Velocity Distribution

- Consider an ideal gas. Each atom can be considered an independent subsystem. So the probability to find the atom with velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, v_z and $v_z + dv_z$ is $\propto e^{-E/k_BT}$ See Picture

$$d\mathcal{P}_{\vec{v}} = C\, e^{-\frac{1}{2}mv^2/k_BT}\, dv_x\, dv_y\, dv_z = P(v_x, v_y, v_z)\, d^3v$$

- Here C is a normalizing constant and $v^2 = \vec{v}^{\,2} = v_x^2 + v_y^2 + v_z^2$, is the speed squared.

- We can find C, since

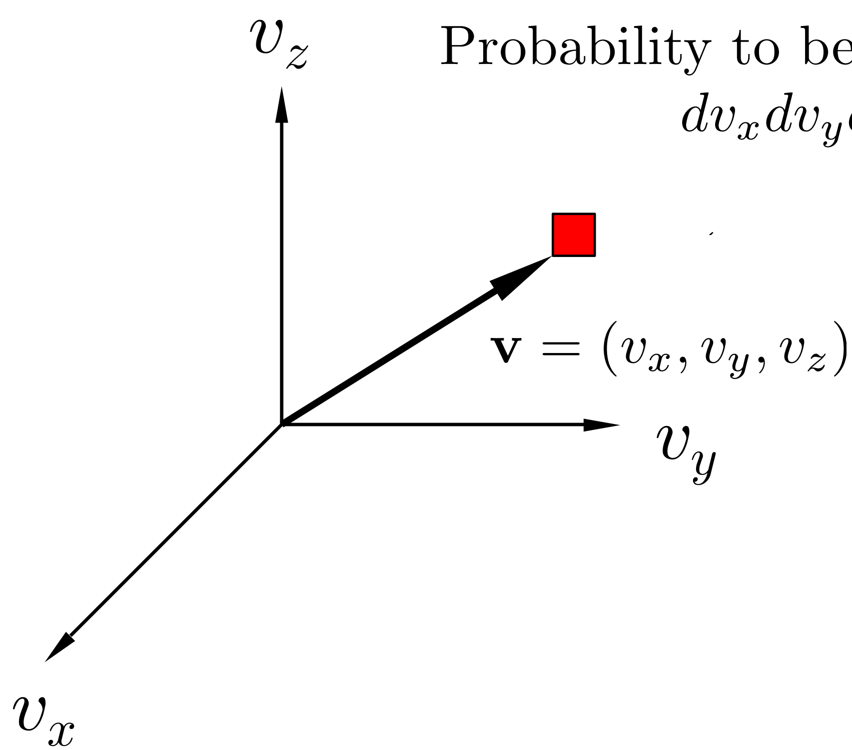
$$1 = \int_{\text{all } \vec{v}} d\mathcal{P} = \int_{\text{all } \vec{v}} C\, e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/k_BT}\, dv_x\, dv_y\, dv_z$$

$$= C \underbrace{\int_{-\infty}^{\infty} dv_x\, e^{-\frac{1}{2}mv_x^2/k_BT}}_{I} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_y^2/k_BT}\, dv_y}_{I} \underbrace{\int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_z^2/k_BT}\, dv_z}_{I}$$

$$I = \int_{-\infty}^{\infty} dv_x\, e^{-v^2/2\sigma^2} = \sqrt{2\pi\sigma^2} \quad \text{with } \sigma^2 = \frac{k_BT}{m}$$

units of $\rightarrow [\sigma] = \left[\sqrt{\frac{k_BT}{m}}\right]$ = velocity

Velocity Probability Distribution



Probability to be in "volume"

$dv_x dv_y dv_z$

So

$$1 = C \left(\frac{2\pi k_B T}{m} \right)^{3/2}$$

So $C = (m/2\pi k_B T)^{3/2}$ And so

$$\boxed{d\mathcal{P} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} \, dv_x \, dv_y \, dv_z}$$

