

Revision Lecture

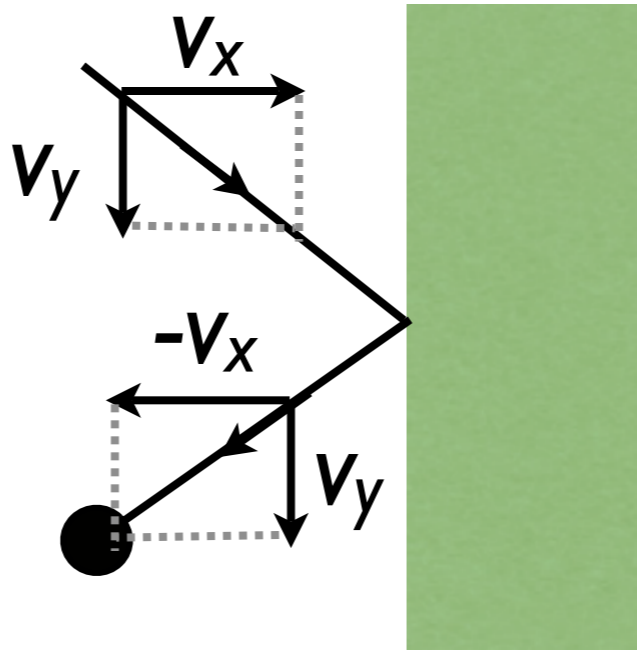
23rd May

Lecture 0

- All common matter made of atoms
- All atoms have a potential that is repulsive at close distance, attractive away from eqm position, and tends to zero at large separation.
- Structure of matter depends on ratio of kinetic energy compared to this potential

Lecture 1

- Gases characterised by P, V, N_{moles}, T - (State Variables)
- Equation of State relates State Variables,
 $PV = N_{moles} RT = N k_B T$
- From kinetic theory, $P = n m \langle v_x^2 \rangle = \frac{1}{3} n m \langle v^2 \rangle$
- Internal energy $PV = \frac{2}{3} U$
(implies $U(T)$ only $U = \frac{3}{2} N k_B T$)
- Equating to the KE per particle $\rightarrow \frac{1}{2} k_B T$ per degree of freedom per particle



NB y momentum unchanged

$$\begin{aligned}\Delta p &= |\text{momentum}| \text{ to wall at each collision} \\ &= |\text{mom. change of part.}| \\ &= 2m|v_x|\end{aligned}$$

(NB this is per collision)

Lecture 2

- * Zeroth law: If system C is in thermal equilibrium (same temperature) with A and B, then A is in thermal equilibrium with B. Allows us to use thermometers.
- * If two systems are not in thermal equilibrium, then heat will flow (conduction, convection, radiation)
- * Heat is a form of energy ($\Delta Q = C \Delta T$)
- * First Law: $dU = \delta Q + \delta W$
- * For gas, $dW = -P dV$, so $dU = dQ - PdV$

