5. Boltzmann's Law

8th May

Recap

- Lecture 0 - all common states of matter made of atom (KE v PE determines state)
- Lecture 1 - ideal gas $PV=Nk_BT$, from kinetic theory $U = \frac{1}{2} n_d Nk_BT$
- Lecture 2 - zeroth law defines T
  first law $\mathrm{d}U = đQ + đW$
  (for gases: $\mathrm{d}U = đQ - P\mathrm{d}V$)

Recap

- Lecture 3 - For gas $dW = -PdV$ - path dependent
  e.g isothermal $dW = -(Nk_BT) \ln(V_1/V_0)$,
  isobaric (followed by isochoric) $dW = -(Nk_BT)(V_1/V_0 - 1)$
- Heat capacity (HC) define $dQ = C\,dT$ - (also path dependent) (molar HC, $dQ = N_m C_m\,dT$, specific HC, $dQ = m\,c\,dT$)
- Ideal gas, $C_v = n_d/2\, Nk_B$ ($C_{vm} = n_d/2\, R$) $C_p = C_v + Nk_B$ ($C_{pm} = C_{vm} + R$)
- Adiabatic eqn of state PV^γ = constant, where $\gamma = C_p / C_v$
- Lecture 4 - Phase Change - Large change in one state variable for a small change in another (usually indicating change in internal order and associated with latent heat).

