Solutions to Problem Set 6

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6.1 Harmonic Oscillator

Reif §6.1: A simple harmonic one-dimensional oscillator has energy levels given by $E_n = (n + \frac{1}{2})\hbar\omega$, where ω is the characteristic (angular) frequency of the oscillator and where the quantum number n can assume the possible integral values $n = 0, 1, 2, \ldots$. Suppose that such an oscillator is in thermal contact with a heat reservoir at temperature T low enough so that $kT/(\hbar\omega) \ll 1$.

(a) Find the ratio of the probability of the oscillator being in the first excited state to the probability of its being in the ground state.

(b) Assuming that only the ground state and first excited state are appreciably occupied, find the mean energy of the oscillator as a function of the temperature T.

(a) We have

$$\frac{P_1}{P_0} = \frac{\exp[-\beta E_1]}{\exp[-\beta E_0]} = \frac{\exp[-\beta(1+1/2)\hbar\omega]}{\exp[-\beta(0+1/2)\hbar\omega]} = \boxed{e^{-\beta\hbar\omega}}$$

(b) The average energy is given by

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \frac{E_o e^{-\beta E_o} + E_1 e^{-\beta E_1}}{e^{-\beta E_o} + e^{-\beta E_1}}$$

which gives

$$\boxed{\bar{E} = \hbar\omega \frac{\frac{1}{2} + \frac{3}{2}\frac{P_1}{P_0}}{1 + \frac{P_1}{P_0}} = \frac{\hbar\omega}{2}\frac{1 + 3e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}}}$$

□

6.2 Two State System

Reif §6.6: A system consists of N weakly interacting particles, each of which can be in either of two states with respective energies ϵ_1 and ϵ_2, where $\epsilon_1 < \epsilon_2$.

(a) Without explicit calculation, make a qualitative plot of the mean energy $\bar{E}$ of the system as a function of its temperature T. What is $\bar{E}$ in the limit of very low and very high temperatures? Roughly near what temperature does $\bar{E}$ change from its low to its high temperature limiting values?

(b) Using the result of (a), make a qualitative plot of the heat capacity C_V (at constant volume) as a function of the temperature T.

(c) Calculate explicitly the mean energy $\bar{E}(T)$ and heat capacity $C_V(T)$ of this system. Verify that your expressions exhibit the qualitative features discussed in (a) and (b).

(a) For a system in contact with heat reservoir we know that the probabilty of the system being in a state with energy E is proportional to $e^{-\beta E}$, the Boltzmann factor. Thus, without detailed calculation, we can deduce that low T limit gives $\bar{E} = N\epsilon_1$ and high T limit $\bar{E} = N\frac{\epsilon_1+\epsilon_2}{2}$. (In low temperatures, particles will prefer to sit in a lower energy state. In high temperatures, particles will fill both state equally likely.) Now, there is one energy scale associated with the difference between the two states $\Delta\epsilon = \epsilon_2 - \epsilon_1$. Roughly, the transition of $\bar{E}$ will occur at $\beta\Delta\epsilon = 1$.

$$\boxed{T = \frac{\epsilon_2 - \epsilon_1}{k}}$$

(b) Qualitatively, the energy should approach $\Delta\epsilon/2$ as $T \to \infty$ and as $T \to 0$, energy goes to 0. Also, the probability ratio of being in the two states is an exponential function, the Boltzmann factor, this is not a linear graph. Thus it should be something like a smooth step function changing its value at around $\Delta\epsilon \sim kT$.

C_V is a first derivative of $E(T)$ thus is should be peaked at around $kT \sim \Delta\epsilon$ according to the argument and should approach zero for high and low temperatures.