Lecture 3

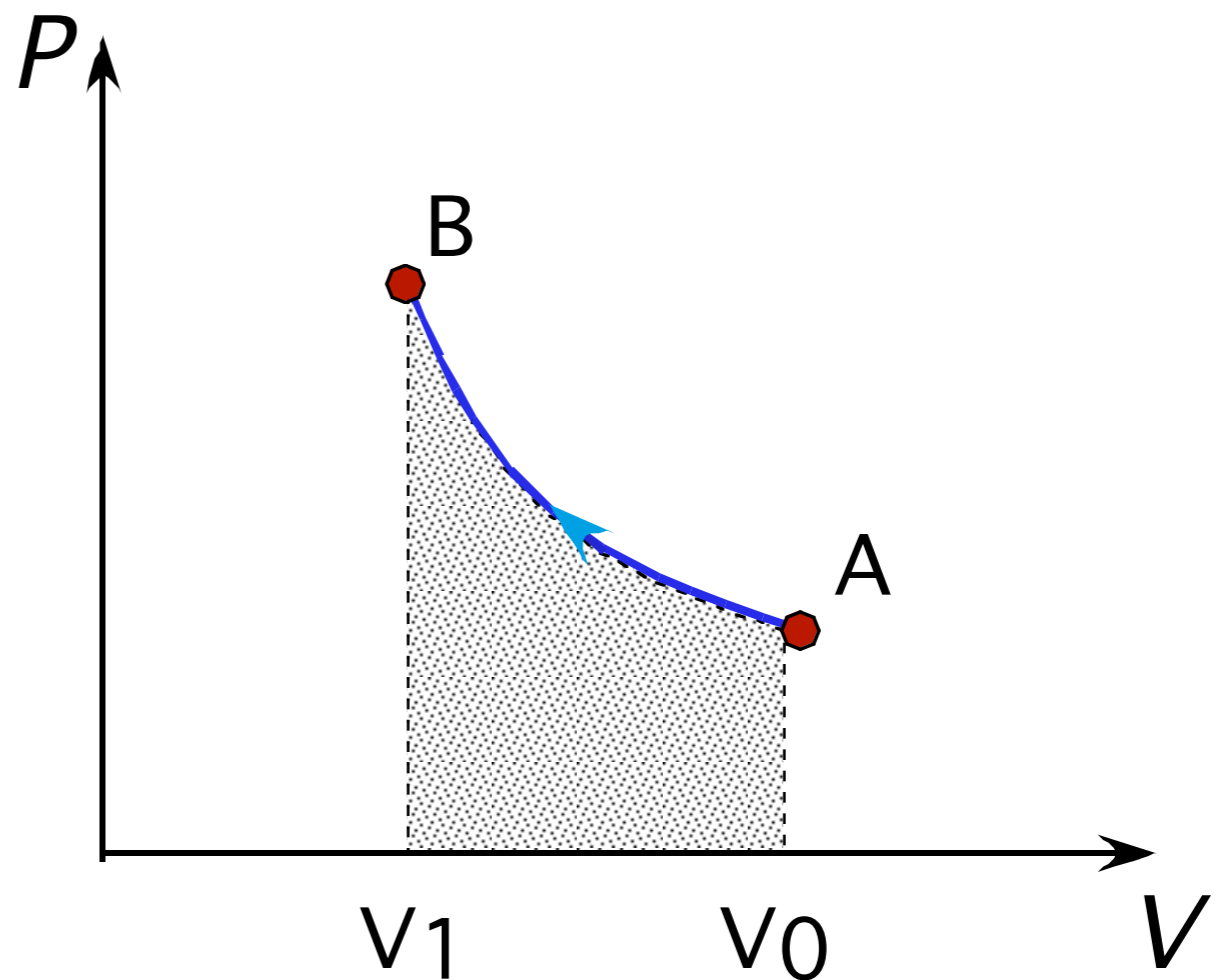
- ◆ For gas $dW = -PdV$ - path dependent
e.g isothermal $dW = (Nk_B T) \ln(V_0/V_1)$,
isobaric (followed by isochoric) $dW = (Nk_B T) (1 - V_1/V_0)$
- ◆ Heat capacity (HC) define $dQ = C dT$
(also path dependent)
(molar HC, $dQ = N_m C_m dT$, specific HC, $dQ = m c dT$)
- ◆ For ideal gas, $C_v = (n_d/2) Nk_B$ ($C_{vm} = n_d/2 R$)
 $C_p = C_v + Nk_B$ ($C_{pm} = C_{vm} + R$)
- ◆ Adiabatic equation of state $PV^\gamma = \text{constant}$,
where $\gamma = C_p / C_v$

Path dependence of W

Consider two paths from A to B on PV diagram at the same temperature:

