Thermodynamics and Statistical Mechanics Homework Assignment 3

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Problem 1

Consider a homogeneous mixture of inert monatomic ideal gases at absolute temperature T in a container of volume V. Let there be ν_1 moles of gas 1, ν_2 moles of gas 2, ..., and ν_k moles of gas k.

a) By considering the classical partition function of this system, derive its equation of state, i.e., find an expression for its total mean pressure $\bar{p}$.

b) How is this total pressure $\bar{p}$ of the gas related to the pressure $\bar{p}_i$ with the ith gas would produce if it alone occupied the entire volume at this temperature?

Solution

a) The partition function for one of our gases is

$$Z_i = \frac{\zeta^{N_i}}{N_i!}$$

where

$$\zeta = V\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}$$

The total partition function will be

$$Z_{tot} = \prod_{i=1}^{k} \frac{\zeta^{N_i}}{N_i!}$$

The average pressure is

$$\langle p \rangle = \frac{1}{\beta}\frac{\partial \ln(Z_{tot})}{\partial V}$$

Using the properties of logarithms, we can separate the total partition function into a sum of individual partition functions. Let's find the pressure for one of the gases.

$$\ln(Z_1) = N_1 \ln(\zeta) - \ln(N_1!) = N_1 \ln(\zeta) - N_1 \ln(N_1) + N_1$$

The terms not directly related to volume will disappear with the derivative which leaves us with

$$\langle p_1 \rangle = \frac{kTN_1}{V}$$

Using the properties of logarithms, we can find the total average pressure by adding up the partial pressures of each of the gases with weights proportional to their molar concentration. This gives us an average pressure of

$$\langle p \rangle = \sum_{i=1}^{k} \frac{kT\nu_i}{V}$$

b) The total average pressure of the gas is equal to the sum of the average pressures each gas produces with sole occupancy.

Problem 2

An ideal monatomic 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 earth's uniform gravitational field on the particle 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 a particle?

Solution

a) We can begin this by looking at the part of the partition function that is responsible for the kinetic energy.

$$Z_K = \frac{1}{h^3} \int d^3p e^{-\beta(\frac{p_x^2+p_y^2+p_z^2}{2m})} = \frac{1}{h^3} \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}$$

We can then find the average kinetic energy by taking the logarithm and differentiating with respect to β.

$$\langle T \rangle = -\frac{\partial \ln(Z_k)}{\partial \beta} = \frac{\partial}{\partial \beta}(\frac{3}{2} \ln(Z_k) + \text{constants}) = \frac{3}{2\beta}$$

b) We can now look at the potential energy part of our partition function to find the average potential energy.

$$Z_P = \int d^3q e^{-\beta mghz} = L^2\Big(\frac{-1}{\beta mg}\Big)(e^{-\frac{\beta mgL}{2}} - e^{\frac{\beta mgL}{2}}) = \frac{2L^2}{\beta mg}\sinh\Big(\frac{\beta mgL}{2}\Big)$$

We can then find the average potential energy in the same way as we found the average kinetic energy in the previous part.

$$\langle V\rangle = -\frac{\partial Z_P}{\partial \beta} = \frac{\partial}{\partial \beta}(\ln\Big(\sinh\Big(\frac{\beta mgL}{2}\Big)\Big) - \ln(\beta)$$

$$= \frac{1}{\beta} - \frac{1}{\sinh\big(\frac{\beta mgL}{2}\big)}\frac{mgL}{2}\cosh\Big(\frac{\beta mgL}{2}\Big) = \frac{1}{\beta} - \frac{mgL}{2}\coth\Big(\frac{\beta mgL}{2}\Big)$$

Problem 3

A thermally insulated container is divided by a partition into two compartments, the right compartment having a volume b times as large as the left one. The left compartment contains ν moles of an ideal gas at temperature T and pressure $\bar{p}$. The right compartment also contains ν moles of an ideal gas at the temperature T. The partition is now removed. Calculate

a) The final pressure of the gas mixture in terms of $\bar{p}_i$

b) The total change of entropy if the gases are different

c) The total change in entropy if the gases are identical.

Solution

a) When the partition is removed, we will have 2ν moles of the gas, and the total volume will be $(1+b)V$ which gives us a final pressure, using ideal gas law, of

$$p_f = \frac{2\nu kT}{(1+b)V}$$

Which is also the sum of the partial pressures of each gas if it took up the whole container

$$p_f = \frac{\nu kT}{(1+b)V} + \frac{\nu kT}{(1+b)V} = \frac{2\nu kT}{(1+b)V}$$

b) The entropy os some ideal gas is

$$S = Nk(\ln\Big(\frac{V}{N}\Big) + \frac{3}{2}\ln(T) + \frac{3}{2}\ln\Big(\frac{2\pi mk}{h^2}\Big) + \frac{5}{2})$$

Since the temperature is the same all around and that energy is conserved, we can ignore the last three terms and focus on just the first one. Since the gases are different, we have to treat their entropies both before and after the partition's removal separately. The change in entropy is then

$$\Delta S = S_{1f} + S_{2f} - S_{1i} - S_{2i}$$
$$= k\nu(2\ln\left(\frac{(1+b)V}{\nu}\right) - \ln\left(\frac{V}{\nu}\right) - \ln\left(\frac{bV}{\nu}\right))$$
$$= k\nu(\ln\left(\frac{(1+b)^2V^2}{\nu^2}\right) - \ln\left(\frac{bV^2}{\nu^2}\right))$$
$$= k\nu\ln\left(\frac{(1+b)^2}{b}\right)$$

c) Since the gases are identical, we can't treat the gases separately in the final total entropy. We can ignore the same terms we did in the previous part and our change in entropy will be

$$\Delta S = S_f - S_{1i} - S_{2i}$$
$$= 2k\nu\ln\left(\frac{(1+b)V}{2\nu}\right) - k\nu\ln\left(\frac{V}{\nu}\right) - k\nu\ln\left(\frac{bV}{\nu}\right)$$
$$= k\nu(\ln\left(\frac{(1+b)^2V^2}{4\nu^2}\right) - \ln\left(\frac{bV^2}{\nu^2}\right))$$
$$= k\nu\ln\left(\frac{(1+b)^2}{4b}\right)$$

