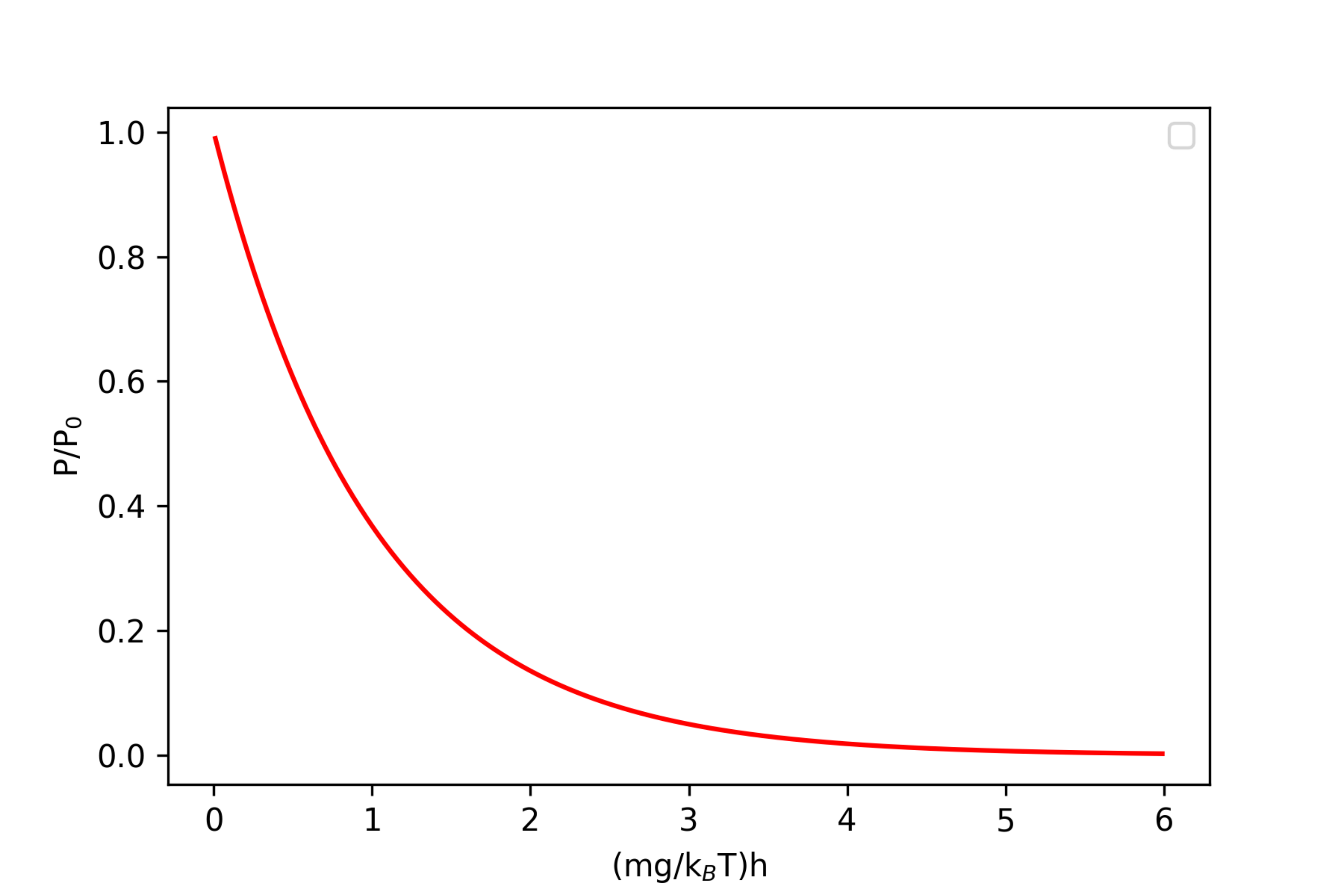
Recap from last time

$$\rho_N(h) = \rho_N(0)\mathrm{e}^{-\left(\frac{mgh}{k_B T}\right)}$$

$$P(h) = P(0)\mathrm{e}^{-\left(\frac{mgh}{k_B T}\right)}$$

$\frac{mgh}{k_B T}$ must be dimensionless, and so $\frac{k_B T}{mg}$ must have dimensions of h -> scale height, h_0

(at which $P(h_0) = P(0)e^{-1}$)



Recap from last time

We have already established that the number density (number of fluid molecules per unit volume), $\rho_N(0)$, can be related to atmospheric pressure, $P_{at}(= P(0))$, by

$$\rho_N(0) = \frac{P_{at}}{k_B T}$$

If we wanted to determine the total number of gas molecules, N, in our slab of atmosphere (with surface area A), we can integrate across all possible heights, $h = 0 \rightarrow h = \infty$,

$$A \int_0^\infty \rho_N(h)\,\mathrm{d}h = N$$

Isothermal model meets probability

We can then, through solving the integral, relate the total number, N, to the number density $\rho_N(0)$:

$$\rho_N(0) = \frac{N}{Ah_0} \qquad \text{With } h_0 = \frac{k_B T}{mg}$$

Here, we can see that $\rho_N(0)$ is in fact the average number density of the slab of atmosphere between $h = 0$ and $h = h_0$

We can then define a new quantity, $Pr(h) = \frac{A\rho_N(h)}{N}$, which is therefore the contribution from one molecule

