HW #5 Solutions

Problems 6.2, 6.3, 6.4

6.2)

6.2 Let the "uniform" ensemble of energy E be defined as the ensemble of all systems of the given type with energy less than E. The equivalence between (6.29) and (6.27) means that we should obtain the same thermodynamic functions from the "uniform" ensemble of energy E as from the microcanonical ensemble of energy E. In particular, the internal energy is E in both ensembles. Explain why this seemingly paradoxical result is true.

As we add more energy to a system, there becomes an increasing number of ways that we can divide this energy across the system. As a quick estimate, consider the number of ways we can organize E units of energy (where E is an integer) is given by $E!$. In thermodynamics, we expect E to be large (recall $U = \frac{3}{2} NkT$ and N is large), therefore, applying Stirling's approximation, we see that the number of ways we can organize E units of energy goes like

$$\sim E^E e^{-E} \sim E^E \quad \text{for large } E$$

Therefore even small increases in E will lead to exponential growth. Because of this exponential growth, even if we increase E by 1, we see that

$$\frac{(E+1)^{E+1}}{E^E} = E\left(1 + \frac{1}{E}\right)^{E+1} = E \exp\left[(E+1)\ln\left(1 + \frac{1}{E}\right)\right] \simeq E \exp\left[1 + \frac{1}{E}\right] \sim E \gg 1$$

Therefore even small increases lead to large growth. Therefore, even if we consider all of the ways we can divide units of energy $E' < E$, they are still subdominant to the number of ways we can organize E units of energy.

$$\frac{\sum\limits_{i=1}^{E+1} (E+1-i)^{E+1-i}}{(E+1)^{E+1}} = \sum\limits_{i=1}^{E+1} E^{-i}\left(1 + \frac{1-i}{E}\right)^{E+1-i} = \sum\limits_{x=0}^{E} E^{x-E-1}\left(\frac{x}{E}\right)^{x} = \frac{1}{E^{E+1}} \sum\limits_{x=0}^{E} x^{x}$$

Plugging in large values of E to the final expression, you would find that this is $\ll 1$.

Now microstates in ensemble represent different ways energy can be used/organized/divided-up among the system. Therefore, based on the analysis above, _most_ of the microstates will have an energy E, because those microstates will overwhelmingly outnumber the microstates of states w/ energies less than E.

Ultimately, whichever ensemble we use will lead to the same result, because in both instances, most microstates have energy E & $\therefore$ E represents the internal energy of the actual thermodynamic system.

(6.3)

6.3 Consider a system of N free particles in which the energy of each particle can assume two and only two distinct values, 0 and E ($E > 0$). Denote by n_0 and n_1 the occupation numbers of the energy level 0 and E, respectively. The total energy of the system is U.

(*a*) Find the entropy of such a system.

(*b*) Find the most probable values of n_0 and n_1, and find the mean square fluctuations of these quantities.

(*c*) Find the temperature as a function of U, and show that it can be negative.

(*d*) What happens when a system of negative temperature is allowed to exchange heat with a system of positive temperature?

Reference. N. F. Ramsey, *Phys. Rev.* **103**, 20 (1956).

(a) This is similar to the problems we tackled in Problem Session 4. In this case we have particles that can take energies $\tilde{E}_j$

$$\tilde{E}_j = jE, \quad j=0,1 \quad ; \quad U = \sum_{j=0}^{1} n_j \tilde{E}_j \quad ; \quad N = \sum_{j=0}^{1} n_j$$

n_j = occupation number defined for each energy level j.

