PHY 407 Chap 5 HW Solutions

(5.2) Let V be volume of room, and $\mathcal{V}$ be the volume under consideration.

The probability of finding a molecule in $\mathcal{V}$ is $\mathcal{V}/V$.

$\therefore$ the probability of not finding a molecule in $\mathcal{V}$ is $1-\mathcal{V}/V$.

Let $N = \#$ of molecules in the room.

Since, under STP conditions (ideal gas conditions) the molecules are considered to be independent, the probability of not finding any molecule in $\mathcal{V}$ is

$$p = \left(1 - \mathcal{V}/V\right)^N = \exp\left(N \ln\left(1-\frac{\mathcal{V}}{V}\right)\right)$$

For $\frac{\mathcal{V}}{V} \ll 1$, we have $\ln\left(1-\frac{\mathcal{V}}{V}\right) \simeq -\frac{\mathcal{V}}{V}$.

$$\therefore \boxed{p \simeq \exp\left(-N\frac{\mathcal{V}}{V}\right)}$$

Let standard temperature and pressure be T_0 and P_0, respectively, and the volume occupied by 1 gm-mole of gas at T_0 and P_0 be V_0. Then

$$P_0 V_0 = R T_0 \quad , \quad V_0 = 2.24 \times 10^4 \text{ cm}^3$$

We have $P_0 V = N k T_0$ for our gas at STP

$$\therefore N = \frac{P_0 V}{k T_0} = \frac{R}{k}\frac{P_0 V}{R T_0} = N_A \frac{V}{V_0}$$

where N_A = Avogadro's # $= R/k = 6.02 \times 10^{23}$

$$\therefore p \simeq \exp\left(-N_A \mathcal{V}/V_0\right)$$

Note that $V = 27 \text{ m}^3 = 27 \times 10^6 \text{ cm}^3 = 2.7 \times 10^7 \text{ cm}^3$

$\mathcal{V}/V = 1/2.7\times10^7 \ll 1$ for $\mathcal{V} = 1 \text{ cm}^3$

$\mathcal{V}/V = 10^{-24}/2.7\times10^7 \lll 1$ for $\mathcal{V} = 1 \text{ Å}^3$

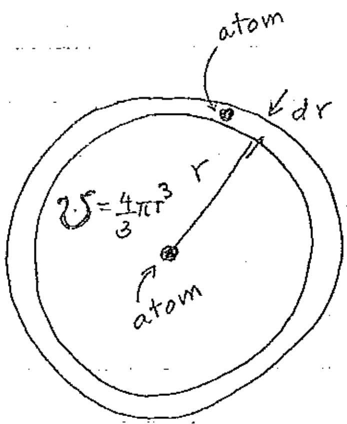
so that in both cases the above assumption $\mathcal{V}/V \ll 1$ is valid.

Finally,

$$p(\mathcal{V} = 1\,\text{cm}^3) \sim \exp\left(\frac{-6.02\times10^{23}\times 1}{2.24\times10^4}\right) = e^{-2.69\times10^{19}} \approx 10^{-10^{19}}$$

$$p(\mathcal{V} = 1\,\text{Å}^3 = 10^{-24}\,\text{cm}^3) \sim \exp\left(\frac{-6.02\times10^{23}\times10^{-24}}{2.24\times10^4}\right) = e^{-2.69\times10^{-5}} \approx 0.99997$$

5.3 Let $p(r)dr$ = probability that an atom has a nearest neighbor between distances r and $r+dr$ at STP.



Let V = volume of gas.

The prob. of finding an atom in a volume dV = dV/V

$\therefore$ probability of finding one atom between r and $r+dr$

$= 4\pi r^2 dr / V$

From the result $p \approx e^{-N\mathcal{V}/V}$ [in 5.2] for the probability of finding no atom in volume $\mathcal{V}$, for $\mathcal{V}/V \ll 1$, we see that

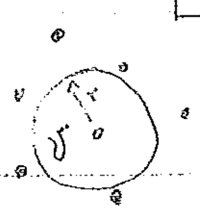
probability of finding no atom in the volume $\frac{4}{3}\pi r^3$

$$= e^{-\frac{N}{V}\cdot\frac{4}{3}\pi r^3} = e^{-\frac{4}{3}\pi n r^3}, \text{ where } n = N/V,$$

$\therefore$ setting $p(r)dr$ = prob. (one atom between r and $r+dr$) $\times$ prob (no atom in sphere of radius r)

we have

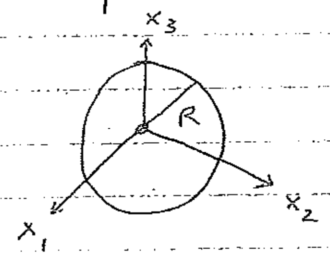
$$\boxed{p(r) = \frac{4\pi r^2}{V}\exp\left(-\frac{4}{3}\pi n r^3\right)}$$



Note: In this problem $\mathcal{V} \approx$ the volume around a particular atom in which there are no other atoms. At STP, it is certainly true that $\mathcal{V}/V \ll 1$.