Isothermal model meets probability

As $A\int_0^\infty \rho_N(h)\,\mathrm{d}h = N$, we can show that

$$\int_0^\infty Pr(h)\,\mathrm{d}h = \frac{A}{N}\int_0^\infty \rho_N(h)\,\mathrm{d}h = \frac{N}{N} = 1$$

Thus, it is clear that the quantity $Pr(h)$ is in some way a probability (normalised to be equal to 1 between 0 and infinity)

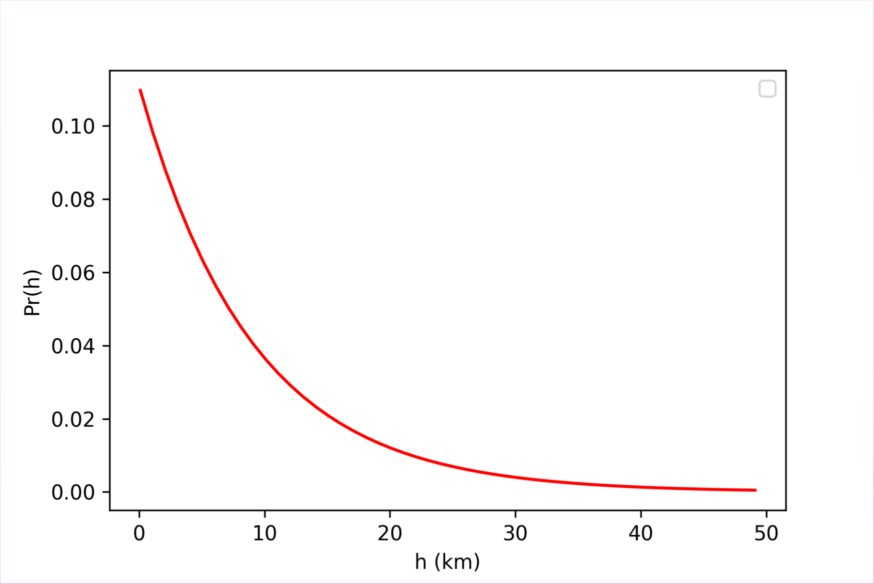
The quantity $Pr(h)\,\mathrm{d}h$ gives the probability of finding a given molecule between h and $h + \mathrm{d}h$

Probability density functions

We can show that the probability, $Pr(h)$, can be related to easily measurable quantities:

$$Pr(h) = \frac{mg}{k_B T} e^{-\left(\frac{mgh}{k_B T}\right)} = \frac{1}{9020} e^{-\left(\frac{h}{9020}\right)}$$

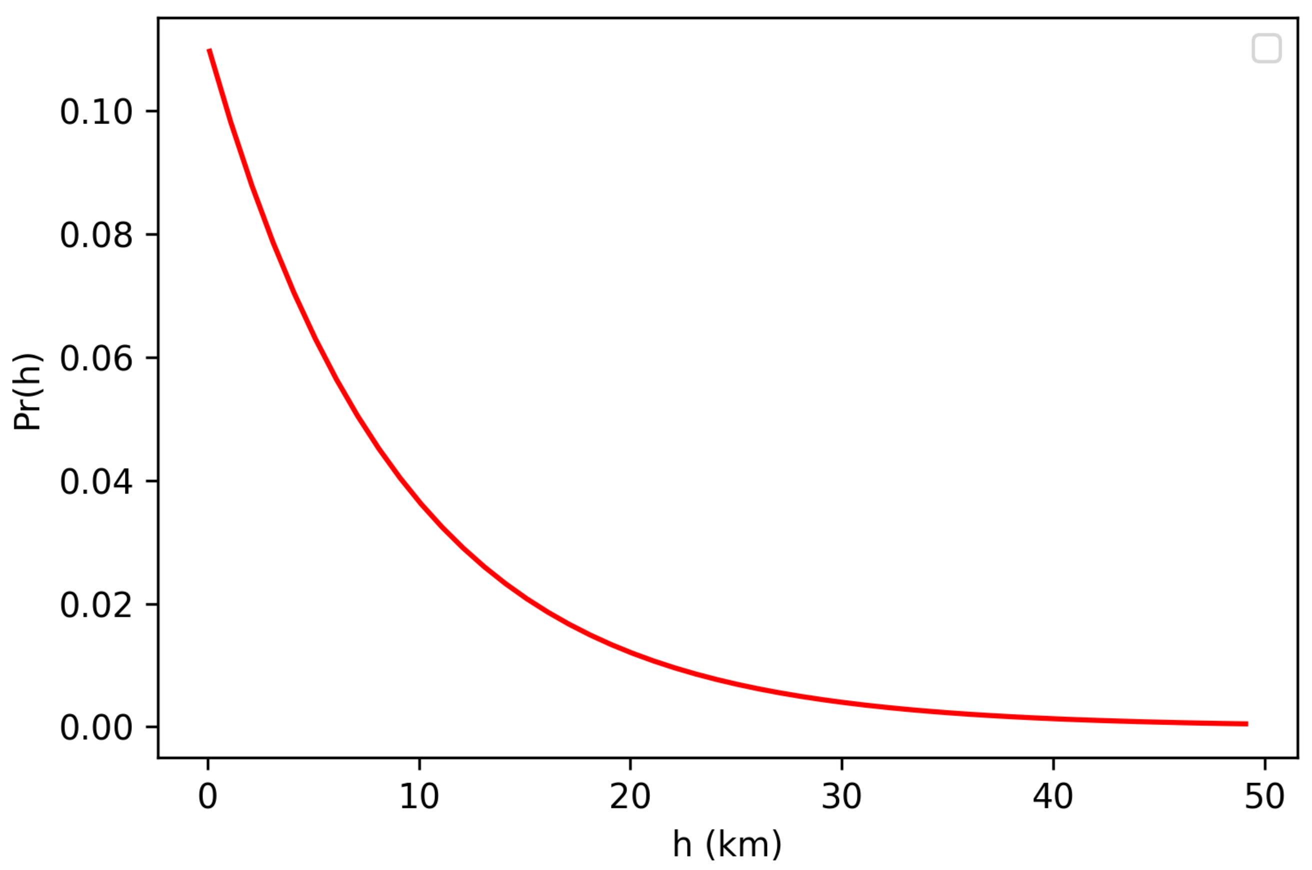
m = 28 amu
g = 9.81 ms^{-1}
T = 298 K
k_B = 1.38 x 10^{-23} m^2 kg s^{-2} K^{-1}



