PHY 460 — Thermodynamics and Statistical Physics

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Assignment: 1

Problem 1

Consider a two-level system consisting of N independent distinguishable particles. Let N_u denote the number of particles in the upper state whose energy is $\varepsilon_u = w$ and N_d the number of particles in the lower state whose energy is $\varepsilon_d = 0$.

(a) Determine the entropy σ in terms of the total energy of the system E.

Solution This question is similar to an exercise we did in class for a single quantum particle. This time there are N independent distinguishable particles. The following conditions apply:

$$N = N_u + N_d$$
$$E = N_u \varepsilon_s + N_d \varepsilon_d = N_u w$$

The first step is to find the multiplicity g in this model. Since this is a binary model we can use the binomial formula to represent the possibilities.

$$(N_u + N_d)^N = \underbrace{\binom{N}{N_d}}_{g} N_u^{N_d} N_d^{N-N_d}$$

$$g = \frac{N!}{N_d!\,(N-N_d)!} = \frac{N!}{N_d! N_u!}$$

$$\sigma = \ln(g) = \ln\left(\frac{N!}{N_d! N_u!}\right) = \ln(N!) - \ln(N_d!) - \ln(N_u!)$$

We apply the Stirling Approximation here, $\ln(n!) = n\ln(n) - n$.

$$\begin{aligned}\sigma &= N\ln(N) - N - N_d\ln(N_d) + N_d - N_u\ln(N_u) + N_u \\ &= N\ln(N) - (N - N_u)\ln(N - N_u) - N_u\ln(N_u) \\ \sigma &= N\ln(N) - \left(N - \frac{E}{w}\right)\ln\left(N - \frac{E}{w}\right) - \frac{E}{w}\ln\left(\frac{E}{w}\right)\end{aligned}$$

(b) Exploit the relation between entropy σ and temperature τ, to find an expression of the energy E in terms of τ.

Solution I will do a change of variables to simplify the computation by exploiting the relationship $E = N_u w$.

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial E} = \frac{1}{w}\frac{\partial \sigma}{\partial N_u}$$

$$\begin{aligned}\frac{w}{\tau} &= \frac{\partial}{\partial N_u}\left[N\ln(N) - (N - N_u)\ln(N - N_u) - N_u\ln(N_u)\right] \\ &= -\left[(0-1)\left(\ln(N-N_u)\right) + (N - N_u)\left(\frac{0-1}{N-N_u}\right)\right] - \left[(1)\left(\ln(N_u)\right) + (N_u)\left(\frac{1}{N_u}\right)\right] \\ &= \ln(N - N_u) - 1 - \ln(N_u) + 1 \\ \frac{w}{\tau} &= \ln\left(\frac{N - N_u}{N_u}\right) \\ \exp\left(\frac{w}{\tau}\right) &= \frac{Nw}{E} - 1 \\ E &= \boxed{\frac{Nw}{\exp\left(\frac{w}{\tau}\right) + 1}}\end{aligned}$$

The result is similar to the energy of a quantum particle as found in lecture, but this time multiplied by N independent and distinguishable particles for the total energy of such a system.

Problem 2

An ideal crystal has N lattice sites and M interstitial locations. Assume that it costs an amount of energy ΔE to remove an atom from a site and place it in an interstitial location when the number n of displaced atoms is much smaller than N or M ($n << N, n << M$).

(a) Obtain an expression of the number of ways of removing n atoms from N sites.

Solution In this case we can assume that both sites are independent and are only connected by the ΔE. Therefore this is also a binary model as there is either an atom at a site N or not.

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

(b) Obtain an expression of the number of ways of placing n atoms on M interstitial locations.

Solution Same idea as part a.

$$g_M = \boxed{\frac{M!}{n!\,(M-n)!}}$$

(c) Determine the entropy σ as a function of total energy $U = n\Delta E$ (use Stirling approximation).

Solution We need the multiplicity of the entire system as a canonical ensemble, which is easily done by multiplying the multiplicities from part a and part b to find the total number of ways of removing n atoms from both N sites and M interstitial locations. Using the general formula $\sigma = \ln g$ and the Stirling approximation $\ln(n!) = n\ln(n) - n$.