(5.6) The volume of a 3-sphere of radius R is $\frac{4}{3}\pi R^3$.
The volume of an n-sphere of radius R is defined by the region

$$x_1^2 + x_2^2 + \dots + x_n^2 \le R^2 .$$



It has the form $\boxed{\Phi_n(R) = C_n R^n}$

To find C_n we realize that the surface area of an n-sphere is given by

$$\boxed{\Sigma_n(R) = \frac{d\Phi_n(R)}{dR} = n C_n R^{n-1}}$$

$\therefore$ the volume of a spherical shell of radius R and thickness dR is $\Sigma_n(R)\,dR = n C_n R^{n-1}\,dR$.

Now consider the integral

$$\int_{-\infty}^{\infty} dx_1\, e^{-\lambda x_1^2} \int_{-\infty}^{\infty} dx_2\, e^{-\lambda x_2^2} \cdots\cdots \int_{-\infty}^{\infty} dx_n\, e^{-\lambda x_n^2} = \left(\sqrt{\frac{\pi}{\lambda}}\right)^n = \left(\frac{\pi}{\lambda}\right)^{n/2}$$

$$= \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-\lambda(x_1^2 + \dots + x_n^2)}$$

$$= n C_n \int_0^{\infty} dR \,.\, R^{n-1} e^{-\lambda R^2} \qquad \text{(converted to spherical coordinates)}$$

Using the definition of the gamma function

$$\boxed{\Gamma(z) = \int_0^{\infty} e^{-t}\, t^{z-1}\, dt} \; ,$$

we see that (letting $\lambda \to 1$ and $t = R^2$)

$$\pi^{n/2} = n C_n \int_0^{\infty} dR\, R^{n-1} e^{-R^2} = \frac{n C_n}{2} \int_0^{\infty} 2R\,dR\, R^{n-2} e^{-R^2} = \frac{n C_n}{2} \int_0^{\infty} dt\, t^{\frac{n}{2}-1} e^{-t} = \frac{n C_n}{2} \Gamma\!\left(\frac{n}{2}\right)$$

(5.6) cont'd

$$\therefore C_n = \frac{2\pi^{n/2}}{n\,\Gamma(\frac{n}{2})} = \frac{2\pi^{n/2}}{2\cdot\underbrace{\frac{n}{2}\Gamma(\frac{n}{2})}_{\Gamma(\frac{n}{2}+1)}} = \boxed{\frac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)}}$$

Note: The Gamma function satisfies the recursion relation

$$\Gamma(z+1) = z\,\Gamma(z).$$

We have

$$\Gamma(\tfrac{1}{2}) = \int_0^\infty dt\, e^{-t} t^{-1/2} = 2\int_0^\infty du\, e^{-u^2} = \sqrt{\pi}$$

$$\therefore \Gamma(\tfrac{3}{2}) = \Gamma(\tfrac{1}{2}+1) = \tfrac{1}{2}\Gamma(\tfrac{1}{2}) = \frac{\sqrt{\pi}}{2}$$

$$\Gamma(\tfrac{5}{2}) = \Gamma(\tfrac{3}{2}+1) = \tfrac{3}{2}\Gamma(\tfrac{3}{2}) = \frac{3}{2}\cdot\frac{\sqrt{\pi}}{2} = \frac{3}{4}\sqrt{\pi} \quad \text{, etc.}$$

$$\Gamma(1) = \int_0^\infty dt\, e^{-t} = 1$$

$$\therefore \Gamma(2) = \Gamma(1+1) = 1\,\Gamma(1) = 1.1 = 1. = 1!$$

$$\Gamma(3) = \Gamma(2+1) = 2\,\Gamma(1) = 2.1 = 2 = 2!$$

$$\Gamma(4) = \Gamma(3+1) = 3\,\Gamma(3) = 3.2! = 3!$$

$$\vdots$$

$$\Gamma(n) = (n-1)!$$

As a check, for $n=3$

$$C_3 = \frac{\pi^{3/2}}{\Gamma(\frac{3}{2}+1)} = \frac{\pi\sqrt{\pi}}{\frac{3}{4}\sqrt{\pi}} = \frac{4}{3}\pi \quad \text{, as expected.}$$