Problem 4

Consider an ideal gas of particle mass m that exists in a d-dimensional cube of space, where d is a positive integer. Take the volume of the gas to be the product of the linear dimension, $V = L^d$ for d dimensions. The gas is in equilibrium with a thermal reservoir of temperature T.

a) Find a general expression for the energy of the gas $U(N,T)$. Compare your result with that for the 3D ideal gas law.

b) Find a general expression for the pressure of the gas $p(N,V,T)$. Compare your result with that for the 3D ideal gas law.

c) Find a general expression for the entropy of the gas $\sigma(N,V,T)$. Compare your result with that for the 3D ideal gas law.

Solution

a) We start by finding the partition function for one particle

$$Z_1 = \frac{1}{h^d}\int d^d p d^d q e^{-\frac{\beta p^2}{2m}} = \left(\frac{L}{h}\right)^d \left(\frac{2\pi m}{\beta}\right)^{\frac{d}{2}}$$

Since these particles are non-interacting, the total partition function will be

$$Z = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{L}{h}\right)^{Nd}\left(\frac{2\pi m}{\beta}\right)^{\frac{Nd}{2}}$$

The log of the partition function will then be

$$\ln(Z) = Nd\ln\left(\frac{L}{h}\right) + \frac{Nd}{2}\ln\left(\frac{2\pi m}{\beta}\right) - \ln(N!)$$

The average energy is then

$$\langle E\rangle = U(T,N) = -\frac{\partial \ln(Z)}{\partial\beta} = \frac{Nd}{2\beta}$$

In the third dimension we would have

$$U = \frac{3N}{2\beta}$$

Which is what we would expect. Every extra dimension seems to add an extra kinetic of $\frac{1}{2}kT$.

b) To find the pressure, we must first find the Helmholtz Free Energy

$$F = -kT\ln(Z) = -kTNd(\ln\left(\frac{L}{h}\right) + \frac{1}{2}\ln\left(\frac{2\pi m}{\beta}\right)) + kT\ln(N!)$$

The pressure is then

$$p = -\frac{\partial F}{\partial V} = \frac{kNT}{L^d} = \frac{kNT}{V}$$

This is the same as the 3D version so changing dimensionality has no effect on pressure.

c) Entropy can be related to the energy and free energy of our system by

$$S = \frac{U-F}{T} = \frac{Nkd}{2} + kN\ln\left(\frac{V}{h^d}\right) - k\ln(N!) + \frac{kNd}{2}\ln\left(\frac{2\pi m}{\beta}\right)$$

$$= \frac{Nkd}{2} + kN + kN\ln\left(\frac{V}{h^d}\right) - kN\ln(N) + \frac{kNd}{2}\ln\left(\frac{2\pi m}{\beta}\right)$$

Let $\eta = \frac{2\pi m}{\beta}$ so

$$S = Nk(\frac{d}{2}+1) + kN\ln\left(\frac{V}{h^d}\right) - kN\ln(N) + kN\ln\left(\eta^{\frac{d}{2}}\right)$$

$$= Nk(\frac{d}{2}+1) + kN\ln\left(\frac{V\eta^{\frac{d}{2}}}{h^d N}\right)$$

In the third dimension this will be

$$Nk(\frac{5}{2} + \ln\left(\frac{V(2\pi m)^{\frac{3}{2}}}{h^3 N\beta^{\frac{3}{2}}}\right)) = Nk(\frac{5}{2} + \ln\left(\frac{V}{N\lambda^3}\right))$$

Using the de-Broglie wavelength λ which is equal to

$$\lambda = \sqrt{\frac{h^2\beta}{2\pi m}}$$

Which is what we would expect.

Problem 5

A very sensitive spring balance consists of a quarta spring suspended from a fixed support. The spring constant is α, i.e., the restoring force of the spring is $-\alpha x$ if the spring is stretched by an amount x. The balance is at a temperature T in a location where the acceleration due to gravity g.

a) If a very small object of mass M is suspended from the spring, what is the mean resultant elongation $\bar{x}$ of the spring?

b) What is the magnitude $\langle(x-\bar{x})^2\rangle$ of the thermal fluctuations of the object about its equilibrium position?

c) It becomes impractical to measure the mass of an object when the fluctuations are so large that $[\langle(x-\bar{x})^2\rangle]^{1/2} = \bar{x}$. What is the minimum mass M which can be measured with this balance?

Solution

a) The force of gravity will equal the spring force at around the mean resultant elongation of the spring

$$Mg = \alpha\langle x\rangle$$

$$\langle x\rangle = \frac{Mg}{\alpha}$$

b) The energy of the spring will be

$$E_K = \frac{1}{2}\alpha \left\langle (x - \langle x \rangle)^2 \right\rangle = \frac{1}{2}kT$$

This will give us

$$\left\langle (x - \langle x \rangle)^2 \right\rangle = \frac{kT}{\alpha}$$

c) We can use the results from the previous two parts to find the minimum mass that can be reasonably measured.

$$\langle x \rangle = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$$

$$\frac{Mg}{\alpha} = \sqrt{\frac{kT}{\alpha}}$$

$$M = \sqrt{\frac{kT\alpha}{g^2}}$$