Process I -
Isothermal

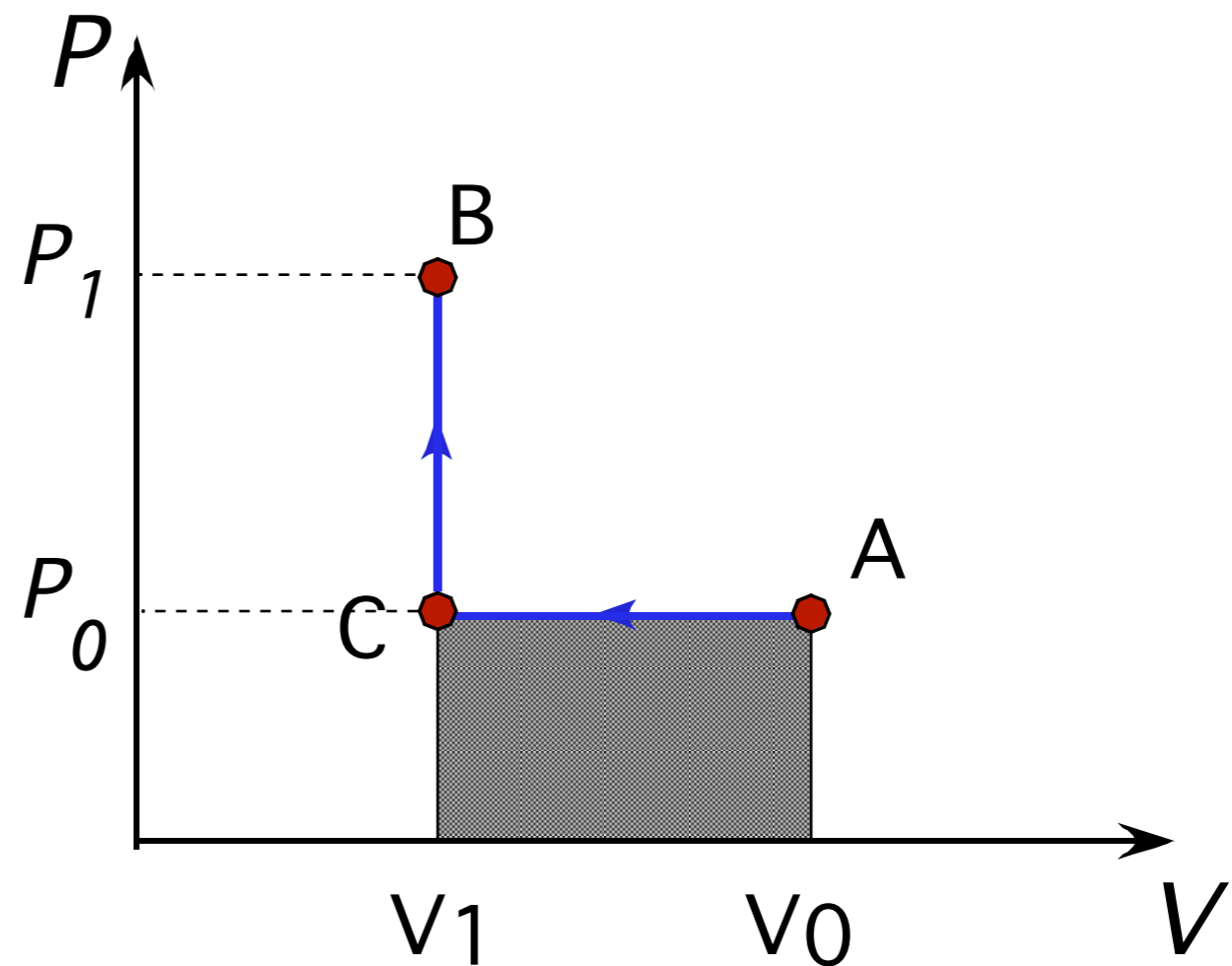
$$PV = Nk_B T \rightarrow P \propto (1/V)$$



Path dependence of W

Consider two paths from A to B on PV diagram at the same temperature:

Process 2 -
Isobaric (constant pressure)
followed by
isochoric (constant volume)