5.7 $\Gamma(E,V) = \frac{\partial \Phi}{\partial E} \cdot \Delta$, where

$$\Phi(E,V) = \int_{H(p,q)<E} dp\,dr = V^N \int_{p_1^2+\dots+p_n^2 < 2mE \equiv R^2} dp_1 dp_2 \dots dp_n \quad \left(\begin{array}{l} n = 3N, \\ N = \#\text{ of molecules} \end{array}\right)$$

$$\therefore \Gamma(E,V) = \frac{\partial \Phi}{\partial R} \frac{dR}{dE} \Delta$$

$$= V^N (3N\, C_{3N}\, R^{3N-1}) \frac{1}{2}\sqrt{\frac{2m}{E}} \cdot \Delta \qquad (R = \sqrt{2mE})$$

$$= V^N \cdot 3N \cdot \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)} (2mE)^{\frac{3N-1}{2}} \cdot \frac{1}{2}\left(\frac{2m}{E}\right)^{1/2} \Delta$$

$$= V^N N \frac{(2\pi m E)^{3N/2}}{(\frac{3N}{2})!} \cdot \frac{3}{2}\left(\frac{\Delta}{E}\right) = V^N \frac{(2\pi m E)^{3N/2}}{(\frac{3N}{2}-1)!}\left(\frac{\Delta}{E}\right)$$

Since $S = k \ln \Gamma$,

$$S = Nk \ln V + \frac{3Nk}{2} \ln (2\pi m E) - k \ln\left(\left(\frac{3N}{2}-1\right)!\right) + k \ln\left(\frac{\Delta}{E}\right)$$

use Stirling's formula $\ln(N!) \simeq N\ln N - N$ for large N

$$S \simeq Nk\ln V + \frac{3Nk}{2} \ln(2\pi m E) - k \ln \left(\frac{3N}{2}\right)! + k \ln\left(\frac{\Delta}{E}\right)$$

$$\simeq Nk\ln V + \frac{3Nk}{2} \ln(2\pi m E) - k\left\{\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2}\right\} + k \ln\left(\frac{\Delta}{E}\right)$$

$$= Nk\ln V + \frac{3Nk}{2} \ln\left(\frac{4\pi m E}{3N}\right) + \frac{3}{2}Nk + k \ln\left(\frac{\Delta}{E}\right)$$

we assume that $\left|\ln\left(\frac{\Delta}{E}\right)\right| \ll N$, so we neglect the last term.

finally,

5.7 cont'd

For an ideal gas, we have the Sacher-Tetrode formula

$$\boxed{S(E,V) \approx Nk \ln V + \frac{3Nk}{2} \ln\left(\frac{4\pi m E}{3N}\right) + \frac{3}{2} Nk}$$

Check this formula by using 'it' to derive thermodynamical results. The first law says that, for reversible processes,

$$dE = T dS - P dV$$

$$\therefore dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV = \frac{1}{T} dE + \frac{P}{T} dV$$

$$\therefore \boxed{\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} , \quad \left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}}$$

Indeed,

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{3Nk}{2} \cdot \frac{3N}{4\pi m E} \cdot \frac{4\pi m}{3N} = \frac{3Nk}{2E} = \frac{1}{T}$$

$$\Rightarrow \frac{E}{N} = \frac{3}{2} kT$$, which is the equipartition theorem

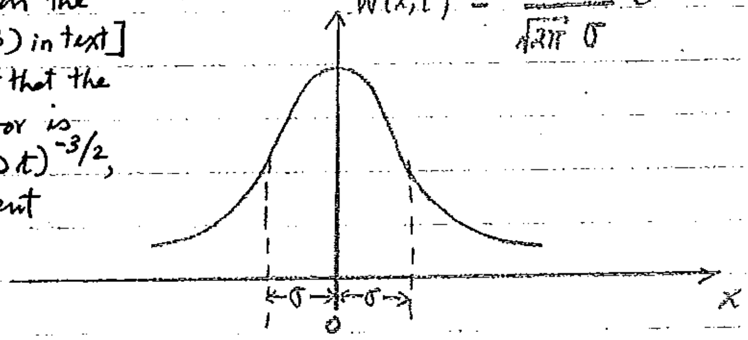
$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{Nk}{V} = \frac{P}{T} \Rightarrow PV = NkT,$$ which is the equation of state for the ideal gas.

