Problem 1A.7

Molecular velocity and mean free path. Compute the mean molecular velocity $\bar{u}$ (in cm/s) and the mean free path λ (in cm) for oxygen at 1 atm and 273.2 K. A reasonable value for d is 3 Å. What is the ratio of the mean free path to the molecular diameter under these conditions? What would be the order of magnitude of the corresponding ratio in the liquid state?

Answers: $\bar{u} = 4.25 \times 10^4$ cm/s, $\lambda = 9.3 \times 10^{-6}$ cm

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Solution

The formula for the mean molecular velocity $\bar{u}$ is given in Eq. 1.4-1 on page 22.

$$\bar{u} = \sqrt{\frac{8\kappa T}{\pi m}} \tag{1.4-1}$$

κ is Boltzmann's constant, $\kappa = 1.38066 \times 10^{-23}$ J/K and $T = 273.2$ K. Since the molecule is O_2, the molar mass is $M = 16.00 + 16.00 = 32.00$ g/mol. We can get the mass of a single molecule by dividing by Avogadro's number.

$$m = \frac{32.00 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ mol}}{6.02214 \times 10^{23} \text{ molecules}} \approx 5.314 \times 10^{-26} \, \frac{\text{kg}}{\text{molecule}}$$

Therefore,

$$\bar{u} \approx \sqrt{\frac{8(1.38066 \times 10^{-23})(273.2)}{\pi(5.314 \times 10^{-26})}} \approx 425 \, \frac{\text{m}}{\text{s}} \times \frac{100 \text{ cm}}{1 \text{ m}} = 4.25 \times 10^4 \, \frac{\text{cm}}{\text{s}}.$$

The formula for the mean free path is given in Eq. 1.4-3 on page 24.

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

$d = 3$ Å $= 3 \times 10^{-10}$ m and n is the number of molecules per unit volume. From the ideal gas law, we have $PV = NRT$. Solve for N/V, plug in the numbers, and change to these units.

$$\frac{N}{V} = \frac{P}{RT} = \frac{1 \text{ atm}}{0.0821 \, \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \cdot 273.2 \text{ K}} \approx 0.0446 \, \frac{\text{mol}}{\text{L}}$$

Change to the proper units.

$$\frac{N}{V} \approx 0.0446 \, \frac{\text{mol}}{\text{L}} \times \frac{6.02214 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3$$

$$n \approx 2.686 \times 10^{25} \, \frac{\text{molecules}}{\text{m}^3}$$

Therefore,

$$\lambda = \frac{1}{\sqrt{2}\pi(3 \times 10^{-10})^2(2.686 \times 10^{25})} \approx 9.3 \times 10^{-8} \text{ m} \times \frac{100 \text{ cm}}{1 \text{ m}} = 9.3 \times 10^{-6} \text{ cm}.$$

The ratio of the mean free path λ to the molecular diameter d is

$$\frac{\lambda}{d} = \frac{9.3 \times 10^{-8} \text{ m}}{3 \times 10^{-10} \text{ m}} \approx 310$$

Because of how close molecules are in the liquid state, they don't get very far before they hit one another, so I expect the ratio λ/d to be on the order of 1.