Statistical Mechanics I HW3

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1 Problem 1

a. The volume of an N-dimensional hypersphere of radius R is:

$$V_N(R) = \frac{\pi^{\frac{N}{2}}}{\Gamma(\frac{N}{2}+1)} R^N \tag{1.1}$$

We find the probability of finding a point inside the sphere of radius 0.99999999 by dividing the volume of that sphere by the volume of the unit sphere (R=1).

$$P_{.99999999} = V_N(.99999999)/V_N(.99999999) \tag{1.2}$$

$$P_{.99999999} = .99999999^N \tag{1.3}$$

b. When N-3 the probability inside the shell is practically 1 $(1 - 3E^{-8})$. For $N = N_A$ the probability inside the shell is practically 0 $(\ll 1E^{-10})$.

c. This demonstrates that for the microcanonical ensemble consisting of very large numbers $(\geq N_A)$ of molecules $\Sigma(E) \approxeq \Gamma(E)$. Therefore the entropy can be defined as either $k \ln \Sigma(E)$ or $k \ln \Gamma(E)$.

2 Problem 2

The harmonic oscillator Hamiltonian is a quadratic form that represents an ellipse in phase space. Writing the Hamiltonian in the common $\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$ form:

$$H = p^2 + (M\omega q)^2 = 2MU \tag{2.1}$$

$$\frac{p^2}{2MU} + \frac{M\omega^2 q^2}{2U} = 1 \tag{2.2}$$

$$a = \sqrt{2MU}, \; b = \sqrt{\frac{2U}{M\omega^2}} \tag{2.3}$$

So we have an ellipse with semimajor axis $\sqrt{2MU}$, semiminor axis $\sqrt{\frac{2U}{M\omega^2}}$, and area $\frac{2\pi U}{\omega}$.

a) With N independent harmonic oscillators the system will consist of N ellipses, each with 2 coordinates, in phase space.

$$\Gamma(U) = \frac{1}{N!}\left(\frac{2\pi U}{\omega}\right)^N \tag{2.4}$$

b) We calculate the entropy from $S = k\ln\Gamma(U)$.

$$\Gamma(U) = \frac{1}{N!}\left(\frac{2\pi U}{\omega}\right)^N \tag{2.5}$$

$$S = k\ln\Gamma(U) \tag{2.6}$$

$$S = k\ln\left(\frac{2\pi U}{\omega}\right)^N - k\ln N! \tag{2.7}$$

$$S = Nk\ln\left(\frac{2\pi U}{\omega}\right) - Nk\ln N + Nk \tag{2.8}$$

$$S = Nk\left(\ln\frac{2\pi U}{N\omega} + 1\right) \tag{2.9}$$

Since the Hamiltonian is quadratic each coordinate contributes $\frac{1}{2}kT$ energy, so $U = NkT$.

$$S = Nk\left(1 + \ln\frac{2\pi kT}{\omega}\right) \tag{2.10}$$

3   Problem 3

a) For the two-level system of N particles the energy U is $n_1 E$. With n_1 and N fixed, n_0 is also fixed. The number of states $\Gamma(U)$ is $\binom{N}{n_1}$. The entropy is then:

$$S = k\ln\frac{N!}{n_0!n_1!} \tag{3.1}$$

b) From the binomial theorem, the total number of states is $\sum_{k=0}^{N}\binom{N}{k} = 2^N$. The statistics for n_0 and n_1 will be calculated in the same manner.

$$<n_0> = \sum_{k=0}^{N}\binom{N}{k}k/2^n \tag{3.2}$$

$$<n_0> = \frac{N2^{N-1}}{2^N} = \frac{N}{2} \tag{3.3}$$

$$<n_0^2> = \sum_{k=0}^{N}\binom{N}{k}k^2/2^n \tag{3.4}$$

$$<n_0^2> = \frac{(N+N^2)2^{N-2}}{2^N} = \frac{N^2+N}{4} \tag{3.5}$$

The mean square fluctuation is:

$$\frac{< n_0^2 > - < n_0 >^2}{< n_0 >^2} = \frac{1}{N} \tag{3.6}$$

The analysis for n_1 is identical.