5.1 Isothermal Atmosphere

Aim: To calculate air pressure as a function of height in equilibrium

Aim: To calculate air pressure as a function of height in equilibrium

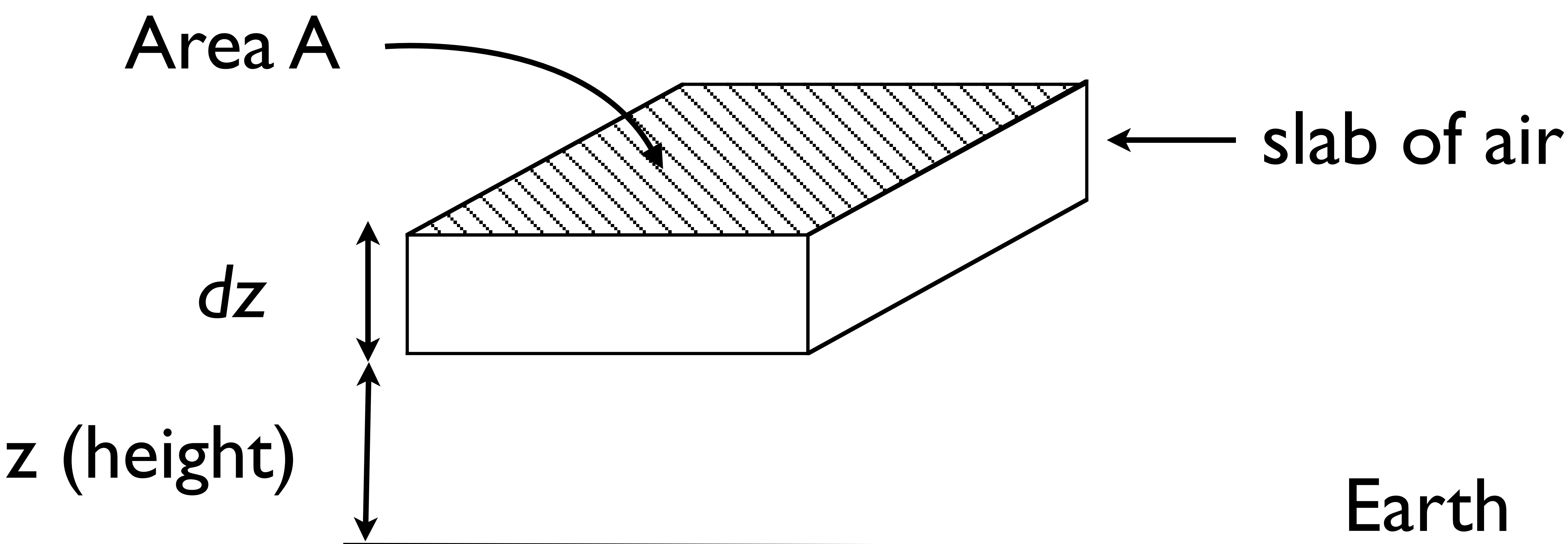
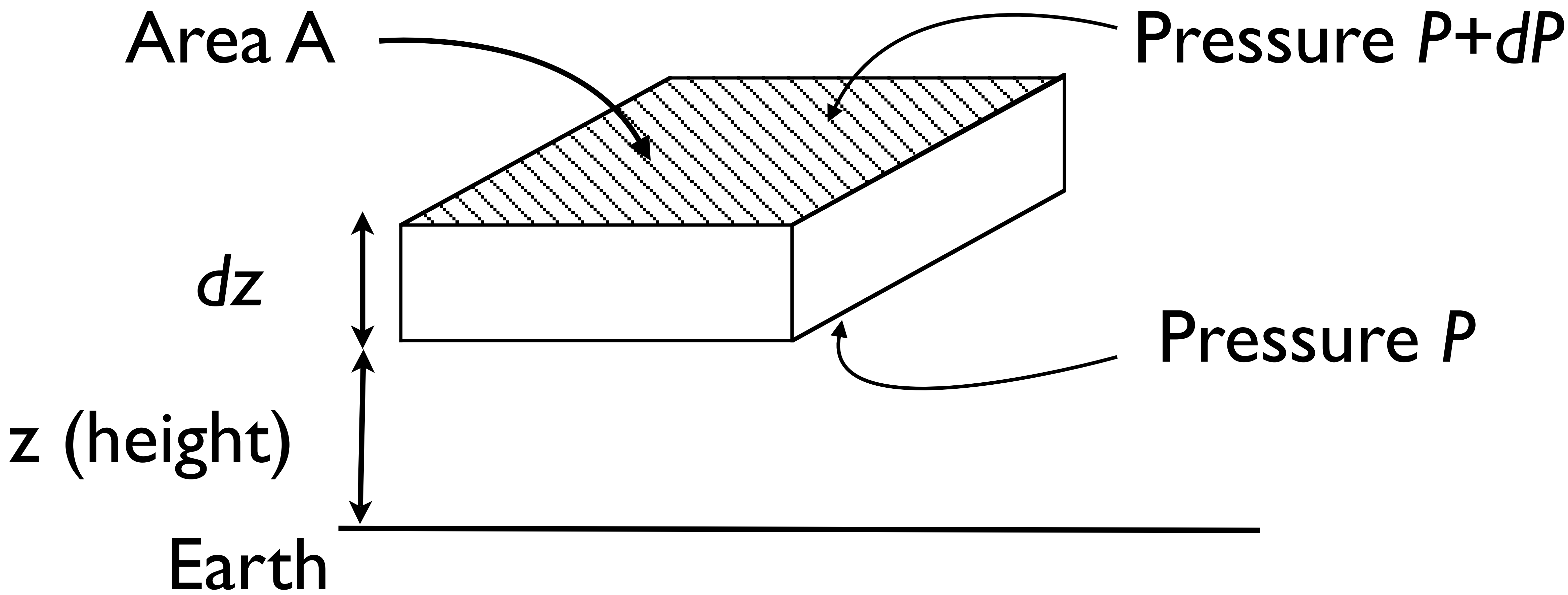


Figure 1



① ② ③

Net upward force = $PA - (P+dP)A - \rho A\, dz\, g$

① pressure from below

② pressure from above (pressure is $P+dP$ at $z+dz$)

[should find that $dP < 0$]

③ weight of slab (ρ = density)

but in equilibrium, net force = 0

$$\rightarrow \qquad PA - PA - AdP - \rho A\, dz\, g = 0$$

$$\rightarrow \qquad \frac{dP}{dz} = -\rho g \qquad (5.1.1)$$

P falls with height.

Rewrite 5.1.1 using $\rho(z) = n(z)\, m$
and assume isothermal ideal gas: $P(z) = n(z)\; k_B T$