- We write $d^3v = dv_x \, dv_y \, dv_z$ and then sometimes say that

$$\frac{d\mathcal{P}}{d^3v} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2}mv^2/k_B T} = P(v_x, v_y, v_z)$$

this is the probability per d^3v

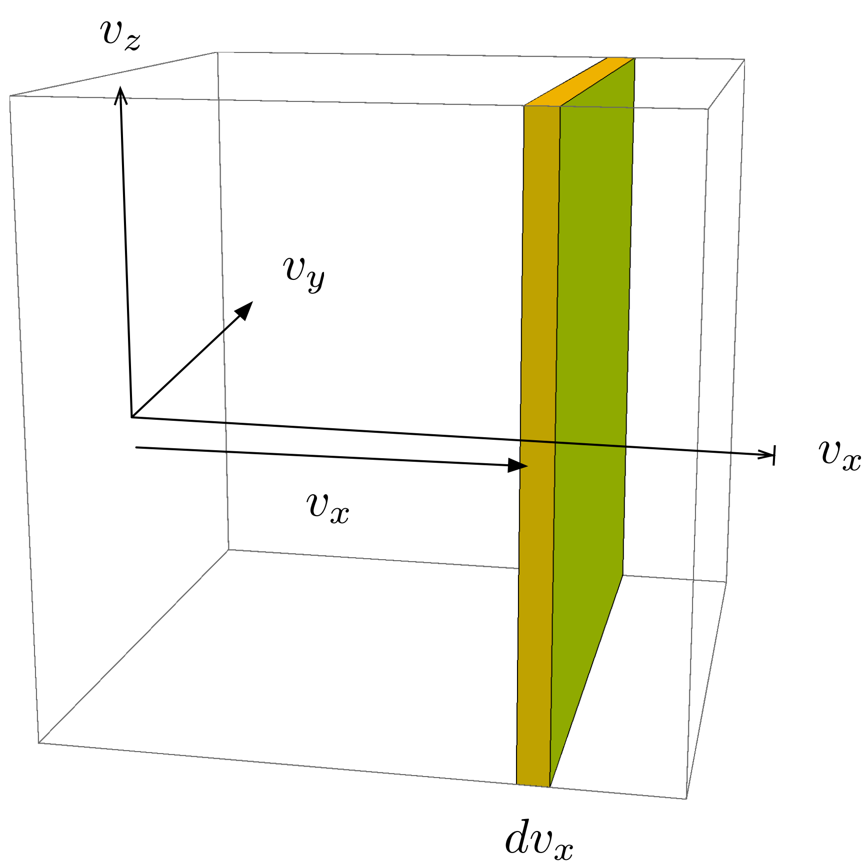
- What is the probability to find the particle with x-component of velocity between v_x and $v_x + dv_x$?

Well, since we don't care what is v_y or v_z we can integrate over these (see picture)

$$d\mathcal{P}(v_x) = \int_{\text{over } v_y, v_z} P(v_x, v_y, v_z) \, dv_x \, dv_y \, dv_z$$

$$\equiv P(v_x) \, dv_x \qquad \left(\text{or } \frac{d\mathcal{P}}{dv_x} = P(v_x) \right)$$

Probability to have x-component of velocity



Integrate over v_y, v_z

- The probabilty density $P(v_x, v_y, v_z)$ factorizes

$$P(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{1}{2}mv_x^2/kT}$$

$$\times \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{1}{2}mv_y^2/kT}$$

$$\times \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{1}{2}mv_z^2/kT}$$

Or:

$$= P(v_x)\, P(v_y)\, P(v_z)$$

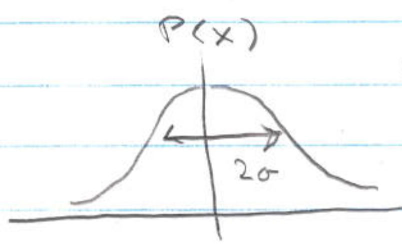
where $P(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{1}{2}mv_x^2}$

