Solution Problem #14

Spring 2000 Comp

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14) (Stat. Mech./Thermo.) 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 earth'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 a particle?

The partition function of a particle is

$$Z = \int_{\vec{p}}\int_{\vec{r}} e^{-\beta E}\, d\vec{p}\, d\vec{r}$$

The energy of the particle is

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

Looking at the partition function

$$Z = \int_{-\infty}^{\infty} e^{-\beta\frac{P_x^2}{2m}} dp_x \int_{-\infty}^{\infty} e^{-\beta\frac{P_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\beta\frac{P_z^2}{2m}} dp_z \int_0^L dx \int_0^L dy \int_0^L e^{-\beta mgz}\, dz$$

from Reif (p 241) we know that the momentum part of the integral is equal to $\left(\sqrt{\frac{2\pi M}{\beta}}\right)^3$

Therefore

$$Z = \left(\sqrt{\frac{2\pi M}{\beta}}\right)^3 L^2 \int_0^L e^{-\beta m g z}\, dz$$

$$= \left(\sqrt{\frac{2\pi M}{\beta}}\right)^3 L^2 \;\frac{\left(1 - e^{-\beta g L m}\right)}{\beta g m}$$

For part a)

The average Kinetic energy is.

$$\langle KE \rangle = \frac{\int_{\vec{p}}\int_{\vec{r}} KE\; e^{-\beta E}\, d\vec{p}\, d\vec{r}}{Z}$$

$$\langle KE \rangle = \frac{\int_{\vec{p}} \frac{\vec{p}^{\,2}}{2m} e^{-\frac{\beta \vec{p}^{\,2}}{2m}}\, d\vec{p} \int_{\vec{r}} e^{-\beta m g z}\, d\vec{r}}{Z}$$

Looking just at the numerator,
and first just at the momentum piece

$$\int_{\vec{p}} \frac{\vec{p}^{\,2}}{2m} e^{-\beta \vec{p}^{\,2}/2m} d\vec{p} = \int_{-\infty}^{\infty} \frac{p_x^2}{2m} e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x dp_y dp_z$$

$$+ \int_{-\infty}^{\infty} \frac{p_y^2}{2m} e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x dp_y dp_z + \int_{-\infty}^{\infty} \frac{p_z^2}{2m} e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x dp_y dp_z$$

We note that

$$\int_{-\infty}^{\infty} \frac{p_i^2}{2m} e^{-\frac{\beta p_i^2}{2m}} dp_i = \frac{1}{2m} \left[\frac{\sqrt{2\pi}}{\left(\frac{\beta}{m}\right)^{3/2}} \right]$$

and again that

$$\int_{-\infty}^{\infty} e^{-\frac{\beta p_i^2}{2m}} dp_i = \sqrt{\frac{2\pi m}{\beta}}$$

Therefore the momentum piece reduces to

$$\frac{1}{2m} \left[\frac{\sqrt{2\pi}}{\left(\frac{\beta}{m}\right)^{3/2}} \right] \times 3 \left(\sqrt{\frac{2\pi m}{\beta}} \right)^2$$

Looking at the space part,

$$\int_0^L dx \int_0^L dy \int_0^L e^{-\beta m g z} dz = \frac{L^2(1-e^{-\beta m g L})}{\beta m g}$$

putting all of this together to get the average kinetic energy

$$\langle KE \rangle = \frac{\frac{1}{2m}\left[\frac{\sqrt{2\pi}}{\left(\frac{\beta}{m}\right)^{3/2}}\right] 3\left(\sqrt{\frac{2\pi m}{\beta}}\right)^2 L^2(1-e^{-\beta m g L})}{\beta m g\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 L^2\left(\frac{1-e^{-\beta m g L}}{\beta m g}\right)}$$

now simplify ...

$$\langle KE \rangle = \frac{3}{2m}\left[\frac{\sqrt{2\pi}}{\left(\frac{\beta}{m}\right)^{3/2}}\right]\frac{1}{\sqrt{\frac{2\pi m}{\beta}}}$$

$$= \frac{3}{2m}\sqrt{\frac{\beta}{m}}\left(\sqrt{\frac{m}{\beta}}\right)^3 = \frac{3}{2m}\frac{m}{\beta} = \frac{3}{2}KT$$

Therefore

$$\boxed{\langle KE \rangle = \frac{3}{2}KT}$$ which is what you would expect.

Now for part b)

$$\langle U \rangle = \frac{\int_{\vec{p}} \int_{\vec{r}} U\, e^{-\beta E}\, d\vec{p}\, d\vec{r}}{Z}$$ is the average potential energy

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

$$= \frac{\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 \int_0^L dx \int_0^L dy \int_0^L mgz\, e^{-\beta mgz}\, dz}{Z}$$

$$= \frac{\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 L^2 \int_0^L mgz\, e^{-\beta mgz}\, dz}{\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 L^2 \left(1 - e^{-\beta mgL}\right) / \beta mg}$$

$$= \frac{\beta mg \int_0^L mgz\, e^{-\beta mgz}\, dz}{\left(1 - e^{-\beta mgL}\right)}$$

$$\int_0^L mgz\, e^{-\beta mgz}\, dz = \frac{e^{-\beta mgL}\left(e^{\beta mgL} - 1 - \beta mgL\right)}{\beta^2 gm}$$

$$\langle U \rangle = \frac{e^{-\beta mgL}\left(e^{\beta mgL} - 1 - \beta mgL\right)}{\beta\left(1 - e^{-\beta mgL}\right)}$$

$$\langle U \rangle = \frac{1 - e^{-\beta mgL} - \beta mgL\, e^{-\beta mgL}}{\beta\left(1 - e^{-\beta mgL}\right)}$$

$$\boxed{\langle U \rangle = \frac{1}{\beta} - \frac{mgL}{\left(e^{\beta mgL} - 1\right)}}$$

which is not what I would expect

To get some physical intuition, look at the limits of this answer when L goes small.

$$\lim_{L \text{ small}} \rightarrow \frac{1}{\beta} - mgL\left(\frac{1}{1 + \beta mgL + \ldots - 1}\right)$$

$$\rightarrow \frac{1}{\beta} - \frac{1}{\beta} \rightarrow 0 \quad \text{which does make sense.}$$