C_V for ideal gas

For ideal gas: $U = n_d \frac{1}{2} N k_B T$, n_d degs. freedom

differentiating $dU = \frac{1}{2} n_d N k_B dT$

1st Law: $dQ = dU - dW = \frac{1}{2} n_d N k_B dT + P dV$

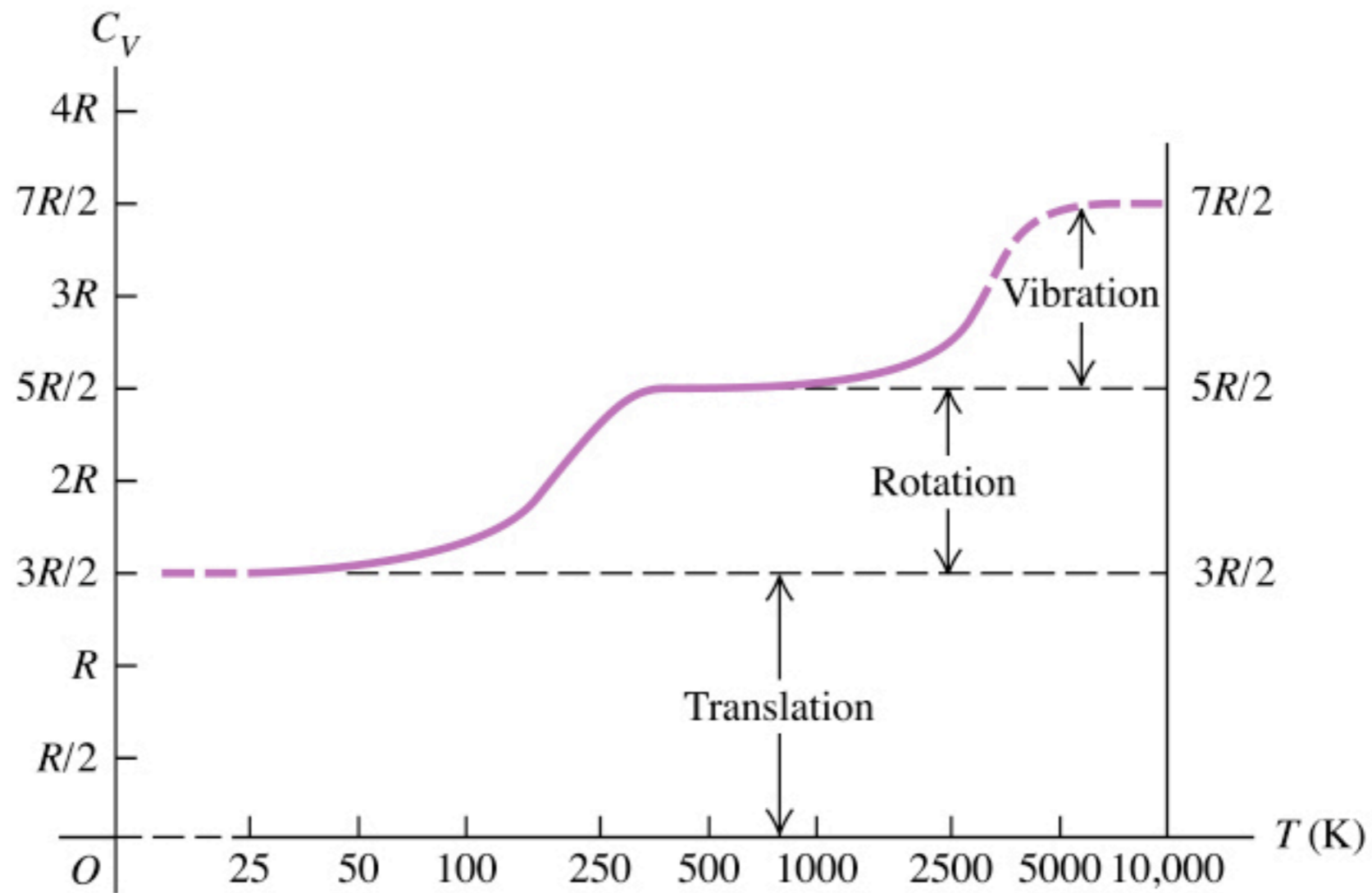
for constant V (*i.e.* $dV = 0$) $\rightarrow dQ = \frac{1}{2} n_d N k_B dT$

