Prof. Anchordoqui

Problems set # 11                    **Physics 303**                    November 18, 2014

1. The partition function of classical particles in 3 dimensions is defined as

$$Z_{\text{class}} = \int d^3p \int d^3r \; \exp[-\beta E(\boldsymbol{p}, \boldsymbol{r})],$$

where $E(\boldsymbol{p}, \boldsymbol{r})$ is the particles energy. Note that this expression has the unit of (momentum $\times$ distance)$^3$, unlike the quantum partition function that is dimensionless. Define the density of states of a free classical particle in a box of volume $V$. By comparing it with the density of states for a quantum particle in a rigid box, find the missing factor in $Z_{\text{class}}$ that would make the classical partition function match the quantum one. This will define a quantum-mechanical "cell" in the phase space of a classical particle. Show that this quantum-mechanical aspect does not contribute into the internal energy and heat capacity of the classical particles.

<u>Solution:</u> The energy of the particle consists of kinetic and potential energy $E(\boldsymbol{p}, \boldsymbol{r}) = \frac{p^2}{2m} + V(\boldsymbol{r})$, so that the classical partition function factorizes $Z_{\text{class}} = \int d^3p \, e^{-\beta p^2/(2m)} \int d^3r \, e^{-\beta V(\boldsymbol{r})})$. For free particles there is no potential energy, and $Z_{\text{class}}$ for particles in a rigid box of volume $V$ becomes $Z_{\text{class}} = V \int d^3p \, e^{-\beta p^2/(2m)}$. Choosing the kineti energy $\varepsilon = p^2/(2m)$ as the integration variable, you can rewrite this in the form $Z_{\text{class}} = \int_0^\infty d\varepsilon \, \rho_{\text{class}}(\varepsilon) \; e^{-\beta \varepsilon}$, where $\rho_{\text{class}}(\varepsilon) = 2\pi V (2m)^{3/2} \sqrt{\varepsilon}$. The quantum mechanical partition function for free particles has the same form with $\rho(\varepsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}$. The two density of states are related by $\rho(\varepsilon) = \frac{\rho_{\text{class}}(\varepsilon)}{(2\pi\hbar)^3}$, which defines the missing factor in the previous definition of the classical partition function. Correcting $Z_{\text{class}}$ as $Z_{\text{class}} = \int \frac{d^3p \, d^3r}{(2\pi\hbar)^3} \; \exp[-\beta E(\boldsymbol{E}, \boldsymbol{r}]$, you obtain the dimensionless quantity that coincides with the classical limit of the quatum partition function $Z$. This expression can also be used in the presence of a potential energy. The interpretation of the above is the following. The $(x, p_x)$ projection of the phase space of the particle is discretized into cells $\Delta x \Delta p_x \sim 2\pi\hbar = h$, and equivalent expressions for the directions $y$ and $z$. The cells have quantum origin and are related to the Heisenberg's uncertainty principle, stating that the product of uncertainties of measuring $x$ and $p_x$ of a quantum particle is of order $h$. The number of quantum cells in a limited region of $x$ and $p_x$ is limited and it defines the number of different states in this region. It is impossible to have more different states because there is no way to distuingush states that are too close both in $x$ and in $p_x$ by any measurement. Similarly, quantum cells can be introduced in many-particle problems and in problems with rotational degrees of freedom. The concept of a quantum cell is na external element in classical statistical physics. Statistical averages of most physical quantities (except for the entropy and related functions) are insensitive to the quantization of the phase space of the system, because the correction factor introduced above cancels.

2. Using the distribution function

$$f(\boldsymbol{p}, \boldsymbol{r}) = \frac{1}{Z_{\text{class}}} \; \exp[-\beta E(\boldsymbol{p}, \boldsymbol{r})]$$

for classical particles with gravity, find the dependence of particle's concentration $n$ and pressure $P$ as the function of the height. Set the minimal height (the earth level) to zero. Calculate the heat capacity of this system and compare it with the one for free particles.

