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Statistical Mechanics Spring, 2002

Problem Set V Solutions v1.11

1) (Counts as 2 problems) a) Show that for a classical ideal gas (of N indistinguishable particles), the observable entropy, $\mathcal{S}$, associated with a coarse-grained distribution function, $\{n_i\}$, is given by $\mathcal{S} = -k\sum n_i \ln n_i$ (apart from an additive constant depending only upon the "cell size" in γ). Thus, in the "continuum limit", for a distribution function $f(\vec{x},\vec{p})$ we have $\mathcal{S} = -k\int f \ln f d^3x d^3p$. Evaluate $\mathcal{S}$ for the Maxwell-Boltzmann distribution function and show that for this "most probable" case, $\mathcal{S}$ equals the "thermodynamic entropy", S, defined by $S = k\ln(\Omega/N!)$.

Solution: The entropy observable entropy is defined as

$$\mathcal{S} = k \ln \frac{\mathcal{V}(\Gamma_{\{n_i\}} \cap \Gamma_E)}{N!}.$$

Since the energy only cares about how many particles are in each state and not which particles are in each state, the volume in phase space is

$$\mathcal{V}(\Gamma_{\{n_i\}} \cap \Gamma_E) = \mathcal{V}(\Gamma_{\{n_i\}}) = \frac{v^N N!}{\Pi_i\,(n_i!)},$$

where v is the volume of an individual cell. Using Stirling's approximation, we find that

$$\mathcal{S} = -k\left(\sum_i n_i \ln n_i\right) + kN\left(\ln v + 1\right).$$

The Maxwell-Boltzmann distribution is given by

$$f(x,p) = \frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{\frac{\beta p^2}{2m}}.$$

This integral is very similar to the one carried out in the last problem of HW#3 and yields

$$\mathcal{S} = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln\frac{2\pi m}{\beta} + \ln v + \frac{5}{2}\right].$$

From HW#2 we know that

$$\Omega = \mathcal{V}(\Gamma_E) = \mathcal{V} = V^N \frac{(2\pi m)^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})} E^{\frac{3N}{2}-1}$$

so that

$$S = k\ln\frac{\Omega}{N!} = k\left[N\ln V + \frac{3N}{2}\ln(2\pi m) + \left(\frac{3N}{2}-1\right)\ln E - \frac{3N}{2}\left(\ln N + \ln\frac{3}{2}\right) - N\ln N\right] =$$

$$= kN\left[\ln V - \ln N - \frac{3}{2}\ln\frac{3N}{4\pi mE} + \frac{5}{2}\right] = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln\frac{2\pi m}{\beta} + \frac{5}{2}\right]$$

where we have dropped the 1 in the coefficient of $\ln E$ since N is very large and also used Stirling's approximation. This formula for the entropy is known as the Sakur-Tetrode equation, and only differs by the factor of $\ln v$ from the observable entropy of the MB distribution. ■

b) For a quantum ideal gas, write down the formula for $\mathcal{S}$ for an arbitrary coarse-grained distribution $\{n_i\}$ of the particles into energy levels for the cases of (i) distinguishable particles, (ii) bosons, and (iii) fermions. Substitute the "most probable" distribution derived in class for each case to obtain the thermodynamic entropy, S. Pass to the continuum limit to get integral expressions for S in terms of the parameters α and β. (You need not evaluate these integrals in the boson and fermion cases.) For distinguishable particles, compare your result with the result of problem 2(c) of set II.

Solution: Quantum mechanically, the entropy (observable or thermodynamic) is simply the natural log of the number of microstates. Since the number of microstates corresponding to a given coarse grained distribution was given in class, we can simply go ahead and take the natural log. Thus we get

$$(i)\quad S = k\ln\frac{N!}{\Pi_i(n_i!)}\Pi_j(g_j)^{n_j} = k\left[N\ln N - \sum_i n_i\ln\frac{n_i}{g_i}\right]$$

$$(ii)\quad S = k\ln\Pi_i\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!} = k\sum_i\left[n_i\ln\left(\frac{n_i+g_i-1}{n_i}\right) + (g_i-1)\ln\left(\frac{n_i+g_i-1}{g_i-1}\right)\right]$$

$$(iii)\quad S = k\ln\frac{g_i!}{n_i!(g_i-n_i)!} = k\sum_i\left[n_i\ln\left(\frac{g_i-n_i}{n_i}\right) - g_i\ln\left(\frac{g_i-n_i}{g_i}\right)\right],$$