- The name $P(v_x) = d\mathcal{P}/dv_x$ is justified since

$$d\mathcal{P} = \int_{y+z} P(v_x, v_y, v_z)\, d^3v = P(v_x)\,dv_x \underbrace{\int_{-\infty}^{\infty} P(v_y)\,dv_y}_{=1} \underbrace{\int_{-\infty}^{\infty} P(v_z)\,dv_z}_{=1}$$

$$= P(v_x)\, dv_x$$

Sketch:



$\sigma = \sqrt{\frac{k_B T}{m}}$

- Note: the book calls $P(v_x)$, $g(v_x)$, but I don't find this a good name

$$\frac{d\mathcal{P}}{dv_x} \equiv P(v_x) \equiv g(v_x) \equiv \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv^2/2kT}, \text{ and}$$

$P(v_x) = \frac{d\mathcal{P}}{dv_x}$ is the probality per dv_x to find the particle vith velocity component v_x irrespective of v_y or v_z

We found

$$P(v_x, v_y, v_z) = P(v_x)\,P(v_y)\,P(v_z)$$

The speed distribution

- We found the velocity distribution

$$d\mathcal{P} = P(v_x, v_y, v_z)\, \underbrace{dv_x\, dv_y\, dv_z}_{\text{"Volume" in velocity space.}}$$

The probability the particle has velocity between (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$

- To find the speed distribution we want to sum up the probabilities for those velocities with speed between v and $v + dv$

$$d\mathcal{P} = \int_{|\vec{v}| \text{ between } v \text{ and } v+dv} P(v_x, v_y, v_z)\, d^3v = \int_{\text{shell}} C \overbrace{e^{-mv^2/2kT}}^{\text{constant on shell}} d^3v$$

$$= C e^{-mv^2/2T} \int_{\text{shell}} d^3v$$

This is the "volume" of a spherical shell in velocity space of radius v and width dv. The volume of this shell is (see figure)

$$4\pi v^2\, dv$$

So

$$\boxed{d\mathcal{P} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv}$$

Probability of speed v

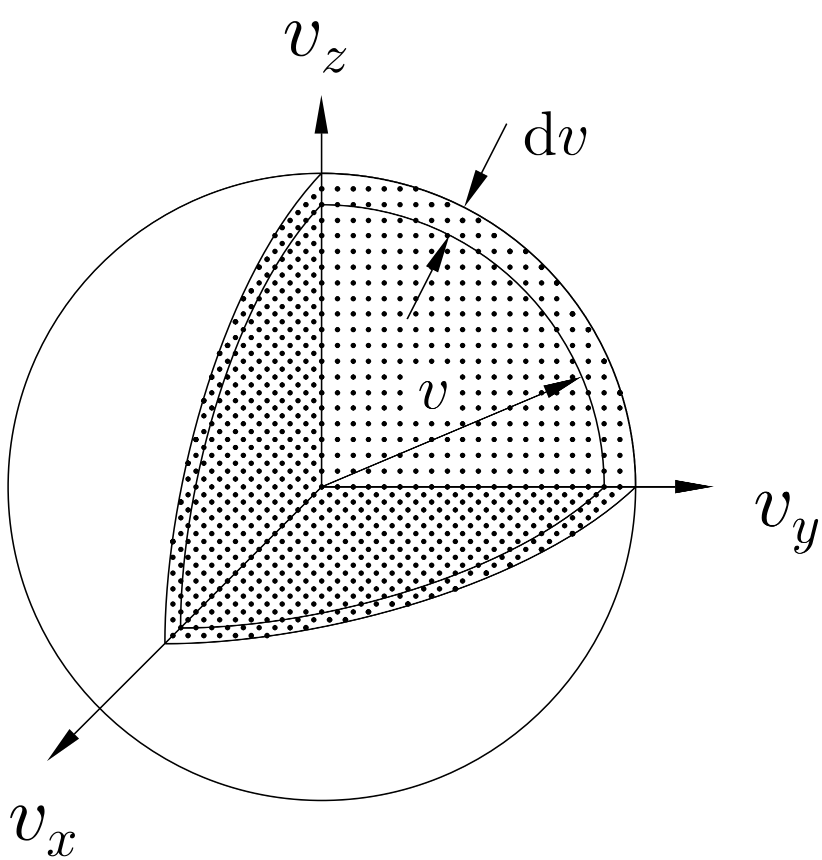


Fig. 5.3 Molecules with speeds between v and $v + \mathrm{d}v$ occupy a volume of velocity space inside a spherical shell of radius v and thickness $\mathrm{d}v$. (An octant of this sphere is shown cut-away.)

