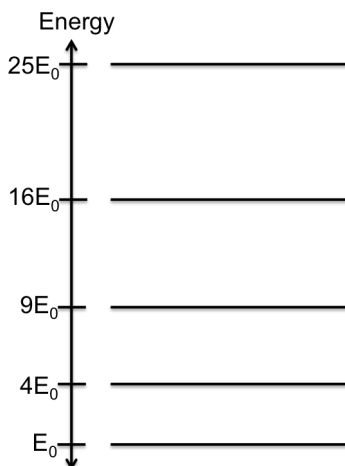
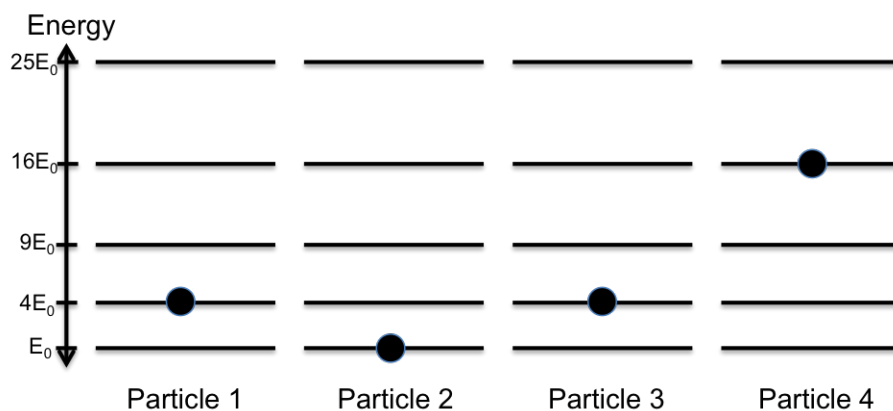


1. (i) See figure.



- (ii) See figure (each person's diagram may look slightly different and that's fine).



- (iii) The occupation number n_j for each of the five possible states, $j = 1 - 5$ is:

$$\begin{aligned} n_1 &= 1 \\ n_2 &= 2 \\ n_3 &= 0 \\ n_4 &= 1 \\ n_5 &= 0 \end{aligned}$$

- (iv) A single particle occupation number is the total number of individual particles that are in a particular state. For example, $n_2 = 2$ above because there are a total of 2 particles in the $j = 2$ single particle state.
- (v) In order to derive the average occupation number for fermions we will begin by calculating the grand canonical partition function, Z . Because we are working with fermions we must restrict the possible values of n_j to either 0 or 1 since each state, j , can only be occupied by a maximum of one particle - this restriction is applied in the summations

over n_j (recall that for bosons there are no restrictions on the number of particles that can occupy a given single particle state). Thus, we have:

$$Z = \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_j=0}^1 \dots e^{-\beta \sum_j n_j \epsilon_j + \beta \sum_j n_j \mu}$$

$$Z = \prod_j \left[\sum_{n_j=0}^1 e^{-\beta(\epsilon_j - \mu)n_j} \right]$$

where in the second step we used the fact that these particles are non-interacting and thus the sums in the exponential can be broken up into products ($e^{x+y} = e^x e^y$). We will now enumerate the two possible values of n_j to obtain the grand canonical partition function:

$$Z = \prod_j \left[e^0 + e^{-\beta(\epsilon_j - \mu)} \right]$$

$$Z = \prod_j \left[1 + e^{-\beta(\epsilon_j - \mu)} \right]$$

the last step is note that $\langle n_j \rangle$ is related to a derivative of the $\ln(Z)$. Specifically,

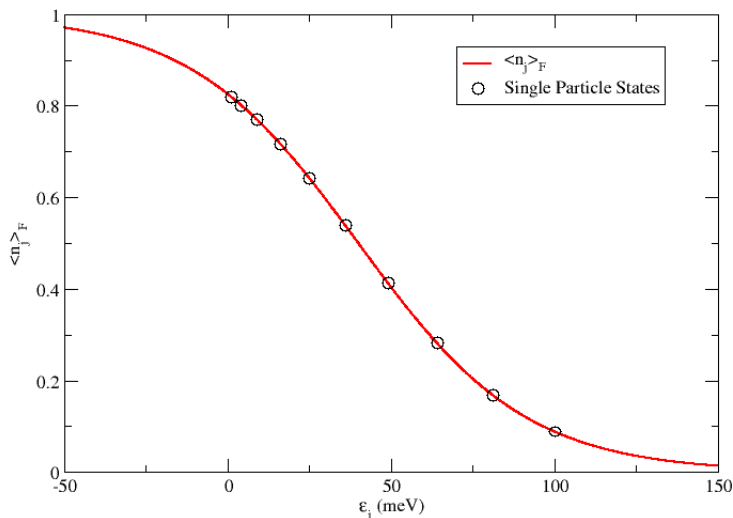
$$\langle n_j \rangle = \frac{\partial \ln Z}{\partial (-\beta \epsilon_j)}$$

$$\langle n_j \rangle = \frac{e^{\beta(\mu - \epsilon_j)}}{1 + e^{\beta(\mu - \epsilon_j)}}$$

$$\langle n_j \rangle_F = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}$$

