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Statistical Mechanics Spring, 2002

Problem Set II Solutions

1) (a) Consider a classical gas composed of N non-interacting point particles, each of mass m, which is confined to a volume V. Calculate the total volume $\mathcal{V}[\Gamma_E]$ of the "energy shell" Γ_E. You may use the fact (shown in Appendix E of Mazenko) that the "area" of a unit sphere in a d-dimensional space is $2\pi^{d/2}/\Gamma(d/2)$, where Γ denotes the gamma-function (so Γ(n)=(n-1)! when n is an integer; Stirling's formula provides an excellent approximation for $\Gamma(x)$ for large x).

Solution: The volume in phase space is defined as $\int dq^N dp^n \delta\left(H-E\right)$. Since the Hamiltonian is independent of postion (the particles are free), the position integral can be performed immediately and yields V^N. The delta-function enforces energy conservation , i.e., $E = \frac{1}{2m}\left(\sum_{i=1}^N \sum_{j=x}^z \left(v_j^{(i)}\right)^2\right)$. This defines a $3N-1$ sphere whose volume is $2\frac{\pi^\alpha}{\Gamma(\alpha)}\left(2mE\right)^{\alpha-\frac{1}{2}}$, with $\alpha = \frac{3N}{2}$. However, there is also a Jacobian coming from evaluating the delta-function, so we must include a factor of $\left|\frac{\partial H}{\partial q_i}\right|^{-1}$ "=" p/m. Since the gradient is normal to a level-set, which in this case is a sphere, the gradient is simply the vector from the origin to the point where it is being evaluted. Its norm is equal to the radius of the sphere, and the net effect of the Jacobian is to reduce the volume by one power of $\frac{\sqrt{2mE}}{m}$. Combining these, we find $\mathcal{V} = V^N\frac{(2\pi m)^\alpha}{\Gamma(\alpha)}E^{\alpha-1}$. ■

(b) Two boxes each have volume V and each contain a classical gas of N particles with energy E, as in part (a). The boxes are now placed in "thermal contact" with each other, so that they can exchange energy with each other, but not change their volume or number of particles. On account of this energy exchange, the energy, E_1, within the first box now may vary between 0 and 2E. Obtain the probability distribution, $p(E_1)dE_1$, that the energy contained within the first box will be within dE_1 of E_1 if one examines the system at a "random time".

Solution: In part (a) we calculated the volume of phase on the energy shell of E. Now we consider the phase space for the product system $\mathcal{S}_1 \times \mathcal{S}_2$. If the first box has energy E_1, then second one has energy $E_2 = 2E - E_1$. Thus, total volume of phase space will be

$$\mathcal{V}(E_1) = \mathcal{V}(\Gamma_{E_1}) \times \mathcal{V}(\Gamma_{2E-E_1}) = V^{2N}\frac{(2m\pi)^{2\alpha}}{\Gamma(\alpha)^2}E_1^{\alpha-1}\left(2E-E_1\right)^{\alpha-1}.$$

Since E_1 specfies the energies of all parts of the system, the total phase space available to the combined system is simply $\int_0^E dE_1\mathcal{V}(E_1)$. This integral can be done in two ways: 1) The hard way, which is to evaluate it in terms of the confluent hypergeometric function and then express that in terms of Γ

functions, and 2) the easy way, which is to think about it physically (thanks to Kosta Ladavac, from whom I'm copying this solution). The combined system consists of $2N$ particles, each of which can be anywhere in some volume V. The only restriction we have on the system is that the total energy is $2E$. Since the particles are free, this is just like having $2N$ particles in a box with energy $2E$, so we get the same answer as in part (a) only with $N \to 2N, E \to 2E$. Thus $\mathcal{V}_{\text{Total}} = V^{2N} \frac{(2\pi m)^{3N}}{\Gamma(3N)} (2E)^{3N-1}$.The probability density is simply the ratio of the phase spaces so it is

$$P(E_1) = \frac{\Gamma(3N)}{\Gamma\left(\frac{3N}{2}\right)^2} \frac{E_1^{\frac{3N}{2}-1} (2E - E_1)^{\frac{3N}{2}-1}}{(2E)^{3N-1}}. \quad \blacksquare$$

2) (Counts as 2 problems) (a) Consider a non-relativistic particle of mass m in one dimension in a box of size L, with infinite potential walls (i.e. $V = 0$ for $0 < x < L$; $V = \infty$ otherwise). Find its energy eigenstates and eigenvalues.

Solution: This is a standard problem from quantum mechanics. We must find the eigenfunctions of the Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m^2} \frac{d^2}{dx^2}$ which vanish at the boundary. With our choice of coordinates, the eigenfunctions are $e_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ with eigenvalues $\frac{n^2\pi^2\hbar^2}{2mL^2}$, $n \in \mathbb{Z}^+$. $\blacksquare$

(b) Now generalize the results of part (a) to the case of N, non-interacting, distinguishable particles in 3-dimensions in a cubic box of size L with infinite potential walls.

