HW 3 Solution.

1 [Easy review question 1]
Due to the ligand field the degeneracy of the d-orbitals of the chromium ion Cr^{3+} is lifted, and the spin Hamiltonian has the following form

$$H = D(S_z^2 - S(S+1)/2),$$

where $D > 0$ is a constant with $S = 3/2$ (the cation is in the term ${}^4\mathrm{F}_{3/2}$).
(1) Obtain the canonical partition function of the system consisting of N such ions (without interactions).
(2) Compute the internal energy of the system
(3) Calculate entropy and the specific heat C.
(4) Show that its high temperature specific heat behaves as $\propto T^{-2}$.
(5) Suppose $C = 0.023 k_B/T^2$ at high temperatures. Determine D in K.

Solution
(1) By definition, and statistical independence of all the spins, we have

$$Z = \left[Tr\, e^{-\beta H}\right]^N.$$

Each spin is with total angular momentum quantum number $S = 3/2$. The eigenstates of H and the simultaneous eigenstates for S and S_z agree. Eigenkets $|\ell, m\rangle$ may be written as $|3/2, \pm 3/2\rangle$ and $|3/2, \pm 1/2\rangle$. Since we know

$$H|3/2, \pm 3/2\rangle = (3D/8)|3/2, \pm 3/2\rangle, \quad H|3/2, \pm 1/2\rangle = -(13D/8)|3/2, \pm 1/2\rangle,$$

$$Z = [2e^{-(3\beta D/8)} + 2e^{13\beta D/8}]^N.$$

(There were several people who multiplied $1/N!$ to this. Well, I did not say anything, but since we are not discussing spatial motion at all (no kinetic energy in this case), you do not need this factor.)

From this we can obtain the occupation probabilities of the microstates as

$$p(m = \pm 3/2) = \frac{1}{2(1+e^{2\beta D})},\ p(m = \pm 1/2) = \frac{e^{2\beta D}}{2(1+e^{2\beta D})}. \tag{1}$$

(2) With the aid of the Gibbs-Helmholtz equation, we have

$$E = -\left.\frac{\partial \log Z}{\partial \beta}\right|_N = N\frac{-(3D/8)e^{-(3\beta D/8)} - (13D/8)e^{13\beta D/8}}{e^{-(3\beta D/8)} + e^{13\beta D/8}} = ND\frac{3 - 13e^{2\beta D}}{8(1+e^{2\beta D})}.$$

(3)

$$\begin{aligned} S &= \frac{E - A}{T} = \frac{ND}{T}\frac{3 - 13e^{2\beta D}}{8(1+e^{2\beta D})} + Nk_B \log\{2[e^{-(3\beta D/8)} + e^{13\beta D/8}]\} \\ &= -2\frac{ND}{T}\frac{e^{2\beta D}}{1+e^{2\beta D}} + Nk_B\log\{2[1+e^{2\beta D}]\} \end{aligned}$$

Actually, this formula is more easily obtained from the Shannon formula. By using (1), the Shannon formula gives us

$$S = -Nk_B\left[\frac{1}{(1+e^{2\beta D})}\log\frac{1}{2(1+e^{2\beta D})} + \frac{e^{2\beta D}}{(1+e^{2\beta D})}\log\frac{e^{2\beta D}}{2(1+e^{2\beta D})}\right]$$

It is clear that this agrees with the thermodynamic result.

The specific heat is obtained by

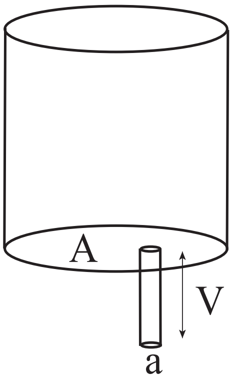
$$\begin{aligned} C &= T\left.\frac{\partial S}{\partial T}\right|_N = -\beta\frac{\partial S}{\partial \beta} = \beta\frac{\partial}{\partial \beta}\left\{2Nk_BD\beta\frac{e^{2\beta D}}{1+e^{2\beta D}} - Nk_B\log\{2[1+e^{2\beta D}]\right\} \\ &= 2Nk_B\beta D\frac{e^{2\beta D}}{1+e^{2\beta D}} + 2Nk_BD\beta^2\left[\frac{2De^{2\beta D}}{1+e^{2\beta D}} - \frac{2De^{4\beta D}}{(1+e^{2\beta D})^2}\right] - \frac{2DNk_Be^{2\beta D}}{1+e^{2\beta D}} \qquad (2) \\ &= 2Nk_BD^2\beta^2\left[\frac{2e^{2\beta D}}{(1+e^{2\beta D})^2}\right] \end{aligned}$$

$\partial E/\partial T$ can also be used. Probably, this is better.

(4) Obvious from (3).