Probability density functions

$$Pr(h) = \frac{1}{9020} e^{-\left(\frac{h}{9020}\right)}$$

Without any microscopic information regarding the motion of these molecules, we can gather the information we're interested in just from this distribution



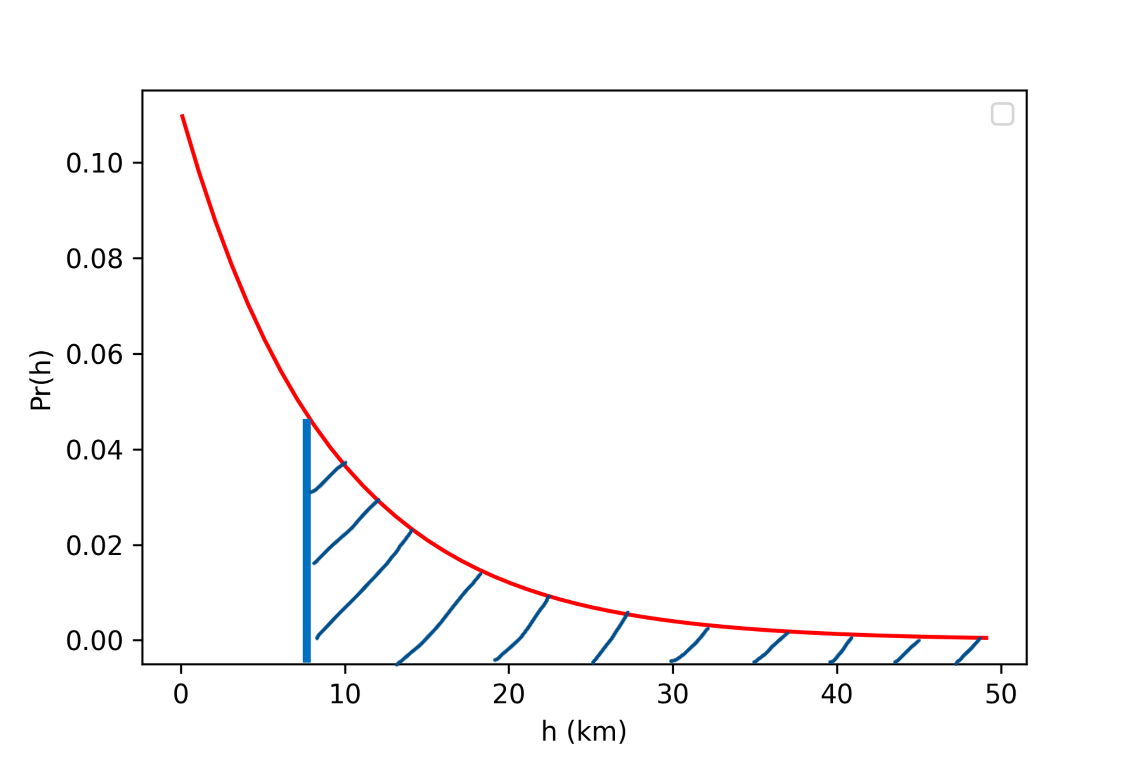
Probability density functions

$$Pr(h) = \frac{1}{9020} e^{-\left(\frac{h}{9020}\right)}$$

Q1: For a random molecule in the atmosphere, what is the probability that it can be found above 8 km?

Q2: At any given time, what proportion of molecules in the atmosphere have a height greater than 8 km?

Q3: Averaged over a long timescale, what fraction of the time does a particular molecule spend at an altitude > 8 km?