(c) Using the Boltzmann factor,

$$\bar{E} = N\frac{\epsilon_1 e^{-\beta\epsilon_1} + \epsilon_2 e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}} = \frac{\epsilon_1 e + \epsilon_2 e^{-\beta(\epsilon_2-\epsilon_1)}}{1 + e^{-\beta(\epsilon_2-\epsilon_1)}}$$

We can easily verify that in the low temperature limit, $\beta \to \infty$, we get $\bar{E} \to \epsilon_1$. For high temperature limit, $\beta \to 0$, the Boltzmann factor approch one, thus $\bar{E} \to \frac{\epsilon_1+\epsilon_2}{2}$. To find C_V we take the derivative of this

$$C_V = \frac{\partial \bar{E}}{\partial T} = N\frac{-\epsilon_2\Delta\epsilon e^{-\beta\Delta\epsilon}(1 + e^{-\beta\Delta\epsilon}) - (\epsilon_1 + \epsilon_2 e^{-\beta\Delta\epsilon})(-\Delta\epsilon e^{-\beta\Delta\epsilon})}{(1 + e^{-\beta\Delta\epsilon})^2}\frac{\partial\beta}{\partial T} = \frac{N}{kT^2}\frac{\epsilon_1 - \epsilon_2 e^{-\beta\Delta\epsilon}}{(1 + e^{-\beta\Delta\epsilon})^2}$$

Plotting these functions we get figures 1 and 2. And from these we can indeed see the features we predicted. C_V is peaked around some value $\sim \Delta\epsilon$, and goes to 0 as T is greater or smaller than the value.

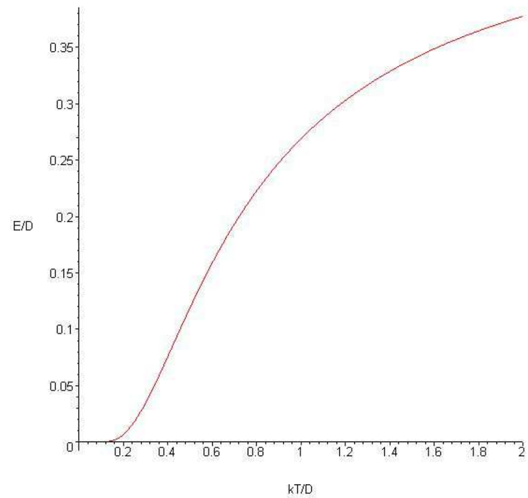

Figure 1: $E/\Delta\epsilon$ vs $kT/\Delta\epsilon$

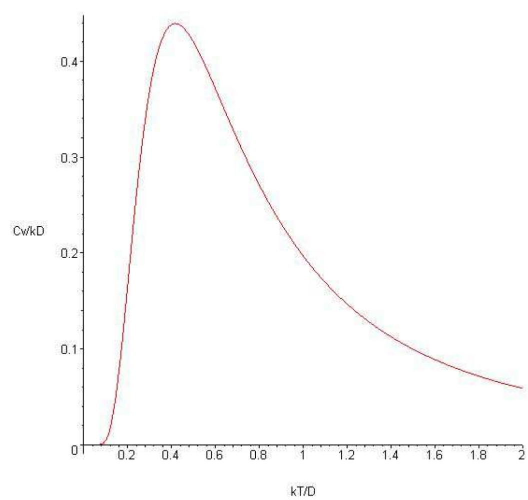

Figure 2: $C_V/k\Delta\epsilon$ vs $kT/\Delta\epsilon$

$\square$

6.3 Centrifuge

(a) For any particular particle located at position (x, y, z), with momentum (p_x, p_y, p_z). We have the energy

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \omega(xp_y - yp_x)$$

Completing the squares in momentum we see

$$E = \frac{1}{2m}\left[p_z^2 + (p_x^2 + 2m\omega y p_x + m^2\omega^2 y^2) + (p_y^2 + 2m\omega x p_y + m^2\omega^2 x^2)\right] - \frac{1}{2}m\omega^2(x^2+y^2)$$

This gives the partition function for a single particle

$$\begin{aligned}
Z_1 &= \frac{1}{h^3}\iiint dy\ dx\ dz \int e^{-\beta p_z^2/2m} dp_z \int e^{-\beta(p_y+m\omega x)^2} dp_y \int e^{-\beta(p_x+m\omega y)^2} dp_x e^{\frac{1}{2}\beta m\omega^2 r^2} \\
&= \frac{1}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \int_0^L dz \int_0^{2\pi} d\phi \int_0^R e^{\frac{1}{2}\beta m\omega^2 r^2} r dr \\
Z_1 &= \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \frac{2\pi L}{m\beta\omega^2}(e^{\frac{1}{2}m\beta\omega^2 R^2} - 1)\ .
\end{aligned}$$

