

Physics 112 Fall 2017
Professor William Holzapfel
Homework 2 Solutions

Problem 1: Magnetization

a) For the paramagnet, we can use the Gaussian approximation to the multiplicity in terms of the total number of spins N and the spin excess s :

$$g(N, s) = g(N, 0)e^{-2s^2/N}$$

The entropy is easily calculated:

$$\begin{aligned}\sigma(s) &= \log g(N, s) = \log(g(N, 0)) - 2s^2/N \\ &= \log(g(N, 0)) - \frac{U^2}{2Nm^2B^2}\end{aligned}$$

where we've substituted U for s using $U = -2smB$. From the definition of temperature we have:

$$\begin{aligned}\frac{1}{\tau} &= \frac{\partial \sigma}{\partial U} = -\frac{U}{Nm^2B^2} \\ \longrightarrow \tau &= -\frac{m^2B^2N}{U}.\end{aligned}$$

Now we can solve for $U(\tau)$ and plug it into the definition of fractional magnetization:

$$\frac{M}{Nm} = \frac{2s}{N} = -\frac{U}{NmB} = \frac{mB}{\tau}.$$

b) Entropy and temperature as functions of energy are plotted in Figures 1 and 2.

We can see that temperature is negative when $U > 0$. The concept of negative temperature is less mysterious when we consider the definition of temperature:

$$\frac{1}{\tau} = \left. \frac{\partial \sigma}{\partial U} \right|_V, \tag{1}$$

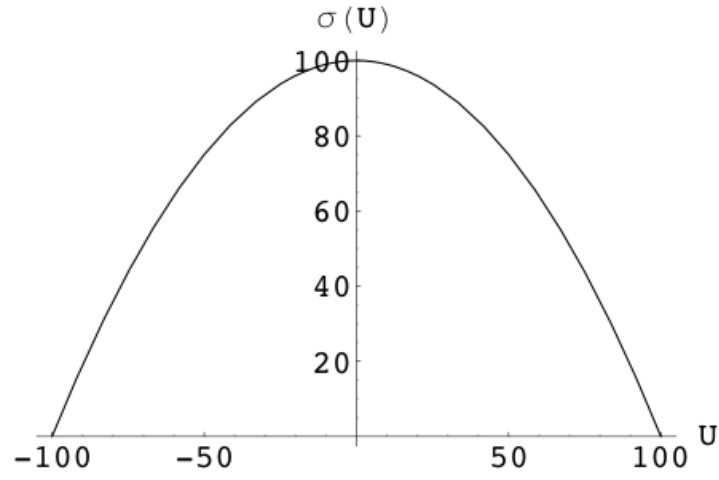


Figure 1: This is the plot of entropy vs. energy for the case $\sigma_0 \approx 100$ and $m^2 B^2 N \approx 100$.

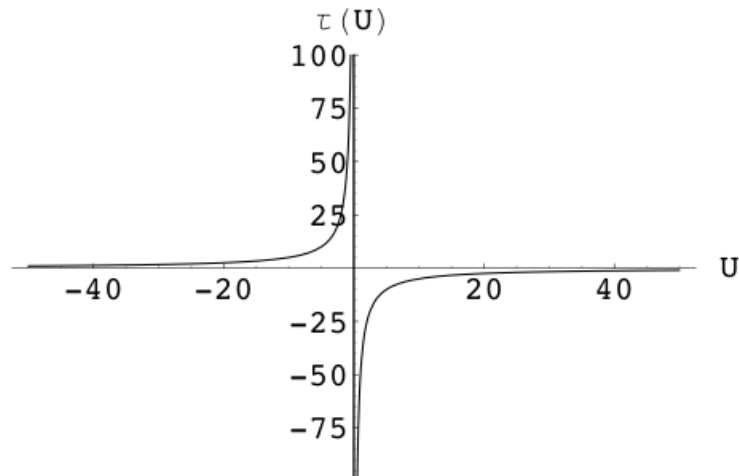


Figure 2: This is the plot of temperature vs. energy for the case $m^2 B^2 N \approx 100$. Notice that the temperature is negative for $U > 0$.

Negative temperature means that $d\sigma/dU$ is negative, and so the entropy increases when the energy decreases. If such a system is brought into contact with a positive temperature system, then energy will flow from the negative T system to the positive T system since that will increase the entropy of both! This is in contrast to what happens when two positive T systems are brought together; in that case one will lose entropy and the other will gain, but the energy will flow in such a way that the *net* entropy change is still positive. In the case of negative T and positive T , *both* systems increase their entropy.