c) We find the temperature from the entropy.

$$S(U) = k \ln \Gamma(U) \tag{3.7}$$

$$S = k \ln \frac{N!}{n_0! n_1!} \tag{3.8}$$

$$\frac{S}{k} = -n_0 \ln \frac{n_0}{N} - n_1 \ln \frac{n_1}{N} \tag{3.9}$$

$$\frac{S}{Nk} = -\frac{n_0}{N} \ln \frac{n_0}{N} - \frac{n_1}{N} \ln \frac{n_1}{N} \tag{3.10}$$

$$\frac{n_0}{N} = \frac{U}{NE}, \ \frac{n_1}{N} = 1 - \frac{U}{NE} \tag{3.11}$$

We now take $\frac{\partial S}{\partial U} = \frac{1}{T}$ and use a numerical program to find the derivative.

$$\frac{S}{Nk} = -\frac{U}{NE} \ln \frac{U}{NE} - (1 - \frac{U}{NE}) \ln 1 - \frac{U}{NE} \tag{3.12}$$

$$\frac{1}{Nk} \frac{\partial S}{\partial U} = \frac{1}{NkT} = \frac{2}{NE} \tanh^{-1} (1 - \frac{2U}{NE}) \tag{3.13}$$

$$T = \frac{E}{2k} \frac{1}{\tanh^{-1} (1 - \frac{2U}{NE})} = \frac{E}{2k} \frac{1}{\tanh^{-1} (1 - \frac{2n_0 E}{NE})} \tag{3.14}$$

When $n_0 > \frac{N}{2}$ the $\tanh^{-1}$ term, and hence the temperature, will be negative. The temperature scale starts at 0 for minimum energy, proceeds to $+\infty$ as $n_0 \to \frac{N}{2}$, then "wraps around" to $-\infty$ and approaches 0^- as the system approaches the maximum energy state.

   d) States with negative temperature have higher energy than states with positive temperature. Heat will flow from the system with negative temperature to the system with positive temeprature.

4   Problem 4

Following Pathria's discussion of the simple harmonic oscillator we take the general coordinate θ and angular momentum L:

$$\theta = \frac{h}{\ell} \cos (\omega t + \phi) \tag{4.1}$$

$$L = m\ell^2 \frac{d\theta}{dt} = -hm\ell\omega \sin (\omega t + \phi) \tag{4.2}$$

We can now write the phase space path in the form of an ellipse:

$$\frac{q^2}{(\frac{h}{\ell})^2} + \frac{p^2}{(hm\ell\omega)^2} = \cos^2\left(\omega t + \phi\right) + \sin^2\left(\omega t + \phi\right) = 1 \qquad (4.3)$$

With semimajor axis $\frac{h}{\ell}$ and semiminor axis $hm\ell\omega$ the area of the ellipse is $\pi m\omega h^2$. The energy of the pendulum is $E = \frac{1}{2}m\omega^2 h^2$ and the period of the pendulum is $\frac{2\pi}{\omega}$. So we find that $E\tau = \pi m\omega h^2$, the area of the ellipse.

5 Problem 5

The uncorrected and corrected entropy formulas are:

$$S_{uncorrected} = Nk \ln V u^{\frac{3}{2}} + s_0 \qquad (5.1)$$

$$S_{corrected} = Nk \ln \frac{V}{N} u^{\frac{3}{2}} + s_1 \qquad (5.2)$$

For dissimilar gasses the N_1 and N_2 cannot be combined into a total N. Each gas expands to take up the total volume $V = V_1 + V_2$. The change in entropy calculated using the uncorrected formula is:

$$\frac{\Delta S}{k} = N_1 \ln V u^{3/2} - N_1 \ln V_1 u^{3/2} + N_2 \ln V u^{3/2} - N_2 \ln V_2 u^{3/2} \qquad (5.3)$$

$$\frac{\Delta S}{k} = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \qquad (5.4)$$