So

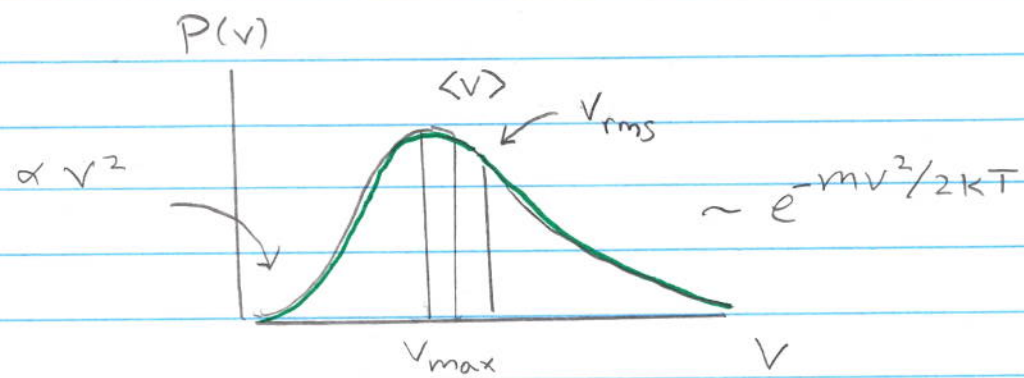
$$\boxed{P(v) = \frac{d\mathcal{P}}{dv} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2kT}\; 4\pi v^2}$$

is the probility per dv of finding the particle with speed v.

- The book calls $P(v)$, $f(v)$, but again I don't find this a good name

$$P(v) \equiv \frac{d\mathcal{P}}{dv} \equiv f(v)$$

- Sketch



★ Lets find the $\sqrt{\langle v^2 \rangle}$. We already know the answer to this:

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \left(\frac{3 k_B T}{m}\right)^{1/2}$$

Proof;

$$\langle v^2 \rangle = \int_0^\infty P(v)\, dv\; v^2$$

$$= \int_0^\infty \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv\; v^2$$

- This integral is like $\sim \int dv\, e^{-v^2/2}\, v^4$.

We can first recognize that the typical velocity is $\sigma = \sqrt{\frac{k_B T}{m}}$. Note $\left(\frac{m}{k_B T}\right)^{3/2} = \frac{1}{\sigma^3}$

So

$$\langle v^2 \rangle = \sigma^2 \int_0^\infty \frac{1}{(2\pi)^{3/2}}\, 4\pi\, e^{-v^2/2\sigma^2} \left(\frac{v}{\sigma}\right)^2 \frac{dv}{\sigma}\; \frac{v^2}{\sigma^2}$$

- So define $u \equiv v/\sigma$, (v in units of the typical v)

$$\langle v^2 \rangle = \sigma^2 \sqrt{\frac{2}{\pi}} \int_0^\infty e^{-u^2/2}\, u^4\, du$$

The integral from $[0,\infty]$ is $1/2$ the one from $[-\infty, \infty]$

$$= \sigma^2 \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{-u^2/2}\, u^4\, du$$

$$\langle v^2 \rangle = 3\sigma^2 = \frac{3k_B T}{m}$$

★ Lots more things can be computed, You will do some of this on homework

For instance

$$\langle v \rangle \equiv \text{average speed} = \sqrt{\frac{8}{\pi}} \left(\frac{k_B T}{m}\right)^{1/2}$$

$$v_{max} \equiv \text{where } P(v) \text{ is maximum} = \sqrt{2} \left(\frac{k_B T}{m}\right)^{1/2}$$