(5.9) The random walk (1-dimensional) distribution is given by

$$W(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-x^2/(4Dt)}$$

Note: For 3D motion the formula [see (5.23) in text] is the same except that the pre-exponential factor is replaced by $(4\pi D t)^{-3/2}$, and in the exponent x^2 is replaced by $r^2 = x^2+y^2+z^2$.

$$W(x,t) = \frac{1}{\sqrt{2\pi}\,\sigma}\, e^{-\frac{x^2}{2\sigma^2}}$$



This is a gaussian centered at $x=0$ with an expanding width as time evolves given by

$$\sigma^2 = 2Dt\,.$$

$\therefore$ An order of magnitude estimate for the time t taken by a gas molecule to diffuse through a distance σ is

$$t \sim \frac{\sigma^2}{2D}, \quad \text{where } D \sim \frac{\lambda^2}{2\tau}$$

At STP, λ = mean free path $\sim 10^{-5}$ cm

τ = mean time between collisions $\sim 10^{-10}$ sec.

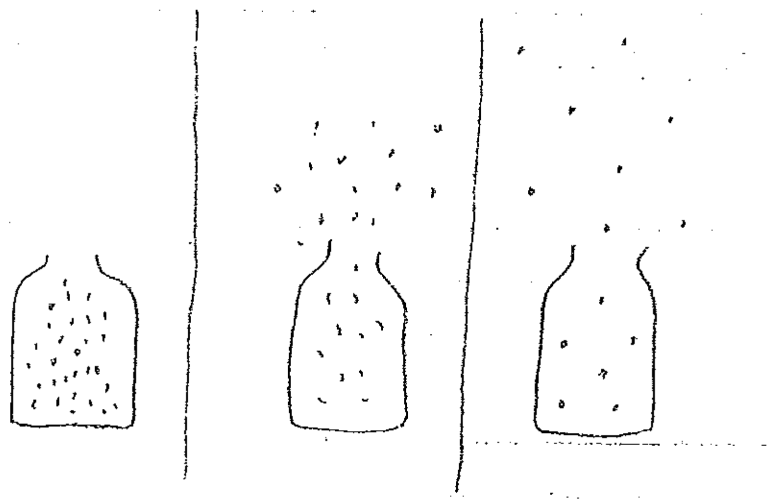
The above implies $\boxed{t \simeq \left(\frac{\sigma}{\lambda}\right)^2 \tau}$

For $\sigma \sim 1\,\text{cm}$, $\left(\frac{\sigma}{\lambda}\right)^2 \sim 10^{10}$ $\therefore t \sim 10^{10} \times 10^{-10}$ sec, or $\boxed{t(1\text{cm}) \sim 1\text{ sec}}$

for $\sigma \sim 1\,\text{m} \sim 10^2\,\text{cm}$, $\left(\frac{\sigma}{\lambda}\right)^2 \sim \left(\frac{10^2}{10^{-5}}\right)^2 \sim 10^{14}$ $\therefore t \sim 10^{14} \times 10^{-10}$ sec.

or $\boxed{t(1\text{m}) \sim 10^4\text{ sec}}$

(5-10) How long does it take the genie to return to its bottle?



We model the movement of the molecules by random walk. By the result $W(k,n) \simeq \sqrt{\frac{2}{\pi n}}\, e^{-k^2/(2n)}$ of prob. 5.9,

The probability that each coordinate returns to its original value after n collisions is $p = \sqrt{\frac{2}{\pi n}}$. For N molecules there are $6N$ coordinates. Suppose they <u>all</u> return to their original values after n collisions. Then the probability P for $6N$ coordinates (treated as independent) to return to their original values after n collisions is

$$P = p^{6N}$$

So the time T that it takes for this to happen is

(recurrence time) $T \sim p^{-6N}(n\tau)$, where τ = collison time

or $T \sim n\tau \exp\left(6N \ln \frac{1}{p}\right) = \exp\left(6N \ln \sqrt{\frac{\pi n}{2}}\right)(n\tau)$

$$\sim (n\tau)\exp\left(3N \ln\left(\frac{\pi n}{2}\right)\right) \approx (n\tau)\, e^{N} \sim \boxed{(n\tau)\, 10^{N/2}}$$

For comparison, the age of the universe $\sim 10^{17}$ sec.