Chemistry 430/530a Practice Midterm 1

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Problem 1.1.

$k_B T =$ 200 cm^{-1}, 0.6 kcal/mol, 2.5 kJ/m

(any unit system)

$Q(N, V, T) =$ $\sum_j e^{-\beta E_j}$

$Q(N, V, E) =$ $\frac{1}{N}$

$S(p_j) =$ $-k_B \sum_j p_j \ln p_j$

$\binom{N}{n} =$ $\frac{N!}{(N-n)!\,n!}$

(how many ways to order N distinguishable particles in n slots)

Problem 1.2.

In class we derived, $\langle E \rangle$ and $\langle E^2 \rangle$. Please derive an expression for the ensemble average energy to the nth power, $\langle E^n \rangle$ using your $Q(N,V,T)$ from Problem 1.1.

Since $\langle E \rangle = -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$ and $\langle E^2 \rangle = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2}$

Try $\langle E^n \rangle \overset{?}{=} \frac{\partial^{(n)} Q}{\partial \beta^{(n)}}$

$$\frac{\partial^{(n)} Q}{\partial \beta^{(n)}} = \sum_j \frac{\partial^{(n)}}{\partial \beta^{(n)}} e^{-\beta E_j}$$

$$= \sum_j (-E_j) \frac{\partial^{(n-1)}}{\partial \beta^{(n-1)}} e^{-\beta E_j}$$

$$= \sum_j (-E_j)^2 \frac{\partial^{(n-2)}}{\partial \beta^{(n-2)}} e^{-\beta E_j}$$

$$\vdots$$

$$= \sum_j (-E_j)^{n-1} \frac{\partial}{\partial \beta} e^{-\beta E_j}$$

$$= \sum_j (-E_j)^n e^{-\beta E_j} = Q(-1)^n \langle E^n \rangle$$

$$\therefore \langle E^n \rangle = \frac{(-1)^n}{Q} \frac{\partial^{(n)} Q}{\partial \beta^{(n)}}$$

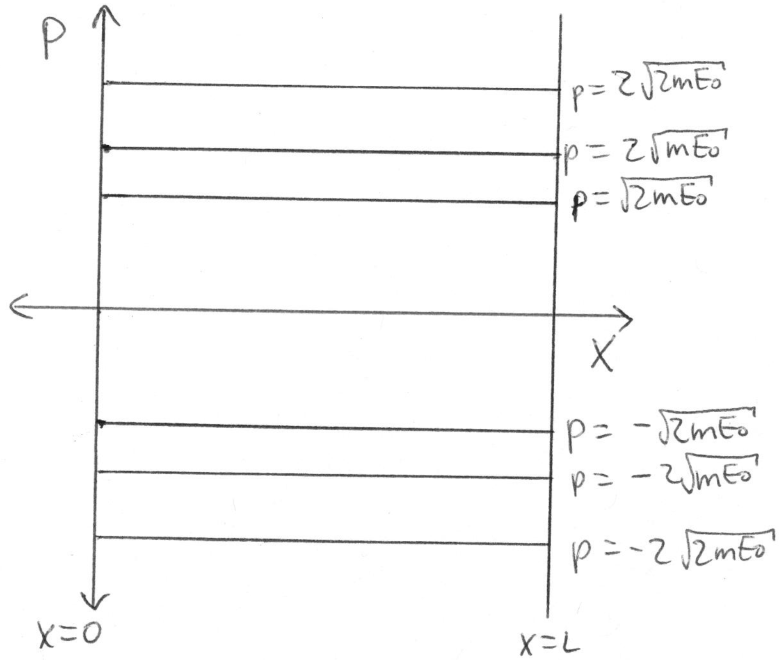
Problem 1.3.

Please draw, roughly to scale, the phase space plot for a classical particle in a 1D box of length L with energies E_0, $2E_0$ and $4E_0$. Please label the axes. How does the distance between contours depend on energy?

Particle in a 1D Box: $X = [0, L]$

$$\frac{p^2}{2m} = E$$

$$p = \sqrt{2mE}$$



$$\frac{p_1}{p_2} = \sqrt{\frac{\cancel{2m} E_1}{\cancel{2m} E_2}} = \sqrt{\frac{E_1}{E_2}}$$

Problem 1.4.
Given

$$Q = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}},$$

please evaluate

$$\begin{aligned} A &= -\frac{1}{\beta} lnQ \\ \langle E \rangle &= -\frac{\partial}{\partial \beta} lnQ \\ S &= klnQ + \frac{\langle E \rangle}{T} \\ C_V &= \frac{\partial \langle E \rangle}{\partial T}, \end{aligned}$$

and show that $C_V = k_B$ *when* $k_B T \gg \hbar\omega$ *using the approximation valid at high temperatures,* $e^{\hbar\omega/k_B T} \approx 1 + \frac{\hbar\omega}{k_B T}$.

$$\ln Q = \frac{-\beta\hbar\omega}{2} - \ln\left[1 - e^{-\beta\hbar\omega}\right]$$

$$A = \frac{\hbar\omega}{2} + \frac{1}{\beta}\ln\left[1 - e^{-\beta\hbar\omega}\right]$$

$$\langle E \rangle = -\frac{\hbar\omega}{2} + \left[1 - e^{-\beta\hbar\omega}\right]^{-1} \frac{\partial}{\partial\beta}\left[1 - e^{-\beta\hbar\omega}\right]$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$S = \cancel{\frac{-k\beta\hbar\omega}{2}} - k\ln\left[1 - e^{-\beta\hbar\omega}\right] + \cancel{\frac{\hbar\omega}{2T}} + \frac{\hbar\omega}{T}\frac{1}{e^{\beta\hbar\omega} - 1}$$