(b) Since the particles do not interact we have the total partition function

$$Z = Z_1^N = \left[\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \frac{2\pi L}{m\beta\omega^2}(e^{\frac{1}{2}m\beta\omega^2 R^2} - 1)\right]^N$$

(c) The Hemlholtz free energy is given by

$$F = -kT\ln Z = -NkT\ln Z_1 = -NkT\left[\frac{3}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + \ln\left(\frac{2\pi L}{m\beta\omega^2}\right) + \ln(e^{\frac{1}{2}m\beta\omega^2 R^2} - 1)\right]\ .$$

(d) First we note that intuitively the pressure should vary with the radius. We have the Helmholtz free energy

$$F = E - TS \qquad \Rightarrow dF = -SdT - p(r)dV = -SdT - \pi R^2 p_{avg} dL - 2\pi r L p(r) dr$$

where p_{avg} is the pressure averaged over the horizontal cross section at $z = L$. Thus we have the pressure

$$p(R) = -\frac{1}{2\pi RL}\left(\frac{\partial F}{\partial R}\right)_{L,T} = \frac{Nm\omega^2}{2\pi L(1 - e^{-m\beta\omega^2 R^2/2})}$$

The total force on the outer wall of the cylinder must then be

$$f(R) = 2\pi RLp(R) = \frac{NmR\omega^2}{(1 - e^{-m\beta\omega^2 R^2/2})}$$

(e) The probability density of a particle being at position r is

$$P(r) = 2\pi L \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} r e^{m\beta\omega^2 r^2/2}/Z_1$$

Thus the number density

$$n(r) = \frac{Nm\beta\omega^2 e^{m\beta\omega^2 r^2/2}}{2\pi L(e^{m\beta\omega^2 R^2/2} - 1)} \ .$$

The pressure is then given as

$$p(r) = \frac{Nm\omega^2 e^{m\beta\omega^2 r^2/2}}{2\pi L(e^{m\beta\omega^2 R^2/2} - 1)} \ .$$

6.4 Statistical Entropy

(a) For the microcanonical ensemble, we know $S = k\ln\Omega$. So we need to show that $-k\sum_r P_r \ln P_r = k\ln\Omega$. For the microcanonical ensemble: $P_r = 1/\Omega$ for $E < E_r < E+\delta E$ and 0 otherwise, thus we have

$$\begin{aligned}
-k\sum_r P_r \ln P_r &= -k\sum_r \frac{1}{\Omega}\ln\frac{1}{\Omega} \\
&= -k\sum_r \frac{1}{\Omega}\ln 1 + k\sum_r \frac{1}{\Omega}\ln\Omega \\
&= k\ln\Omega\ .
\end{aligned}$$

(b) Reif §6.13

$$\begin{aligned}
S &= -k\sum_r\sum_s P_{rs}\ln P_{rs} = -k\sum_r\sum_s P_r P_s \ln(P_r P_s) \qquad \text{since } P_r \text{ and } P_s \text{ are independant} \\
&= -k\sum_s P_s \sum_r P_r \ln P_r - k\sum_r P_r \sum_s P_s \ln P_s = -k(1)(-S_1/k) - k(1)(-S_2/k) \\
&= S_1 + S_2 \qquad (1)
\end{aligned}$$