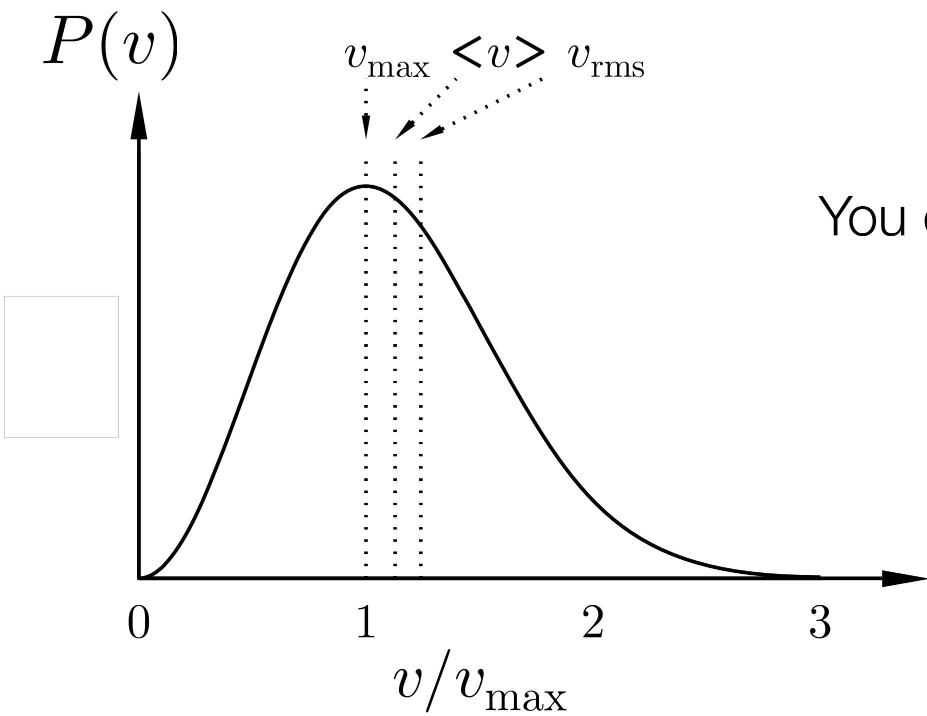
So we have:

$$v_{max} < \langle v \rangle < v_{rms}$$

$$\sqrt{2} \left(\frac{k_B T}{m}\right)^{1/2} < \sqrt{\frac{8}{\pi}} \left(\frac{k_B T}{m}\right)^{1/2} < \sqrt{3} \left(\frac{k_B T}{m}\right)^{1/2}$$

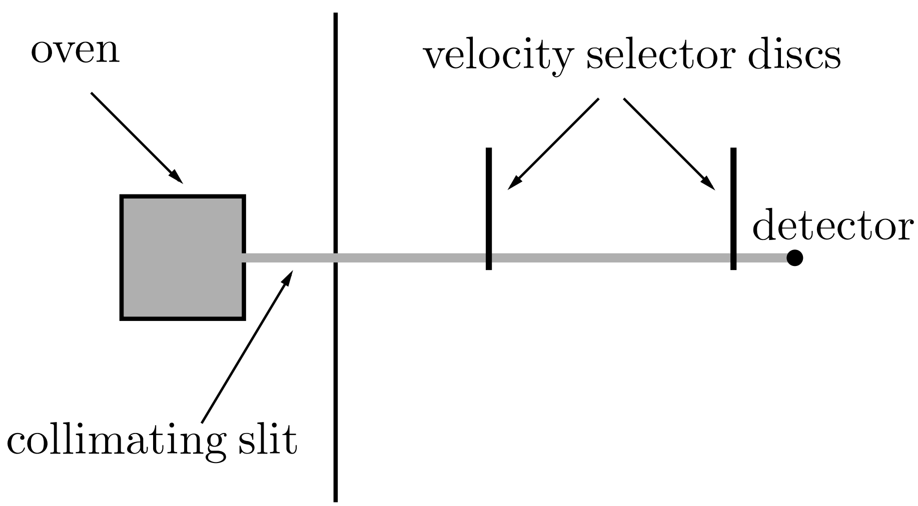
See the next page for how these things are related

More things to compute — in homework :)