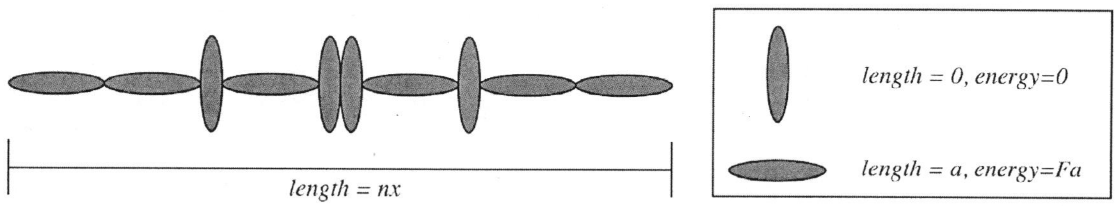
$$= -k\ln\left[1 - e^{-\beta\hbar\omega}\right] + \frac{\hbar\omega k}{\beta}\frac{1}{e^{\beta\hbar\omega} - 1}$$

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{\partial\langle E\rangle}{\partial\beta}\cdot\frac{\partial\beta}{\partial T} = \frac{\partial\langle E\rangle}{\partial\beta}\cdot\left(\frac{-1}{kT^2}\right)$$

$$= \frac{-\hbar\omega}{kT^2}\left[-\left(e^{\beta\hbar\omega} - 1\right)^{-2}\right]e^{\beta\hbar\omega}\cdot\hbar\omega = \frac{\hbar^2\omega^2}{kT^2}\frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

As $kT \gg \hbar\omega$ or $\beta \ll \hbar\omega$, $C_V \to \frac{\hbar^2\omega^2}{kT^2}\frac{(1 + \beta\hbar\omega)}{(\beta\hbar\omega)^2} = \frac{\cancel{\hbar^2\omega^2}}{kT^2\beta^2\cancel{\hbar^2\omega^2}} + \cancel{\frac{\hbar^2\omega^2}{kT^2\beta\hbar\omega}} \to 0$
$= k$

Problem 1.5. *Here we consider a one-dimensional chain of n segments, as illustrated below. Each segment can exist in two states- length $x = a$ or length $x = 0$. When tension F is applied, the energy of a segment is $F \cdot x$, or $a \cdot F = aF$ for extended or $0 \cdot F = 0$ for contracted segments, respectively. Thus by changing F, we can change the energy difference between the two states.*



What is the partition function, Q, for one segment at temperature T and tension F?

$$Q = 1 + e^{-\beta Fa} = 1 + e^{-Fa/kT}$$

Using this result, calculate the average length, $\langle x \rangle$ of one segment as a function of T.

$$\langle x \rangle = \frac{(0)1 + (a)e^{-Fa/kT}}{1+e^{-Fa/kT}} = \frac{a\, e^{-Fa/kT}}{1+e^{-Fa/kT}}$$

For n segments, the length will be $n\langle x \rangle$. Verify that this result leads to Hooke's Law, $n\langle x \rangle = c_0 + c_1 F$, at high temperatures where the limit $e^{-Fa/k_BT} \approx 1 - \frac{Fa}{k_BT}$ is applicable.

$$n\langle x \rangle = \frac{na\, e^{-Fa/kT}}{1+e^{-Fa/kT}}$$

As $kT \gg Fa$, $n\langle x \rangle \rightarrow \dfrac{na(1 - Fa/kT)}{(2 \cancel{-Fa/kT})^{0}} = \dfrac{na}{2} - \dfrac{na^2F}{2kT}$

$C_0 = \dfrac{na}{2}$, $C_1 = \dfrac{-na^2}{2kT}$ (F<0 for spring to stretch with increasing tension.)

Problem 1.6. *Recall the 1D Ising model with N spins, each situated at a lattice site, and each spin may be up or down.*

$$\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}\cdots\boxed{\downarrow}$$

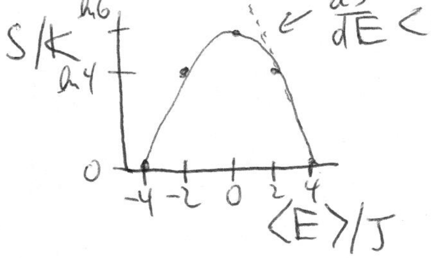
We will treat four spins with no nearest neighbor coupling. If we represent an $\boxed{\uparrow}$ with $s_i = +1$ and $\boxed{\downarrow}$ with $s_i = -1$, then the energy function for the system, the Hamiltonian, is

$$H = -J \sum_{i=1}^{4} s_i. \tag{1}$$

*For **four spins**, please write out all possible energy levels and the degeneracy for each energy level.*

States	Energy	Ω	S/k
↑↑↑↑	$-4J$	1	$\ln 1 = 0$
↑↑↑↓ ↑↑↓↑ ↑↓↑↑ ↓↑↑↑	$-2J$	4	$\ln 4$
↑↑↓↓ ↑↓↑↓ ↓↓↑↑ ↓↑↓↑ ↑↓↓↑ ↓↑↑↓	0	6	$\ln 6$
↓↓↓↑ ↓↓↑↓ ↓↑↓↓ ↑↓↓↓	$2J$	4	$\ln 4$
↓↓↓↓	$4J$	1	$\ln 1$

Sketch a plot of how the entropy S changes as a function of the energy of the system. Recall that we define the temperature $\frac{1}{T} = \frac{dS}{dE}$. Show that the temperature is negative as $E \to E_{max}$. Does negative temperature mean the system is "colder"?



$\frac{dS}{dE} < 0 \therefore T < 0$

These are non-thermal configurations with high internal energy — not "cold" in the conventional sense.