$$5.1.1 \qquad \rightarrow \qquad k_B T \frac{dn}{dz} = -mng$$

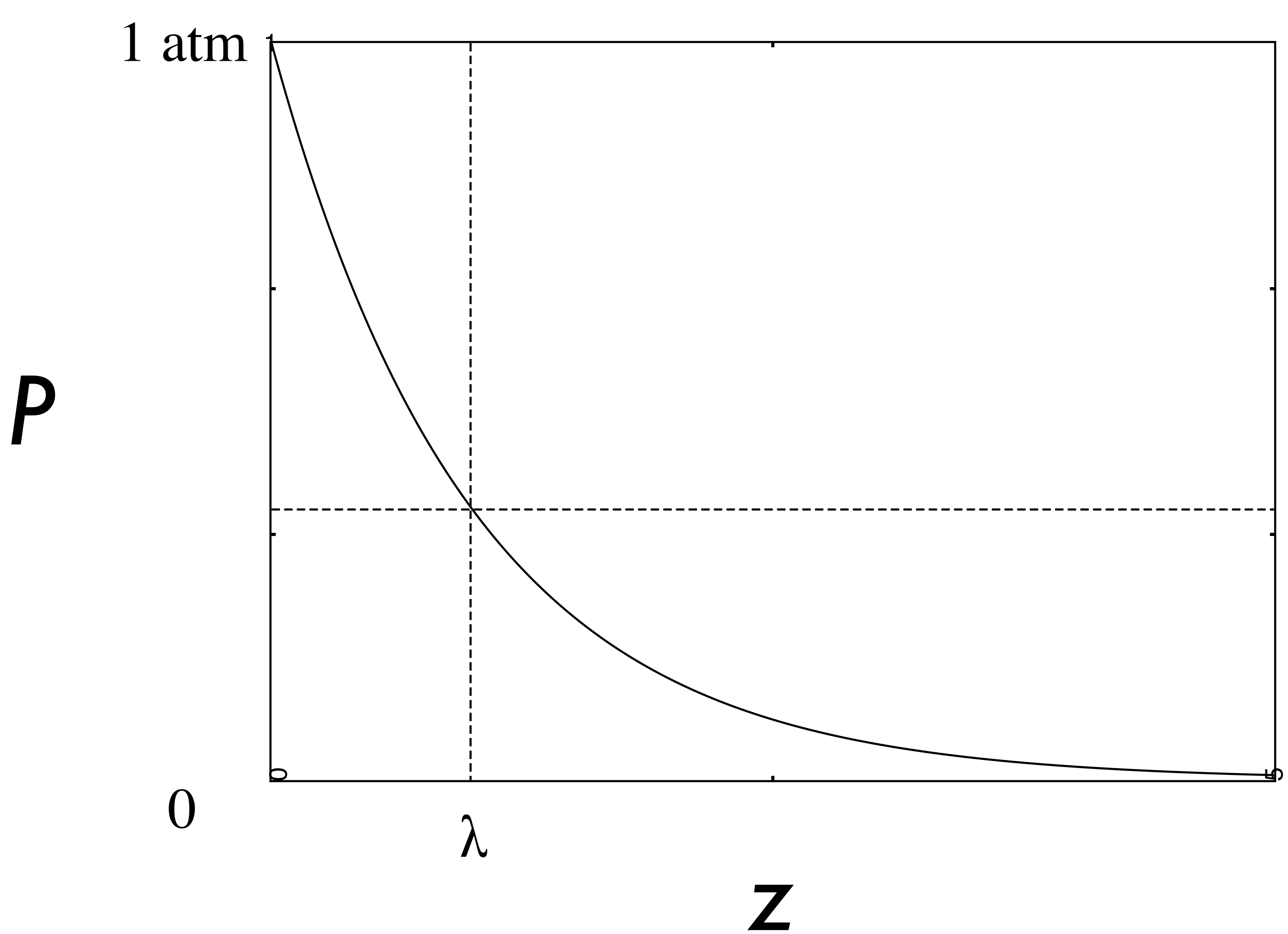
$$\rightarrow \qquad \frac{dn}{dz} = -\frac{mg}{k_B T} n$$

$$\therefore \quad n = n_0\, e^{-z/\lambda} \tag{5.1.2}$$

where $n_0 = n(z = 0)$ [ie. at ground level],

$\lambda = k_B T/mg$ = scale length

also $P = nk_B T = P_0\, e^{-z/\lambda}$



$\lambda \approx$ 8.5 km, which is the height of Everest

human habitation only up to about 5 km (in Tibet & Andes)

So Everest (8.5 km) only conquered after lightweight oxygen canisters.