Solution: The energy of a particle has the form $E = \frac{p^2}{2m} + mgz$ The classical partition function factorizes $Z_{\text{class}} = \int d^3p \int d^3r \, \exp[-\beta E(\boldsymbol{p}, \boldsymbol{r})] = Z_{\text{kinetic}} Z_{\text{potential}}$, where $Z_{\text{kinetic}} = \int d^3p \, e^{-\beta p^2/(2m)}$ and $Z_{\text{potential}} = \int d^3r e^{-\beta mgz}$. The kinetic part of the classical partition function can be calculated as $Z_{\text{kinetic}} = \left[\int_{-\infty}^{+\infty} dp_x e^{-\beta p_x^2/(2m)}\right]^3 = (2\pi mkT)^{3/2}$. Assuming that the particles are contained to a vertical cylinder of cross section $S$, for the potential partition function you obtain $Z_{\text{potential}} = S \int_0^\infty dz e^{-\beta mgz} = \frac{SkT}{mg}$. Therefore, $Z_{\text{class}} = \frac{S}{g}(2\pi)^{3/2} m^{1/2} (kT)^{5/2}$. Now, suppose the are $N$ particles in the system. The number of particles in the element of phase space is $dN = Nf dp_x dp_y dp_z dx dy dz$, where $f$ is the distribution function. The concentration of particles is defined as $n = \int d^3p \frac{dN}{dxdydz} = N \int d^3p f$. Since $f$ and $Z_{\text{class}}$ factorize, the integrals over momentum cancel out and you obtain $n = \frac{N}{Z_{\text{potential}}} e^{-\beta mgz}$. You can verify that integration this over the volumes yields the identity $N = N$. Using the expression for $Z_{\text{potential}}$ you obtain $n = \frac{mgN}{SkT} e^{-\beta mgz}$, that is $n$ exponetially decreases with height. For the pressure you obtain the equation of state of the ideal gas $P = kkT = \frac{mgN}{S} e^{-\beta mgz}$. The average internal energy is given by $U = -N \frac{\partial \ln Z_{\text{class}}}{\partial \beta} = -N \frac{\partial \ln \beta^{-5/2}}{\partial \beta} = \frac{5}{2} \frac{N}{\beta} = \frac{5}{2} NkT$. The heat capacity is $C = \frac{\partial U}{\partial T} = \frac{5}{2} Nk$. This result might be unexpected. The three translational degrees of freedom contribute $\frac{3}{2} Nk$ to the heat capacity. In addition, there is a potenatil energy for the motion in the vertical direction. Its contribution is $Nk$ instead of the expected $\frac{1}{2} Nk$, as it would be the case or a vibrational degree of freedom. The reason for a different result is that the theorem of equidistribution of the energy over degrees of freedom is valid in cases where the energy is a quadratic function of the momenta and the deviations from the equilibrium position (see problem 4). For the problem at hand, the potential energy is linear rather than a quadratic function of $z$.

3. Consider two interacting Ising spins, *i.e.* a model of two coupled spins with the Hamiltonian

$$\hat{H} = -g\mu_B B(S_{1,z} + S_{2,z}) - JS_{1,z}S_{2,z},$$

where $B$ is the external magnetic field and $J$ is the so-called exchange interaction, ferromagnetic for $J > 0$ and antiferromagnetic for $J < 0$. The energy levels of this system are given by

$$\varepsilon_{m_1 m_2} = -g\mu_B B(m_1 + m_2) - Jm_1 m_2,$$

where the quantum numbers take the values $-S \leq m_1, m_2 \leq S$. Write down the expression for the partition function of the system. Can it be calculated analytically for a general $S$? If not, perform the calculation for $S = 1/2$. Calculate the internal energy, heat capacity, magnetization induced by the magnetic field, and the magnetic susceptibility (in the zero field limit). Analyze ferro- and antiferromagnetic cases.

Soultion: The partition function of the system is given by $Z = \sum_{m_1, m_2 = -S}^{S} e^{-\beta \varepsilon_{m_1 m_2}}$. For a general spin you can perform analytically one summation. You can use the results for a single spin in a magnetic field and with $h \equiv g\mu_B B$ write $Z_S = \sum_{m_1 = -S}^{S} e^{\beta h m_1} \sum_{m_2 = -S}^{S} e^{\beta(h + Jm_1)m_2} =$

