Ex5022: Perssure via the virial theorem and the Lenard Jones Potential

Submitted by: Tal Malinovitch

The problem:

A gas of f N particles is confined in a box of volume V with temprature of T.

(a)Write the virial theorem for a system with interparticle interaction $u(r) \sim r^{-\gamma}$. Deduce that the mean kinetic energy is

$$K = -\mathcal{V}/2 = (3PV - \gamma U)/2 = \frac{1}{2-\gamma}(3PV - \gamma E)$$

where $E = K + U$. What happens for $\gamma = 2$?

(b) For the Lenard Jones two body interaction given by: $u(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$, find an expression for the pressure via the virial theorem, assumeing that the moments $\langle r^n \rangle_T$ are known.

(c) In the case above, Using the virial expansion, find an explicit expression for the pressure in both high and low temperatures.

(d) For high temperatures, can you find a single length scale? that is, a single r_0 that determine the relvent moments of the problem?

The solution:

(a) The virial theroeml states that:

$$P = \frac{< p\frac{\partial K}{\partial p} > - < r\frac{\partial u}{\partial r} >}{3V}$$

For inter-particle interaction of the form $u(r) = Ar^{-\gamma}$, and kinetic term of the form $K(p) = \frac{p^2}{2m}$, the following holds :

$$< p\frac{\partial K}{\partial p} >= \sum_{i=1}^{n} \frac{p_i^2}{m} = 2K$$

$$< r\frac{\partial u}{\partial r} >= \sum_{<ij>} -\gamma A r_{ij}^{-\gamma} = -\gamma u$$

So the virial theorem will be (noting that $E = u + K$):

$$P = \frac{2K + \gamma u}{3V} = \frac{2K + \gamma E - \gamma K}{3V}$$

So it follows that:

$$K = \frac{3PV - \gamma u}{2} = \frac{3PV - \gamma E}{2 - \gamma}$$

A special case is for $\gamma = 2$, that leads to the equipartition theroem :

$$P = \frac{2K + \gamma u}{3V} = \frac{2K + 2u}{3V} = \frac{2E}{3V}$$

And in other words:

$$K = \frac{E}{2} = \frac{3PV}{4}$$

(b) For the Lenard Jones potential, given by: $u\left(r\right) = \frac{a}{r^{12}} - \frac{b}{r^{6}}$ the virial theorem will be:

$$P = \frac{1}{V}(NT - \frac{1}{3} < \sum_{<ij>} r_{ij}\frac{\partial u}{\partial r_{ij}} >)$$

Noting that :

$$< \sum_{<ij>} r_{ij}\frac{\partial u}{\partial r_{ij}} > = < \sum_{ij} \frac{-12a}{r_{ij}^{12}} + \frac{6b}{r_{ij}^{6}} > = \frac{N(N-1)}{2}(-12a < r^{-12} > + 6b < r^{-6} >)$$

Since $N \gg 1$, we could approximate $N(N-1) \approx N^2$, and write:

$$P = \frac{NT}{V} + \frac{N^2}{V}(2a < r^{-12} > - b < r^{-6} >)$$

(c) Using the virial expansion we could write:

$$P = \frac{NT}{V}(1 + a_2(\frac{N}{V}))$$

where :

$$a_2 = -\frac{1}{2}\int\int\int(e^{-\beta u(r)} - 1)d^3r = -\frac{1}{2}\int\int\int(e^{-\beta(\frac{a}{r^{12}} - \frac{b}{r^{6}})} - 1)d^3r$$