Problem 2: Crystal Disorientations

a) First we need to choose which M of the total of N atoms will be removed from their lattice sites; clearly there are $\binom{N}{M}$ ways of doing this. Then we need to choose which interstitial sites to put the M atoms in. For a square lattice of N sites, there are N interstitial sites, so there are also $\binom{N}{M}$ ways to place the displaced atoms in the interstitial sites. So the total multiplicity is:

$$g(N, M) = \binom{N}{M} \binom{N}{M} = \left(\frac{N!}{M!(N-M)!} \right)^2.$$

b) This part of the problem is analogous to problem 1: first we write σ as a function of U and then take the derivative to find τ :

$$\begin{aligned} \sigma &= \log g(N, M) = 2(\log N! - \log M! - \log(N-M)!) \\ &= 2(N \log N - M \log M - (N-M) \log(N-M)) \\ &= 2N \left(\log \frac{N}{N-M} - \frac{M}{N} \log \frac{M}{N-M} \right) \\ &= 2N \left(\log \frac{1}{1 - \frac{U}{U_0}} - \frac{U}{U_0} \log \frac{\frac{U}{U_0}}{1 - \frac{U}{U_0}} \right) \\ \Rightarrow \frac{1}{\tau} &= \left. \frac{\partial \sigma}{\partial U} \right|_{U_0=N\epsilon} \\ &= 2N \left(\frac{1}{U_0 - U} - \frac{1}{U_0} \left[\log \frac{U}{U_0} - \log \left(1 - \frac{U}{U_0} \right) \right] - \frac{1}{U_0} - \frac{U}{U_0(U_0 - U)} \right) \\ &= -\frac{2N}{U_0} \log \left(\frac{U}{U_0 - U} \right) = -\frac{2}{\epsilon} \log \left(\frac{M}{N-M} \right) \end{aligned}$$

where we have used $U = N\epsilon$, $U_0 = M\epsilon$. We can solve for M/N by taking the exponential of the above expression:

$$\frac{M}{N-M} = e^{-\epsilon/2k_B T}$$

$$\Rightarrow \frac{M}{N} = \frac{1}{e^{\epsilon/2k_B T} + 1}.$$

Problem 3: More Crystal Disorientations

- a) In this problem, we still need to pick M atoms to displace first, so we again have $\binom{N}{M}$ ways of doing this. Now for each atom we displace there are only β interstitial sites in which we can place it (compare this with the previous problem where any of the M displaced atoms could go into any of N interstitial sites). So there are β configurations for each displaced atom, and therefore β^M ways to displace the atoms. (Clearly we are ignoring any potential complications due to the fact that in a real lattice, neighboring atoms may share interstitial sites between them. If $M \ll N$ this is not a problem.) Our total multiplicity becomes:

$$g(N, M) = \binom{N}{M} \beta^M = \frac{N!}{M!(N-M)!} \beta^M.$$

The rest of the problem follows our calculation in problem 2:

$$\begin{aligned} \sigma &= \log g(N, M) = M \log \beta + \log N! - \log M! - \log(N-M)! \\ &= \frac{U}{\epsilon} \log \beta + N \left(\log \frac{1}{1 - \frac{U}{U_0}} - \frac{U}{U_0} \log \frac{\frac{U}{U_0}}{1 - \frac{U}{U_0}} \right) \\ \Rightarrow \frac{1}{\tau} &= \left. \frac{\partial \sigma}{\partial U} \right|_{U_0 = N\epsilon} \\ &= \frac{1}{\epsilon} \log \beta - \frac{N}{U_0} \log \left(\frac{U}{U_0 - U} \right) = \frac{1}{\epsilon} \log \beta - \frac{1}{\epsilon} \log \left(\frac{M}{N-M} \right) \\ \Rightarrow \frac{M}{N} &= \frac{\beta}{\beta + e^{\epsilon/\tau}}. \end{aligned} \tag{2}$$

- b) Before considering various limits, it's important to note that a formula such as (2) has no meaning if the system is isolated, since in that case the

energy of the system U is fixed and we have $M/N = U/\epsilon N$. An equation such as (2), in which M/N is expressed as a function of temperature, is only meaningful if the system is in contact with another system at a known temperature, such as a reservoir. This will be the context of our discussion below.