(vi) A plot of $\langle n_j \rangle_F$ at $T = 298.15K$ and $\mu = 40meV$ is shown in red with (g) below.

(vii) See plot. The circles indicate the location of of energy eigenvalues $j = 1 - 10$.



- (viii) Plugging in the numbers: $k_B = 8.617 \times 10^{-2} \text{meV} \cdot K^{-1}$, $T = 298.15 K$, $\mu = 40 \text{meV}$, $\epsilon_4 = 1 \text{meV} \cdot (4)^2 = 16 \text{meV}$, and $\epsilon_7 = 1 \text{meV} \cdot (7)^2 = 49 \text{meV}$ into the equation for $\langle n_j \rangle_F$ we get:

$$\begin{aligned}\langle n_4 \rangle_F &= \frac{1}{e^{\frac{1}{8.616 \times 10^{-2} \cdot 298.15} (16-40)} + 1} \\ \langle n_4 \rangle_F &= 0.718 \\ \langle n_7 \rangle_F &= \frac{1}{e^{\frac{1}{8.616 \times 10^{-2} \cdot 298.15} (49-40)} + 1} \\ \langle n_7 \rangle_F &= 0.413\end{aligned}$$

- (ix) The temperature determines the energy interval in which the FD distribution changes from 1 to 0. The center of this change is at μ , which can readily be seen from setting $\epsilon = \mu$:

$$\begin{aligned}\langle n_{\epsilon=\mu} \rangle_F &= \frac{1}{e^0 + 1} \\ \langle n_{\epsilon=\mu} \rangle_F &= \frac{1}{2}\end{aligned}$$

And when you combine this with the knowledge that after the exponent becomes large (in magnitude) then e to this exponent will approach either become extremely large or extremely small very quickly. In other words, if x in e^x becomes large in magnitude then it will approach either infinity or 0 very quickly. The magnitude of x in the FD distribution is controlled by the temperature and the difference between the energy and of the state the chemical potential ($\epsilon_j - \mu$). Specifically, it is controlled by the ratio of these: $x \propto \frac{\epsilon_j - \mu}{T}$. Thus, the temperature is very important because the states within kT of μ will be the ones for which the magnitude of the exponent is not large which makes the population of these states very sensitive to the temperature.

2. (i) In the first excited state, any one of the N particles may be excited. In the second excited state, any one of the remaining $(N - 1)$ particles may be excited. The degeneracy is thus $N(N - 1)$. To account for the fact that the particles are fixed at a particular lattice site, we divide $N(N - 1)$ by 2.

Then we have that

$$W(2) = \frac{N(N - 1)}{2}.$$

- (ii) This answer to this question can be rephrased as the number of ways to put n spins up in a sea of $N - n$ spins down. Even though the particles are distinguishable, being fixed at particular lattice sites has the same probabilistic effect as the particles being indistinguishable. So, the result is just the binomial coefficient:

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

- (iii) We know that $S = k_B \ln W$, so let's calculate $\ln W(n)$, making use of Stirling's approx-

imation along the way.

$$\begin{aligned}
 \ln W(n) &= \ln N! - \ln(N-n)! - \ln n! \\
 &= N \ln N - N - (N-n) \ln(N-n) + (N-n) - n \ln n + n \\
 &= N \ln N - (N-n) \ln(N-n) - n \ln n \\
 &= N \ln N - N \ln(N-n) + n \ln(N-n) - n \ln n \\
 &= N \ln N - N \ln \left[N \left(1 - \frac{n}{N} \right) \right] + n \ln \left[n \left(\frac{N}{n} - 1 \right) \right] - n \ln n \\
 &= N \ln N - N \ln N - N \ln \left(1 - \frac{n}{N} \right) + n \ln n + n \ln \left(\frac{N}{n} - 1 \right) - n \ln n \\
 &= -N \ln \left(1 - \frac{n}{N} \right) + n \ln \left(\frac{N}{n} - 1 \right) \\
 &= N \left[-\ln \left(1 - \frac{n}{N} \right) + \frac{n}{N} \ln \left(\frac{N}{n} - 1 \right) \right].
 \end{aligned}$$