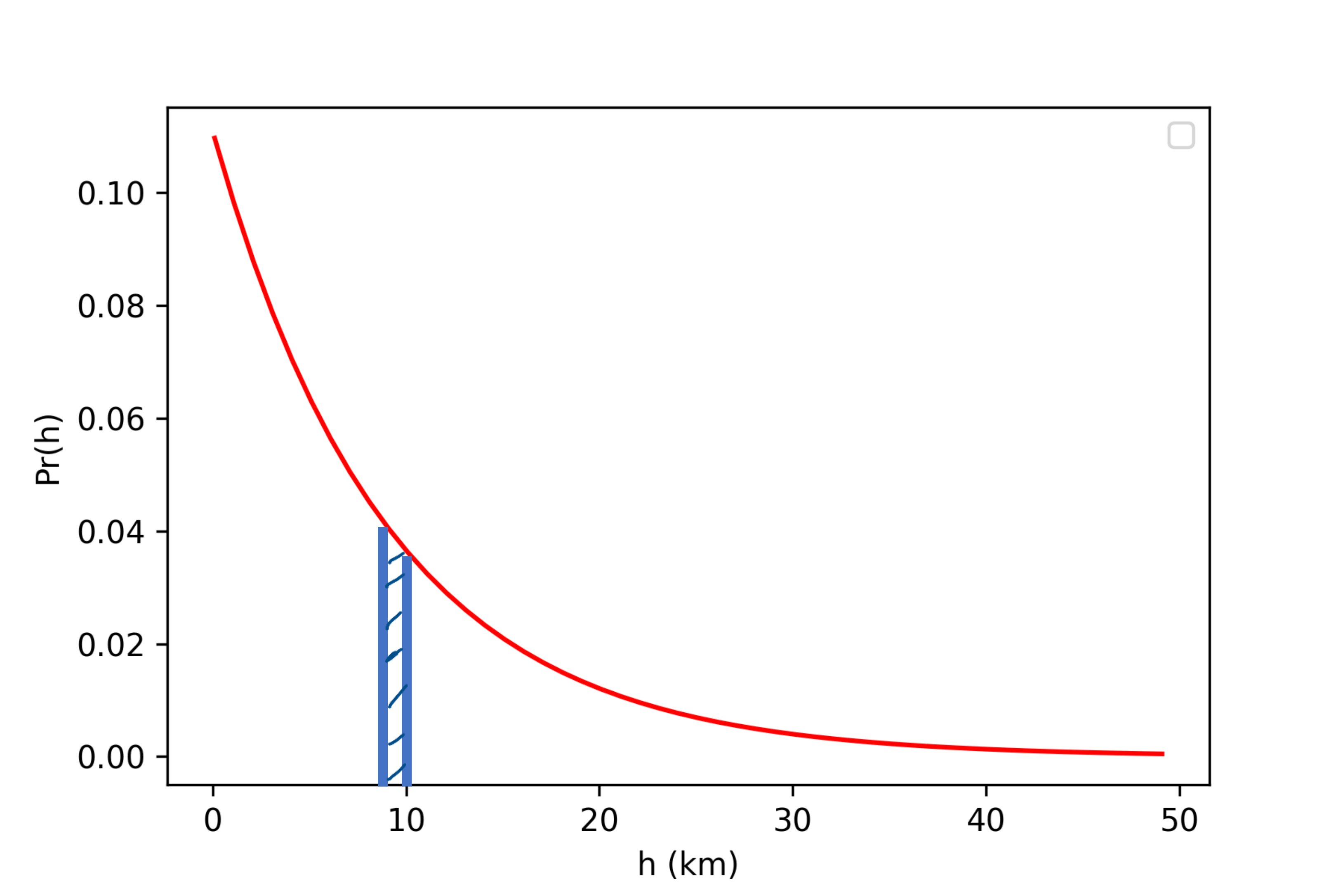
Identical questions!

A: $Pr(h > 8\ km) = \int_{8\ \mathrm{km}}^{\infty} Pr(h)\, \mathrm{d}h = 0.41$

More PDF examples

Roughly, what is the probability of finding a particle between 9 km and 10 km?

A: ~ 0.04



Boltzmann factors

Remember that the quantity $\frac{mgh}{k_B T}$ must be dimensionless… what physically does it mean?

mgh = (gravitational) potential energy

$k_B T$ = thermal energy

$$Pr(h) = \frac{A\rho_N(h)}{N} = \frac{mg}{k_B T}\,\mathrm{e}^{-\left(\frac{mgh}{k_B T}\right)}$$

$$Pr(E_i) \propto \mathrm{e}^{-\frac{E_i}{k_B T}}$$

This is the Boltzmann factor – gives the probability of measuring a certain energy state at a given temperature