Figure 2

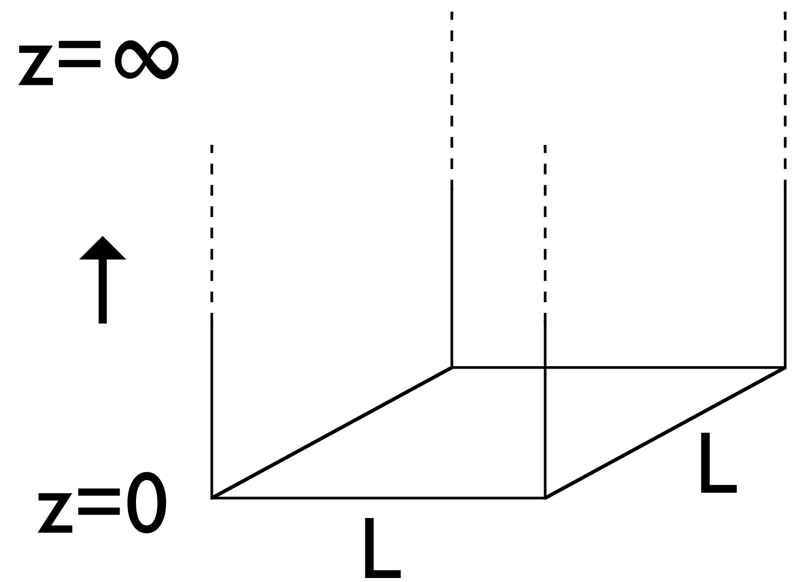


Figure 3

Consider a column of air, area L^2, infinitely high:

Number of particles between z and $z+dz = n_0 \exp(-z/\lambda)L^2 dz$

$$
\begin{aligned}
\therefore \text{N} = \text{total number of particles} &= \int n_0 \exp(-z/\lambda)L^2 dz \\
&= -n_0 L^2 \lambda [e^{-\infty} - e^0] \\
&= n_0 L^2 \lambda \qquad (5.1.3)
\end{aligned}
$$

Under pressure

Commercial airliners fly at abut 32,000 ft 9-10km, which is why airliners are pressurised, but NOTE airliners only pressurised to 0.85 Atmospheres (to keep thickness required down

$$n_0 = \frac{P}{k_B T} = \frac{10^5}{k_B 293} = 2.5 \times 10^{25}\ \mathrm{m}^{-3}$$

So total of particles above each $\mathrm{m}^2 = n_0 L^2 \lambda$

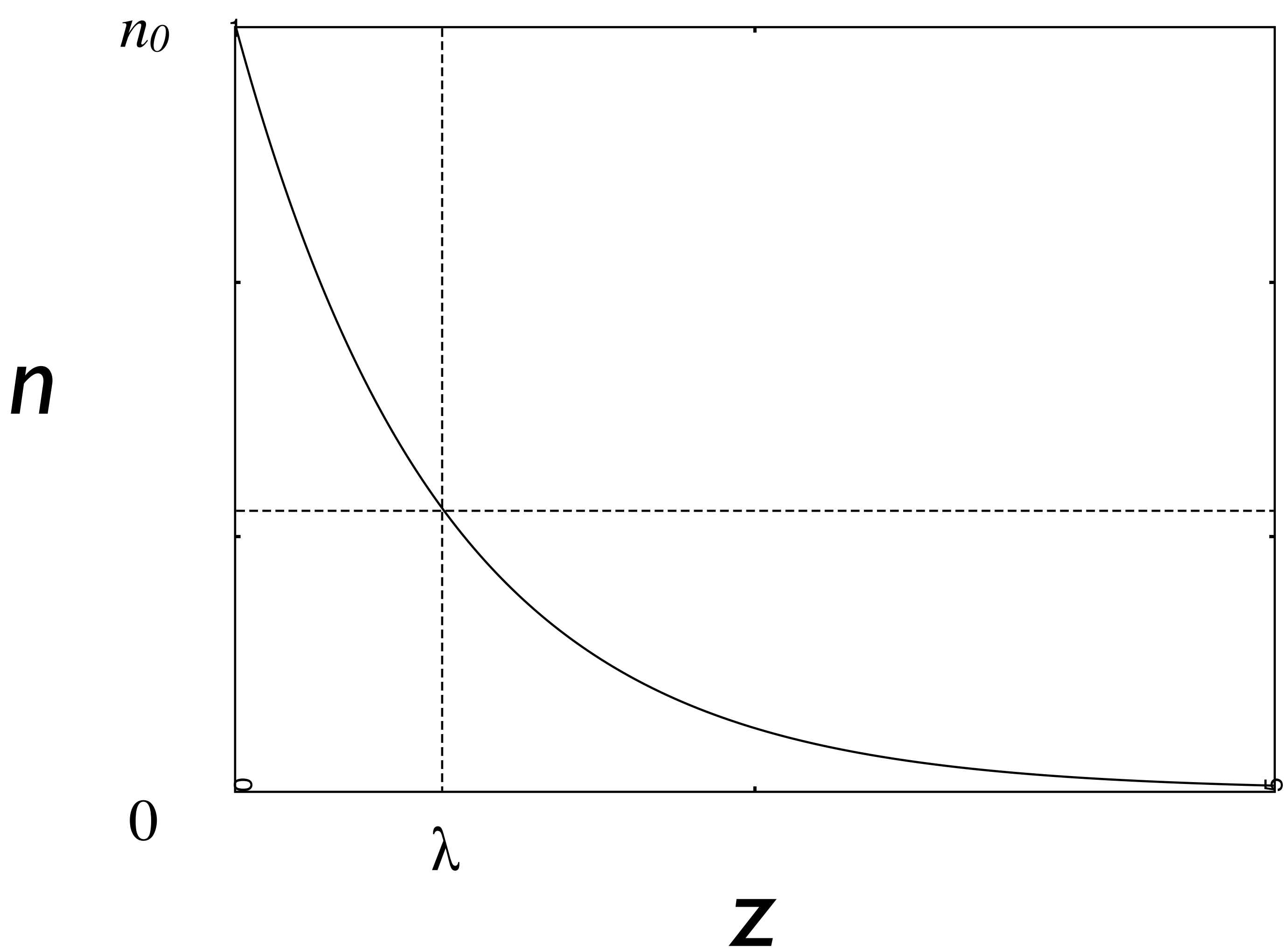
$$\approx 2.5 \times 10^{25} \times 8.5 \times 10^3 = 2.1 \times 10^{29}$$