- i) If $\beta \rightarrow \infty$, the exponential in the denominator of (2) is negligible, so $M/N \rightarrow 1$, i.e. all the atoms are displaced. Why should this happen? Remember that energy transfer from the reservoir to the system will only take place if that transfer increases the *total* entropy of the system. Since the reservoir is at a fixed T , the entropy loss *of the reservoir* for a transfer of energy ϵ (corresponding to the displacement of one atom) will be $\delta S = \frac{\epsilon}{T}$, which is independent of β . However, the entropy gain *of the system* will have a contribution $\ln \beta$ since it gains a multiplicity of β when one additional atom is displaced. Thus, for β large enough the entropy gain in the system will outweigh the entropy loss of the reservoir, and so it will be entropically favorable for each atom to be displaced.
- ii) For $T \rightarrow \infty$, we have $M/N \rightarrow \frac{\beta}{\beta+1}$. This makes sense because at infinite T there is unlimited energy available and so an atom is just as likely to be at any one of its $\beta + 1$ available sites. Thus, the probability of being displaced is just $\frac{\beta}{\beta+1}$.
- iii) For $T \rightarrow 0$, $M/N \approx 0$. At $T = 0$ the lowest energy state, where all the atoms are on the lattice, is selected.

Problem 4: Paramagnetic Entropy

a) We know the multiplicity and energy of a paramagnet are given by:

$$\begin{aligned} g(N, s) &= \frac{N!}{(N/2 + s)!(N/2 - s)!} \\ U(s) &= -2msB \end{aligned}$$

The entropy is then simply, $S = k_b \sigma = k_b \ln(g)$, which we can calculate the usual

way with Stirling's approximation:

$$\begin{aligned}
\sigma &= \ln g = \ln N! - \ln(N/2 + s)! - \ln(N/2 - s)! \\
&= N \ln N - \frac{N}{2} \ln \left(\frac{N^2}{4} - s^2 \right) - s \ln \left(\frac{N/2 + s}{N/2 - s} \right) \\
&= N \ln N - \frac{N}{2} \ln \left(\frac{1}{4} \left[N^2 - \frac{U^2}{m^2 B^2} \right] \right) + \frac{U}{2mB} \ln \left(\frac{N - U/(mB)}{N + U/(mB)} \right)
\end{aligned}$$

To get temperature in the picture, we start from the definition of temperature:

$$\begin{aligned}
\frac{1}{\tau} &= \left. \frac{\partial \sigma}{\partial U} \right|_{N,m,B} \\
&= \frac{NU/(m^2 B^2)}{N^2 - U^2/(m^2 B^2)} + \frac{1}{2mB} \ln \left(\frac{N - U/(mB)}{N + U/(mB)} \right) - \frac{U}{2mB} \left(\frac{1/(mB)}{N - U/(mB)} + \frac{1/(mB)}{N + U/(mB)} \right) \\
&= \frac{1}{2mB} \ln \left(\frac{N - U/(mB)}{N + U/(mB)} \right).
\end{aligned}$$

Introducing $x = \frac{mB}{k_b T}$, we get:

$$\left(\frac{N - U/(mB)}{N + U/(mB)} \right) = e^{2x}$$

which can be solved for U in terms of x :

$$\begin{aligned}
U &= -NmB \frac{1 - e^{2x}}{1 + e^{2x}} \\
&= -NmB \tanh x
\end{aligned}$$

Now we can plug this into our expression for σ above:

$$\begin{aligned}
\sigma &= N \ln N + \frac{N}{2} \ln 4 - \frac{N}{2} \ln (N^2 - N^2 \tanh^2 x) - \frac{N}{2} \tanh x \ln \left(\frac{N + N \tanh x}{N - N \tanh x} \right) \\
&= N \ln 2 + N \ln(\cosh x) - N \tanh x \ln \left(\frac{1 + \tanh x}{1 - \tanh x} \right)^{1/2} \\
&= N \ln(2 \cosh x) - Nx \tanh x. \\
S &= k_b \sigma = Nk_b (\ln(2 \cosh x) - x \tanh x)
\end{aligned}$$

b) Entropy is plotted as a function of $k_b T/mB$ in Figure 3. We can see that as $T \rightarrow 0$, $S \rightarrow 0$, and S goes to some constant value for $T \rightarrow \infty$. To understand this behavior, let's look at the expression from part (a) in the two limits.