where g_i is the density of states. The most probable distribution is

$$n_i = \frac{g_i e^{-\alpha-\beta\epsilon_i}}{1+\lambda e^{-\alpha-\beta\epsilon_i}} \equiv \frac{g_i G_i}{1+\lambda G_i},$$

where λ is equal to 0, -1, and 1 for Boltzmanns, bosons, and fermions, respectively, α and β also depend on the kind of particle. Hence, the thermodynamic entropy is

$$(i)\quad \mathcal{S} = k\left[N\ln N + \sum_i(\alpha+\beta\epsilon_i)g_iG_i\right] \;=\; k\left[N\ln N + \alpha N + \beta E\right]$$

$$(ii)\quad \mathcal{S} = k\sum_i g_i\left[\frac{\alpha+\beta\epsilon_i}{G_i^{-1}-1} - \ln(1-G_i)\right] = k\left[\alpha N + \beta E - \sum_i g_i\ln(1-G_i)\right]$$

$$(iii)\quad \mathcal{S} = k\sum_i g_i\left[\frac{\alpha+\beta\epsilon_i}{G_i^{-1}+1} - \ln(1+G_i)\right] = k\left[\alpha N + \beta E - \sum_i g_i\ln(1+G_i)\right],$$

where we have used $g_i - 1 \approx g_i$ in case (ii). Recall that in the continuum limit, the density of states becomes $g(\epsilon)d\epsilon = \frac{V\eta\sqrt{2m^3\epsilon}d\epsilon}{2\pi^2\hbar^2}$. To get the continuum limit, we substitute

$g(\epsilon)$ for g_i and integrate with respect ϵ in place of summing over i. The only interesting case is case (i), where we can actually evaluate the integrals necessary to find α and β. For ideal gas $\beta E = \frac{3}{2}N$ and

$$\alpha = \ln\left(\frac{\eta V}{Nh^3}\right) + \frac{3}{2}\ln\left(\frac{3N}{4\pi m E}\right).$$

Thus we find that

$$(i) \quad S = kN\left[\ln\left(\frac{\eta V}{h^3}\right) - \frac{3}{2}\ln\left(\frac{3N}{4\pi E m}\right) + \frac{3}{2}\right] = kN\left[\ln(\eta V) + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right) - \ln h^3 + \frac{3}{2}\right].$$

Notice that the right-hand most side is very similar to the Sackur-Tetrode equation. By comparing terms, we can see that this corresponds to a coarse-graining where each cell has volume h^3, which is the source of the statement that each quantum mechanical state occupies a volume h in phase space (for a 1-d problem you would have h in lieu of h^3). However, there are also two differences: the numerical constant has changed by one and the first logarithm is missing a factor of N^{-1}. These stem from the fact classically one defines the entropy as $k\ln\frac{\mathcal{V}}{N!}$, whereas quantum mechanically the formula is $k\ln n$, where n is the number of states. For indistinguishable particles these two formulae agree, but for distinguishable particles they differ by a factor of $N!$. The reason for these conventions is that one explicitly divides by $N!$ in the classical formula to make the entropy additive, which follows naturally in the quantum analysis of indistinguishable particles but not for distinguishable particles.

Finally, recall that in HW#2, we found an expression number of states between E and $E + \Delta E$. Thus, the entropy associated with that number of microstates is

$$S = k\ln\left[\frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})}\left(\frac{V}{h^3}\right)^N (2mE)^{\frac{3N}{2}}\frac{\Delta E}{E}\right] = kN\left[\ln(\eta V) - \frac{3}{2}\ln\left(\frac{\beta}{2\pi m}\right) - \ln h^3 + \frac{3}{2}\right] - k\ln\left(\frac{\Delta E}{E}\right),$$

which is the same apart from the irrelevant additive constant at the end. ■

c) Show that in all 3 cases of part (b), the temperature, T, of the gas is related to the Lagrange multiplier β by $\beta = 1/kT$.

Solution: By definition $T = \left(\frac{\partial S}{\partial E}\right)^{-1}_{N,V}$. When evaluating this derivative, one must be careful to obey the constraints, especially in the fermionic and bosonic cases: one cannot treat α and β as constant and differentiate with respect to E because if one changes E while holding N fixed, then α and β must change. We therefore proceed as follows. Let

$$S = k\left[\alpha N + \beta E - \sum_i \ln(1 \pm G_i)\right],$$

where we choose the minus sign for bosons and the plus sign for fermions. Then we have that

$$\frac{\partial S}{\partial \beta} = k\left[\frac{\partial \alpha}{\partial \beta}N + E + \beta\frac{\partial E}{\partial \beta} - \sum_i g_i\frac{\left(\frac{\partial \alpha}{\partial \beta} + \epsilon_i\right)G_i}{1 \pm G_i}\right] = k\beta E$$

