Chemistry 4000/5000/7000 Fall 2021
Assignment 1 solutions

1. It is probably simplest to calculate the two energies numerically to start:

$$\begin{aligned}
\epsilon_{\pm\frac{1}{2}} &= \mp\frac{1}{2}\hbar\gamma B_z \\
&= \mp\frac{1}{2}(1.054\,571\,818 \times 10^{-34}\,\mathrm{J\,s})(2.675\,22 \times 10^{8}\,\mathrm{T^{-1}s^{-1}})(16.4\,\mathrm{T}) \\
&= \mp 2.313\,39 \times 10^{-25}\,\mathrm{J}
\end{aligned}$$

   Let $x = \epsilon_-/k_BT$. Note that $\epsilon_+/k_BT = -x$.

$$x = \frac{2.313\,39 \times 10^{-25}\,\mathrm{J}}{(1.380\,649 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})} = 5.619\,94 \times 10^{-5}$$

   Quite a small value!

   In terms of this x, the partition function is

$$\begin{aligned}
q &= e^{-\epsilon_+/k_BT} + e^{-\epsilon_-/k_BT} \\
&= e^{x} + e^{-x} \\
&\approx (1 + x) + (1 - x) \\
&= 2
\end{aligned}$$

   Thus,

$$\begin{aligned}
P(\epsilon_+) &= e^{-\epsilon_+/k_BT}/q = e^{x}/q \\
&\approx \frac{1+x}{2} \\
\therefore P(\epsilon_+) - \frac{1}{2} &\approx \frac{1}{2}x \\
&= 2.809\,97 \times 10^{-5}
\end{aligned}$$

   The probability of being in the lower energy state is *barely* more than $\frac{1}{2}$, but the extreme sensitivity of the NMR experiment still allows us to detect the magnetization resulting from this small excess.

2. (a)

$$\begin{aligned}
\overline{u^2} &= \int_0^\infty u^2 p(u) du \\
&= \int_0^\infty u^2 \left[4\pi u^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(\frac{-mu^2}{2k_B T} \right) \right] du \\
&= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^4 \exp\left(\frac{-mu^2}{2k_B T} \right) du
\end{aligned}$$

To solve this integral, let

$$\begin{aligned}
y^2 &= \frac{mu^2}{2k_B T} \\
\therefore y &= \sqrt{\frac{m}{2k_B T}} u \\
\therefore u &= \sqrt{\frac{2k_B T}{m}} y \\
\therefore du &= \sqrt{\frac{2k_B T}{m}} dy \\
\therefore \overline{u^2} &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty \left(\sqrt{\frac{2k_B T}{m}} y \right)^4 e^{-y^2} \sqrt{\frac{2k_B T}{m}} dy \\
&= \frac{8k_B T}{m\sqrt{\pi}} \int_0^\infty y^4 e^{-y^2} dy \\
&= \frac{8k_B T}{m\sqrt{\pi}} \frac{3\sqrt{\pi}}{8} \\
&= \frac{3k_B T}{m} \\
\therefore \sigma_u &= \sqrt{\overline{u^2} - \overline{u}^2} \\
&= \sqrt{\frac{3k_B T}{m} - \frac{8k_B T}{\pi m}} \\
&= \sqrt{\frac{k_B T}{m} \left(3 - \frac{8}{\pi} \right)}
\end{aligned}$$

(b)

$$
\begin{aligned}
\mathrm{CV} &= \sigma_u/\bar{u} \\
&= \frac{\sqrt{\frac{k_BT}{m}\left(3-\frac{8}{\pi}\right)}}{\sqrt{\frac{8k_BT}{\pi m}}} \\
&= \sqrt{\frac{3\pi}{8}-1} \approx 0.42
\end{aligned}
$$

3. From the NIST web site "Atomic Weights and Isotopic Compositions with Relative Atomic Masses" (`https://www.nist.gov/pml/atomic-weights-and-isotopic-compositions-relative-atomic-masses`), we find that the relative atomic mass (numerically equal to the molar mass)[1] of ^{40}Ar is 39.962 383 1237. The relative atomic mass of a ^{35}Cl atom is 34.968 852 68. The relative mass of a $^{35}Cl_2$ molecule is therefore 69.993 7705.

$$
\begin{aligned}
\mu_m &= \left(69.993\,7705^{-1} + 39.962\,383\,1237^{-1}\right)^{-1}\ \mathrm{g\,mol^{-1}} \\
&= 25.543\,1075\,\mathrm{g\,mol^{-1}} \equiv 2.554\,310\,75\times10^{-2}\,\mathrm{kg\,mol^{-1}} \\
\therefore \bar{u}_{\mathrm{rel}} &= \sqrt{\frac{8RT}{\pi\mu_m}} \\
&= \sqrt{\frac{8(8.314\,462\,618\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{\pi(2.554\,310\,75\times10^{-2}\,\mathrm{kg\,mol^{-1}})}} \\
&= 498.22\,\mathrm{m\,s^{-1}}
\end{aligned}
$$