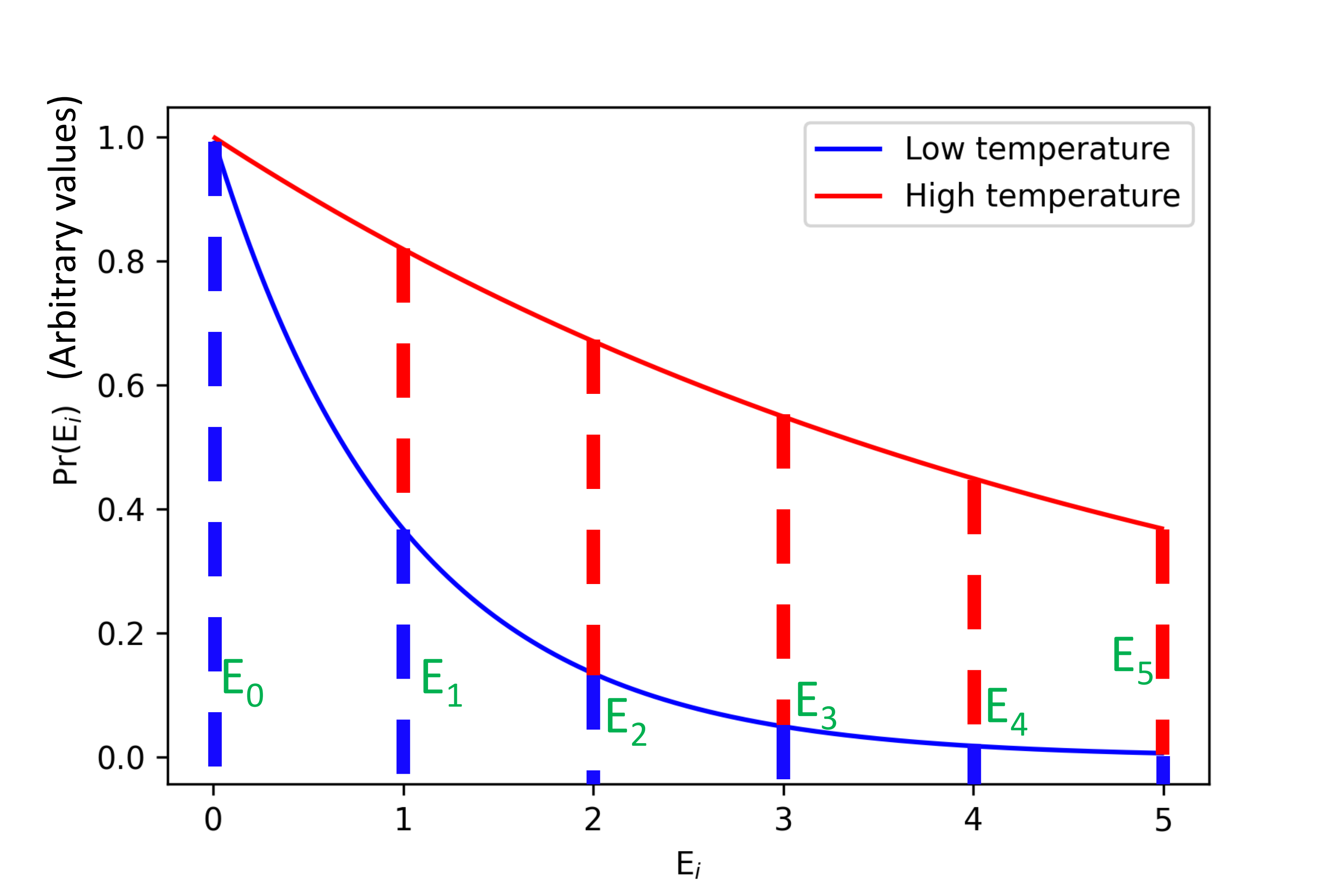
Boltzmann factors

$$Pr(E_i) \propto \mathrm{e}^{-\frac{E_i}{k_B T}}$$

As temperature increases, rate of decay decreases

Can describe continuous energy distributions (e.g. gravitational potential energy)…

… and discrete ones!