$\sum_{m=-S}^{S} e^{\beta hm} \frac{\sinh[(S+1/2)\beta(h+Jm)]}{\sinh[\beta(h+Jm)/2]}$. The remaining sum most probably cannot be calculated analyt-ically. For $S = 1/2$ the partition function simplifies to $Z_{1/2} = \sum_{m=-1/2}^{1/2} e^{\beta hm} 2 \cosh\left[\frac{\beta(h+Jm)}{2}\right]$, that is $Z_{1/2} = 2\left\{e^{\beta h/2} \cosh\left[\frac{\beta(h+J/2)}{2}\right] + e^{-\beta h/2} \cosh\left[\frac{\beta(h-J/2)}{2}\right]\right\}$. This expression can be simpli-fied to $Z_{1/2} = 2\left[e^{\beta J/4} \cosh(\beta h) + e^{-\beta J/4}\right]$. In the zero field limit the result further simplifies to $Z_{1/2} = 4\cosh(\beta J/4)$. The internal energy in the zero field limit is $U = -N \frac{\partial \ln Z}{\partial \beta} = -\frac{NJ}{4} \tanh\left(\frac{\beta J}{4}\right)$, where $N$ is the number of two-spin systems. In the limit of low temperatures the hyperbolic tan-gent tends to 1 and so $U = -NJ/4$ (the two coupled spins are parallel for $J > 0$). In the case of antiferromagnetic coupling, $J < 0$ and so $\tanh(\beta J/4) \to -1$ for $T \to 0$, so that for both ferro-and antiferromagnetic coupling it follows that $U = -N|J|/4$ at zero temperature. The average spin value per two-spin system is $\langle S_z \rangle = \langle m_1 + m_2 \rangle = \frac{1}{Z} \frac{\partial Z}{\partial(\beta h)}$. Use the $Z_{1/2}$ partition function to obtain $\langle S_z \rangle = \frac{e^{\beta J/4} \sinh(\beta h)}{e^{\beta J/4} \cosh(\beta h) + e^{\beta J/4}} = \frac{\sinh(\beta h)}{\cosh(\beta h) + e^{-\beta J/2}}$. The susceptibility can be obtained by differe-tiating this expression with respect to the magnetic field, $\chi \propto \frac{\beta[\cosh^2(\beta h) + \cosh(\beta h)e^{-\beta J/2} - \sinh^2(\beta h)]}{(\cosh(\beta h) + e^{-\beta J/2})^2} = \frac{\beta[1 + \cosh(\beta h)e^{-\beta J/2}]}{(\cosh(\beta h) + e^{-\beta J/2})^2}$. In particular, at zero field $\chi \propto \frac{\beta}{1 + e^{-\beta J/2}}$. In the ferromagnetic case $J > 0$, the exponential is very small at low temperatures, $\beta J \gg 1$, so that the susceptibility has a regular value comparable with that of an isolated spin. On the contrary, in the antiferromagnetic case $J < 0$ the exponential is large and therefore the susceptibility is very small.

4. Consider classical particles with the potential energy $V(\boldsymbol{r}) = \kappa r^2/2$ in 3 dimensions. Calcu-late the partition function, internal energy and heat capacity.

Soultion: Start by calculating the classical partition funtion which factorizes into the kinetic and potentail parts: $Z_{\text{class}} = \int d^3p\, e^{-\beta p^2/(2m)} \int d^3r\, e^{-\beta \kappa r^2/2} = Z_{\text{kinetic}} Z_{\text{potential}}$, where $Z_{\text{kinetic}} = \left[\int_{-\infty}^{+\infty} dp_x\, e^{-\beta p_x^2/(2m)}\right]^3 = (2\pi mkT)^{3/2}$ and $Z_{\text{potential}} = \left[\int_{-\infty}^{+\infty} dx\, e^{-\beta \kappa x^2/2}\right]^3 = (2\pi kT/\kappa)^{3/2}$; hence $Z_{\text{class}} \propto T^3$. The internal energy and heat capacity are given by $U = -N \frac{\partial \ln Z_{\text{class}}}{\partial \beta} = 3NkT$ and $C = \frac{\partial U}{\partial T} = 3Nk$. The factor of 3 here is due to the three translational degrees of freedom of the system. Per each degree of freedom there is $Nk/2$ due to kinetic energy and the same amount due to potential energy. This problem illustrates the equidistribution of energy over degrees of freedom in classical statistical physics.