# Linear Molecules (04/05)

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## 1 Solution

We propose that the rotational degrees of freedom do not affect the pressure of a gas inside a wide box. This argument is presented in detail in Appendix A. The results in Appendix A hold in the present two-dimensional case as well and this can be seen both statistically (volume is just replaced by surface) as well as microscopically. In any case, the rotational degrees of freedom do not contribute to the total pressure. The only way in which the nature of the molecules (specifically: their size) can contribute to the pressure is by imposing constraints upon the CM motion. This would make the allowed surface for the CM of each molecule less than the geometrical surface $S$ that would be allowed if the molecules were point-like. We assume linear molecules of length $L$. Then the partition function will contain a factor:

$$(2\pi S)^N = \left(\int dx\ dy\ d\theta\right)^N , \tag{1}$$

which is the equivalent "volume" $V^N$ over the allowed values of the degrees of freedom $x, y, \theta$. We denote by $x, y$ the CM coordinates of each rod ($0 \leq y \leq d$) and by $\theta$ ($-\pi/2 \leq \theta \leq \pi/2$) the angle between the rod and the $y$-axis (measured from the CM). Since the $x$-length of the box is not of interest (considered infinite) we disregard it by setting it equal to unity. The integral, thus, becomes:

$$2\pi S = \int dy\ d\theta. \tag{2}$$

The calculation of this integral breaks into two parts. First we compute its value over the regions where $y$ and $\theta$ are independent. Clearly, there is no such constraint in the region $L/2 \leq y \leq d - L/2$. So the contribution to the above integral in this region is $2\pi(d-L)$. The remaining regions break into two parts: the upper one and the lower one. Both of these regions are identical and have equal contributions to the integral. Thus, we can write (2) as $2\pi S = 2\pi(d-L) + 2I_{lower}$, where $I_{lower}$ is the contribution to the integral from the lower region. In the lower region ($y \leq L/2$) we sum over all the values of $\theta$, that is, from 0 to $2\pi$ and *subtract* the values of $\theta$ in the "forbidden" range $-\theta_0 \leq \theta \leq \theta_0$, $\pi - \theta_0 \leq \theta \leq \pi$, and $-\pi \leq \theta \leq -\pi + \theta_0$ where $\theta_0 = \arccos(2y/L)$. Taking this constraint into account we have:

$$I_{lower} = \int_0^{L/2} dy \left\{ \int_0^{2\pi} d\theta - \int_{-\theta_0}^{\theta_0} d\theta - \int_{\pi-\theta_0}^{\pi} d\theta - \int_{-\pi}^{-\pi+\theta_0} d\theta \right\} =$$

$$2\pi(L/2) - 4\int_0^{L/2} dy\ \arccos(2y/L) = \pi L - 2L. \tag{3}$$

Therefore, equation (2) becomes:

$$2\pi S = 2\pi(d-L) + 2(\pi-2)L, \tag{4}$$

or

$$S = d\left(1 - \frac{2L}{\pi d}\right). \tag{5}$$

Therefore, the pressure becomes

$$P_{lin} = P_p \left(1 - \frac{2L}{\pi d}\right)^{-1} \approx P_p\left(1 + \frac{2L}{\pi d} + \ldots\right), \tag{6}$$

where $P_p$ is the pressure of the gas if the particles were point-like.

In the case of rigid circles the situation is less complicated. Since their radius is $L/2\pi$ the allowed "surface" is $d - L/\pi$ and thus:

$$P_{circ} = P_p \left(1 - \frac{L}{\pi d}\right)^{-1} \approx P_p\left(1 + \frac{L}{\pi d} + \ldots\right). \tag{7}$$

We note that the correction term in the case of the rigid rods is just twice that of the circles. The reason for that simple relation lies, of course, in the choice of the diameter of the circle $L/\pi$. This is just the diameter of the circle we would obtain by "bending" the rigid rod and connecting its endpoints. We will demonstrate the reason behind this simple relation below. We first notice that the mean "height" of the CM of the rods that hit the wall is $\langle y \rangle = (L/2)(2/\pi)\int_0^{\pi/2} d\theta\ \cos\theta = L/\pi$. Therefore, we can replace the rods by rigid circles of radius $\langle h \rangle = L/\pi$ without affecting the pressure. The allowed "surface" of those "virtual" circles would be $S_v = d - 2L/\pi$, which is just the result obtained analytically in (5). The "surface" correction $2L/\pi$ for the rods is just twice the correction $L/\pi$ for the circles, simply because the mean hight of the CM of the rods ($\langle h \rangle = L/\pi$) is twice the mean hight of the CM of the circles ($L/2\pi$). In other words, the "virtual" circles described above have twice the radius of the "real" rigid circles of the problem. Therefore, we would expect to find the correction in the pressure in the case of rods to be twice the correction in the case of circles, simply by noticing that the bending of the rods into circles (connecting their endpoints) would just reduce the mean CM into half.