = 0.7\,\hbar/2 + 0.3(-\hbar/2) = 0.2\hbar$

For our "system", the probability to be in state s is

$$\mathcal{P}(s) = \frac{1}{Z} e^{-\beta E(s)} \qquad \beta = \frac{1}{k_B T} \quad \text{(this is standard notation)}$$

$$\bar{E} = \sum_s E(s)\,\mathcal{P}(s) = \frac{1}{Z} \sum_s E(s)\, e^{-\beta E(s)}$$

In general if there is a quantity $X(s)$ [X might be spin, KE, position ...]

$$\bar{X} = \sum_s X(s)\,\mathcal{P}(s) = \frac{1}{Z} \sum_s E(s)\, e^{-\beta E(s)}$$

Suppose you have N identical objects make up your system (objects are independent and distinguishable)
The total energy is $N \times$ average energy of 1

$U = N\bar{E}$ (Note trick! Can get U by doing 1 object.)

For quantum system how does U behave at low T?

$$\bar{E} = E_1 \mathcal{P}(1) + E_2 \mathcal{P}(2) \cong E_2 \frac{\Omega_2}{\Omega_1} e^{-E_2/k_B T}$$

$$\Rightarrow \quad U = N E_2 \frac{\Omega_2}{\Omega_1} e^{-E_2/k_B T}$$

The heat capacity $$C_V/Nk_B = \frac{1}{Nk_B}\left(\frac{\partial U}{\partial T}\right)_N = \left(\frac{E_2}{k_B T}\right)^2 \frac{\Omega_2}{\Omega_1} e^{-E_2/k_B T}$$

$C_V \to 0$ as $T \to 0$

Prob 6.16 Prove $\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z$

$$Z = \sum_s e^{-\beta E(s)} \Rightarrow -\frac{\partial Z}{\partial \beta} = \sum_s E(s) e^{-\beta E(s)} = \overline{E}\cdot Z$$

Prob 6.17 Standard deviation

a) $\overline{E} = 3\,eV$ $\quad \Delta E_1 = 0 - 3eV = -3eV,\ \Delta E_2 = 1eV,\ \Delta E_3 = 4eV$

b) $\overline{\Delta E} = \frac{2}{5}(-3eV) + \frac{2}{5}1eV + \frac{1}{5}4eV = 0$?!!

$\overline{\Delta E^2} = \frac{2}{5}9eV^2 + \frac{2}{5}1eV^2 + \frac{1}{5}16eV^2 = \frac{36}{5}eV^2$

$\sigma_E \equiv \sqrt{\overline{\Delta E^2}} = \frac{6}{\sqrt{5}}eV \approx 2.7eV$ reasonable?

c) $\sigma_E^2 = \sum_i (E_i - \overline{E})^2 P_i = \sum_i (E_i^2 - 2E_i\overline{E} + \overline{E}^2)P_i$

$= \sum_i E_i^2 P_i - 2\overline{E}\sum_i E_i P_i + \overline{E}^2 \sum_i P_i$

$= \overline{E^2} - 2\overline{E}^2 + \overline{E}^2 = \overline{E^2} - \overline{E}^2$

d) $\overline{E^2} = 0eV^2\frac{2}{5} + 16eV^2\frac{2}{5} + 49eV^2\frac{1}{5} = \frac{81}{5}eV^2$

$\overline{E^2} - \overline{E}^2 = \frac{81}{5}eV^2 - 9eV^2 = \frac{36}{5}eV^2$ ✓

Prob 6.18 Prove $\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$

$$Z = \sum_s e^{-\beta E(s)} \qquad \frac{\partial^2 Z}{\partial \beta^2} = \sum_s E(s)^2 e^{-\beta E(s)} = Z\,\overline{E^2}$$

Now compute $\sigma_E^2 = \overline{E^2} - \overline{E}^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$

Remember $\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$ $\qquad \frac{\partial \overline{E}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{1}{Z}\right)\frac{\partial Z}{\partial \beta} - \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$

$= \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 - \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$

$\Rightarrow \sigma_E^2 = -\frac{\partial \overline{E}}{\partial \beta}$

Want answer in terms of $\frac{\partial \overline{E}}{\partial T} = \frac{\partial \overline{E}}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial \overline{E}}{\partial \beta} = \frac{\sigma_E^2}{k_B T^2}$

$\Rightarrow \sigma_E = k_B T\sqrt{\frac{\partial \overline{E}}{\partial T}/k_B} = k_B T\sqrt{C/k_B}$ $\qquad$ C = heat capacity!

What does this mean for energy fluctuation of macroscopic system? $\sigma_E \propto \sqrt{N}$, but $U \propto N$

$\Rightarrow$ relative size of fluctuation $\sigma_E/U \propto 1/\sqrt{N}$

For low T system $C = \frac{\Omega_2 k_B E_2^2}{\Omega_1 k_B^2 T^2} e^{-E_2/k_B T}$ $\Rightarrow \sigma_E = E_2\sqrt{\frac{\Omega_2}{\Omega_1}}\, e^{-\frac{E_2}{2k_B T}} \to 0$ as $T \to 0$

Does this make sense?