The dominent contribution in given by r close to the minimum point of the potential, so the high and low temperatures will be determined by those r's . the minimum of the potential r_0 will obey the following equation:

$$\frac{\partial u}{\partial r}\mid_{r=r_0} = 0$$

$$-12\frac{a}{r_0^{13}} + 6\frac{b}{r_0^{6}} = 0$$

$$r_0 = (\frac{2a}{b})^{\frac{1}{6}}$$

For low temperatue ($-\frac{u(r)}{T} \gg 1$, for r around r_0), we could approximate the potential by a quadratic expression around r_0:

$$u\left(r\right) \approx u\left(r_0\right) + \frac{\partial u\left(r\right)}{\partial r}\mid_{r=r_0}(r - r_0) + \frac{1}{2}\frac{\partial^2 u\left(r\right)}{\partial^2 r}\mid_{r=r_0}(r - r_0)^2$$

first, we will calculate the coefficients ($r_0 = (\frac{2a}{b})^{\frac{1}{6}}$):

$$u\left(r_0\right) = \frac{a}{r_0^{12}} - \frac{b}{r_0^{6}} = a(\frac{b}{2a})^2 - b(\frac{b}{2a}) = \frac{b^2}{4a} - \frac{b^2}{2a} = -\frac{b^2}{4a}$$

$$\frac{\partial u(r_0)}{\partial r} = 0$$

$$\frac{\partial^2 u(r_0)}{\partial^2 r} = 12 * 13\frac{a}{r_0^{14}} - 6 * 7\frac{b}{r_0^8} = 6[26a(\frac{b}{2a})^{\frac{7}{3}} - 7b(\frac{b}{2a})^{\frac{4}{3}}] =$$

$$= 6(\frac{b}{2a})^{\frac{1}{3}}[26a(\frac{b}{2a})^2 - 7b(\frac{b}{2a})] = 6(\frac{b}{2a})^{\frac{1}{3}}[13\frac{b^2}{2a} - 7\frac{b^2}{2a}] = 36(\frac{b}{2a})^{\frac{1}{3}}\frac{b^2}{2a}$$

for convenience we will use $k = 18(\frac{b}{2a})^{\frac{1}{3}}\frac{b^2}{a}$ so the second virial coefficient will be:

$$a_2 = -\frac{1}{2}\int\int\int(e^{-\beta u(r)} - 1)d^3r = -\frac{1}{2}\int\int\int(e^{-\beta(u(r_0)+\frac{k}{2}(r-r_0)^2)} - 1)d^3r =$$

$$= -\frac{1}{2}e^{\beta\frac{b^2}{4a}}\int\int\int e^{-\beta\frac{k}{2}(r-r_0)^2}d^3r + \frac{V}{2} = \frac{V}{2} - \frac{1}{2}e^{\beta\frac{b^2}{4a}}(\frac{2\pi}{k\beta})^{\frac{3}{2}}$$

so the pressure will be:

$$P = \frac{NT}{V}(1 + \frac{NV}{2V} - \frac{1}{2}e^{\beta\frac{b^2}{4a}}(\frac{2\pi}{k\beta})^{\frac{3}{2}}(\frac{N}{V}))$$

$$P = \frac{NT}{V}(1 + \frac{N}{2} - \frac{N}{2V}e^{\beta\frac{b^2}{4a}}(\frac{2a\pi}{18b^2\beta}(\frac{2a}{b})^{\frac{1}{3}})^{\frac{3}{2}})$$

$$P = \frac{NT}{V}(1 + \frac{N}{2} - \frac{N}{2V}e^{\beta\frac{b^2}{4a}}(\frac{a\pi}{9b^2\beta})^{\frac{3}{2}}\sqrt{\frac{2a}{b}})$$

$$P = \frac{NT}{V}(1 + \frac{N}{2} - \frac{N}{54b^3V}e^{\frac{b^2}{4aT}}(aT\pi)^{\frac{3}{2}}\sqrt{\frac{2a}{b}})$$

For high temperatures ($-\frac{u(r)}{T} \ll 1$, for r around r_0), we will divide the potential to two sections: for $r > r_0$ we will use the approximation: $e^{-\beta u(r)} \approx 1 - \beta u(r)$ and for $r < r_0$ we will approximate the potential to $+\infty$ so that :$e^{-\beta u(r)} \approx 0$ introducing that approximation the second coefficient will be:

$$a_2 = -\frac{1}{2}\int\int\int(e^{-\beta u(r)} - 1)d^3r = -\frac{1}{2}\int_0^\infty\int_{-1}^1\int_0^{2\pi}(e^{-\beta(u(r_0)+\frac{k}{2}(r-r_0)^2)} - 1)r^2 d\phi d\cos\theta dr =$$