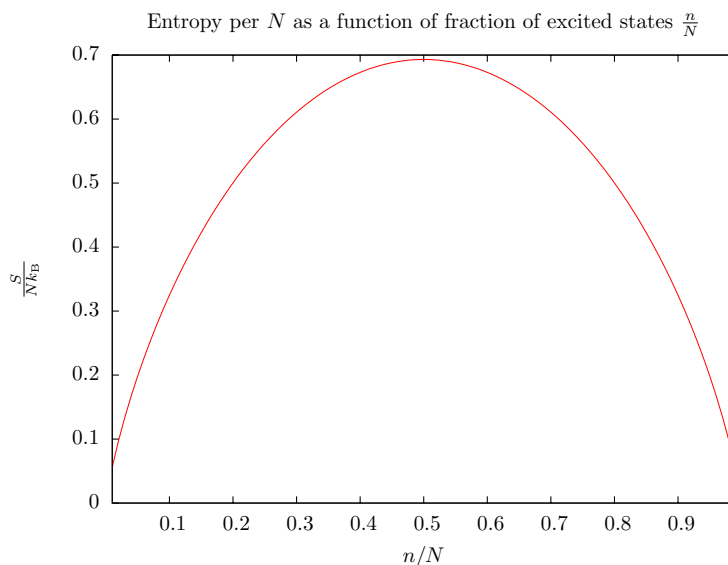
Let $f = n/N$:

$$\begin{aligned}
 \ln W(n) &= N \left[-\ln(1-f) + f \ln \left(\frac{1}{f} - 1 \right) \right] \\
 \ln W(n) &= N \left[-\ln(1-f) + f \ln \left(\frac{1-f}{f} \right) \right] \\
 \ln W(n) &= -N \left[(1-f) \ln(1-f) + f \ln f \right]
 \end{aligned}$$

Then the entropy is

$$\begin{aligned}
 S &= k_B \ln W(n) \\
 &= k_B N \left[-\ln(1-f) + f \ln \left(\frac{1-f}{f} \right) \right] \\
 &= -k_B N \left[(1-f) \ln(1-f) + f \ln f \right].
 \end{aligned}$$

Since entropy is proportional to N , it clearly is extensive. Below is a plot of the entropy S/k_B per particle N as a function of n/N .



- (iv) Before proceeding further, note that a means to calculate the temperature of any system is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N$$

Since S is a function of f , it would be more convenient to calculate $(\partial S / \partial f)_N$, which can be done using the chain rule:

$$\left(\frac{\partial S}{\partial E} \right)_N = \left(\frac{\partial S}{\partial f} \right)_N \left(\frac{\partial f}{\partial n} \right)_N \left(\frac{\partial n}{\partial E} \right)_N$$

From the expression for energy, we find that

$$\left(\frac{\partial E}{\partial n} \right)_N = \epsilon$$

and we know that

$$\left(\frac{\partial f}{\partial n} \right)_N = \frac{1}{N}.$$

Then

$$\frac{1}{T} = \frac{1}{N\epsilon} \left(\frac{\partial S}{\partial f} \right)_N$$

Taking the derivative of entropy, we find that

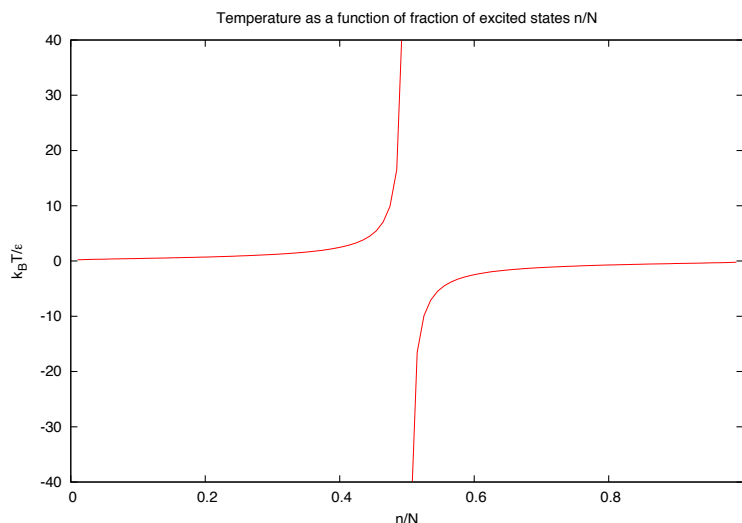
$$\begin{aligned} \frac{1}{T} &= \frac{1}{N\epsilon} k_B N \left\{ \frac{1}{1-f} + \ln \frac{1-f}{f} + f \left[\frac{f}{1-f} \left(\frac{-1}{f} - \frac{1-f}{f^2} \right) \right] \right\} \\ &= \frac{1}{N\epsilon} k_B N \left\{ \frac{1}{1-f} + \ln \frac{1-f}{f} + f \left[\frac{f}{1-f} \left(-1 - \frac{1-f}{f} \right) \right] \right\} \\ &= \frac{1}{N\epsilon} k_B N \left\{ \frac{1}{1-f} + \ln \frac{1-f}{f} + \left[-\frac{f}{1-f} - 1 \right] \right\} \end{aligned}$$

