CHEM 26300 (Chemical Kinetics and Dynamics) Problem Sets

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Contents

1 The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

Chapter 27

27-5. Arrange the following gases in order of increasing root-mean-square speed at the same temperature: O_2, N_2, H_2O, CO_2, NO_2, ${}^{235}UF_6$, ${}^{238}UF_6$.

27-7. The speed of sound in an ideal monatomic gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

Derive an equation for the ratio $u_{\text{rms}}/u_{\text{sound}}$. Calculate the root-mean-square speed for an argon atom at 20 °C and compare your answer to the speed of sound in argon.

27-12. We can use the equation for $f(u_x)$ to calculate the probability that the x-component of the velocity of a molecule lies within some range. For example, show that the probability that $-u_{x0} \leq u_x \leq u_{x0}$ is given by

$$\begin{aligned}\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= \sqrt{\frac{m}{2\pi k_\text{B}T}} \int_{-u_{x0}}^{u_{x0}} \mathrm{e}^{-mu_x^2/2k_\text{B}T}\,\mathrm{d}u_x \\ &= 2\sqrt{\frac{m}{2\pi k_\text{B}T}} \int_{0}^{u_{x0}} \mathrm{e}^{-mu_x^2/2k_\text{B}T}\,\mathrm{d}u_x\end{aligned}$$

Now let $mu_x^2/2k_\text{B}T = w^2$ to get the cleaner looking expression

$$\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} = \frac{2}{\sqrt{\pi}} \int_0^{w_0} \mathrm{e}^{-w^2}\,\mathrm{d}w$$

where $w_0 = u_{x0}\sqrt{m/2k_\text{B}T}$.

It so happens that the above integral cannot be evaluated in terms of any function that we have encountered up to now. It is customary to express the integral in terms of a new function called the **error function**, which is defined by

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^{z} \mathrm{e}^{-x^2}\,\mathrm{d}x$$

The error function can be evaluated as a function of z by evaluating its defining integral numerically. Some values of $\text{erf}(z)$ are

z	$\text{erf}(z)$	z	$\text{erf}(z)$
0.20	0.22270	1.20	0.91031
0.40	0.42839	1.40	0.95229
0.60	0.60386	1.60	0.97635
0.80	0.74210	1.80	0.98909
1.00	0.84270	2.00	0.99532

Now show that

$$\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} = \text{erf}(w_0)$$

Calculate the probability that $-\sqrt{2k_\text{B}T/m} \leq u_x \leq \sqrt{2k_\text{B}T/m}$.

27-20. Show that the variance of the equation $I(\nu) \propto \mathrm{e}^{-mc^2(\nu-\nu_0)^2/2\nu_0^2 k_\text{B}T}$ is given by $\sigma^2 = \nu_0^2 k_\text{B}T/mc^2$. Calculate σ for the $3p\ {}^2P_{3/2}$ to $3s\ {}^2S_{1/2}$ transition in atomic sodium vapor (see Figure 8.4 on McQuarrie and Simon (1997, p. 307)) at 500 K.

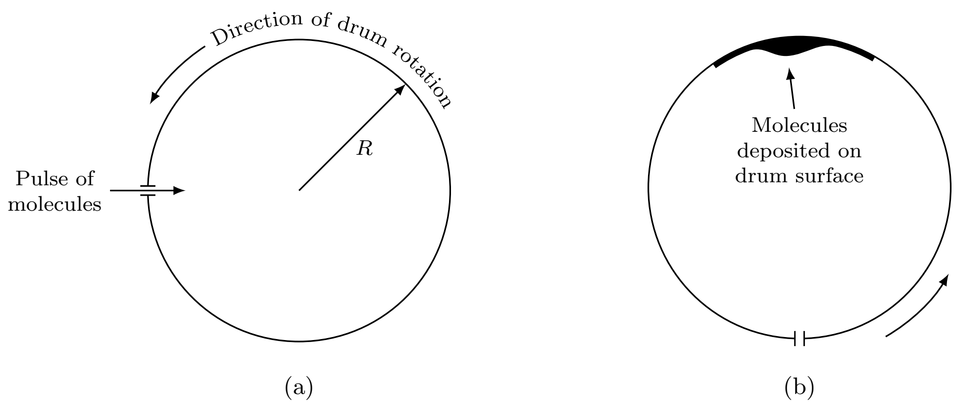
27-24. Show that the probability that a molecule has a speed less than or equal to u_0 is given by

$$\text{Prob}\{u \le u_0\} = \frac{4}{\sqrt{\pi}} \int_0^{x_0} x^2 \mathrm{e}^{-x^2}\,\mathrm{d}x$$

where $x_0 = u_0\sqrt{m/2k_\mathrm{B}T}$. This integral cannot be expressed in terms of any known function and must be integrated numerically. Use Simpson's rule or any other integration routine to evaluate $\text{Prob}\{u \le \sqrt{2k_\mathrm{B}T/m}\}$.

27-27. Derive an expression for $\sigma_\varepsilon^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$ from the equation for $F(\varepsilon)\,\mathrm{d}\varepsilon$. Now form the ratio $\sigma_\varepsilon / \langle \varepsilon \rangle$. What does this say about the fluctuation in ε?

27-34. The figure below illustrates another method that has been used to determine the distribution of molecular speeds.



A pulse of molecules collimated from a hot oven enters a rotating hollow drum. Let R be the radius of the drum, ν be the rotational frequency, and s be the distance through which the drum rotates during the time it takes for a molecule to travel from the entrance slit to the inner surface of the drum. Show that

$$s = \frac{4\pi R^2 \nu}{u}$$

where u is the speed of the molecule.

Use the equation for $\mathrm{d}z_\text{coll}$ to show that the distribution of molecular speeds emerging from the over is proportional to $u^3 \mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u$. Now show that the distribution of molecules striking the inner surface of the cylinder is given by

$$I(s)\,\mathrm{d}s = \frac{A}{s^5} \mathrm{e}^{-m(4\pi R^2\nu)^2/2k_\mathrm{B}Ts^2}\,\mathrm{d}s$$

where A is simply a proportionality constant. Plot I versus s for various values of $4\pi R^2\nu/\sqrt{2k_\mathrm{B}T/m}$, say 0.1, 1, and 3. Experimental data are quantitatively described by the above equation.

27-36. On the average, what is the time between collisions of a xenon atom at 300 K and...

(a) One torr;

(b) One bar.

27-40. The following table gives the pressure and temperature of the Earth's upper atmosphere as a function of altitude.

Altitude (km)	Pressure (mbar)	Temperature (K)
20.0	56	220
40.0	3.2	260
60.0	0.28	260
80.0	0.013	180

Assuming for simplicity that air consists entirely of nitrogen, calculate the mean free path at each of these conditions.

References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach.* University Science Books.