Problem 1:

A perfect crystal comprises N atoms placed on N lattice sites. Defects are formed when an atom moves from a lattice site onto and interstitial site. There are M interstitial sites available in the crystal. Each atom moving from the lattice site to an interstitial site requires an energy ϵ.

(a) Suppose n atoms move onto interstitial sites, requiring a total energy $E = n\epsilon$. How many ways are there of removing n atoms from the lattice sites? How many ways are there of distributing the n atoms among the M interstitial sites? By multiplying these together, obtain the total number of ways W of moving n atoms onto interstitial sites.

Solution:

The number of ways of removing n atoms from the lattice sites is $\binom{N}{n}$. The number of ways of distributing the n atoms among the M interstitial sites is identical to the number of ways of distributing n identical balls into M distinct boxes, which is $\binom{M+n-1}{n}$. By multiplying these together, we obtain the total number of ways W of moving n atoms onto interstitial sites:

$$W = \binom{N}{n}\binom{M}{n} \tag{1}$$

(b) Using the microcanonical ensemble, calculate the entropy for n defect atoms, with energy $E = n\epsilon$ and so calculate the temperature.

Solution:

The entropy is given by the Boltzmann formula:

$$S = k_B \ln W = k_B \ln \left[\binom{N}{n}\binom{M}{n}\right] \tag{2}$$

By using Stirling's approximation ($\log n! \approx n \log n - n$), we have:

$$\begin{aligned}
S &= k_B \log W \\
&= k_B \log \left[\binom{N}{n}\binom{M}{n}\right] \\
&= k_B \log \left[\frac{N!}{n!(N-n)!}\frac{M!}{n!(M-n)!}\right] \\
&= k_B \log \left[\frac{N!}{n!(N-n)!}\right] + k_B \log \left[\frac{(M+n-1)!}{n!(M-1)!}\right] \\
&= k_B \left[\log N! - \log n! - \log(N-n)!\right] + k_B \left[\log(M+n-1)! - \log n! - \log(M-1)!\right] \\
&= k_B \left[N \log N - n \log n - (N-n)\log(N-n)\right] + k_B \left[(M+n-1)\log(M+n-1) - n\log n - (M-1)\log(M-1\right. \\
&= k_B \left[2\log n - \log(N-n) - \log(M-n)\right]
\end{aligned}$$

The temperature is given by the inverse of the derivative of the entropy with respect to the energy:

$$
\begin{aligned}
\frac{1}{T} &= \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} = \frac{k_B}{\epsilon}\frac{\partial}{\partial n}\ln\left[\binom{N}{n}\binom{M}{n}\right] \\
&= \frac{k_B}{\epsilon}\frac{\partial}{\partial n}\left[N\log N - n\log n - (N-n)\log(N-n) + (M+n-1)\log(M+n-1) - n\log n - (M-1)\log(M-1\right. \\
&= \frac{k_B}{\epsilon}\left[-(\log n + 1) + -(\log(N-n)+1) + (\log(M+n-1)+1) - (\log n + 1) - (\log(M-1)+1)\right] \\
&= \frac{k_B}{\epsilon}[\log(N-n) + \log(M-n) - 2\log n]
\end{aligned}
$$

Thus,

$$
\begin{aligned}
-\frac{\epsilon}{k_B T} &= 2\log n - \log(N-n) - \log(M-n) \\
&= \log\left(\frac{n^2}{(N-n)(M-n)}\right)
\end{aligned}
$$

Taking the exponential of both sides, we have:

$$
\exp\left(-\frac{\epsilon}{k_B T}\right) = \frac{n^2}{(N-n)(M-n)}
$$

Problem 4:

(a) Can you show taht the work done by an external pressure p in changing the volue of a a system by ΔV is

$$
\Delta W = -p\Delta V. \tag{3}
$$

Solution:

The work done by an external pressure p in changing the volume of a system by ΔV is given by:

$$
\Delta W = \int_{V_1}^{V_2} p\mathrm{d}V \tag{4}
$$

Since p is constant, we have:

$$
\begin{aligned}
\Delta W &= \int_{V_1}^{V_2} p\mathrm{d}V \\
&= p\int_{V_1}^{V_2} \mathrm{d}V \\
&= p(V_2 - V_1) \\
&= -p(V_1 - V_2) \\
&= -p\Delta V
\end{aligned}
$$

(b) What is the conjugate force for an angle of rotation θ of some object in the system?