The weight of these particles is $1.66 \times 10^{-27} * 29 * 2.1 \times 10^{29} = 10^4 kg = 10$ tonnes!

Of course the force due to 10^4 kg $\approx 10^5\ \mathrm{N/m^{-2}} =$ atmospheric pressure.

5.2 Particle probabilities

$$n = n_0 \, e^{-z/\lambda} \qquad (5.1.2)$$



λ ≈ 8.5 km, which is the height of Everest

human habitation only up to about 5 km (in Tibet & Andes)

So Everest (8.5 km) only conquered after lightweight oxygen canisters.

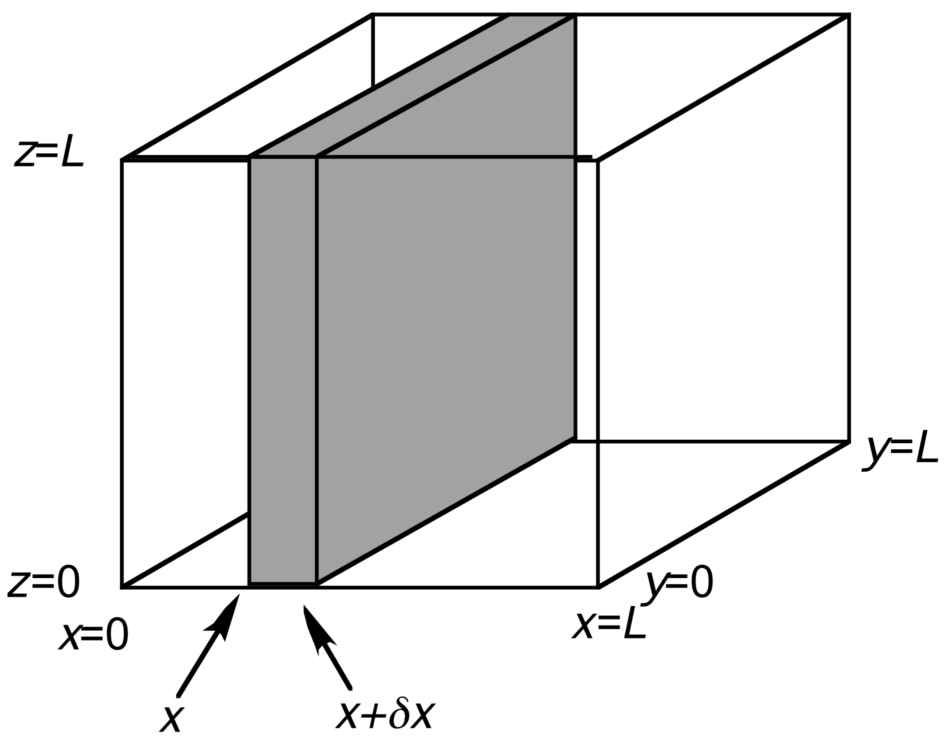


Figure 4

Probability of given molecule being in a region of the box = no. of particles in region / N