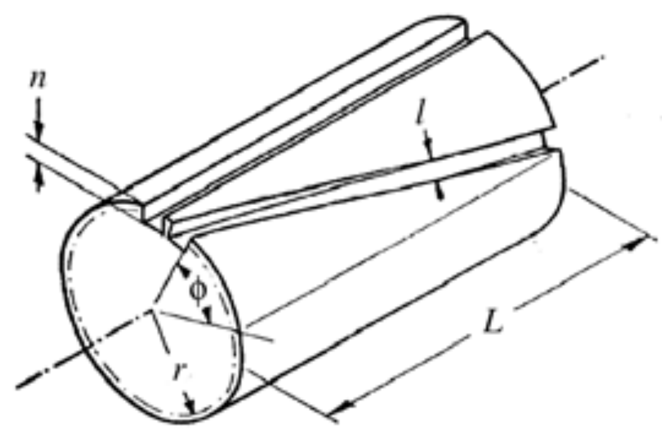


You can find $v_{\max}$ (the most probable speed)
by differentiation $dP(v)/dv = 0$

Measuring the velocity distribution (see book for details)



Velocity selector: A turning drum with a slot



If the speed is $v = \omega L / \phi$ then the molecule gets through the slot.

Measured Velocity Distribution

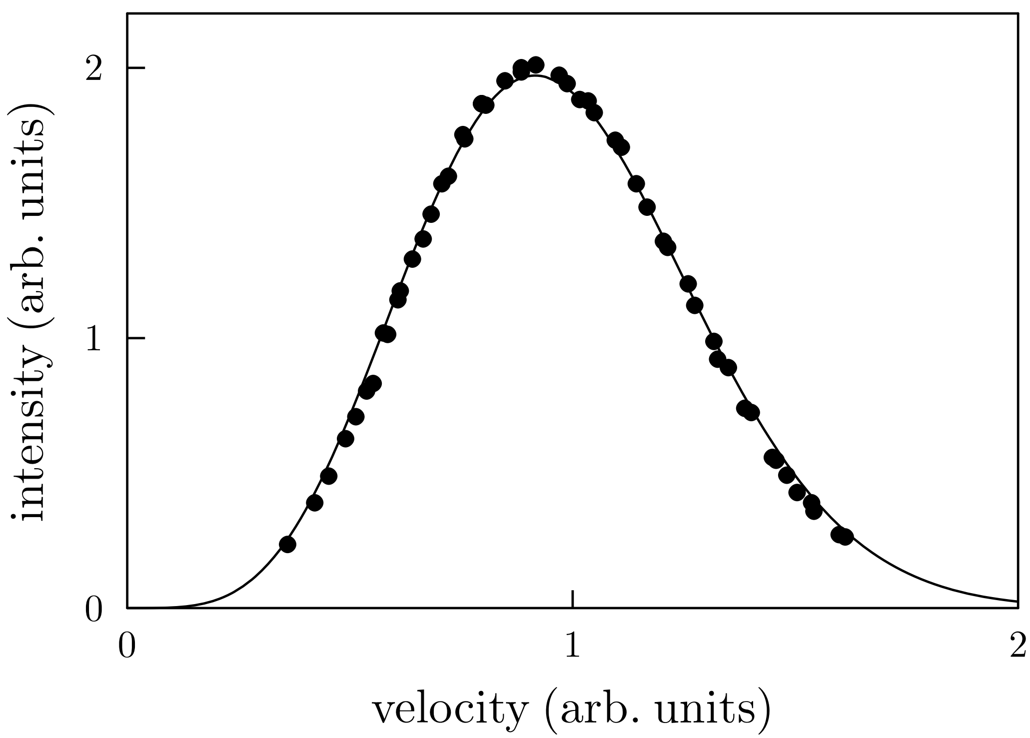


Fig. 5.7 Intensity data measured for potassium atoms using the velocity selector shown in Fig. 5.6 (from R. C. Miller and P. Kusch, Phys. Rev. **99**, 1314 (1955), Copyright (1955) by the American Physical Society). The line

Can be used to fit k_B !