To find the entropy we want to find the number of microstates in which N particles can be arranged in the two energy states to satisfy a total energy U for the system. Only particles in the $\tilde{E}_1$ state contribute to U.

$$\Rightarrow n_1 = U/\tilde{E}_1 = U/E$$

The number of microstates can be calculated by determining the amount of ways we can split up U among the N particles. But only n_1 particles contribute to the energy; therefore, alternatively we can think of the number of microstates as the number of ways we can arrange N particles into a subset of n_1 particles, given by $n_1 = U/E$. This is simply given by

$$\Omega = \binom{N}{n_1} = \frac{N!}{(N-U/E)! \, U/E!}$$

Ω = # of microstates

$\binom{n}{k}$ = binomial coefficient

Taking the natural log & applying Stirling's approximation of $\ln n! \simeq n \ln n - n$

$$S \simeq k\left[N\ln N - \cancel{N} - (N-U/E)\ln(N-U/E) + \cancel{N} - U/E - U/E\ln U/E + \cancel{U/E}\right]$$

$$= k\left[N\ln N - (N-U/E)\ln(N-U/E) - U/E\ln U/E\right]$$

Or defining $\alpha \equiv U/NE$

$$\boxed{S \simeq Nk\left[\ln\left(\frac{1}{1-\alpha}\right) + \alpha \ln\left(\frac{1-\alpha}{\alpha}\right)\right]}$$

b) Recall that the mean square fluctuations of a variable x are

$$\langle (x-\bar{x})^2 \rangle = \langle x^2 \rangle + \bar{x}^2 - 2\bar{x}\langle x \rangle$$

where $\bar{x}$ is the average value & $\langle x \rangle$ is the most probable value of x and $\langle x^2 \rangle$ is the most probable value of x^2. In statistical mechanics we understand the average as the most probable value, so that

$$\langle (x-\bar{x})^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

For this system, given energy U, then n_1 must be equal to U/E. Therefore, even when considering an ensemble of these systems, all system must have $n_1 = U/E$ & $n_0 = N - U/E$ given energy U. Fluctuations can only exist if there is some uncertainty in U.

$$\therefore \quad \langle (n_1 - \bar{n}_1)^2 \rangle = [\langle U^2 \rangle - \langle U \rangle^2]/E^2$$

$$\langle (n_0 - \bar{n}_0)^2 \rangle = [\langle (N-U/E)^2 \rangle - \langle N-U/E \rangle^2]$$

$$= [N^2 - 2N\langle U \rangle/E + \langle U^2 \rangle/E^2 - N^2 - \langle U \rangle^2/E^2 + 2N\langle U \rangle/E]$$

$$= [\langle U^2 \rangle - \langle U \rangle^2]/E^2$$

$\therefore$ the mean square fluctuations of both n_0 & n_1 depend on the mean square fluctuations of U.

c) From the microcanonical ensemble framework, the temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{d\alpha}{dU}\left(\frac{\partial S}{\partial \alpha}\right) = \frac{d\alpha}{dU}\left[\frac{Nk}{1-\alpha} - \frac{Nk\alpha}{1-\alpha} - \frac{Nk\alpha}{\alpha} + Nk\ln\left(\frac{1-\alpha}{\alpha}\right)\right]$$

Note that the first 3 terms cancel & $d\alpha/dU = 1/NE$

$$\Rightarrow \boxed{\frac{1}{T} = \frac{k}{E}\ln\left(\frac{NE}{U}-1\right)} \quad \leftarrow \text{We see that this is negative iff}$$

$$\frac{NE}{2} < U < NE$$

using $N = n_0 + n_1$ & $U = En_1$

$$\Rightarrow \boxed{\frac{n_0+n_1}{2} < n_1 < n_0+n_1}$$

Obviously the upper bound is always satisfied $\therefore$ the defining criteria is when

$$\frac{n_0+n_1}{2} < n_1 \qquad \Rightarrow \qquad \boxed{n_0 < n_1}$$

d) I think it is helpful to first examine the types of bounds a negative temperature puts on the entropy. So consider when $U = jNE$ where $j \in [\frac{1}{2}, 1] \Rightarrow \alpha = j$

$$\Rightarrow \frac{S}{Nk} = \ln\left(\frac{1}{1-j}\right) + j \ln\left(\frac{1-j}{j}\right)$$

Therefore as j increases from $\frac{1}{2} \to 1$ (i.e. as we increase the energy of the system) we find that

$$\frac{\Delta S}{Nk} < 0 \qquad \textcolor{blue}{\leftarrow \text{This can be seen by plotting } j \text{ from } \frac{1}{2} \to 1}$$

In fact if we look @ the critical points of $S(j)$

$$\Rightarrow \quad 0 = (1-j) + \ln\left(\frac{1-j}{j}\right) - \frac{j^2}{1-j} \quad \Rightarrow \quad j = \frac{1}{2}$$

By plotting S, we indeed see that S is maximized when $U = \frac{NE}{2}$, i.e. when $n_0 = n_1$. Therefore negative temperature describes a system that decreases in entropy as you pump energy into the system. In this case, this effect is caused by bounding the energy.

