Two State

$$\langle \varepsilon \rangle = 0 \cdot P_0 + \Delta P_1$$

$$P_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{1 + e^{-\beta \Delta}}$$

$$\boxed{\langle \varepsilon \rangle = \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}}$$

$$\langle \varepsilon^2 \rangle = 0^2 P_0 + \Delta^2 \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})}$$

So

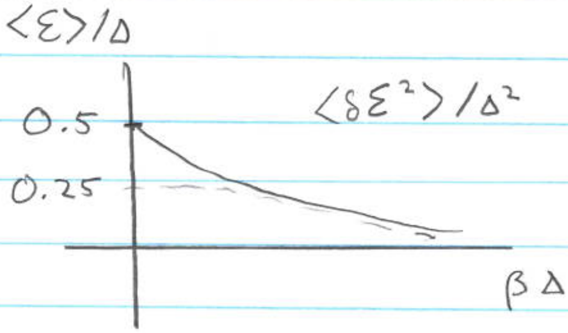
$$\langle \delta \varepsilon^2 \rangle = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$$

$$= \Delta^2 \quad \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})} - \frac{e^{-2\beta \Delta}}{(1 + e^{-\beta \Delta})^2}$$

$$= \Delta^2 \left[e^{-\beta \Delta} (1 + e^{-\beta \Delta}) - e^{-2\beta \Delta} \right] / (1 + e^{-\beta \Delta})^2$$

$$\boxed{\delta \varepsilon^2 = \Delta^2 \left(\frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2} \right)}$$

So



$\langle \delta \varepsilon^2 \rangle / \Delta^2$ is dashed line. When $\beta \Delta \simeq 0$, then the atoms are equally likely to be in either state $\langle \varepsilon \rangle = 0 \cdot \frac{1}{2} + \Delta \frac{1}{2}$

Speed Distribution

So

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

- Maximizing $P(v)$ we have

$$P(v) = C\, e^{-v^2/2\sigma^2} v^2 \quad \text{with} \quad \sigma \equiv \left(\frac{kT}{m}\right)^{1/2}$$

$$P' = Ce^{v^2/2\sigma^2}\left(\frac{v^3}{\sigma^2} + 2v\right)$$

- So P is maximized when $P'(v) = 0$ or

$$v^2 = 2\sigma^2 \implies \boxed{v_* = \sqrt{\frac{2kT}{m}}}$$

b) $$\mathcal{P} = \int_{v_*}^{2v_*} \left(\frac{m}{(2\pi kT)}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$$

- Substituting

$u = \dfrac{v}{(kT/m)^{1/2}}$ this becomes

$$\mathcal{P} = \int_{\sqrt{2}}^{2\sqrt{2}} \frac{1}{(2\pi)^{3/2}} 4\pi \, e^{-u^2/2} \, u^2 \, du$$

- So

$$\mathcal{P} = \sqrt{\frac{2}{\pi}} \int_{\sqrt{2}}^{2\sqrt{2}} e^{-u^2/2} \, u^2 \, du$$

$$\simeq 0.53$$

See program

```python
from math import *

xmin = sqrt(2.)
xmax = sqrt(2.)*2.

n = 1000
dx = (xmax - xmin)/n

s = 0.
for i in range(0, n):
    x = i * dx + xmin
    s = s + dx * sqrt(2./pi) * exp(-x*x/2.) * x * x
    print(s)
```

Energies

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

$$v = \left(\frac{2E}{m}\right)^{1/2} \qquad dv = \frac{1}{2\left(\frac{2E}{m}\right)^{1/2}} \frac{2E}{m} = \frac{dE}{(2mE)^{1/2}}$$

- So

$$P(\varepsilon)\,d\varepsilon = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\varepsilon/kT}\; \frac{2\varepsilon}{m}\; \frac{d\varepsilon}{\sqrt{2m}\,\varepsilon^{1/2}}$$

$$= 2\pi\; \frac{2^{3/2}}{2^{3/2}}\; \frac{m^{3/2}}{m^{3/2}}\; \frac{\varepsilon^{1/2}\,d\varepsilon}{(k_B T)^{3/2}}\; \frac{1}{\pi^{3/2}}\; e^{-\varepsilon/kT}$$

$$\boxed{P(\varepsilon)\,d\varepsilon = \frac{2}{\sqrt{\pi}}\, \beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon}$$