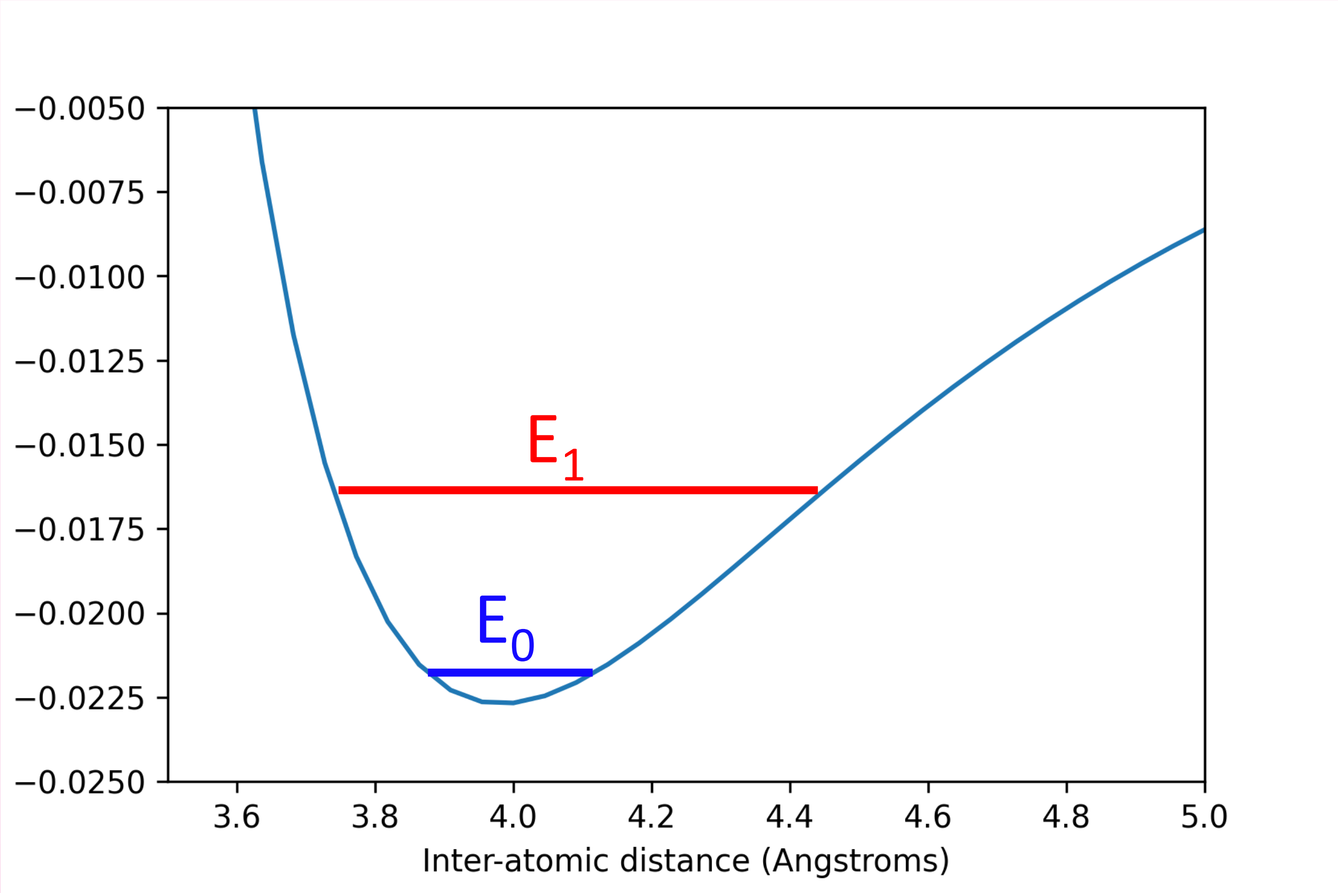
Simple quantum system

A simple atom/molecule with two energy levels, E_0 and E_1

What is the probability of finding the atom/molecule in the state E_0?

$$Pr(E_0) = Ce^{-\frac{E_0}{k_B T}}$$

$$Pr(E_1) = Ce^{-\frac{E_1}{k_B T}}$$



Simple quantum system

By requiring normalisation of the probability, we can determine the constant C and so

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}}$$

Interesting cases: 1) $T \to 0 : Pr(E_0) = 1, Pr(E_1) = 0$

2) $T \to \infty : Pr(E_0) = 0.5, Pr(E_1) = 0.5$ (unbiased)

Low and high temperature limits

Interesting cases:

