Physics 35200 Statistical Mechanics

R. Wald Spring, 2002

Problem Set III Solutions

1) Consider a classical, ideal gas of N point particles, confined by a spherical box, so that the total angular momentum, $\vec{J}$, is conserved. In this case, dynamical motion will be confined to a $(6N-4)$-dimensional surface, $\Gamma_{E,\vec{K}}$, in Γ defined by the equations $H = E$ and $\vec{J} = \vec{K}$. If the dynamical evolution is appropriately ergodic on $\Gamma_{E,\vec{K}}$, the time-averaged behavior of the gas will be described by the "modified microcanonical ensemble" $\delta(H-E)\delta^3(\vec{J}-\vec{K})d^{3N}xd^{3N}p$. Parallel the arguments given in class to obtain the most probable distribution function, $f(\vec{x},\vec{p})$, in this case. (You may express your answer in terms of certain constants which you need not evaluate, but you must specify clearly what integrals need to be done to evaluate them.) Show that when $\vec{K} = 0$, we again obtain the Maxwell-Boltzmann distribution.

Solution: Consider carving up phase space (of a single particle) into cells of volume $\mathcal{V}$ and labeled by i. Let n_i, ϵ_i, and $\vec{j}_i$ denote the number of particles in, the energy of, and the angular momentum of the i^{th} cell, respectively. Finding the most probable distribution function means maximizing the volume of accessible phase space (of the whole system), which is equal to $\mathcal{V}^N \frac{N!}{\Pi_i (n_i!)}$. Using the standard tricks of ignoring the constant out front, taking the logarithm, and expanding using Stirling's approximation, we find that the function to be maximized is $F(n_i) = -\sum_i (n_i \ln n_i - n_i)$. Of course, we must maximize F relative to the constraints $\sum_i n_i = N$, $\sum_i n_i\epsilon_i = E$, and $\sum_i n_i\vec{j}_i = \vec{K}$. We use the Lagrange parameters α, β, and $\vec{\gamma}$, respectively, and obtain the non-trivial equation

$$\frac{\partial F}{\partial n_i} = 0 = -\ln n_i - \alpha - \beta\epsilon_i - \vec{\gamma}\cdot\vec{j} \Rightarrow n_i = e^{-\alpha-\beta\epsilon_i-\vec{\gamma}\cdot\vec{j}_i}$$

as well as the constraint equations. Taking the continuum limit and substituting for ϵ and $\vec{j}$ in terms of $\vec{x}$ and $\vec{p}$, we find that

$$f(\vec{x},\vec{p};\alpha,\beta,\vec{\gamma}) = e^{-\alpha-\frac{\beta p^2}{2m}-\vec{\gamma}\cdot(\vec{x}\times\vec{p})}$$

and that the Lagrange constants are found by solving the system of equations

$$\int d^3xd^3p f(\vec{x},\vec{p};\alpha,\beta,\vec{\gamma}) = N$$

$$\int d^3xd^3p \frac{p^2}{2m} f(\vec{x},\vec{p};\alpha,\beta,\vec{\gamma}) = E$$

$$\int d^3xd^3p\, (\vec{x}\times\vec{p})\, f(\vec{x},\vec{p};\alpha,\beta,\vec{\gamma}) = \vec{K}.$$

Now suppose $\vec{K}=0$. We want to show that we recover the Maxwell-Boltzmann distribution, i.e., $\vec{\gamma}=0$ and α and β are given as in the MB distribution. It is clear that if $\gamma=0$, the first two constraint equations reduce that those from the MB distribution, so showing that $\gamma=0$ is a solution suffices. However, if $\gamma=0$, the integrand in the angular momentum constraint equation is an odd function of $\vec{x}$ (since $\vec{x}$ only appears in the $\vec{x}\times\vec{p}$ out front) and so the integral vanishes. Hence we recover the MB distribution. ■

2) Consider a classical ideal gas of N particles of mass m in a volume V in a state described by the Maxwell-Boltzmann distribution.
(a) Calculate the average magnitude of velocity, $< |\vec{v}| >$, of the particles, and the "root mean square dispersion", $\Delta v = [< v^2 > - < |\vec{v}| >^2]^{1/2}$, about $< |\vec{v}| >$.