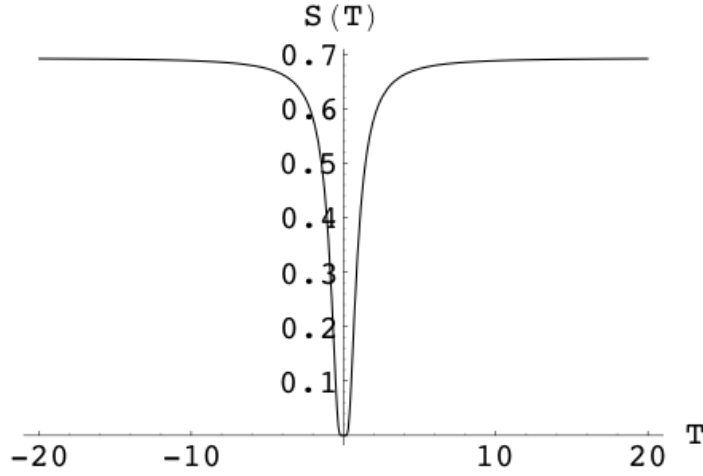


Figure 3: Entropy vs. T for $Nk_b \approx 1$, $N \approx 10^{23}$ and $k_b \approx 10^{-23}$.

When $T \rightarrow 0$, $x \rightarrow \infty$. For large x , $\cosh(x) \approx \frac{1}{2}e^x$, and $\tanh(x) \approx 1$, so we have:

$$S \approx N \ln\left(2 * \frac{1}{2}e^x\right) - Nx = 0$$

This agrees with our intuitive picture that entropy should tend to zero as $T \rightarrow 0$. For $T \rightarrow \infty$, $x \rightarrow 0$, in which case $\cosh(x) \approx 1$ and $\tanh(x) \approx 0$. So we have:

$$S = Nk_b \ln 2 = k_b \ln 2^N$$

which should be the maximum possible value for the entropy. Is that correct? We know that the highest entropy state has $s = 0$, in which case the entropy is

$$\begin{aligned} S &= k_b \ln \left(\frac{N}{N/2} \right) \\ &\approx k_b (N \ln N - 2 \cdot N/2 \ln(N/2)) \\ &= Nk_b \ln 2 \end{aligned}$$

as desired (we skipped a little algebra in the calculation). You might find this result odd, since it also corresponds to a multiplicity of 2^N which is the number of *all* states of the paramagnet, but to the accuracy that we're working with we have $2^N \approx \binom{N}{N/2}$, as you can check.

As noted in the question, $S(x)$ is an even function of x , so we get the same entropies for negative temperatures as for positive temperatures. Remembering what

we said in problem 1, negative temperatures correspond to a magnetization aligned opposite to the magnetic field; so moving from $T \rightarrow -T$ is the same as flipping the direction of the magnetic field. However, the multiplicity, and therefore the entropy, should not depend on the direction of the field; these quantities simply count the number of states in a particular configuration, independent of the energy of the configuration.

Problem 5. Quantum Harmonic Oscillator.

a) Starting with the multiplicity $g(N, q) = \frac{(q+N-1)!}{q!(N-1)!}$ and using the Stirling approximation in the rough form $N! \approx N^N e^{-N}$ as well as the approximation $N-1 \approx N$ we get

$$\begin{aligned} g &\approx \frac{(q+N)!}{q!N!} \\ &\approx \frac{(q+N)^{q+N}}{q^q N^N} \\ &= \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N. \end{aligned}$$

b) The entropy follows simply from a):

$$\begin{aligned} S &= k_b \ln g = k_b [(q+N) \ln(q+N) - q \ln q - N \ln N] \\ &= k_b \frac{1}{\epsilon} \left[(U + U_0) \ln \left(\frac{U + U_0}{\epsilon} \right) - U \ln \left(\frac{U}{\epsilon} \right) - U_0 \ln \left(\frac{U_0}{\epsilon} \right) \right] \end{aligned}$$

I'll skip the algebra, but the steps are the same as usual:

c) Using $U = q\epsilon$ and $U_0 = N\epsilon$, we start from the definition of temperature:

$$\frac{1}{\tau} = \left. \frac{\partial \sigma}{\partial U} \right|_{N\epsilon=U_0} = \frac{1}{\epsilon} \ln \left(\frac{U + U_0}{U} \right)$$

d) and solve for the energy as a function of temperature:

$$U = \frac{U_0}{e^{\epsilon/\tau} - 1} = \frac{N\epsilon}{e^{\epsilon/(k_b T)} - 1}.$$

e) To simplify the algebra, we'll substitute $\epsilon/(k_b T) = \epsilon/\tau = x$

$$\begin{aligned} C_V &= \left. \frac{\partial U}{\partial T} \right|_V = \frac{N k_b \epsilon^2}{(k_b T)^2} \frac{e^{\epsilon/(k_b T)}}{(e^{\epsilon/(k_b T)} - 1)^2} \\ &= N k_b x^2 \frac{e^x}{(e^x - 1)^2} \end{aligned}$$