(5) Since $C \simeq k_B(D\beta)^2 = k_BD^2/k_B^2T^2 = 0.023k_B/T^2$, so $(D/k_B)^2 = 0.023$. Hence $D/k_B = 0.023^{1/2} = 0.152$ K. I made a careless error in the original solution (but I never subtract any point for not outrageous careless errors).

2 [Easy review question 2]



In a very deep cylindrical hole is a 'putting green' and a cup. That is, there is a 2d system confined to a area of A in which there is a potential hole of depth V and area a ($\ll A$), At temperature T, what it the relation among A, a and V if a particle resides evenly inside and outside the 'cup'? [This trivial-looking question has some relation to biomolecular conformation changes.]

Solution

The canonical partition function for a single particle is (as a 2D system)

$$Z = A + a\,e^{\beta V}.$$

Thus, $A = a\,e^{\beta V}$ is required.

The flat 'green' corresponds to a disordered (high entropy state) and the states in the cup corresponds to an ordered low energy state. This is a for to of a model of the first order phase transition between liquid and crystal or proteins between folded and denatured states.

3. [Jarzynski's equality]

With a certain protocol, starting from a canonical distribution at temperature 300 K, work has been added to an isolated system to modify the initial Hamiltonian H_0 to the final one H_1 by tweaking the control parameter. The observed work needed to change the parameter in the Hamiltonian was found to obey a Gaussian distribution with average 38 pNnm per particle and the standard deviation 17 pN·nm.

(1) Find the free energy difference between the equilibrium state defined by the initial Hamiltonian H_0 and that defined by the final Hamiltonian H_1 at 300 K.

(2) What is the entropy change between these two equilibria?

(3) We know the average of the work W is (significantly) larger than the reversible work. What is the difference? You should have realized that if the distribution of W is sharp, then Jarzynski's equality is hardly possible. Can you imagine what kind of unusual fluctuations are required to make Jarzynski's equality to hold? Explain why your life is too short to confirm the equality if the system contains 10^{15} particles.

Solution
(1) Although it is a well-known integral, let us do it honestly

$$\begin{aligned}
\left\langle e^{-\beta W}\right\rangle &= \int dW\, e^{-\beta W}\frac{1}{\sqrt{2\pi\sigma^2}}e^{-(W-\langle W\rangle)^2/2\sigma^2} && (3)\\
&= \frac{1}{\sqrt{2\pi\sigma^2}}e^{-\beta\langle W\rangle}\int dx\, e^{-\beta x-x^2/2\sigma^2} && (4)\\
&= \frac{1}{\sqrt{2\pi\sigma^2}}e^{-\beta\langle W\rangle}\int dx\, e^{-(x+\beta\sigma^2)^2/2\sigma^2+(1/2)\beta^2\sigma^2} && (5)\\
&= e^{-\beta\langle W\rangle+\beta^2\sigma^2/2}. && (6)
\end{aligned}$$

This formula is more easily computed by the so-called cumulant expansion (see Chapter 4 for details):

$$\begin{aligned}
\log\left\langle e^{-\beta W}\right\rangle &= \log\left\langle 1-\beta W+\frac{1}{2}\beta^2W^2+\cdots\right\rangle\\
&= \log\left[1-\beta\langle W\rangle+\frac{1}{2}\beta^2\langle W^2\rangle+\cdots\right]\\
&= -\beta\langle W\rangle+\frac{1}{2}\left(\beta^2\langle W^2\rangle-\beta^2\langle W\rangle^2\right)+\cdots
\end{aligned} \tag{7}$$

but for a Gaussian distributions, only the first and the second cumulants survive (i.e., $\cdots = 0$). Therefore,

$$\log\left\langle e^{-\beta W}\right\rangle = -\beta\langle W\rangle+\frac{1}{2}\beta^2\sigma^2$$

Consequently,

$$\Delta A = k_BT(\beta\langle W\rangle-\beta^2\sigma^2/2) = \langle W\rangle-\frac{1}{2}\beta\sigma^2.$$

Therefore, numerically, noting $k_BT = 4.14$ pN·nm, we estimate $\Delta A = 38 - 17^2/8.28 = 3.1$ pN·nm.

(2) This is a 'trap question.' Perhaps a bit unkind. It is true that we can obtain ΔA. To get ΔS we need ΔE (or if you wish to use the Gibbs-Helmholtz equation, we need the T dependence of ΔA). Can we obtain ΔE? The system is not energetically closed, so the heat generated by the irreversible work (since $W \gg \Delta A$, definitely the work is mostly irreversible) leaves the system. Therefore, we cannot obtain ΔE. Therefore, it is absolutely impossible to obtain δE. Do not confuse dissipated energy and entropy increase.

(3) Since this asks about the time scale, there is no way to quantitatively answer this question. I simply ask for an intuitive answer.