$$= -\frac{1}{2}4\pi(\int_0^{r_0}(e^{-\beta u(r)} - 1)r^2dr + \int_{r_0}^\infty(e^{-\beta u(r)} - 1)r^2dr) \approx -2\pi(-\int_0^{r_0}r^2dr - \int_{r_0}^\infty\beta u(r)r^2dr) =$$

$$= 2\pi(\frac{1}{3}r^3 |_{r=0}^{r=r_0} + \beta\int_{r_0}^\infty(\frac{a}{r^{10}} - \frac{b}{r^4})dr = 2\pi(\frac{1}{3}r_0^3 - \beta\frac{a}{9r^9} |_{r=r_0}^{r=\infty} + \beta\frac{b}{3r^3} |_{r=r_0}^{r=\infty}) =$$

$$= 2\pi(\frac{1}{3}r_0^3 + \beta\frac{a}{9r_0^9} - \beta\frac{b}{3r_0^3})$$

remembering that $r_0 = (\frac{2a}{b})^{\frac{1}{6}}$ we will get:

$$a_2 = 2\pi(\frac{1}{3}\sqrt{\frac{2a}{b}} + \beta\frac{a}{9}(\frac{b}{2a})^{\frac{3}{2}} - \beta\frac{b}{3}\sqrt{\frac{b}{2a}}) = 2\pi\sqrt{\frac{b}{2a}}(\frac{2a}{3b} + \beta\frac{ab}{18a} - \beta\frac{b}{3}) =$$

$$= 2\pi\sqrt{\frac{b}{2a}}(\frac{2a}{3b} + \beta\frac{b}{18} - \beta\frac{b}{3}) = 2\pi\sqrt{\frac{b}{2a}}(\frac{2a}{3b} - \beta\frac{5b}{18})$$

that is:

$$a_2 = \frac{\pi}{3}\sqrt{\frac{2b}{a}}(\frac{2a}{b} - \beta\frac{5b}{6})$$

so that the pressure will be:

$$P = \frac{NT}{V}[1 + \frac{N}{V}\frac{\pi}{3}\sqrt{\frac{2b}{a}}(\frac{2a}{b} - \beta\frac{5b}{6})]$$

$$P = \frac{NT}{V} + \frac{N^2T\pi}{3V^2}\sqrt{\frac{2b}{a}}(\frac{2a}{b} - \beta\frac{5b}{6})$$

$$P = \frac{NT}{V} + \frac{2N^2T\pi}{3V^2}\sqrt{\frac{2a}{b}} - \frac{5bN^2\pi}{18V^2}\sqrt{\frac{2b}{a}}$$

(d)
In (b) we received the result:

$$P = \frac{NT}{V} + \frac{N^2}{V}(2a < r^{-12} > -b < r^{-6} >)$$

note that this and in (c) for high temperatures we received:

$$P = \frac{NT}{V} + \frac{2N^2T\pi}{3V^2}\sqrt{\frac{2a}{b}} - \frac{5bN^2\pi}{18V^2}\sqrt{\frac{2b}{a}}$$

from the comperison we can write:

$$< r^{-12} >= \frac{2N^2T\pi}{3V^2}\sqrt{\frac{2a}{b}}\frac{V}{N^2 2a} = \frac{2\pi}{3V}\frac{T}{\sqrt{2ab}}$$

on the other hand we could also write:

$$< r^{-6} >= \frac{5bN^2\pi}{18V^2}\sqrt{\frac{2b}{a}}\frac{V}{N^2 b} = \frac{5\pi}{18V}\sqrt{\frac{2b}{a}}$$

From here it is clear that there are two different length scales that are defined in the system.
The first scale comes from the ratio between the attractive part and repulsive part of the interaction, relates to minimum of the potenial, and is described by: $\frac{a}{b} \sim r_0^6$
The other scale comes from the ratio between the interaction and the temperature, that is more related to the fluctuations, given by: $\frac{T}{\sqrt{ab}}$