4.9: Pressure Variations for Macroscopic Samples

At 300 K, the standard deviation of N_2 speeds is about 40% of the average speed. Clearly the relative variation among molecular speeds in a sample of ordinary gas is very large. Why do we not observe macroscopic effects from this variation? In particular, if we measure the pressure at a small area of the container wall, why do we not observe pressure variations that reflect the wide variety of speeds with which molecules strike the wall?

Qualitatively, the answer is obvious. A single molecule whose scalar velocity is v contributes $P_1\left(v\right)=mv^2/3V$ to the pressure on the walls of its container. (See problem 20.) When we measure pressure, we measure an average squared velocity. Even if we measure the pressure over a very small area and a very short time, the

number of molecules striking the wall during the time of the measurement is very large. Consequently, the average speed of the molecules hitting the wall during any one such measurement is very close to the average speed in any other such measurement.

We are now able to treat this question quantitatively. For N_2 gas at 300 K and 1 bar, roughly $3{\times}10^{15}$ molecules collide with a square millimeter of wall every microsecond. (See problem 12.) The standard deviation of the velocity of an N_2 molecule is $201\ \mathrm{m\ s}^{-1}$. Using the central limit theorem, the standard deviation of the average of 3×10^{15} molecular speeds is

$$\frac{201\ m\ s^{-1}}{\sqrt{3\times 10^{15}}}\approx 4\times 10^{-6}\mathrm{ms}^{-1}$$

The distribution of the average of 3×10^{15} molecular speeds is very narrow indeed.

Similarly, when molecular velocities follow the Maxwell-Boltzmann distribution function, we can show that the expected value of the pressure for a single-molecule collision is $\left\langle P_1\left(v\right)\right\rangle =kT/V$. (See problem 21.) The variance of the distribution of these individual pressure measurements is $\sigma^2_{P_1\left(v\right)}=2k^2T^2/3V^2$, so that the magnitude of the standard deviation is comparable to that of the average:

$$\sigma_{P_1\left(v\right)}/\left\langle P_1\left(v\right)\right\rangle =\sqrt{2/3}$$

For the distribution of averages of 3×10^{15} pressure contributions, we find

$$\begin{aligned} P_{avg} &=\left\langle P_1\left(v\right)\right\rangle \\ &=\sqrt{3/2}\sigma_{P_1\left(v\right)} \\ \sigma_{avg} &=\frac{\sigma_{P_1\left(v\right)}}{\sqrt{3\times 10^{15}}} \end{aligned}$$

and

$$\frac{\sigma_{avg}}{P_{avg}}\approx 1.5\times 10^{-8}$$