$\boxed{5}$

p12–24. Read "Statistical Physics".

<u>Free Energy</u>. System with states labelled i, they have energies ε_i

then we know the partition function is $\boxed{Z = \sum_i e^{-\varepsilon_i/k_B T}}$

then probability is $P_i = \frac{1}{Z} e^{-\varepsilon_i/k_B T}$.

Let's take logs, i.e. $\underline{\ln P_i} = -\frac{\varepsilon_i}{k_B T} - \ln Z$.

We also know that $S = -N k_B \sum_i P_i \underline{\ln P_i}$

$$= N k_B \sum_i P_i \left(\frac{\varepsilon_i}{k_B T} + \ln Z \right)$$

We know that internal energy $U = N \sum_i P_i \varepsilon_i$ so

the entropy becomes : $S = \frac{U}{T} + N k_B \ln Z$

$$\Rightarrow U - TS = -N k_B T \ln Z = F$$

Recall that free energy $F = U - TS$

i.e. $\boxed{F = -N k_B T \ln Z}$

The partition function is the basis of all thermodynamic quantities.

Summarize Statistical Thermodynamics.

$$\beta = \frac{1}{k_B T} \Rightarrow \frac{\partial}{\partial T} = \frac{\partial}{\partial \beta} \frac{\partial \beta}{\partial T}$$

But $\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$ hence $\frac{\partial}{\partial \beta} = \boxed{-k_B T^2} \frac{\partial}{\partial T}$

$$\frac{\partial}{\partial T} = -k_B \beta^2 \frac{\partial}{\partial \beta}$$

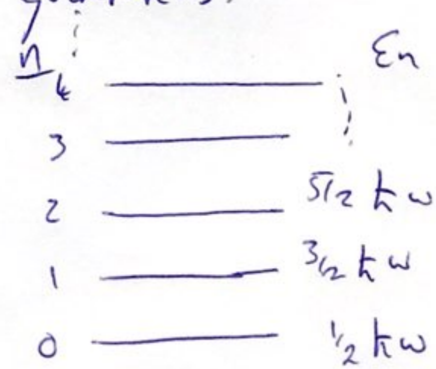
Also free energy $F = -N k_B T \ln Z$

$$U = -N \left[\frac{\partial \ln Z}{\partial \beta} \right]_V = N k_B T^2 \left[\frac{\partial \ln Z}{\partial T} \right]_V$$

Entropy $S = \frac{1}{T}(U - F) = \ldots$

Heat capacity : $C_v = \left[\frac{\partial U}{\partial T}\right]_v = \dots$

<u>Example</u>. A system of one-dimensional harmonic oscillators. Calculate its partition function and hence other thermodynamic quantities.



Energy states $\underline{\varepsilon_n = (n + 1/2)\hbar\omega}$

$$Z = \sum_{n=0}^{\infty} e^{-\varepsilon_n / k_B T} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}$$

$$= e^{-1/2\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}$$

$$Z = \left(e^{-\beta\hbar\omega/2}\right)\left(\left(e^{-\beta\hbar\omega}\right)^0 + \left(e^{-\beta\hbar\omega}\right)^1 + \left(e^{-\beta\hbar\omega}\right)^2 + \cdots\right)$$

(Recall that $1 + x + x^2 + x^3 + \cdots = \dfrac{1}{1-x}$, $|x| < 1$.)

Hence $Z = \left(e^{-\beta\hbar\omega/2}\right)\left(\dfrac{1}{1-e^{-\beta\hbar\omega}}\right)$.

$$\boxed{Z = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}}$$

For Free energy we need $\ln Z$, i.e.

$$\ln Z = \ln\left(\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right) = -\frac{\beta\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right).$$

Also require $$-\partial/\partial\beta \ln Z = \hbar\omega/2 + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

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

Hence $$U = -N\frac{\partial \ln Z}{\partial\beta} = N\frac{\hbar\omega}{2} + \frac{N\hbar\omega}{e^{-\beta\hbar\omega}-1}.$$

$$F = -\frac{N}{\beta}\ln Z = \frac{N\hbar\omega}{2} + \frac{N}{\beta}\ln\left(1-e^{-\beta\hbar\omega}\right).$$

$$S = \frac{1}{T}(U - F) = k_B \beta (U - F)$$

$$= N k_B \left(\frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln\left[1 - e^{-\beta \hbar \omega}\right] \right)$$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = -k_B \beta^2 \frac{\partial U}{\partial \beta} = \frac{N k_B (\beta \hbar \omega)^2 e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1\right)^2}$$

Plot these: set $\hbar\omega = 1$ and $k_B = 1$.