1) $T \to 0 : Pr(E_0) = 1,$
$Pr(E_1) = 0$

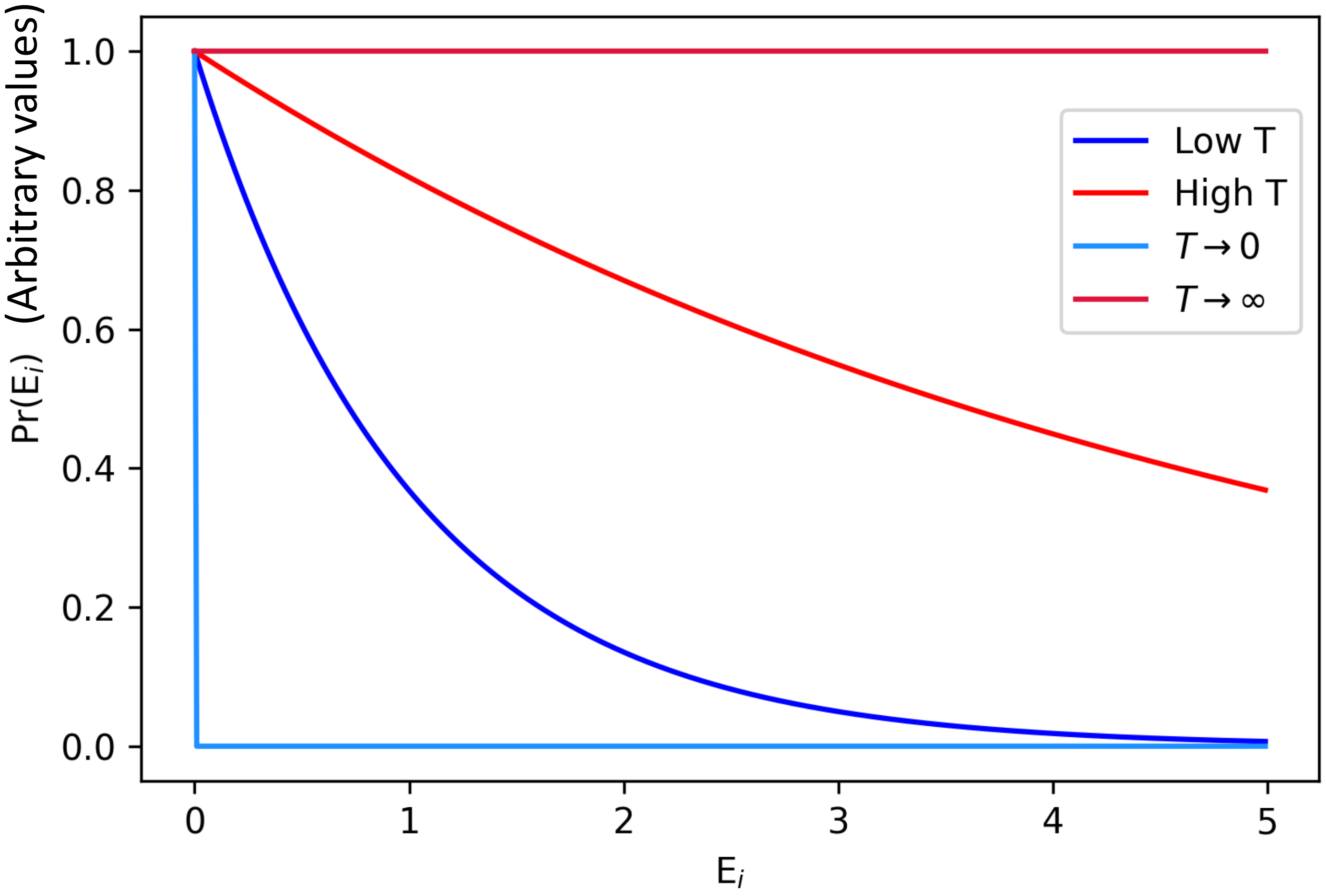
$$k_B T \ll E_1 - E_0$$

2) $T \to \infty : Pr(E_0) = 0.5,$
$Pr(E_1) = 0.5$ (unbiased)

$$k_B T \gg E_1 - E_0$$

Usual cases

$$k_B T \approx E_1 - E_0$$



Negative temperatures

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}}$$

If T = -τ, where τ is some positive number, then

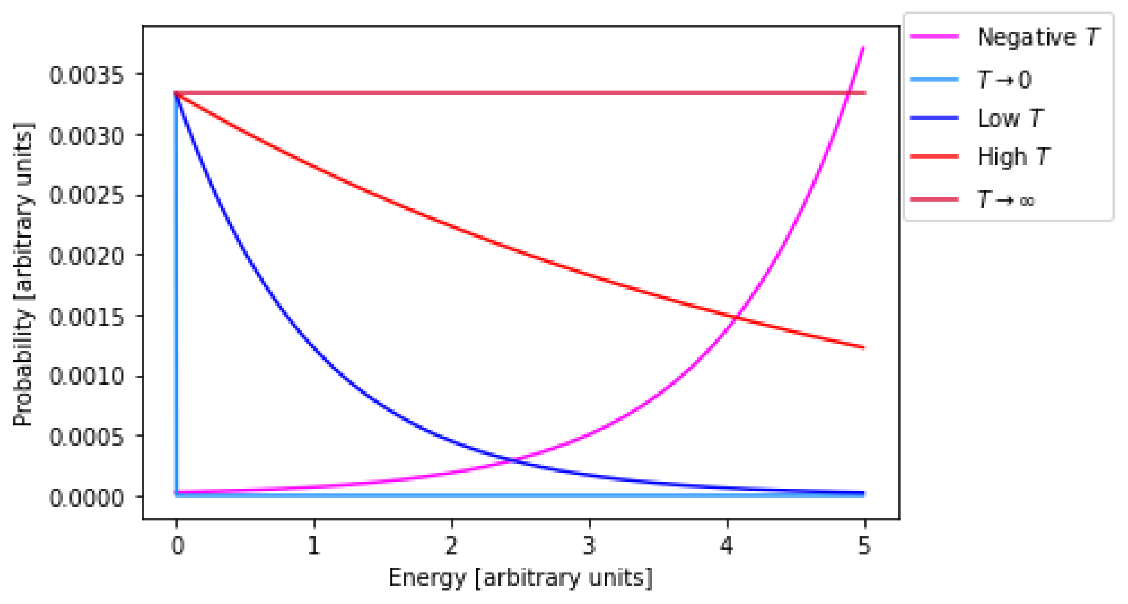
$$Pr(E_i) = \frac{e^{\frac{E_i}{k_B \tau}}}{e^{\frac{E_0}{k_B \tau}} + e^{\frac{E_1}{k_B \tau}}}$$

Negative temperatures

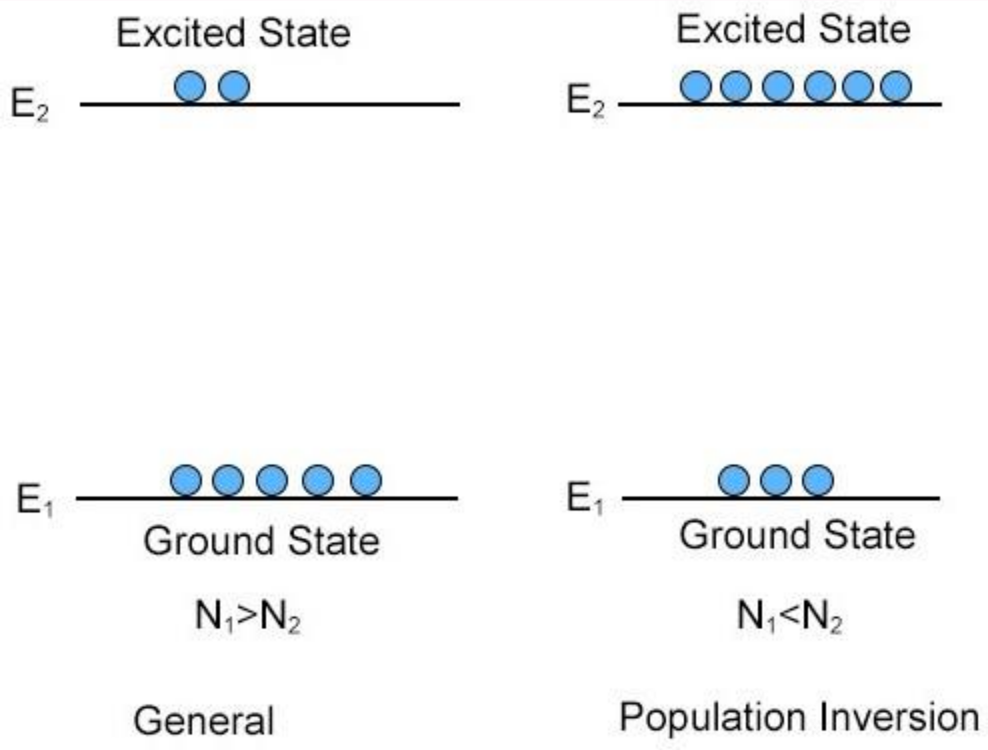
$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}}$$

