Problem : Statistical mechanics of quantum harmonic oscillator/s

Recall that the energy eigenstates $|n\rangle$ of a single harmonic oscillator have the energy $E_n = \epsilon\left(n + \frac{1}{2}\right)$ where $n = 1, 2, \ldots$

Problem (a)

: Calculate the canonical partition function for one harmonic oscillator $Z_1(\beta) = \sum_{n=1}^{\infty} e^{-\beta E_n}$

Solution

Use the definition for E_n in Z_1,

$$\begin{aligned}
Z_1(\beta) &= \sum_{n=1}^{\infty} e^{-\beta E_n} \\
&= \sum_{n=1}^{\infty} \exp\left\{-\beta\epsilon\left(n + \frac{1}{2}\right)\right\} \\
&= \sum_{n=1}^{\infty} \exp\left\{-\beta\epsilon n - \frac{\beta\epsilon}{2}\right\} \\
&= \sum_{n=1}^{\infty} \exp\{-\beta\epsilon n\} \cdot \underbrace{\exp\left\{-\frac{\beta\epsilon}{2}\right\}}_{\text{No } n \text{ dependence}} \\
&= \exp\left\{-\frac{\beta\epsilon}{2}\right\} \sum_{n=1}^{\infty} \exp\{-\beta\epsilon n\} \\
&= \exp\left\{-\frac{\epsilon\beta}{2}\right\} \underbrace{\sum_{n=1}^{\infty} \left(\exp\{-\beta\epsilon\}\right)^n}_{\text{Geometric series}}
\end{aligned}$$

Remark : Geometric series

$$\sum_{n=1}^{\infty} ar^n = \frac{1}{1-r} \qquad \text{if } \|r\| < 1$$

Comparing our Geometric series with the one in the remark we have

$$\sum_{n=1}^{\infty} \underbrace{1}_{a} \left(\underbrace{\exp\{-\beta\epsilon\}}_{r}\right)^n = \frac{1}{1-r} = \frac{1}{1-\exp\{-\beta\epsilon\}} \tag{1}$$

We know that our $\|r\| < 1$ as $\epsilon > 0$ and $\beta > 0$

Plugging in the geometric series in our solution we get

$$Z_1(\beta) = \exp\left\{-\frac{\epsilon\beta}{2}\right\} \cdot \frac{1}{1-\exp\{-\beta\epsilon\}} \tag{2}$$

Problem (b)

Calculate the canonical partition function $Z_N(\beta)$ for a system of N independent harmonic oscillators in terms of that found for the single harmonic oscillator.

Solution

(Not sure if this is all that is needed for explanation, but the answer is correct)
For N independent (keyword) harmonic oscillators, our partition function can be defined as

$$Z_n(\beta) = Z_1 Z_2 Z_3 \dots Z_n = \prod_{i=1}^{n} Z_i$$

We do have n independent harmonic oscillators, hence,

$$Z_n(\beta) = \left(\frac{\exp\left\{-\frac{\beta\epsilon}{2}\right\}}{1 - \exp\{-\beta\epsilon\}} \right)^n \tag{3}$$

Problem (c)

Calculate the mean energy E

Solution

Let us start by the definition of the mean energy E,

$$\langle E_N \rangle = -\frac{\partial \ln Z_N}{\partial \beta} \tag{4}$$

Rewrite our Z_N into a more convenient format using hyperbolic functions to prepare it for differentiation with respect to β and also makes it easier for interpretation/graphing.

$$Z_N(\beta) = \left(\frac{1 - \exp\{-\beta\epsilon\}}{\exp\left\{-\frac{\beta\epsilon}{2}\right\}} \right)^{-N}$$

Recall that

$$\sinh x = \frac{\exp(x) - \exp(-x)}{2} = \frac{1 - \exp(-2x)}{2\exp(-x)}$$
$$2 \cdot \sinh x = \frac{1 - \exp(-2x)}{\exp(-x)}$$

where we get the last equality by multiplying+dividing with $\exp(-x)$

Sustitute $\xi = \frac{\beta\epsilon}{2}$ in Z_N, so we get a sinh equation

$$Z_N = \left(\frac{1 - \exp(-2\xi)}{\exp(-\xi)} \right)^{-N}$$

We can easily see that this equation is the in the same form as the $2\sinh x$ equation from above.

Hence we can write,

$$Z_N = (2 \cdot \sinh \xi)^{-N} = \left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)^{-N}$$

All that is left, is doing the differentiation as in the definition of $\langle E_N \rangle$,

$$\begin{aligned}
\langle E_N \rangle &= -\frac{\partial}{\partial\beta}\left\{\ln\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)^{-N}\right\} \\
&= -(-N)\frac{\partial}{\partial\beta}\left\{\ln\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)\right\} \\
&= N \cdot \frac{1}{\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)}\frac{\partial}{\partial\beta}\left\{\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)\right\} \\
&= 2N \cdot \frac{1}{\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)} \cdot \cosh\left(\frac{\beta\epsilon}{2}\right)\frac{\partial}{\partial\beta}\left(\frac{\beta\epsilon}{2}\right) \\
&= 2N \cdot \frac{1}{\left(2 \cdot \sinh \frac{\beta\epsilon}{2}\right)} \cdot \cosh\left(\frac{\beta\epsilon}{2}\right) \cdot \left(\frac{\epsilon}{2}\right) \\
&= \left(\frac{N\epsilon}{2}\right) \cdot \frac{\cosh \frac{\beta\epsilon}{2}}{\sinh \frac{\beta\epsilon}{2}} = \left(\frac{N\epsilon}{2} \cdot \coth\left(\frac{\beta\epsilon}{2}\right)\right)
\end{aligned}$$

P.S : $\cot x = \frac{1}{\tan x}$ (NOT arctan / $\tan^{-1}$)

Problem (d)

•The free energy is $F = E - TS$. Show that the first law of thermodynamics takes the form

$$\mathrm{d}F = -S\mathrm{d}T + \mu \mathrm{d}N \tag{5}$$

in terms of F. (Noting that $\mathrm{d}V = 0$ in this question).

•Give a formula for the chemical potential μ in terms of a derivative of $F(T, N)$.

• Using the formula $F(\beta, N) = -\beta^{-1} \log Z_N(\beta)$, calculate μ for the present system. (Where $\beta = \frac{1}{k_B T}$)

Solution

Given : $F = E - TS$

Taking differential of the above given equation (one forms to be more precise)

$$\mathrm{d}F = \mathrm{d}E - \mathrm{d}(TS) = \mathrm{d}E - S\mathrm{d}T - T\mathrm{d}S \tag{$\star$}$$

Independent from the above equation, from the first law of thermodynamics we (should) know,

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu \mathrm{d}N \tag{$\star\star$}$$

Plug in $\mathrm{d}E$ from ($\star\star$) in ($\star$),

$$\begin{aligned}\mathrm{d}F &= \cancel{T\mathrm{d}S} - P\mathrm{d}V + \mu\mathrm{d}N - S\mathrm{d}T - \cancel{T\mathrm{d}S} \\ &= \mu\mathrm{d}N - P \underbrace{\mathrm{d}V}_{=0 \text{ (Given)}} - S\mathrm{d}T \\ &= \mu\mathrm{d}N - S\mathrm{d}T\end{aligned}$$

Compare the above equation with this one,

$$\mathrm{d}\{F(T, N)\} = \underbrace{\frac{\partial F}{\partial T}}_{-S} \mathrm{d}T + \underbrace{\frac{\partial F}{\partial N}}_{\mu} \mathrm{d}N$$

□