using the definitions of E and N. Thus we find that

$$kT = \left(\frac{\partial S}{\partial E}\right)^{-1}_{N,V} = \frac{\left(\frac{\partial E}{\partial \beta}\right)_{N,V}}{\left(\frac{\partial S}{\partial \beta}\right)_{N,V}} = \frac{1}{\beta},$$

as desired. For the case of distinguishable particles, we have

$$S = k\left[N \ln N + \alpha N + \beta E\right]$$

so that

$$\frac{\partial S}{\partial \beta} = k\left[0 + \frac{\partial \alpha}{\partial \beta}N + E + \beta\frac{\partial E}{\partial \beta}\right].$$

We can obtain an explicit expression for $\frac{\partial \alpha}{\partial \beta}$ by differentiating N with respect to β:

$$\frac{\partial N}{\partial \beta} = 0 = \frac{\partial}{\partial \beta}\sum_i g_i G_i = \sum_i \left(-\frac{\partial \alpha}{\partial \beta} - \epsilon_i\right) g_i G_i = -\frac{\partial \alpha}{\partial \beta}N - E \quad \Rightarrow \quad \frac{\partial \alpha}{\partial \beta} = -\frac{E}{N}.$$

Plugging this into expression for the derivative of S, we find that

$$\frac{\partial S}{\partial \beta} = k\beta\frac{\partial E}{\partial \beta} \Rightarrow \beta = \frac{1}{kT},$$

as before. **Note:** for the special case of distinguishable particles in the MB distribution, we also have explicit formulae for the entropy and β:

$$S = kN\left[\left(\frac{\eta V}{h^3}\right) + \frac{3}{2}\ln\left(\frac{3N}{4\pi E m}\right) + \frac{3}{2}\right] \quad ; \quad \beta = \frac{3N}{2\beta}.$$

This formula for entropy **can** be naively differentiated with respect to E since everything is in terms of N, E, and constants. This yields

$$kT = k\left(kN\left[\frac{3}{2}\frac{1}{E}\right]\right)^{-1} = \frac{1}{\beta},$$

in complete agreement. ■

2) Consider a lattice with N sites. At each site is placed a spin-1/2 particle with magnetic moment μ. A magnetic field B is applied, so the energy of each particle is $-\mu B$ if its spin is "up" and $+\mu B$ if its spin is "down".

a) Calculate the density of quantum states of the system with total energy E and thereby obtain a formula for the entropy, $S(E, N)$. Does it make any difference whether the particles are treated as distinguishable or as fermions?

Solution: The number of states with n particles spin up and $N - n$ particles spin down is $\mathcal{N} = \frac{N!}{n!(N-n)!}$. These states, and only these states, have energy

$$E = n(-\mu B) + (N - n)(\mu B) = (N - 2n)\mu B \quad \Rightarrow \quad n = \frac{N\mu B - E}{2\mu B}.$$

Hence the total number of states is

$$\mathcal{N} = \frac{N!}{\left(\frac{N\mu B - E}{2\mu B}\right)!\left(\frac{N\mu B + E}{2\mu B}\right)!}.$$

Letting $x = \dfrac{E}{N\mu B}$ we find that the entropy is

$$k \ln \mathcal{N} = k\left[N \ln\left(\frac{2N}{\sqrt{N^2 - \frac{E^2}{\mu^2 B^2}}}\right) - \frac{E}{2\mu B}\left(\frac{1 + \frac{E}{\mu B N}}{1 - \frac{E}{\mu B N}}\right)\right] = kN\left[\ln\frac{2}{\sqrt{1-x^2}} - x\tanh^{-1} x\right].$$

The statistics of the particles do not enter into the calculation because each particle is automatically in a different state because each one is in a different eigenstate of the position operator. (More accurately, when antisymmetrizing the states over the particles, we need to consider both position and spin parts of the state, and that will lead to the above counting.) ■

b) Calculate the temperature, T, as a function of E and N. Under what conditions is T negative?

Solution: The thermodynamic temperature is defined by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,B} = \frac{1}{\mu B}\ln\frac{1-x}{1+x} = \frac{-\mu B}{k\tanh^{-1} x}$$

using the expressions given above and bit of algebra. The temperature will be negative if $E > 0$. This is because when $E > 0$ is a high energy-state for the system, with more spins anti-aligned than aligned. Increasing the energy means making more spins anti-aligned, so the number of available microstates, and hence the entropy, actually decreases. ■