$\therefore C_V = \frac{1}{2} n_d N k_B$ - Heat capacity constant volume

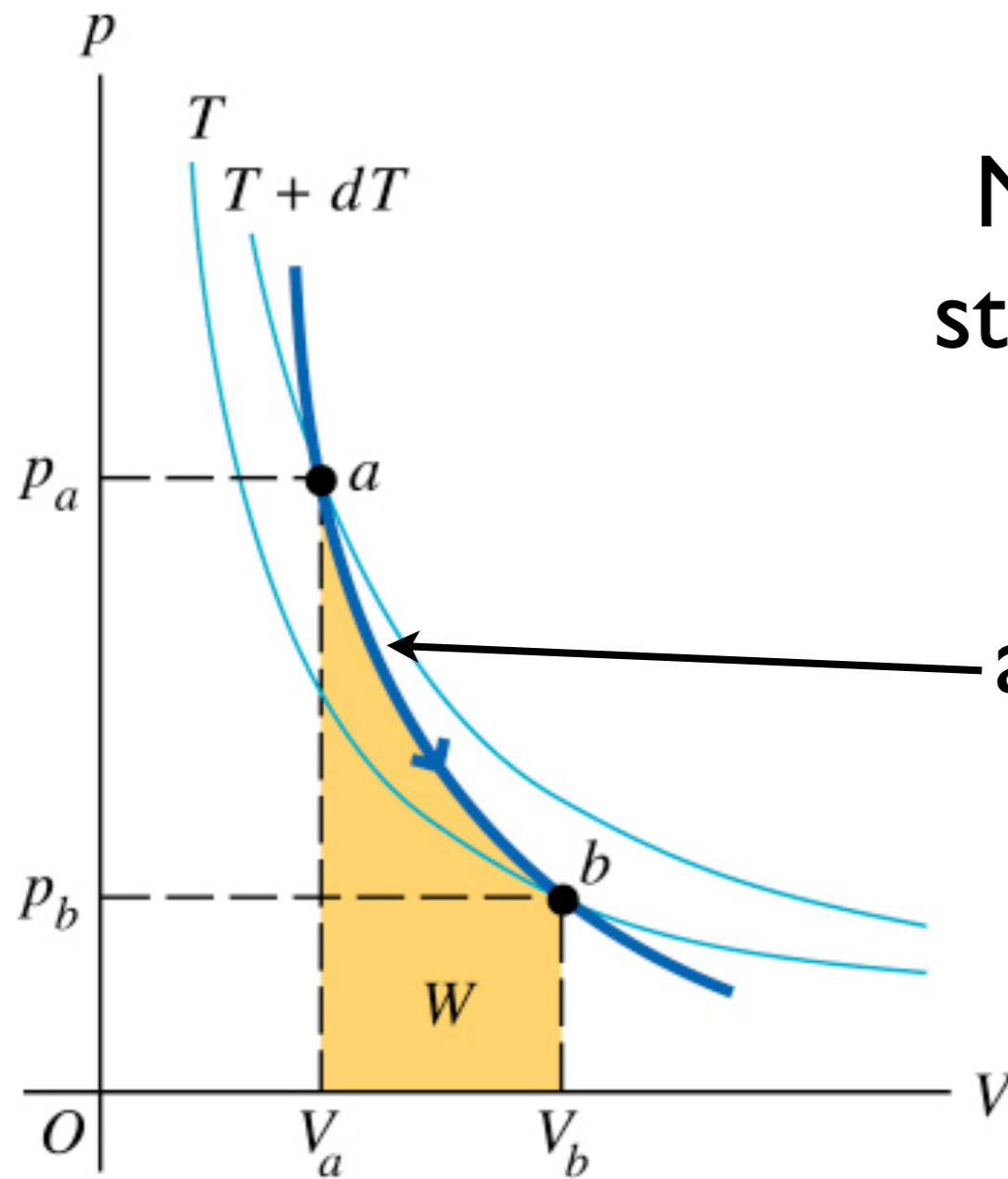
\therefore can write $U = C_V T$ (for an ideal gas)

For 1 mole of gas $C_{V_m} = \frac{n_d}{2} R$.