(b) Reif §6.15

$$S = -k\sum_r P_r \ln P_r \qquad S_o = -k\sum_r P_r^{(o)}\ln P_r^{(o)}$$

$$\begin{aligned}
S - S_o &= k\sum_r \left[-P_r\ln P_r + P_r^{(o)}\ln P_r^{(o)}\right] \\
&= k\sum_r \left[-P_r\ln P_r + P_r\ln P_r^{(o)} - P_r\ln P_r^{(o)} + P_r^{(o)}\ln P_r^(o)\right] \\
&= k\sum_r P_r \ln\frac{P_r^{(o)}}{P_r} + k\sum_r\left[P_r(-\beta E_r - \ln Z) + P_r^{(o)}(-\beta E_r - \ln Z)\right] \\
&\quad (\text{Since } \ln P_r^{(o)} = -\beta E_r - \ln Z) \\
&= k\sum_r P_r \ln\frac{P_r^{(o)}}{P_r} + k\underbrace{(\sum_r P_r\beta E_r - \sum_r P_r^{(o)}\beta E_r)}_{0} + k\ln Z\underbrace{(\sum_r P_r - \sum_r P_r^{(o)})}_{0} \\
&= k\sum_r P_r\ln\frac{P_r^{(o)}}{P_r}\ .
\end{aligned}$$

We also note that $\ln x \le x - 1$ which implies

$$S - S_o = k\sum_r P_r \ln\frac{P_r^{(o)}}{P_r} \le k\sum_r (P_r^{(o)} - P_r) = 0$$

Thus we must have

$$S \leq S_o$$

where equality represents the most likely canonical distribution.

6.5 Ideal Gas in a Gravitational Field

Reif §7.2: An ideal monoatomic gas of N particles, each of mass m, is in thermal equilibrium at absolute temperature T. The gas is contained in a cubical box of side L, whose top and bottom sides are parallel to the earth's surface. The effect of the earths's uniform gravitational field on the particles should be considered, the acceleration due to gravity being g.

(a) What is the average kinetic energy of a particle?

(b) What is the average potential energy of the particle?

This problem is most easily approached by first determining the partition function for a gas molecule in the gravitational field. We have

$$E = \frac{p^2}{2m} + mgz$$

Treating the system classically we have

$$\begin{aligned}
Z &= \frac{1}{h_0^3} \iiint_{-L/2}^{L/2} \iiint_{-\infty}^{\infty} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)-\beta mgz} dp_x dp_y dp_z dx dy dz \\
&= \frac{1}{h_0^3} \iint_{-L/2}^{L/2} dx dy \iint_{-\infty}^{\infty} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)} dp_x dp_y dp_z \int_{-L/2}^{L/2} e^{-\beta mgz} dz \\
&= \left(\frac{L}{h_0}\right)^3 \left(\sqrt{\frac{\pi 2m}{\beta}}\right)^3 \int_{-L/2}^{L/2} \frac{1}{L} e^{-\beta mgz} dz \qquad \text{(doing the Gaussian integral)} \\
&= \left(\frac{L^2 \pi 2m}{h_0^2 \beta}\right)^{3/2} \left[\frac{2}{\beta mgL} \sinh\left(\frac{\beta mgL}{2}\right)\right]
\end{aligned}$$

The first term in the product is the kinetic term, which is the same as for a normal ideal gas. The second term in the product is the potential term.

(a) The kinetic energy can be given either by the equipartition thereom as $\bar{E}_k = \frac{3}{2}kT$ or by taking a derivatives of the partition function

$$\bar{E}_k = -\frac{\partial \ln Z_k}{\partial \beta} = \frac{\partial}{\partial \beta}\frac{3}{2} \ln \beta = \frac{3}{2\beta} = \frac{3}{2}kT$$

(b) The potential energy can be found by taking derivatives of the potential part of the partition function

$$\bar{E}_p = -\frac{\partial \ln Z_p}{\partial \beta} = \frac{1}{\beta} - \frac{1}{\sinh(\beta mgL/2)} \frac{\partial \sinh(\beta mgL/2)}{\partial \beta} = kT - \frac{mgL}{2} \frac{\cosh(\beta mgL/2)}{\sinh(\beta mgL/2)}$$

This gives

$$\boxed{\bar{E}_p = kT - \frac{mgL}{2} \coth(mgL/2kT)}$$

Checking the zero gravity limit: $g \to 0$ we have $\coth(mgL/2kT) \to \frac{2kT}{mLg} + \frac{mgL}{6kT} + O(g^3)$, Thus we have $\bar{E}_p \to kT - \frac{mgL}{2}\frac{2kT}{mgL} = kT - kT = 0$ as expected.

□