Solution: The properly normalized Maxwell-Boltzmann distribution is $f(\vec{x},\vec{p}) = \frac{1}{V}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{\frac{\beta p^2}{2m}}$. By definition,

$$\langle v\rangle = \int v f(\vec{x},\vec{p}) d^3x d^3p = \left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} \int_0^\infty \frac{p}{m} e^{-\frac{\beta p^2}{2m}} p^2 dp d\Omega = \sqrt{\frac{8}{\pi m\beta}}.$$

The average square velocity can be computed in the same manner, or by noting that the equipartition theorem tells us that $\left\langle \frac{p^2}{2m}\right\rangle = \frac{3}{2\beta}$ so that $\langle v^2\rangle = \frac{3}{m\beta}$. Hence,

$$\langle \Delta v\rangle = \sqrt{\left(3-\frac{8}{\pi}\right)\frac{1}{m\beta}}. \quad ■$$

(b) Calculate the pressure exerted by the gas on a wall resulting from elastic collisions of the gas with the wall.

Solution: Consider particles incident on the wall with an angle θ with respect the normal. These particles will have their normal momentum changed by a factor of $2p\cos\theta$, where p is the magnitude of each particle's momentum. If A is the area of the wall, the volume of such particles which hit the wall in a time Δt is $A\Delta t\frac{p}{m}\cos\theta$. The number of particles hitting the wall will be this volume times the density of particles with momentum $\vec{p}$, which is $\frac{N}{V}$ times the "momentum part" of the MB distribution. The pressure exerted by these particles will be impulse/time per unit area, or

$$P(\vec{p}) = \frac{2Np^2\cos^2\theta}{Vm}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{\frac{\beta p^2}{2m}}.$$

To find the total pressure, we integrate over all momenta; however, we need to add a factor of one-half because only half of the momenta point toward the wall instead of away from it. Thus we obtain

$$P_{\text{total}} = \int d^3p P(\vec{p}) = \frac{N}{V\beta},$$

as we were taught in freshman chemistry. ■

3) Define the "Schmaxwell-Boltzmann" distribution function of a gas with N particles of mass m and total energy E by

$$F(\vec{x}, \vec{p}) = ap^{-2} \exp(-bp^2/2m)$$

where $b = N/2E$ and $a = V^{-1}(N/2\pi)^{3/2}(2mE)^{-1/2}$. If one examines the gas at a "random time", what is the relative probability that the gas will be well described by the Schmaxwell-Boltzmann distribution rather than the Maxwell-Boltzmann distribution?

Solution: Since all microstates are equally likely, probability is proportional to the accessible volume in phase space. In order to compare probabilities, we need simply compare volumes. As shown in class, the volume accessible when the distribution of states is described by a function $f(\vec{x}, \vec{p})$ is $e^{\int d^3x d^3p f \ln f - f}$. If we let f denote the Maxwell-Boltzmann (MB) distribution, then the natural log of the relative probability of Schmaxwell-Boltzmann (SB) to MB is

$$\ln P = \ln \frac{\mathcal{V}_{\mathrm{SB}}}{\mathcal{V}_{\mathrm{MB}}} = \int d^3x d^3p F \ln F - F - f \ln f + f$$

$$= -\int d^3x d^3p \left[a\, p^{-2} e^{-\frac{bp^2}{2m}} \left(\ln a - 2 \ln p - \frac{bp^2}{2m} - 1 \right) - C e^{-\frac{\beta p^2}{2m}} \left(\ln C - \frac{\beta p^2}{2m} - 1 \right) \right]$$

with $C = \frac{N}{V} \left(\frac{3N}{4\pi m E} \right)^{\frac{3}{2}}$. From here on out, all that's left is evaluating the integrals and doing algebra. The first term in the brackets integrates to

$$2\pi a V \sqrt{\frac{2m\pi}{b}} \left[\ln \frac{2ab}{m} + \gamma - \frac{3}{2} \right] = N \left[\ln \frac{2ab}{m} + \gamma - \frac{3}{2} \right] \quad (\gamma = \text{Euler's Constant}),$$

and the second one yeilds

$$4\pi C V \left(\frac{2m\pi}{\beta} \right)^{\frac{3}{2}} \left[\ln C - \frac{5}{2} \right] = N \left[\ln C - \frac{5}{2} \right] \text{ since } C = \frac{N}{V} \left(\frac{\beta}{2m\pi} \right)^{\frac{3}{2}}.$$

Hence we find that

$$\ln P = -N \left[\ln \frac{2ab}{mC} + \gamma + 1 \right] = -N \left[\ln \left(2 \cdot 3^{-\frac{3}{2}} \right) + \gamma + 1 \right]$$

using the definitions of a, b, and C. Now the smoke finally clears and we find that

$$P = \frac{\mathcal{V}_{\mathrm{SB}}}{\mathcal{V}_{\mathrm{MB}}} = \left(\frac{\left(\sqrt{3}\right)^3 e^{-(\gamma+1)}}{2} \right)^N \approx 0.54^N.$$

This probability rapidly decreases with N and is totally negligible at any macroscopic number. ■