e.g. if uniformly distributed
$n = N/L^3$

$\therefore$ number of particles between x and $x + \delta x = n\delta x L^2$

$$= (N/L^3)\delta x L^2$$

so probability of given particles being between x and $x + \delta x$:
$p(x)\delta x = \delta x / L$

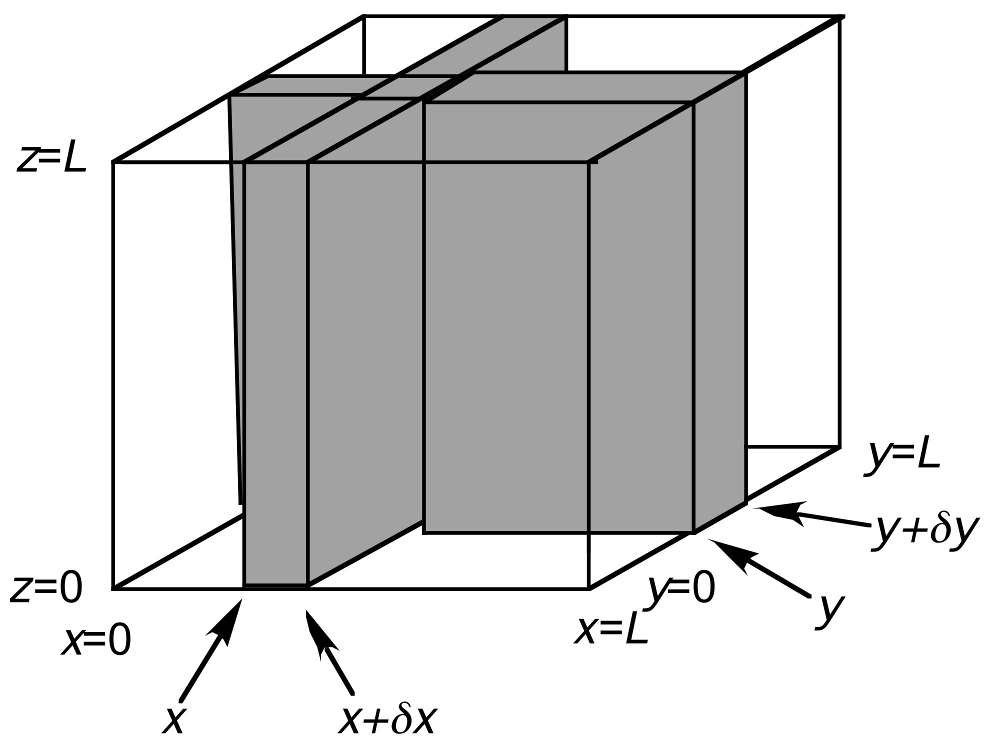


Figure 5

Number of such particles
$= N\delta x\delta y/L^2$
$= (N/L^3) \times L\delta x\delta y$
$(= n \times \text{volume of region})$

e.g. prob. of a particle being between x and $x+\delta x$ and also between y and $y+\delta y$

$$p(x,y)\,\delta x\delta y = \delta x\delta y/L^2$$

$\therefore$ if two events are independent,
prob. of both = prob(1)×prob(2)

For isothermal atmosphere:

5.2.1 $\rightarrow$ prob. of particles being between z & $z + dz$ is $p(z)\,dz$

$$\begin{aligned} p(z) &= (\text{no. of particles between } z \ \& \ z+dz)/N \\ &= n_0 \exp(-z/\lambda) L^2 dz / n_0 L^2 \lambda \\ &= (mg/k_B T) \exp(-mgz/k_B T) dz \qquad (5.2.2) \end{aligned}$$

NB Particles are actually moving through out the gas, so for any given particle, this is also the probability of where you would find it through-out its history.

Also note that equilibrium implies, stationary or constant state, but actually in a gas, though state variables are constant, underlying motion at atomic scale is far from stationary!