We also need [Ar]. We get this from the ideal gas law:

$$
\begin{aligned}
[\mathrm{Ar}] &= \frac{n}{V} = \frac{p}{RT} \\
&= \frac{0.50\times10^{5}\,\mathrm{Pa}}{(8.314\,462\,618\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})} \\
&= 20\,\mathrm{mol\,m^{-3}}
\end{aligned}
$$

Next, we need the cross-section, which means that we need radii for Cl_2 and Ar. For Cl_2, the bond length is a reasonable estimate of the

[1] Not quite true in the new SI system, but close enough.

radius. According to Silberberg et al., *Chemistry*, 2nd Canadian Edition, p. 319, the bond length in Cl_2 is 199 pm. The bond length is a reasonable estimate of the radius of a molecule. If you used a van der Waals radius of a chlorine atom, you would end up with a much larger estimate of the radius of the molecule since van der Waals radii tend to be large, and you have to double that to get the radius of a molecule. The same book gives the radius of an argon atom as 98 pm on p. 286. This is a radius from an argon crystal. If you used a van der Waals radius, you would again have a much larger value. To summarize: I'm using values at the smaller end of the range for the required radii. If you use van der Waals radii, you are using values at the larger end of the reasonable range of values. Neither is better than the other since there is always considerable uncertainty about what is meant by a radius for a spongy object.

$$\begin{aligned}
r_{AB} &= 199 + 98\,\text{pm} = 297\,\text{pm} \\
\therefore \sigma &= \pi r_{AB}^2 = \pi(297 \times 10^{-12}\,\text{m})^2 \\
&= 2.77 \times 10^{-19}\,\text{m}^2 \\
\therefore Z_A &= \sigma \bar{u}_{\text{rel}} L[\text{Ar}] \\
&= (2.77 \times 10^{-19}\,\text{m}^2)(498.22\,\text{m}\,\text{s}^{-1})(6.022\,140\,76 \times 10^{23}\,\text{mol}^{-1})(20\,\text{mol}\,\text{m}^{-3}) \\
&= 1.7 \times 10^{9}\,\text{s}^{-1} \\
\therefore l_{\text{free}} &= \bar{u}_{\text{rel}}/Z_A = 3.0 \times 10^{-7}\,\text{m} \\
&\equiv 350\,\text{nm} \\
\tau_{\text{coll}} &= Z_A^{-1} = 6.0 \times 10^{-10}\,\text{s} \\
&\equiv 600\,\text{ps}
\end{aligned}$$

So a chlorine molecule doesn't travel for very long or very far before it has a collision with an argon atom.

4. There are two key conditions we must meet. The target speed should satisfy

$$u = n_s d\nu,$$

where n_s is the number of regularly spaced slits, d is the distance between the discs, and ν is the rotation frequency. Moreover, the thickness of the discs must satisfy

$$\frac{n_s dw}{4\pi r_b} < z < \frac{n_s dw}{2\pi r_b}$$

where w is the width of the slits and r_b is the radial coordinate of the point where the molecular beam crosses the disc.

Since $\nu \leq 400\,\text{Hz}$, $u \leq 400 n_s d$. We want to measure speeds up to $800\,\text{m}\,\text{s}^{-1}$, so we must have $800 \leq 400 n_s d$, or $n_s d \geq 2\,\text{m}$. Since d should be no more than $10\,\text{cm}$, n_s must be at least 20. Suppose we fix $d = 10\,\text{cm}$ and $n_s = 20$. Then $u = (2\,\text{m})\nu$, and we can measure speeds from 100 to $800\,\text{m}\,\text{s}^{-1}$ by varying the rotational speed from 50 to 400 Hz, which falls within the design specifications.

We can now look at the relationship between the thickness of the discs and width of the slits:

$$\frac{n_s d w}{4\pi r_b} = \frac{(20)(10\,\text{cm})w}{4\pi(3.5\,\text{cm})} = 4.55w.$$

Similarly,

$$\frac{n_s d w}{2\pi r_b} = 9.09w.$$

Therefore,

$$4.55w < z < 9.09w.$$

If we take a slit width w of 0.1 mm, then the thickness z must be between 0.46 and 0.91 mm.

Final design specifications:

Number of slits:	20
Distance between discs:	10 cm
Width of slits:	0.1 mm
Thickness of discs:	0.5 mm