

PHYS7721 Homework 2

Ryan Carelli

Due Thursday March 2, 2017

Exercise 1. By evaluating the "volume" of the relevant region of its phase space, show that the number of microstates available to a rigid rotator with angular momentum $\leq M$ is $(M/\hbar)^2$. Hence determine the number of microstates that may be associated with the quantized angular momentum $M_j = \sqrt{j(j+1)}\hbar$, where $j = 0, 1, 2, \dots$ or $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. Interpret the result physically.

Solution. We desire the total volume in phase space,

$$\int d\theta d\phi dp_\theta dp_\phi$$

where θ and ϕ represent the orientation of the rotator in real space. We have that the area of an ellipse $A = \pi ab$ where a is the length of the major axis and b is the length of the semimajor axis. The general formula for an ellipse is,

$$1 = \frac{a^2}{x^2} + \frac{b^2}{y^2}$$

Consider $M^2 = p_\theta^2 + (p_\phi^2/\sin^2\theta)$. We get

$$1 = \frac{p_\theta^2}{M^2} + \frac{p_\phi^2}{M^2 \sin^2\theta}$$

which gives us the values for a and b . The momentum cross section is therefore $\pi M^2 \sin\theta$ and our integral is reduced to,

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} \pi M^2 d\phi = 4\pi^2 M^2.$$

Thus the number of microstates is $\frac{4\pi^2 M^2}{\hbar^2} = \left(\frac{M}{\hbar}\right)^2$ as desired. For a particular quantized angular momentum, we estimate with the range of a particular quanta.

$$\frac{1}{\hbar} \left[M_{j+\frac{1}{2}}^2 - M_{j-\frac{1}{2}}^2 \right] = 2j + 1$$

simply plugging in the chosen values of j . □

Exercise 2. Following the method of Appendix C, replacing equation (C.4) by the integral

$$\int_0^\infty e^{-r} r^2 dr = 2,$$

show that

$$V_{3N} = \int \dots \int_{0 \leq \sum_{i=1}^N r_i \leq R} \prod_{i=1}^N (4\pi r_i^2 dr_i) = (8\pi R^3)^N / (3N)!$$

Using this result, compute the "volume" of the relevant region of the phase space of an extreme relativistic gas ($\epsilon = pc$) of N particles moving in three dimensions. Hence, derive expressions for the various thermodynamic properties of this system and compare your results with those of Problem 1.7.

Solution. $V_{3N} = AR^{3N}$ and $dV_{3N} = 3ANR^{3N-1}dR$.

$$\int_0^\infty \dots e^{-\sum_{i=1}^N r_i} \prod_{i=1}^N r_i^2 dr_i = 2^N$$

by substitution of the given integral. Write the LHS,

$$\int_0^\infty e^{-R} 4^{-N} \pi^{-N} dV_{3N} = (4\pi)^{-N} 3A N \Gamma(3N)$$

$$2^N = (4\pi)^{-N} 3A N \Gamma(3N) \implies A = \frac{(8\pi)^N}{(3N)!}$$

where we use the definition of the gamma function to get the factorial. By $V_{3N} = AR^{3N}$ this yields the desired expression for V_{3N} .

Now to find the volume of the region of the phase space,

$$\int \prod_{i=1}^{3N} dq_i dp_i = V^N \int \prod_{i=1}^N 4\pi p_i^2 dp_i = V^N \frac{\left(\frac{8\pi E^3}{c^3}\right)^N}{(3N)!}$$

Divide by h^3 to give the number of microstates contained in this volume.

$$\left(\frac{\partial(k \ln \Sigma)}{\partial E}\right)_{N,V} = \frac{3Nk}{E} = \frac{1}{T}$$

as expected. Since VE^3 is a constant we get VT^3 a constant which gives us $\gamma = \frac{4}{3}$ and now taking partial derivatives we can get the thermodynamic quantities we desire matching those in 1.7. \square

Exercise 3. Making use of the fact that the Helmholtz free energy $A(N, V, T)$ of a thermodynamic system is an extensive property of the system, show that

$$N\left(\frac{\partial A}{\partial N}\right)_{V,T} + V\left(\frac{\partial A}{\partial V}\right)_{N,T} = A$$

[Note that this result implies the well-known relationship: $N\mu = A + PV (= G)$.]