Using the corrected entropy formula:

$$\frac{\Delta S}{k} = N_1 \ln \frac{V}{N_1} u^{3/2} - N_1 \ln \frac{V_1}{N_1} u^{3/2} + N_2 \ln \frac{V}{N_1} u^{3/2} - N_2 \ln \frac{V_2}{N_2} u^{3/2} \qquad (5.5)$$

$$\frac{\Delta S}{k} = N_1 \ln \frac{V/N_1}{V_1/N_1} + N_2 \ln \frac{V/N_2}{V_2/N_2} \qquad (5.6)$$

$$\frac{\Delta S}{k} = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \qquad (5.7)$$

So for different gasses the corrected entropy formula gives the same result as the uncorrected formula.
For identical gasses the uncorrected entropy gives the same result, which is incorrect. The corrected entropy formula gives:

$$\frac{\Delta S}{k} = N \ln \frac{V}{N} u^{3/2} - N_1 \ln \frac{V_1}{N_1} u^{3/2} - N_2 \ln \frac{V_2}{N_2} u^{3/2} \qquad (5.8)$$

Since the ratios $\frac{V}{N} = \frac{V_1}{N_1} = \frac{V_2}{N_2}$ we can write this as:

$$\frac{\Delta S}{k} = N \ln \frac{V}{N} u^{3/2} - (N_1 + N_2) \ln \frac{V}{N} u^{3/2} = 0 \qquad (5.9)$$

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So the corrected entropy formula gives no change in entropy as expected.
We find the internal energy $U(S, V)$ by rearranging the entropy equations.
Ignoring the constant term, the uncorrected entropy formula gives:

$$S = Nk \ln V u^{\frac{3}{2}} \tag{5.10}$$

$$\frac{S}{Nk} = \ln V u^{\frac{3}{2}} \tag{5.11}$$

$$e^{S/Nk} = V u^{\frac{3}{2}} \tag{5.12}$$

$$u = V^{-2/3} e^{\frac{2S}{3Nk}} \tag{5.13}$$

$$U = NV^{-2/3} e^{\frac{2S}{3Nk}} \tag{5.14}$$

For the corrected entropy formula:

$$S = Nk \ln \frac{V}{N} u^{\frac{3}{2}} \tag{5.15}$$

$$\frac{S}{Nk} = \ln \frac{V}{N} u^{\frac{3}{2}} \tag{5.16}$$

$$e^{S/Nk} = \frac{V}{N} u^{\frac{3}{2}} \tag{5.17}$$

$$u = (\frac{N}{V})^{2/3} e^{\frac{2S}{3Nk}} \tag{5.18}$$

$$U = \frac{N^{5/3}}{V^{2/3}} e^{\frac{2S}{3Nk}} \tag{5.19}$$

$$\tag{5.20}$$

To find the temperature we take $\left(\frac{\partial S}{\partial U}\right)_{N,V}$. For the uncorrected entropy formula:

$$U = NV^{-2/3} e^{\frac{2S}{3Nk}} \tag{5.21}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{2}{3kV^{2/3}} e^{\frac{2S}{3Nk}} \tag{5.22}$$

For the corrected entropy formula:

$$U = \frac{N^{5/3}}{V^{2/3}} e^{\frac{2S}{3Nk}} \tag{5.23}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{2}{3k} \left(\frac{N}{V}\right)^{2/3} e^{\frac{2S}{3Nk}} \tag{5.24}$$

We now find the chemical potential from $\mu = (\frac{\partial U}{\partial N})_{S,V}$. For the uncorrected

entropy formula:

$$U = NV^{-2/3}e^{\frac{2S}{3Nk}} \tag{5.25}$$

$$\mu = (\frac{\partial U}{\partial N})_{S,V} \tag{5.26}$$

$$\mu = V^{-2/3}\left(1 - \frac{2S}{3kN}\right)e^{\frac{2S}{3kN}} \tag{5.27}$$

For the corrected entropy formula:

$$U = \frac{N^{5/3}}{V^{2/3}}e^{\frac{2S}{3Nk}} \tag{5.28}$$

$$\mu = (\frac{\partial U}{\partial N})_{S,V} \tag{5.29}$$

$$\mu = V^{-2/3}\left(\frac{5}{3}N^{2/3} - \frac{2S}{3kN^{1/3}}\right)e^{\frac{2S}{3kN}} \tag{5.30}$$