5.3 Boltzmann's Law

5.2.2 $\rightarrow$ prob of particles being between z & $z + dz \propto \exp(-mgz/k_B T)dz$

but $E(z) = mgz =$ p.e.

so $p(z) \propto p(E) \propto \exp(-E(z)/k_B T)$

IN FACT generally when in thermal equilibrium,

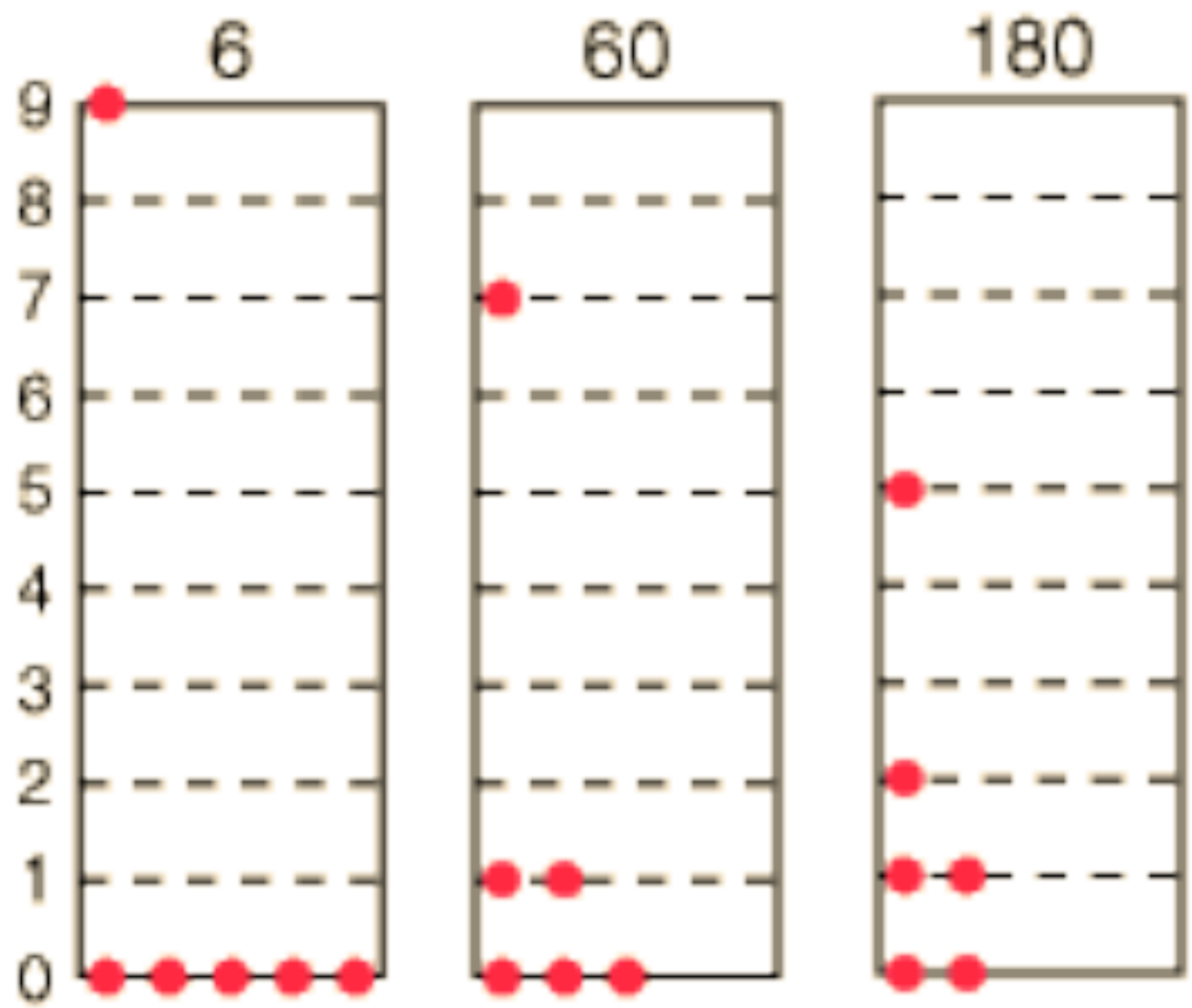
$p(E) \propto \exp(-E/k_B T)$ (Boltzmann's Law)