Put in contact with a reservoir of positive temperature, the systems will reach equilibrium by maximizing their entropy, $dS \geq 0$

Since $\qquad\qquad dQ = T\,dS \qquad \& \qquad T < 0 \text{ w/ } dS \geq 0$

We see that heat can only flow from the system. Therefore we interpret the negative temperature system as "hotter."

(6.4)

6.4 Using the corrected entropy formula (6.62), work out the entropy of mixing for the case of different gases and for the case of identical gases, thus showing explicitly that there is no Gibbs paradox.

Let's begin by writing Eqn (6.62) in the form

$$\frac{S}{k} = N \log\left[\frac{V}{N}\left(\frac{3kT}{2}\right)^{3/2}\right] + \frac{3}{2}N\left(\frac{5}{3} + \log\frac{4\pi m}{3h^2}\right) \quad (6.62)$$

$$= N \log\left(\frac{V}{N} u^{3/2}\right) + N S_0$$

$$S_0 \equiv \frac{3}{2}\left(\frac{5}{3} + \log\frac{4\pi m}{3h^2}\right)$$

$$u = \frac{3}{2}kT$$

Where u & S_0 are quantities that do not depend on N or V. I believe that, in this problem, when asked for the entropy of mixing, Huang is asking for the change in entropy due to mixing the gases.

Therefore, assume I have two gases. The first gas has N_1 particles that occupy V_1 volume, while the second gas has N_2 particles that occupy a volume V_2. If the gases are kept separate, their combined entropy is just the sum of the separate entropy for each gas:

$$\frac{S}{k} = N_1 \log\left(\frac{V_1}{N_1} u^{3/2}\right) + N_2 \log\left(\frac{V_2}{N_2} u^{3/2}\right) + N_1 S_0^{(1)} + N_2 S_0^{(2)}$$

← recall that S_0 depends on mass of individual particles, so
⇒ $S_0^{(i)} = S_0$ using mass of particles in gas (i).

Now, if we let the two the gases mix, we can calculate the total entropy of the system by summing the entropy of each gas, but we must now take into consideration that each gas now occupies a volume $V_1 + V_2$

$$\Rightarrow \frac{S_{mix}}{k} = N_1 \log\left(\frac{V_1+V_2}{N_1} u^{3/2}\right) + N_2 \log\left(\frac{V_1+V_2}{N_2} u^{3/2}\right) + N_1 S_0^{(1)} + N_2 S_0^{(2)}$$

$$\Rightarrow \frac{\Delta S}{k} = \frac{S_{mix}-S}{k} = N_1 \log\left(\frac{V_1+V_2}{V_1}\right) + N_2 \log\left(\frac{V_1+V_2}{V_2}\right)$$

Which we can rewrite as $\boxed{\Delta S = N_1 k \log(V/V_1) + N_2 k \log(V/V_2)}$ $V \equiv V_1 + V_2$

If we are dealing with identical gases at the same temperature & pressure, then the ratio $N_1/V_1 = N_2/V_2 = N_1+N_2/V_2$ is constant. Additionally, once the gases begin to mix, we have to treat this mixture as 1 gas with $N = N_1 + N_2$ particles in a volume V

$$\Rightarrow S_{mix} = Nk \log\left(\frac{V}{N} u^{3/2}\right) + N k s_0$$

due to the "indistinguishability of particles"

$$\Rightarrow \boxed{\Delta S = 0}$$ just as we would expect. Therefore there is no Gibbs Paradox in this instance.