Solution: Since the particles are distinguishable, the Hilbert space of states is simply the 3N-fold tensor product of the 1d particle in box. Thus, the eigenstates are $e_{n_x^1, n_y^1, n_z^1, \ldots, n_x^N, n_y^N, n_z^N} = \Pi_{i=1}^N \Pi_{j \in \{x,y,z\}} \sin\left(\frac{n^{(i)}{}_j \pi x}{L}\right)$ with energies $E_{n_x^1, n_y^1, n_z^1, \ldots, n_x^N, n_y^N, n_z^N} = \sum_{i=1}^N \sum_{j \in \{x,y,z\}} \frac{\left(n_j^{(i)}\right)^2 \pi^2 \hbar^2}{2mL^2}$ and each $n_j^{(i)} \in \mathbb{Z}^+$. $\blacksquare$

(c) For the situation of part (b), derive a formula for the number of quantum states with total energy between E and $E + \Delta E$, where $\Delta E/E << 1$, but ΔE is large enough to include many states. (Hint: Find the average density of states in $3N$-dimensional "k-space" from part (b) and multiply by the appropriate volume.)

Solution: The energy of the system only depends on the "length-squared" of the "wave-vector" $n_j^{(i)}$. Thus, the number of states with energy less than or equal to E will be proportional the volume of a $3N$-1-ball of radius $r = \left(\frac{2mEL^2}{\pi^2\hbar^2}\right)^{\frac{1}{2}}$. However, since we are the states are labeled by positive integers, we must insert a factor of $\frac{1}{2}^{2\alpha}$ to take into account that we only want the volume in the first "quadrant." Hence, the number of states is $S = 2^{1-2\alpha} \frac{\pi^\alpha}{2\alpha\Gamma(\alpha)} \left(\frac{2mL^2E}{\pi^2\hbar^2}\right)^\alpha$, $\alpha = \frac{3N}{2}$ is the number of states with energy $\leq E$. Note that this simplifes to $\frac{\pi^\alpha}{\alpha\Gamma(\alpha)} \left(\frac{V}{h^3}\right)^N (2mE)^\alpha$, so we do get a factor of V^N as expected classically. Differentiating the expression, we find the density of states $\rho = \frac{dS}{dE}$ at energy E is equal to $= \frac{\pi^\alpha}{\Gamma(\alpha)} \left(\frac{V}{h^3}\right)^N \frac{(2mE)^\alpha}{E}$. We conclude that the number of states in the desired range is

$$\rho \Delta E = \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2})} \left(\frac{V}{h^3}\right)^N (2mE)^{\frac{3N}{2}} \frac{\Delta E}{E}. \quad \blacksquare$$

(d) For a 1m^3 box of (monatomic) gas at ordinary pressure and room temperature conditions we have $N \sim 10^{25}$ and the total energy is $E = \frac{3}{2}NkT \sim 10^{12}$ ergs. Assume that the mass of each particle is $m \sim 10^{-22}$gm. Use the result of (c) to estimate the number of quantum states with total energy within 1 erg of $E = 10^{12}$ ergs, assuming that the particles in the gas are distinguishable.

Solution: To our desired precision $\alpha = 1.5 \times 10^{25}$, $\frac{\Delta E}{E} = 10^{-12}$, and $\left(\frac{V}{h^3}\right)^1 (2mE)^{\frac{3}{2}} = 9.7 \times 10^{69}$. The hard part is computing the volume of the unit sphere, for which we need Sterling's approximation $n! \approx e^{-n} n^n \sqrt{2\pi n}$. For $N = 10^{25}$, $N \ln N - N \approx 5.65 \times 10^{26}$. Thus we get (converting all numbers raised to ridiculous powers to e^something)

$$\frac{e^{\ln(\pi) 1.5 \times 10^{25}}}{e^{5.65 \times 10^{26}}} \left(e^{160}\right)^{1 \times 10^{25}} \left(10^{-12}\right) \approx e^{10^{27}}. \quad \blacksquare$$

(e) For the system of part (d), estimate the probability that a given "single particle energy level" will be occupied by more than one particle, i.e., compare the number of single particle levels in the relevant energy range to the number of particles. (If this probability is small, a boson or fermion gas will behave in the same manner as a gas of distinguishable particles.)

Solution: We want to find the number of states available to a single particle in the energy range $0 \leq E \leq 10^{12}$. Since we're looking at a single particle, what we want is the volume of the 3-ball of radius r, where r is given by the length-squared of the "wave-vector" as before, so $r = \left(\frac{2mL^2E}{\pi^2\hbar^2}\right)^{\frac{1}{2}}$ and the number of states is

$$\frac{4\pi}{3} \left(\frac{2mL^2E}{\pi^2\hbar^2}\right)^{\frac{3}{2}} \frac{1}{8} = 4 \times 10^{70}.$$

Thus the average occupance of a single particle state is about 2.5×10^{-46}, which is very small indeed; it is irrelevant if our gas is made up of bosons or fermions. $\blacksquare$