Solution:

The conjugate force for an angle of rotation θ of some object in the system is the torque τ. The work done by the torque is given by:

$$\Delta W = \int_{\theta_1}^{\theta_2} \tau \mathrm{d}\theta \tag{5}$$

Problem 6:

(a) A single quantum harmonic oscillator has states with energies $E = m\epsilon$ where $m = 1, 2, \cdots$. Write down the partition function, and energy, the free energy and the entropy of the oscillator. hence obtain the average energy, the free energy and the entropy of the oscillator.

Solution:

The partition function is given by:

$$\begin{aligned}
Z &= \sum_{m=1}^{\infty} e^{-\beta m \epsilon} \\
&= \frac{e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}}
\end{aligned}$$

The energy is given by:

$$\begin{aligned}
E &= -\frac{\partial}{\partial \beta} \ln Z \\
&= -\frac{\partial}{\partial \beta} \ln \left(\frac{e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} \right) \\
&= -\frac{\partial}{\partial \beta} \left(-\beta\epsilon - \ln(1 - e^{-\beta\epsilon}) \right) \\
&= \epsilon + \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} \\
&= \epsilon \frac{1 + e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}}
\end{aligned}$$

The free energy is given by:

$$\begin{aligned}
F &= -k_B T \ln Z \\
&= -k_B T \ln \left(\frac{e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} \right) \\
&= -k_B T \left(-\beta\epsilon - \ln(1 - e^{-\beta\epsilon}) \right) \\
&= k_B T \left(\beta\epsilon + \ln(1 - e^{-\beta\epsilon}) \right) \\
&= k_B T \left(\frac{\epsilon}{k_B T} + \ln(1 - e^{-\beta\epsilon}) \right) \\
&= \epsilon + \frac{k_B T}{\beta} \ln(1 - e^{-\beta\epsilon})
\end{aligned}$$

The entropy is given by:

$$\begin{aligned}
S &= \frac{E-F}{T} \\
&= \frac{\epsilon\frac{1+e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}} - \epsilon - \frac{k_B T}{\beta}\ln(1-e^{-\beta\epsilon})}{T} \\
&= \frac{\epsilon\frac{1+e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}} - \epsilon - \frac{k_B T}{\beta}\ln(1-e^{-\beta\epsilon})}{k_B T} \\
&= \frac{\epsilon\frac{1+e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}} - \epsilon - \frac{\epsilon}{\beta}\ln(1-e^{-\beta\epsilon})}{\epsilon} \\
&= \frac{1+e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}} - 1 - \frac{1}{\beta}\ln(1-e^{-\beta\epsilon})
\end{aligned}$$

(b) For N identical but distinguishable harmonic oscillators, write down the partition function, and hence obtain the average energy, the free energy and the entropy.

Solution:

The partition function is given by:

$$\begin{aligned}
Z &= \sum_{m=1}^{\infty} e^{-\beta m\epsilon} \\
&= \sum_{m=1}^{\infty} \left(e^{-\beta\epsilon}\right)^m \\
&= \frac{e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}}
\end{aligned}$$

Problem 10:

"A fair dice always has a greater entropy than a biased dice". Is this statement true? Explain your answer.

Solution:

Yes, this statement is true. The entropy of a dice is given by:

$$S = -k_B \sum_{i=1}^{6} p_i \ln p_i \tag{6}$$

Note that $\ln(x)$ is a concave function (The second derivative of $\ln(x)$ is $-\frac{1}{x^2}$, which is always negative.), using Jensen's inequality, we have:

$$
\begin{aligned}
S &= -k_B \sum_{i=1}^{6} p_i \ln p_i \\
&= k_B \sum_{i=1}^{6} p_i \ln \left(\frac{1}{p_i} \right) \\
&\leq k_B \ln \left(\sum_{i=1}^{6} p_i \frac{1}{p_i} \right) \\
&= k_B \ln 6
\end{aligned}
$$

Thus, the entropy of a dice is always less than or equal to $k_B \ln 6$. Since a fair dice has $p_i = \frac{1}{6}$ for all i, the entropy of a fair dice is $k_B \ln 6$. Since the entropy of a biased dice is less than or equal to $k_B \ln 6$, the entropy of a fair dice is always greater than the entropy of a biased dice.