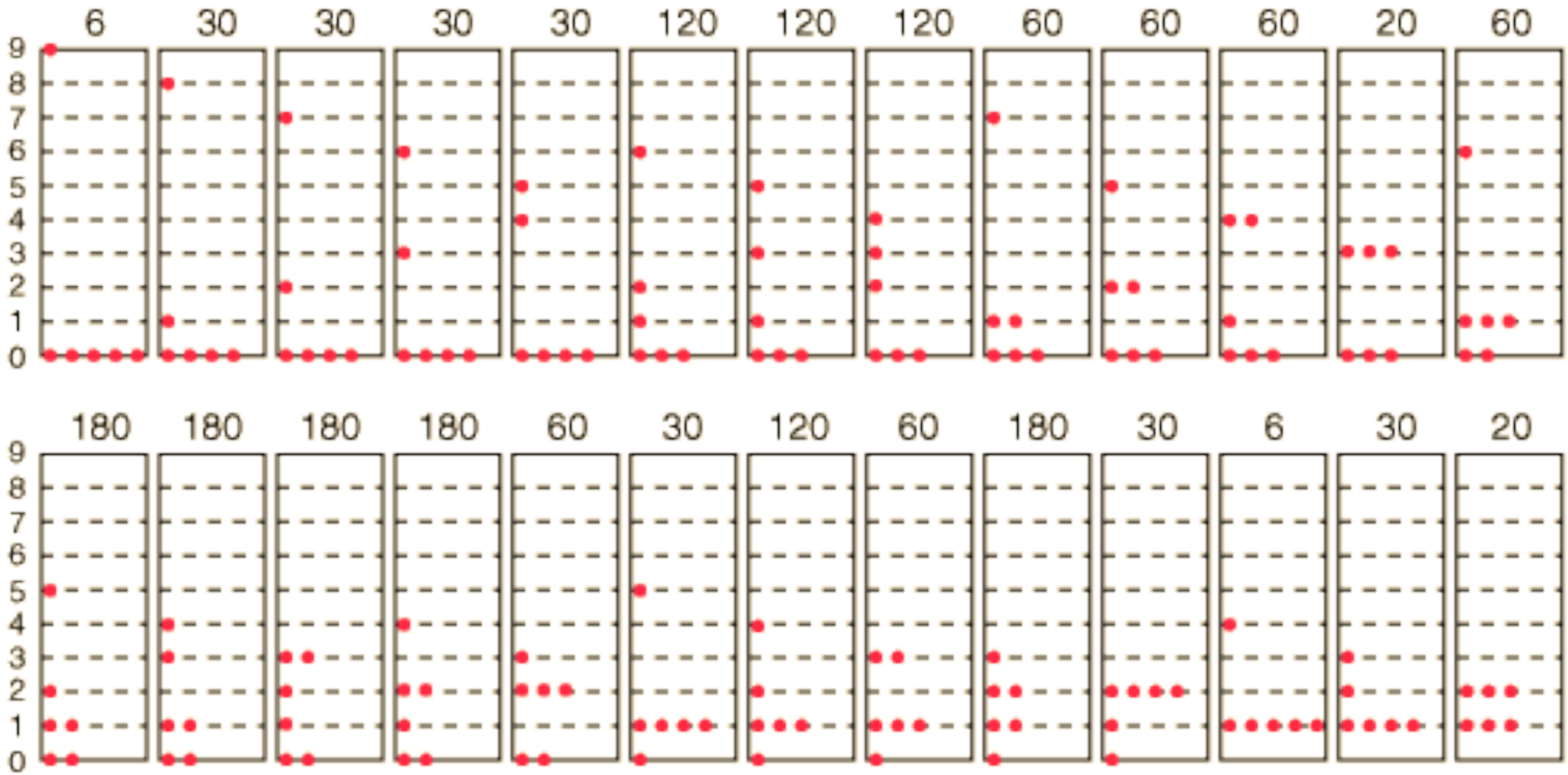
(E can be any general potential)

Counting states:

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbol.html#c2

How many ways can you distribute 9 units of energy among 6 particles?





Answer: 26 distributions, but for distinguishable particles 2002 possible arrangements

Energy level number	Average
0	2.143
1	1.484
2	0.989
3	0.629
4	0.378
5	0.21
6	0.105
7	0.045
8	0.015
9	0.003