After some algebra, this becomes

$$\frac{1}{T} = \frac{k_B}{\epsilon} \ln \frac{1-f}{f}$$

$$T = \frac{\epsilon}{k_B} \left[\ln \frac{1-f}{f} \right]^{-1}.$$

Since there is no N dependence in the above expression, temperature is intensive, as it should be. It only depends on the fraction of the system that is excited, or f . A plot of this expression is shown below.



(v) As shown above, the temperature can be negative under certain conditions. Above $n/N = 1/2$ entropy actually decreases with increasing energy. This occurs because the system is isolated with a finite number of places for the system to distribute its energy. (Think "population inversion", spectroscopists.) In the natural world, systems are not isolated, and there always exist higher energy levels to place particles upon excitation – thus there never is a natural case where there is a true population inversion or negative temperature.

(vi) For the first case, where $f^{(1)} = 1/4$,

$$T = \frac{\epsilon}{k_B} \left[\ln \frac{1-f}{f} \right]^{-1}$$

$$= \frac{\epsilon}{k_B} \left[\ln \frac{1-0.25}{0.25} \right]^{-1}$$

$$= \frac{\epsilon}{k_B} \left[\ln 3 \right]^{-1}$$

For the second case, where $f^{(2)} = 3/4$,

$$\begin{aligned} T &= \frac{\epsilon}{k_B} \left[\ln \frac{1-f}{f} \right]^{-1} \\ &= \frac{\epsilon}{k_B} \left[\ln \frac{1-0.75}{0.75} \right]^{-1} \\ &= -\frac{\epsilon}{k_B} \left[\ln 3 \right]^{-1} \end{aligned}$$

- (vii) If we assumed that temperature flows from high to low temperature we would assume that, since $T^{(1)} > T^{(2)}$, heat would flow from system 1 to system 2. If that were the case, eventually all the spins in system 1 would be down, and all the spins in system 2 would be up...which means that all of system 1's energy would go to system 2. This certainly is not equilibrium.
- (viii) Before proceeding, recall that the system obeys the conservation of energy:

$$E_{total} = E_f^{(2)} + E_f^{(1)} = E_i^{(2)} + E_i^{(1)} = 0$$

Let us define ΔE as the energy that flows from system 2 to system 1:

$$\begin{aligned} E_f^{(1)} &= E_i^{(1)} + \Delta E \\ E_f^{(2)} &= E_i^{(2)} - \Delta E \end{aligned}$$

Then, by the second law,

$$\Delta S = \Delta E \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \geq 0$$

If $1/T^{(1)} - 1/T^{(2)} > 0$ then $\Delta E > 0$, and heat flows from system 2 to system 1. If $1/T^{(1)} - 1/T^{(2)} < 0$ then $\Delta E < 0$, and heat flows from system 1 to system 2.

Case a: If $T^{(1)} > 0$ and $T^{(2)} > 0$, then the final temperature will also be positive. Without loss of generality, take $T^{(1)} < T^{(2)}$ so that $\Delta E > 0$ and heat flows from system 2 to 1.

Case b: If $T^{(1)} < 0$ and $T^{(2)} < 0$, then the final temperature will also be negative. Without loss of generality, take $T^{(1)} > T^{(2)}$ so that $\Delta E < 0$ and heat flows from system 1 to 2.

Case c: It is impossible to tell what the sign of the final temperature will be. Nonetheless, since $T^{(2)} < 0$ and $T^{(1)} > 0$, $1/T^{(1)} - 1/T^{(2)} > 0$ and $\Delta E < 0$, which means heat flows from system 2 to 1.