$$g_{N+M} = g_N \cdot g_M = \frac{N!M!}{(n!)^2(N-n)!(M-n)!}$$

$$\begin{aligned}
\sigma &= \ln(g_{N+M}) \\
&= [N\ln(N) - N] + [M\ln(M) - M] - [2n\ln(n) - 2n] \\
&\quad - [(N-n)\ln(N-n) - (N-n)] - [(M-n)\ln(M-n) - (M-n)] \\
&= N\ln(N) + M\ln(M) - (N-n)\ln(N-n) - n\ln(n) - (M-n)\ln(M-n) - n\ln(n) \\
&= N\ln(N) + M\ln(M) \\
&\quad - (N-n)\ln\Big(1 - \frac{n}{N}\Big) - (N-n)\ln(N) - n\ln(n) \\
&\quad - (M-n)\ln\Big(1 - \frac{n}{M}\Big) - (M-n)\ln(M) - n\ln(n) \\
&= N\ln(N) + M\ln(M) \\
&\quad - (N-n)\ln\Big(1 - \frac{n}{N}\Big) - N\ln(N) + n\ln(N) - n\ln(n) \\
&\quad - (M-n)\ln\Big(1 - \frac{n}{M}\Big) - M\ln(M) + n\ln(M) - n\ln(n) \\
&= n\ln\Big(\frac{N}{n}\Big) - (N-n)\ln\Big(1 - \frac{n}{N}\Big) + n\ln\Big(\frac{M}{n}\Big) - (M-n)\ln\Big(1 - \frac{n}{M}\Big) \\
\sigma &= \frac{U}{\Delta E}\ln\Big(\frac{\Delta E N}{U}\Big) - (N - \frac{U}{\Delta E})\ln\Big(1 - \frac{U}{\Delta E N}\Big) + \frac{U}{\Delta E}\ln\Big(\frac{\Delta E M}{U}\Big) - (M - \frac{U}{\Delta E})\ln\Big(1 - \frac{U}{\Delta E M}\Big)
\end{aligned}$$

If we apply the approximation $n << N, M$.

$$\sigma = n\ln\Big(\frac{N}{n}\Big) + n\ln\Big(\frac{M}{n}\Big) = \frac{U}{\Delta E}\ln\Big(\frac{\Delta E N}{U}\Big) + \frac{U}{\Delta E}\ln\Big(\frac{\Delta E M}{U}\Big)$$

(d) Determine the temperature τ.

Solution Using the relation between the temperature τ and σ. I will use the non approximated σ from last part. It seems that approximating within the logarithm is bad practice.

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U} = \frac{1}{\Delta E}\frac{\partial \sigma}{\partial n}$$

$$\begin{aligned}
\frac{\Delta E}{\tau} &= \frac{\partial}{\partial n}\left[n\ln\left(\frac{N}{n}\right) - (N-n)\ln\left(1-\frac{n}{N}\right) + n\ln\left(\frac{M}{n}\right) - (M-n)\ln\left(1-\frac{n}{M}\right)\right] \\
&= \left[(1)\left(\ln\left(\frac{N}{n}\right)\right) + (n)\left(\frac{-N/n^2}{N/n}\right)\right] - \left[(0-1)\left(\ln\left(1-\frac{n}{N}\right)\right) + (N-n)\left(\frac{0-\frac{1}{N}}{1-\frac{n}{N}}\right)\right] \\
&\quad - \left[(1)\left(\ln\left(\frac{M}{n}\right)\right) + (n)\left(\frac{-M/n^2}{M/n}\right)\right] - \left[(0-1)\left(\ln\left(1-\frac{n}{M}\right)\right) + (M-n)\left(\frac{0-\frac{1}{M}}{1-\frac{n}{M}}\right)\right] \\
&= \ln\left(\frac{N}{n}\right) - 1 + \ln\left(1-\frac{n}{N}\right) + 1 + \ln\left(\frac{M}{n}\right) - 1 + \ln\left(1-\frac{n}{M}\right) + 1 \\
\frac{\Delta E}{\tau} &= \boxed{\ln\left(\frac{N}{n}-1\right) + \ln\left(\frac{M}{n}-1\right)}
\end{aligned}$$

(e) Determine an expression for the average number of displaced atoms n in terms of τ and ΔE.

Solution Continuing on from the answer from part d. We can apply the approximation $n << N, M$ here.

$$\begin{aligned}
\frac{\Delta E}{\tau} &= \ln\left(\frac{N}{n}-1\right) + \ln\left(\frac{M}{n}-1\right) \\
\exp\left[\frac{\Delta E}{\tau}\right] &= \left(\frac{N}{n}-1\right)\left(\frac{M}{n}-1\right) \\
\exp\left[\frac{\Delta E}{\tau}\right] &= \frac{(N-n)(M-n)}{n^2} \approx \frac{NM}{n^2} \\
n &= \boxed{\sqrt{NM}\exp\left[-\frac{\Delta E}{2\tau}\right]}
\end{aligned}$$

(f) Use this model for defects in a solid with $N = M$ and $\Delta E = 1\,\mathrm{eV}$ to find the defect concentration $\frac{n}{N}$ at $T = 300K$ and at $T = 1000K$. (Note that $\tau = k_\mathrm{B}T$).

Solution Applying the conditions to the formula found in part e.

$$\begin{aligned}
n &= \sqrt{N^2}\exp\left[-\frac{1\,\mathrm{eV}}{2k_\mathrm{B}T}\right] \\
\frac{n}{N}(T) &= \exp\left[-\frac{1\,\mathrm{eV}}{2k_\mathrm{B}T}\right] \\
\frac{n}{N}(300\,\mathrm{K}) &= \exp\left[-\frac{1\,\mathrm{eV}}{2(8.63\times10^{-5}\,\mathrm{eV\,K^{-1}})(300\,\mathrm{K})}\right] = \boxed{4.1\times10^{-9}} \\
\frac{n}{N}(1000\,\mathrm{K}) &= \exp\left[-\frac{1\,\mathrm{eV}}{2(8.63\times10^{-5}\,\mathrm{eV\,K^{-1}})(1000\,\mathrm{K})}\right] = \boxed{3.05\times10^{-3}}
\end{aligned}$$