C_v for H_2



Adiabat steeper than isotherm



Not that adiabats are steeper than isotherms

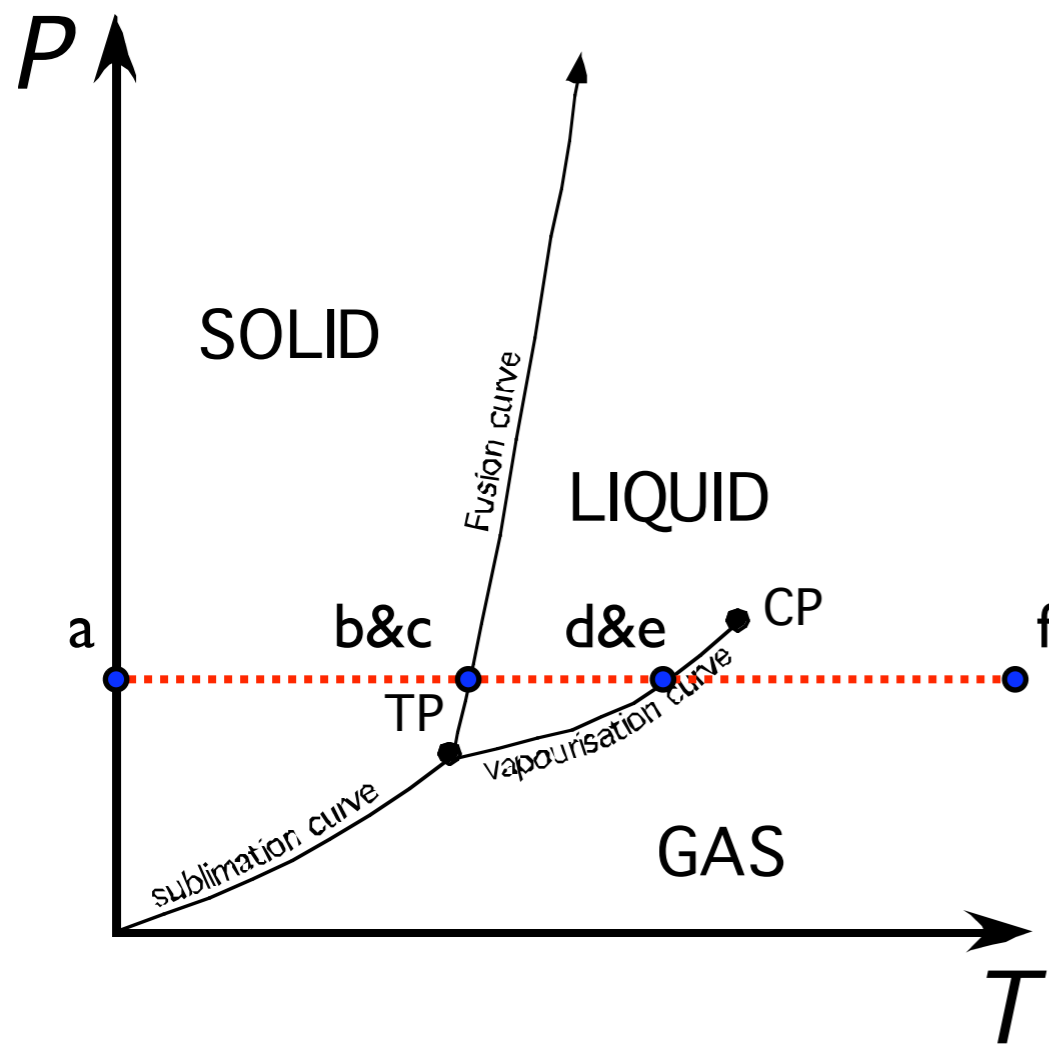
adiabat

NB light blues are isotherms, lines of equal (but different!) T

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): represented by boundaries on PVT diagram
- Regions of mixed phase on PV diagram. Energy overcomes latent heat.
- All states exist at triple point. Evaporation curve ends at critical point liquids exist for $T_{tp} < T < T_c$
- Latent heat of sublimation can be related to binding energy by $L_s = N_0 (n/2) \epsilon$