Solution. An extensive property increases linearly with N . We want to express A as a process of intensive variables and N ,

$$A(N, V, T) = Na(v, T).$$

$$V\left(\frac{\partial A}{\partial V}\right)_{N,T} = VN\left(\frac{\partial a}{\partial v}\right)_T \frac{\partial v}{\partial V} = VN\left(\frac{\partial a}{\partial v}\right)_T \frac{1}{N}$$

$$N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\left(a + N\left(\frac{\partial a}{\partial v}\right)_T \frac{-V}{N^2}\right)$$

and summing,

$$VN\left(\frac{\partial a}{\partial v}\right)_T \frac{1}{N} + N\left(a + N\left(\frac{\partial a}{\partial v}\right)_T \frac{-V}{N^2}\right) = Na(v, T) = A$$

\square

Exercise 4. (a) Assuming that the total number of microstates accessible to a given statistical system is Ω , show that the entropy of the system, as given by the equation (3.3.13), is maximum when all Ω states are equally likely to occur.

(b) If, on the other hand, we have an ensemble of systems sharing energy (with mean value \bar{E}), then show that the entropy, as given by the same formal expression, is maximum when $P_r \propto e^{-\beta E_r}$, β being a constant to be determined by the given value of \bar{E} .

- (c) Further, if we have an ensemble of systems sharing energy (with mean value \bar{E}) and also sharing particles (with mean value \bar{N}), then show that the entropy, given by a similar expression, is maximum when $P_{r,s} \propto e^{-\alpha N_r - \beta E_s}$, α and β being constants to be determined by the given values of \bar{N} and \bar{E} .

Solution. This problem is an application of the Lagrange Multiplier method discussed in class. Consider first the constraints,

$$\sum_s E_s P_{r,s} = \bar{E}, \quad \sum_s N_s P_{r,s} = \bar{N}$$

These are the most general constraints allowing variation in \bar{N} and \bar{E} , and we can remove these one by one to get all of the desired expressions. As in Eq. 3.2.8 in the book, slightly vary P and we get,

$$\sum_{r,s} (-(1 + \ln P_{r,s}) - \gamma - \beta E_s - \alpha N_r) \delta P_{r,s} = 0$$

But then

$$-(1 + \ln P_{r,s}) - \gamma - \beta E_s - \alpha N_r = 0$$

which implies from simple rearrangement (c), $P_{r,s} \propto e^{-\beta E_s - \alpha N_r}$. Now remove the constraint from \bar{N} and we are left with (b) $P_r \propto e^{-\beta E_r}$ by the same process. Finally if we remove the constraint from \bar{E} we get $P_r = k$ where k is a constant (a).

□

Exercise 5. If the "free volume" \bar{V} of a classical system is defined by the equation

$$\bar{V}^N = \int e^{(\bar{U} - U(\bar{q}_i)/kT} \prod_{i=1}^N d^3 q_i,$$

where \bar{U} is the average potential energy of the system and $U(\bar{q}_i)$ the actual potential energy as a function of the molecular configuration, then show that

$$S = Nk \left(\ln \left(\frac{\bar{V}}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right)$$

In what sense is it justified to refer to the quantity \bar{V} as the "free volume" of the system? Substantiate your answer by considering a particular case - for example, the case of a hard sphere gas.

Solution. To derive S , we want to find the partition function. Start with the equation for classical systems,

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q, p)} d\omega$$

and substitute the Hamiltonian for a system of particles $H(q, p) = \sum_i \frac{p_i^2}{2m} + U(q)$.

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \sum_i \frac{p_i^2}{2m} + U(q)} d\omega$$

which becomes,

$$Q_N(V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \int e^{-U(q)/kT} d^{3N} q$$

Now apply the Stirling Approximation and let $Z_N = \int e^{-U(q)/kT} d^{3N} q$

$$\begin{aligned} A &= NkT \left(\ln \left(N \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right) - 1 \right) - kT \ln Z \\ \Rightarrow S &= Nk \left(\frac{1}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + \frac{5}{2} + kT \left(\frac{\partial \ln Z}{\partial T} \right)_{N, V} + k \ln Z \end{aligned}$$

Evaluating the partial derivative,

$$kT \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} = \frac{\bar{U}}{T}$$

$$k \ln Z = Nk \ln \bar{V} - \frac{\bar{U}}{T}$$

which gives the result stated in the problem. For a hard sphere of gas,

$$U(q) = \sum_{i < j} u(r_{ij}) \implies e^{\beta U(q)} = \prod_{i < j} e^{-\beta u(r_{ij})}$$

But now when we evaluate Z , we find that \bar{V} represents a volume element of the molecules considered. \square