In the present case W/k_BT is about 10, so you could expect even $W = -\langle W\rangle$ is realizable easily (for our time scale). Therefore, even though $\langle W \rangle$ is significantly larger than the reversible work, still you need not live long to verify Jarzynski's equality. Suppose the system contains about 10^{15} particles (it is about 10^{-9} moles, so this corresponds to about 2 to 3 cubic micrometers of water; it is roughly a size of bacterium cell. Now, you apply some work that can affect the cell position or shape, then it is about 10^{10} times as large as the work (semi macroscopic work) considered in this problem. If you consider the Boltzmann factor, it is clear that such fluctuations of scale of order $\sqrt{10^{10}}$ is impossible.

4. [Entropy-information conversion]
Show that 1 eu (cal/K·mol) is about 0.72 bit (per molecule) as noted in the lecture notes, but I wish you to confirm this by yourself.

Solution
$1eu = Nk_B \log p$, so for a single molecule $\log p = 4.2/R = 4.2/8.31 = 0.505$. We must convert this to bits: $\log_2 p = \log p / \log 2$, so 1 eu is equal to $0.505/\log 2 \simeq 0.726$. [I should revised the value in the lecture notes.]

5. [Information gained by cheating]
In a test students must answer whether given statement is correct or incorrect. It is known that two possibilities have equal probabilities. A student cannot guess the answer at all, so he decides to exploit an opportunity that the best student in his class is just in his convenient neighborhood. He knows that the best student's success rate is 75 % when he says 'correct,' and 95 % when he says 'incorrect.' What is the information (in bits) he can gain by looking at the best student's answer?

Solution
We must assume that the best student's choice is on the average even; this must be so, since the correct cases are even. When he says correct: The remaining entropy is obtained by the Shannon formula, so

$$S = -(3/4)\log_2(3/4) - (1/4)\log_2(1/4) = 0.81$$

This means, you can gain $1 - 0.81 = 0.19$ bits. In case, he says incorrect,

$$S = -0.95\log_2(0.95) - 0.05\log_2(0.05) = 0.286$$

That is , you can get $1 - 0.286 = 0.714$ bits. On the average about 0.45 bits.

Is this averaging procedure correct? Let p_1 be the best student to say 'incorrect', and p_2 to say 'correct.' Then, $0.95p_1 + .25p_2$ must be the probability that 'incorrect' is the correct choice. Similarly, $0.05p_1 + 0.75p_2$ must be the probability that 'correct' is the correct choice. They are even, so $0.95p_1 + 0.25p_2 = 0.05p_1 + 0.75p_2 = 1/2$, or $0.9p_1 = 0.5p_2$. Thus, the probability to see his choice is 'incorrect' is only 5/14, and 'correct' 9/14. Hence, 0.38 bits should be the correct estimate. The expected score of this best student is about 82, miserable.

If the cheater looks at the answer of the best student (actually this student is not so good as we have seen), what the cheater sees is answer 'yes' or 'no' irrespective of the true answer. Therefore, we must classify the cases according to the answer. The answer 'no' is much more reliable: 95% correct! Thus, the remaining entropy (= uncertainty) is 0.286 bits. Initially, nothing is known, so the amount of ignorance is 1bit (do not forget that the problem is a yes-no question; those who gave more than 1 bit for the answer get nice penalty), so $1 - 0.286 = 0.714$ bits is the information gain. The answer 'yes' gives only $1 - 0.81 = 0.19$

bits. These gains must be averaged over both the cases.

Information and Entropy
[I realized that the relation between these concepts were not explained well in my notes. This is an appendix.]

Entropy measures the extent of randomness; we do not know which choice/possibility is realized, so entropy may be understood as a measure of our ignorance. Therefore, if the entropy of the 'collection of choices' decreases from S_I to S_F, then $\Delta S = S_F - S_I < 0$ (the decrease of entropy); our knowledge should have increased by $-\Delta S$, which is called (the gain of) information: $I = -\Delta S$.

HOWEVER, sometimes S is identified with information itself. An example is already in the lecture notes. We introduced Shannon's formula asking how much information we can send using n letters. As can be read there, the information we can send by a sentence increases with the number of possible sentences we can compose. Therefore, the entropy of the sentences may be understood as the amount of information we can send. In such contexts, entropy is identified with information.

6. [Information in the message]
(1) If you are given a positive integer, it must start with 1, 2, $\cdots$, or 9. If all the numbers appear evenly, what is the information in the message that actually the first digit was 9 (in bits)?
(2) Actually, it is well known that the first digit D does not distribute evenly, but empirically follows the so-called first digit law: $P(D) = \log_{10}(1 + 1/D)$ (approximately). Then, what is the information you can gain by knowing the first digit law (relative to the equal distribution 'prejudice.')?
(3) Now knowing this, you are told again the first digit was 9. What is the information of this message (in bits)?

The solution is in the lecture notes.