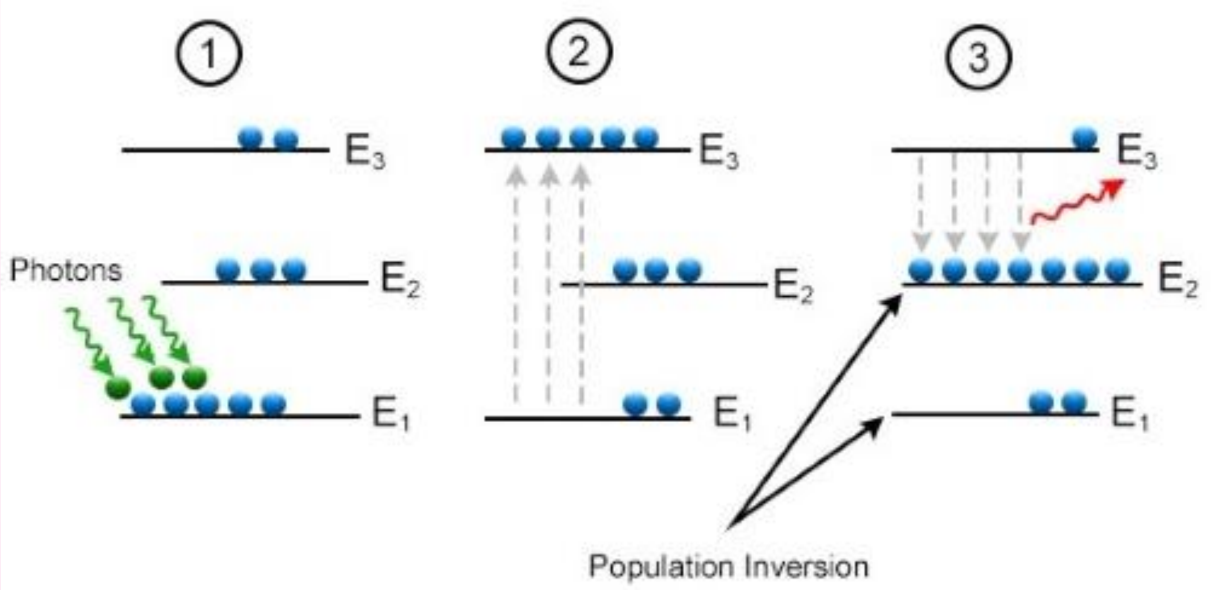
If T = -τ, where τ is some positive number, then

$$Pr(E_i) = \frac{e^{\frac{E_i}{k_B \tau}}}{e^{\frac{E_0}{k_B \tau}} + e^{\frac{E_1}{k_B \tau}}}$$



Higher energy levels have more particles than lower energy states!





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More complicated quantum systems

For an atomic system with 2 levels E_0 and E_1 (with $E_1 < E_0$), we have

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}}$$

Increasing to N levels, we have

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{j=0}^{N-1} e^{-\frac{E_j}{k_B T}}}$$

Interesting cases:

1) $T \rightarrow 0 : Pr(E_0) = 1,$
$Pr(E_{n!=0}) = 0$

2) $T \rightarrow \infty : Pr(E_0) = 1/N,$
$Pr(E_{n!=0}) = 1/N$
(unbiased)

Example question

A type of atom has 4 possible energy levels, $E_0 = 0$, $E_1 = 0.08$ meV, $E_2 = 0.24$ meV and $E_3 = 0.48$ meV

For a single mole of atoms with a temperature at 50 K, how many of the atoms are in the E_2 (second excited state)?

$$Pr(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{j=0}^{N-1} e^{-\frac{E_j}{k_B T}}} = \frac{e^{-\frac{E_2}{50 k_B}}}{\sum_{j=0}^{3} e^{-\frac{E_j}{50 k_B}}} = \frac{e^{-\frac{E_2}{50 k_B}}}{e^{-\frac{E_0}{50 k_B}} + e^{-\frac{E_1}{50 k_B}} + e^{-\frac{E_2}{50 k_B}} + e^{-\frac{E_3}{50 k_B}}}$$

Degeneracies

In reality, electrons in atoms can have the same energy in multiple ways (spin up vs spin down, for example).

The is a degeneracy of 2 (we can fit two electrons) in the n=1 subshell, 8 in the n=2 etc

Boltzmann factor changes accordingly:

$$Pr(E_i) \propto g(E)e^{-\left(\frac{E_i}{\kappa_B T}\right)}$$

n = 1, g(E) = 2; n = 2, g(E) = 8… g(E) represents the degeneracy