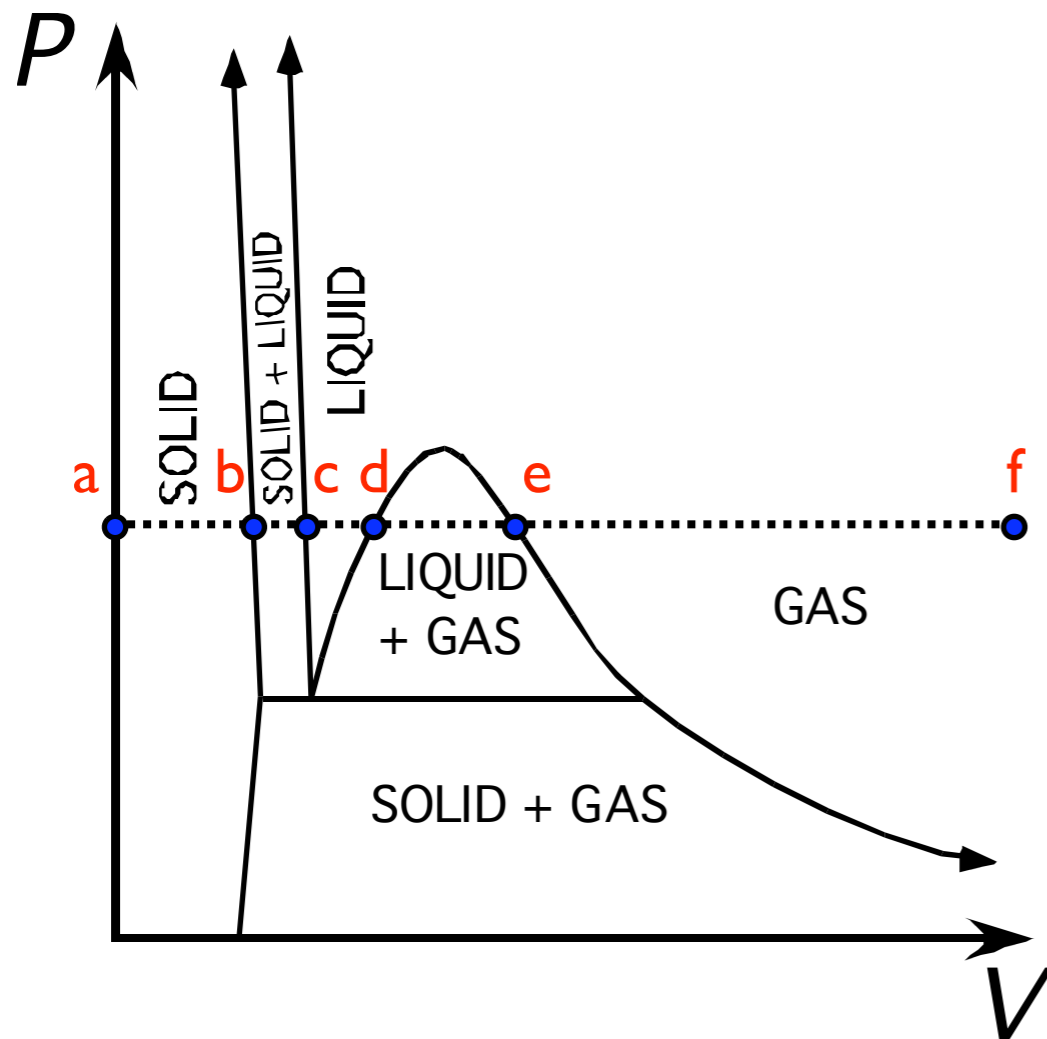
PT projection



- $a \rightarrow b$: solid T rises
- b : starts to melt
- $b \rightarrow c$: solid / liquid co-exist, T const.
- $c \rightarrow d$: liquid, T rises
- d : starts to vapourise
- $d \rightarrow e$: liquid / gas coexist, T const.
- $e \rightarrow f$: gas, T rises

PV projection

Adding heat at constant pressure



$a \rightarrow b$: solid T rises

b : starts to melt

$b \rightarrow c$: solid / liquid co-exist, T const.