So

- $$\langle\varepsilon\rangle = \int_0^\infty \varepsilon\, P(\varepsilon)\, d\varepsilon$$

$$= \int_0^\infty \frac{2}{\sqrt{\pi}}\, \beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon \times \varepsilon$$

• Change vars $u = \beta \varepsilon$

$$\langle \varepsilon \rangle = \frac{1}{\beta} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{3/2} \, du$$

$$\boxed{\langle \varepsilon \rangle} = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \Gamma(5/2) = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$$

Similarly

$$= 1/\beta \cdot 2 \cdot \frac{3}{2} \cdot \frac{1}{2} = \boxed{\frac{3}{2} k_B T}$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{5/2} \, du$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \frac{2}{\sqrt{\pi}} \Gamma(7/2)$$

So

$$\boxed{\langle \varepsilon^2 \rangle} = \frac{1}{\beta^2} \cdot \frac{2}{\sqrt{\pi}} \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \Gamma(1/2)$$

$$= \frac{1}{\beta^2} 2 \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} = \boxed{\frac{1}{\beta^2} \frac{15}{4}}$$

So

$$\boxed{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{1}{\beta^2} \left(\frac{15}{4} - \frac{9}{4} \right) = \frac{3}{2} (k_B T)^2}$$

<u>Distribution on Sphere</u>

a) The probability per area is constant

$$d\mathcal{P} \propto dA \propto R^2\, d\Omega$$

- The normalization constant is $1/\text{total } A = 1/4\pi R^2$

So,

$$\boxed{d\mathcal{P}_{\theta,\phi} = \frac{R^2\, d\Omega}{4\pi R^2} = \frac{d\Omega}{4\pi} = \frac{\sin\theta\, d\theta\, d\phi}{4\pi}}$$

- If we don't care about ϕ, we can integrate over ϕ

$$d\mathcal{P}_\theta = \int_0^{2\pi} d\phi\, dP_{\theta,\phi} = \int_0^{2\pi} \frac{d\phi\, \sin\theta\, d\theta}{4\pi}$$

$$\boxed{d\mathcal{P}_\theta = \frac{1}{2}\sin\theta\, d\theta}$$

This is how the book writes

$$d\mathcal{P}_\theta = \frac{1}{2}\sin\theta\, d\theta$$

So

$$\langle \cos^2\theta \rangle = \int_0^{\pi} \cos^2\theta\, \frac{1}{2}\sin\theta\, d\theta = \frac{-1}{6}\cos^3\theta \Big|_0^{\pi} = \frac{1}{3}$$

b) So

$$\int d\mathcal{P} = 1 \quad \leftarrow \text{normalization condition}$$

$$\int_0^{\pi} C(1+\cos^2\theta)\ \frac{1}{2}\sin\theta\, d\theta = 1$$

$$C\left(-\frac{1}{2}\cos\theta - \frac{1}{6}\cos 3\theta\right)\Big|_0^{\pi} = 1$$

$$C\left(1+\frac{1}{3}\right) = 1 \quad \text{or} \quad \boxed{C = 3/4}$$

- So

$$d\mathcal{P} = \frac{3}{4}(1+\cos^2\theta)\ \frac{\sin\theta\, d\theta\, d\phi}{4\pi}$$

Integrating over ϕ as in part (a), $\frac{d\Omega}{4\pi} \to \frac{1}{2}\sin\theta\, d\theta$
So the probability is

$$\boxed{d\mathcal{P}_\theta = \frac{3}{4}(1+\cos^2\theta)\ \frac{1}{2}\sin\theta\, d\theta}$$

Change vars, $u = \cos\theta$, $\frac{du}{d\theta} = -\sin\theta\, d\theta$.

$u = [-1 .. 1]$ since $\theta \in [0 ... \pi]$

Note $\boxed{d\theta = du/|du/d\theta|}$ when we use unoriented integrals.

$$d\mathcal{P}_u = \frac{3}{8}(1+\cos^2\theta)\frac{\sin\theta}{\left|\frac{du}{d\theta}\right|}du$$

$$\boxed{d\mathcal{P}_u = \frac{3}{8}(1+u^2)\,du \qquad \text{with} \qquad u = [-1, \ldots 1]}$$

So

$$\langle\cos^2\theta\rangle_{\text{sphere}} = \langle u^2\rangle_u = \int_{-1}^{1}\frac{3}{8}(1+u^2)\,u^2\,du$$

$$= \frac{2}{5}$$