As $T \rightarrow \infty$, $x \rightarrow 0$, so we get $0/0$. Using L'Hopital's rule twice, we see that $\lim_{x \rightarrow 0} \frac{e^x}{(e^x - 1)^2} = 1$, so $C \rightarrow N k_b$. This makes sense when we think about the equipartition theorem: as $T \rightarrow \infty$, we should get the classical result for N harmonic oscillators, where each harmonic oscillator contributes k_b to the specific heat. (Even though a harmonic oscillator has only one degree of freedom, it contributes k_b instead of $\frac{1}{2}k_b$ because what the equipartition theorem actually states is that you get $\frac{1}{2}k_b$ per *quadratic term in the Hamiltonian*, and so the 1D free particle with just a p^2 term gets $\frac{1}{2}k_b$ but the 1D oscillator with an additional q^2 term gets k_b .)

f) The heat capacity is plotted vs. temperature in Figure 4. We already discussed the high temperature limit, and we see that $C_v \rightarrow 0$ for $T \rightarrow 0$. At low temperatures, there will not be enough thermal energy to excite the oscillators into their first excited states, so the energy will not change as we increase the temperature infinitesimally. Now because diamond is much harder than lead, we expect the spring constants in the harmonic oscillator model of a solid to be stiffer for diamond than for lead; this means $\epsilon_{\text{diamond}} > \epsilon_{\text{lead}}$. Figure 5 shows a plot of C_v vs. $k_b T/\epsilon$ for two different values of epsilon; the higher value of ϵ appears as the lower curve. These curves are a result of the larger spacing of the diamond energy levels: because at lower temperatures there are more modes which can accept energy for lead than for diamond, the heat capacity for diamond is lower. At high temperatures, C_v is independent of the energy spacing because all levels are accessible, so we get the classical result for N oscillators.

g) Here we expand part b):

$$\begin{aligned}
C_v &= Nk_b x^2 e^x / (e^x - 1)^2 = Nk_b x^2 \frac{1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots}{(x + \frac{x^2}{2} + \frac{x^3}{6} + \dots)^2} \\
&= Nk_b \frac{1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots}{1 + x + \frac{7x^2}{12} + \dots} \\
&= Nk_b \left(1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots \right) \left(1 - x - \frac{7x^2}{12} - \dots + x^2 + \dots \right) \\
&\approx Nk_b \left(1 + x + \frac{x^2}{2} \right) \left(1 - x + \frac{5x^2}{12} \right) \\
&= Nk_b \left(1 - \frac{1}{12} x^2 \right) = Nk_b \left[1 - \frac{1}{12} \left(\frac{\epsilon}{k_b T} \right)^2 \right].
\end{aligned}$$

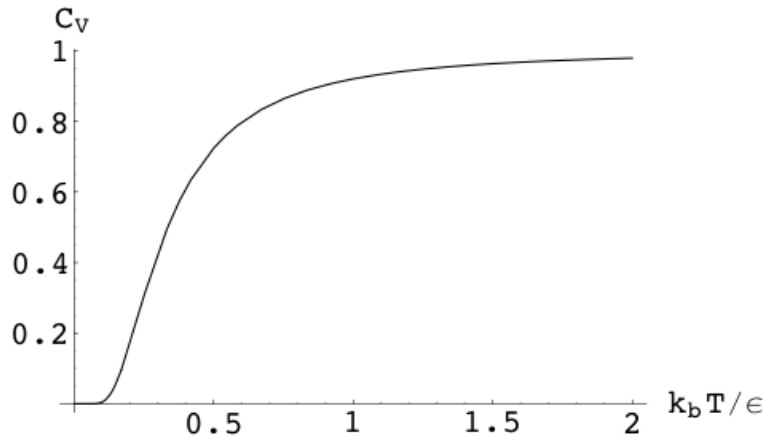


Figure 4: Heat capacity vs. temperature with $Nk_b = 1$

Problem 6: Entropy and Reversibility

a) To find the change in entropy of the water we need to find a relationship between entropy and temperature at fixed volume. Looking at the thermodynamic identity, $dU = TdS - pdV$, at constant volume we have: $dS = \frac{dU}{T}$. Using the definition of specific heat $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ we have the familiar relationship, $dS = \frac{C_V dT}{T}$. So we can integrate over the temperature change:

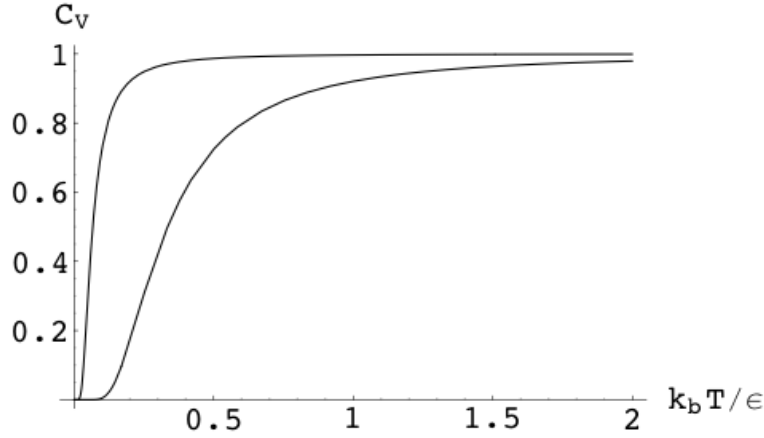


Figure 5: Heat capacity of lead (upper curve) and diamond (lower curve)

$$\begin{aligned}
 \Delta S_w &= C_V \int_{T_i}^{T_f} \frac{dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right) \\
 &= 4.2 \text{ KJ/K} \times \ln\left(\frac{373}{273}\right) = 1310 \text{ J/K.}
 \end{aligned} \tag{3}$$

The entropy change of the reservoir is even simpler, as the temperature of the reservoir is constant.

$$\Delta S_r = \frac{\Delta U}{T_r} = \frac{-C_V(T_f - T_i)}{T_r} = \frac{-4.2 \text{ KJ/K} * 100\text{K}}{373\text{K}} = -1126 \text{ J/K.}$$

So the total entropy change of the universe will be $\Delta S_u = \Delta S_w + \Delta S_r = 184 \text{ J/K}$.

b) This is easy now that we know the entropy: $\Delta \sigma_w = \Delta S_w / k_b = \ln g_f - \ln g_i$

$$\begin{aligned}
 \Rightarrow \frac{g_f}{g_i} &= e^{\Delta \sigma_w} = e^{\Delta S_w / k_b} \\
 &= e^{\frac{1310\text{J/K}}{1.381 \times 10^{-23}\text{J/K}}} = e^{9.49 \times 10^{25}}.
 \end{aligned}$$

c) The entropy change of the water for this two step process is the same as in a), because all we are doing is dividing the integral into two pieces, $0 \rightarrow 50$ and

50 \rightarrow 100. The entropy change for the reservoirs is different now because the energy is transferred at two different temperatures:

$$\begin{aligned}\Delta S_{r,1} &= \frac{\Delta U}{T_{r,1}} = \frac{-4.2\text{KJ/K} * 50K}{323K} = -650\text{J/K} \\ \Delta S_{r,2} &= \frac{\Delta U}{T_{r,2}} = \frac{-4.2\text{KJ/K} * 50K}{373K} = -563\text{J/K} \\ \longrightarrow \Delta S_{r,\text{total}} &= -1213 \text{ J/K.} \\ \longrightarrow \Delta S_u &= 97.7 \text{ J/K.}\end{aligned}$$

We see that the total entropy increases less in the two step process than in the one step process.

d) When we take an infinite number of steps, the entropy change of the water is still the same, but now we can integrate over the infinitesimal steps of the different reservoirs at the intermediate temperatures.

$$\begin{aligned}\delta S_r &= \frac{\delta U}{T} = -C_V \frac{dT}{T} \\ \longrightarrow \Delta S_r &= -C_V \int_{T_f}^{T_i} \frac{dT}{T} = -C_V \ln \left(\frac{T_f}{T_i} \right).\end{aligned}$$

This is exactly the opposite of the entropy change of the water, so the total entropy of the universe is doesn't change. Clearly, in the limit of taking an infinite number of steps the process is reversible.