- (ix) This problem addresses the issue of thermodynamic stability in the context of temperature and entropy. Here realistic systems always have positive temperature; this means that the derivative of entropy with respect to energy is always increasing. In real systems, there are more degrees of freedom in which to put energy, and therefore any system with this sort of finite energy level is an artifact of an isolated system with finite energy level. Additionally, a negative temperature system is an unstable situation because if it were placed in contact with a positive temperature system it would result in the systems going to temperatures of negative and positive infinity, which means they would not approach an equilibrium state in which their temperatures would be equal.

3. (i) Because the stretching is done reversibly, at each instant the "internal" force equals the "external" force, and so we can just take a simple integral:

$$\begin{aligned}
 work &= \int dw \\
 &= \int F_{ext} d\kappa' \\
 &= \int_0^\kappa \alpha \kappa' e^{-T/T_0} d\kappa' \\
 &= \alpha \frac{\kappa'^2}{2} e^{-T/T_0} \Big|_0^\kappa \\
 &= \alpha \frac{\kappa^2}{2} e^{-T/T_0}
 \end{aligned}$$

- (ii) Now to apply simple laws of thermodynamics:

$$\begin{aligned}
 \Delta E &= \text{heat} + \text{work} \\
 \Delta E - \text{work} &= \text{heat} \\
 \Delta E &= E - E_0(T) = \frac{1}{2} \alpha \kappa^2 \left(1 + \frac{T}{T_0} \right) e^{-T/T_0} \\
 \Delta E - \text{work} &= \frac{1}{2} \alpha \kappa^2 \left(1 + \frac{T}{T_0} \right) e^{-T/T_0} - \alpha \frac{\kappa^2}{2} e^{-T/T_0} \\
 \text{heat} = \Delta E - \text{work} &= \frac{1}{2} \alpha \kappa^2 \left(\frac{T}{T_0} \right) e^{-T/T_0}
 \end{aligned}$$

- (iii) For an isothermal process:

$$\begin{aligned}
 \text{heat} &= T \Delta S \\
 \Delta S &= \frac{1}{T} \text{heat} \\
 &= \frac{1}{T} \cdot \frac{1}{2} \alpha \kappa^2 \left(\frac{T}{T_0} \right) e^{-T/T_0} \\
 &= \frac{1}{2} \alpha \kappa^2 \left(\frac{1}{T_0} \right) e^{-T/T_0}
 \end{aligned}$$

4. See solutions manual.

5. (i) For convenience, let the molecule H be designated 1 and the molecule H_2 as 2. By the conservation of mass

$$\Delta N = \Delta N_2 = -\frac{1}{2} \Delta N_1.$$

For a spontaneous reaction,

$$\Delta S = \Delta S_1 + \Delta S_2 \geq 0.$$

Combining these two expressions and taking appropriate derivatives, we have that

$$\begin{aligned} \left(\frac{\partial S_1}{\partial N_1}\right)_{E,V,N_2} \Delta N_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E,V,N_1} \Delta N_2 &\geq 0 \\ -\frac{\mu_1}{T}(-2\Delta N) - \frac{\mu_2}{T}(\Delta N) &\geq 0 \\ \frac{\Delta N}{T}(2\mu_1 - \mu_2) &\geq 0 \end{aligned}$$

For the number of H_2 molecules to increase, $\Delta N > 0$, so then it must be that $2\mu_1 - \mu_2 > 0$, or that $2\mu_1 > \mu_2$.

- (ii) Since all microstates are equally likely, the most probable number of molecules is determined by the degeneracy. Moreover, we can state that the total number of configurations is

$$\Omega_{total} = \Omega_H \Omega_{H_2}.$$

The chemical potential of the individual species characterizes the change of accessible configurations with respect to the change in the number of molecules of that species. Thus the system will move spontaneously towards the state with more microstates, as determined by the balance of the chemical potentials of the species involved.

- (iii) From the first part, if $\Delta N < 0$, $2\mu_1 - \mu_2 < 0$, so $2\mu_1 < \mu_2$.
 (iv) For chemical equilibria criteria to be met, it is clear that we must have $2\mu_1 = \mu_2$.
 (v)

$$dE = dW + dQ$$

Since the process is adiabatic, $dE = dW$. Recall the definition of the differential of energy:

$$dE = TdS - pdV + \sum_i \mu_i dN_i$$

Since the process is reversible and in a rigid container, $dS = dV = 0$. Then we have

$$dE = \sum_i \mu_i dN_i$$

So then combining the expressions yields

$$\begin{aligned} dE = dW &= \sum_i \mu_i dN_i = -2\mu_1 dN + \mu_2 dN \\ dW &= (-2\mu_1 + \mu_2) dN. \end{aligned}$$