Paramagnetism (revisit 3.3)

$1 = \uparrow \quad E_1 = -\mu B \qquad 2 = \downarrow \quad E_2 = \mu B$

$$Z = e^{\mu B \beta} + e^{-\mu B \beta} = 2\cosh(\beta \mu B)$$

$$P_1 = \frac{e^{\mu B\beta}}{Z} = \frac{e^{\mu B \beta}}{2\cosh(\beta\mu B)} \qquad P_2 = \frac{e^{-\mu B\beta}}{2\cosh(\beta \mu B)} \checkmark$$

$$\bar{E} = -\mu B P_1 + \mu B P_2 = -\mu B (P_1 - P_2) = -\mu B \frac{\sinh(\beta\mu B)}{\cosh(\beta \mu B)}$$
$$= -\mu B \tanh(\beta \mu B) \checkmark$$

$$U = N\bar{E} = -N\mu B \tanh(\beta\mu B) \checkmark$$

$$\bar{\mu}_z = \mu P_1 - \mu P_2 = \mu(P_1 - P_2) = \mu \tanh(\beta \mu B)$$

$$M = N\bar{\mu}_z = N\mu \tanh(\beta \mu B) \checkmark$$

All results reproduced with much less effort!

Rotation of diatomic molecules (simplified version)

Remember from classical mechanics $E = \frac{L^2}{2I}$ for rotational KE

$\Rightarrow \quad E = \ell(\ell+1)\,\varepsilon \qquad \varepsilon = \frac{\hbar^2}{2I}$

$\ell = 0, 1, 2, 3, \ldots$

How many states for each ℓ?

$\ell = 0 \quad m = 0 \qquad 1 = 2\ell + 1$

$\ell = 1 \quad m = -1, 0, 1 \qquad 3 = 2\ell+1$

$\ell = 2 \quad m = -2, -1, 0, 1, 2 \qquad 5 = 2\ell + 1$

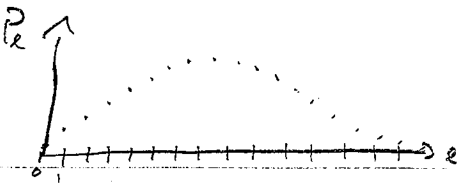
$$\Rightarrow Z_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\ell(\ell+1)\varepsilon/k_BT}$$

If $\varepsilon/k_BT > 1$ then only a few levels will contribute

From prev. pages $\quad U \approx N\, 2\varepsilon \cdot 3\, e^{-2\varepsilon/k_BT}$ and $C_V/Nk_B \approx \left(\frac{2\varepsilon}{k_BT}\right)^2 3\, e^{-2\varepsilon/k_BT}$

At higher T, $\varepsilon/k_BT \ll 1$, you can use a different approximation. A huge number of levels contribute to the sum in Z so convert it to integral.

High T



$$Z_{rot} \cong \int_0^\infty (2\ell+1)\, e^{-\ell(\ell+1)\varepsilon/k_BT}\, d\ell = -\frac{k_BT}{\varepsilon}\int_0^\infty \left[\frac{d}{d\ell} e^{-(\ell^2+\ell)\varepsilon/k_BT}\right] d\ell$$

$$\Rightarrow Z_{rot} \cong \frac{k_BT}{\varepsilon} = \frac{1}{\beta\varepsilon}$$

$$\bar{E}_{rot} = -\frac{1}{Z_{rot}}\frac{\partial Z_{rot}}{\partial\beta} = -\beta\varepsilon\frac{\partial}{\partial\beta}\left(\frac{1}{\beta\varepsilon}\right) = \frac{1}{\beta} = k_BT \;!!$$

Equipartition Thm rears its ugly head!

Couple problems with rotation of diatomic molecules:

1) If the electron part of wave function has nonzero $\vec{J}$, then ℓ not correct. Need total angular momentum.

2) Identical atoms the wave function needs appropriate symmetry. 2 spin 0 atoms only even ℓ allowed
At high T $\Rightarrow Z_{rot} \cong \frac{1}{2}\frac{k_BT}{\varepsilon}$ however $\bar{E}_{rot} = k_BT$ still.

Prob 6.24 pg 236 $\quad \varepsilon = 0.00018\,\text{eV} \Rightarrow \varepsilon/k_BT = \dfrac{0.00018\,\text{eV}\; 1.6\times10^{-19}\,\text{J/eV}}{1.38\times10^{-23}\,\text{J/K}\; 300\,\text{K}} = 6.96\times10^{-3}$

$$\Rightarrow Z \cong \frac{1}{2}\frac{k_BT}{\varepsilon} = 72$$

Prob 6.27 pg 237

kT/ε	Z_{exact}
0	1
1	1.418
2	2.370
3	3.357
4	4.351
6	6.345
10	10.340
15	15.338
30	30.336
60	60.334

From excel

$$Z_{exact} \overset{?}{\cong} \frac{k_BT}{\varepsilon} + \frac{1}{3} = \frac{1}{\beta\varepsilon} + \frac{1}{3}$$

$\Rightarrow$ the $\frac{1}{3}$ doesn't mess up $\bar{E}_{rot}$

$$\bar{E}_{rot} = -\frac{1}{\frac{1}{\beta\varepsilon}+\frac{1}{3}}\frac{\partial}{\partial\beta}\left(\frac{1}{\beta\varepsilon}+\frac{1}{3}\right) = \frac{k_BT}{1+\frac{\varepsilon}{3k_BT}}$$

To see where the $\frac{1}{3}$ comes from note $\int_0^\infty F(x)\,dx \cong \frac{5}{12}F_0 + \frac{13}{12}F_1 + F_2 + F_3 + \dots$

$$\Rightarrow F_0 + F_1 + F_2 + \dots \cong \int_0^\infty F(x)\,dx + \frac{7}{12}F_0 - \frac{1}{12}F_1$$

$$= \frac{k_BT}{\varepsilon} + \frac{7}{12}1 - \frac{1}{12}3e^{-2\varepsilon/k_BT}$$

$$= \frac{k_BT}{\varepsilon} + \frac{7}{12} - \frac{3}{12} = \frac{k_BT}{\varepsilon} + \frac{1}{3}\;!$$