p85

Fall 1993 #14

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 gravitational field should be considered, the acceleration due to gravity being g.

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

The partition function for a single molecule is:

$$z = \sum_r e^{-\beta E_r}$$

Where:

$$E_r = \frac{p_r^{\,2}}{2m} + mgz$$

For box dimensions large compared to the DeBroglie wavelength of a molecule, the values of E_r are closely spaced and the summation can be written as an integral.

$$z = \iint e^{-\beta\left(\frac{p^2}{2m}+mgz\right)} d^3\vec{p}\, d^3\vec{r}$$

The average kinetic energy can now be written as:

$$\overline{KE} = \frac{\int \frac{p^2}{2m} e^{-\beta\frac{p^2}{2m}} d^3\vec{p} \int e^{-\beta mgz} d^3\vec{r}}{\int e^{-\beta\frac{p^2}{2m}} d^3\vec{p} \int e^{-\beta mgz} d^3\vec{r}} = -\frac{\partial}{\partial\beta}\ln \int e^{-\beta\frac{p^2}{2m}} d^3\vec{p}$$

$$\overline{KE} = -\frac{\partial}{\partial\beta}\ln\left[\int_{-\infty}^{\infty} e^{-\beta\frac{p_x^2}{2m}} dp_x \int_{-\infty}^{\infty} e^{-\beta\frac{p_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\beta\frac{p_z^2}{2m}} dp_z\right]$$

$$\overline{KE} = -\frac{\partial}{\partial\beta}\ln\left[\int_{-\infty}^{\infty} e^{-\beta\frac{p^2}{2m}} dp\right]^3$$

The integral in brackets above is a Gaussian integral, which can be evaluated using:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{1/2}$$

Thus, with the substitution $\alpha = \beta/2m$ one finds

$$\overline{KE} = -\frac{\partial}{\partial\beta}\ln\left[\sqrt{\pi}\left(\frac{\beta}{2m}\right)^{-1/2}\right]^3$$

$$\overline{KE} = -3\frac{\partial}{\partial\beta}\left[\frac{1}{2}\ln\pi - \frac{1}{2}\ln\beta + \frac{1}{2}\ln(2m)\right]$$

$$\overline{KE} = \frac{3}{2\beta} = \frac{3}{2}kT$$

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

Following the same procedure as in a)

$$\overline{PE} = \frac{\int e^{-\beta\frac{p^2}{2m}} d^3\vec{p} \int mgze^{-\beta mgz} d^3\vec{r}}{\int e^{-\beta\frac{p^2}{2m}} d^3\vec{p} \int e^{-\beta mgz} d^3\vec{r}} = -\frac{\partial}{\partial\beta} \ln \int_0^L e^{-\beta mgz} dz$$

$$\overline{PE} = -\frac{\partial}{\partial\beta} \ln\left[\left(\frac{-1}{\beta mg}\right)\left[e^{-\beta mgz}\right]_0^L\right]$$

$$\overline{PE} = -\frac{\partial}{\partial\beta} \ln\left[\left(\frac{1}{\beta mg}\right)\left(e^0 - e^{-\beta mgL}\right)\right]$$

$$\overline{PE} = -\frac{\partial}{\partial\beta}\left[-\ln\beta - \ln(mg) + \ln\left(1 - e^{-\beta mgL}\right)\right]$$

$$\overline{PE} = \frac{1}{\beta} + \frac{1}{\left(1 - e^{-\beta mgL}\right)}\left(-mgL\right)e^{-\beta mgL}$$

$$\overline{PE} = \frac{1}{\beta} - mgL\left(\frac{e^{-\beta mgL}}{e^{-\beta mgL}}\right)\left(\frac{1}{e^{\beta mgL} - 1}\right)$$

$$\overline{PE} = kT + mgL\left(\frac{1}{1 - e^{-mgL/kT}}\right)$$