$c \rightarrow d$: liquid, T rises

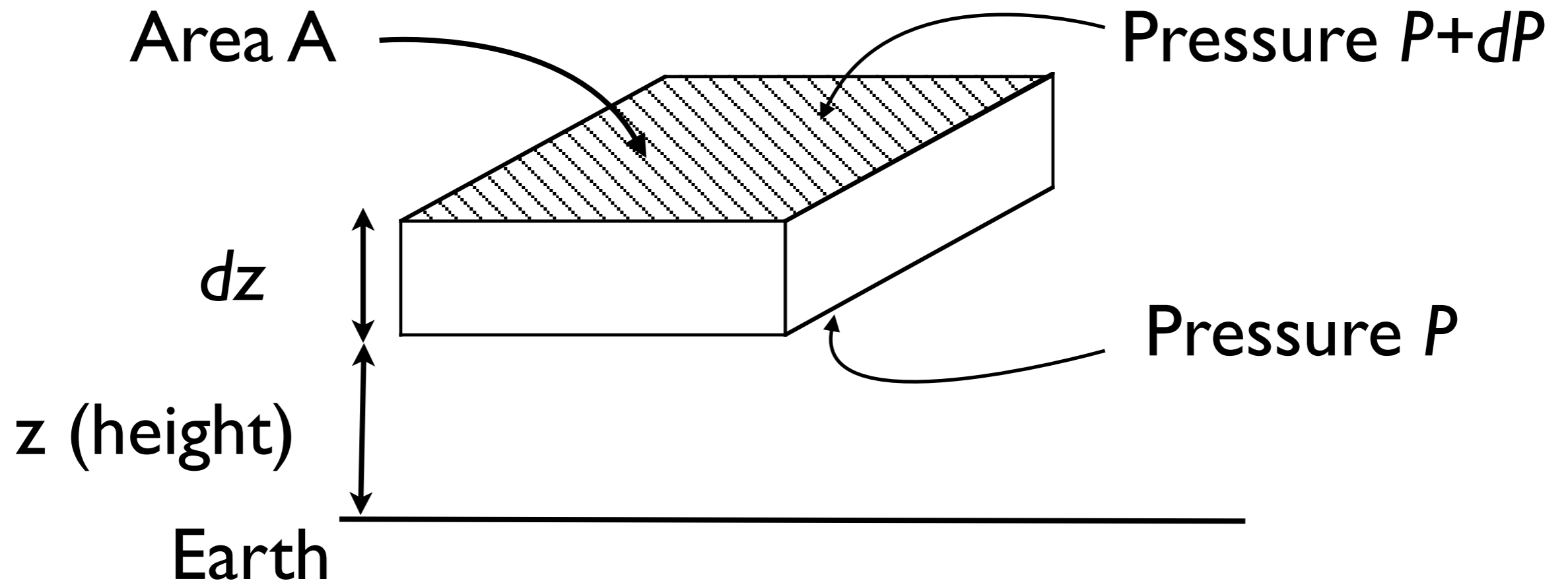
d : starts to vapourise

$d \rightarrow e$: liquid / gas coexist, T const.

$e \rightarrow f$: gas, T rises

Lecture 5

- Isothermal model of the atmosphere,
 $n = n_0 e^{(-z/\lambda)}$ and $P = P_0 e^{(-z/\lambda)}$,
where $\lambda = k_B T / mg$
- Probability of particle being within z and $z + dz$, $p(z) dz = n(z) A dz / N$, so $p(z) \propto e^{(-mgz/kT)}$
- For two independent co-ordinates to be correlated, $Prob_{\text{Tot}} = Prob_1 \times Prob_2$
- **Boltzmann's Law, $p(E) \propto e^{(-E/kT)}$**



①

②

③

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

① pressure from below

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

[should find that $dP < 0$]

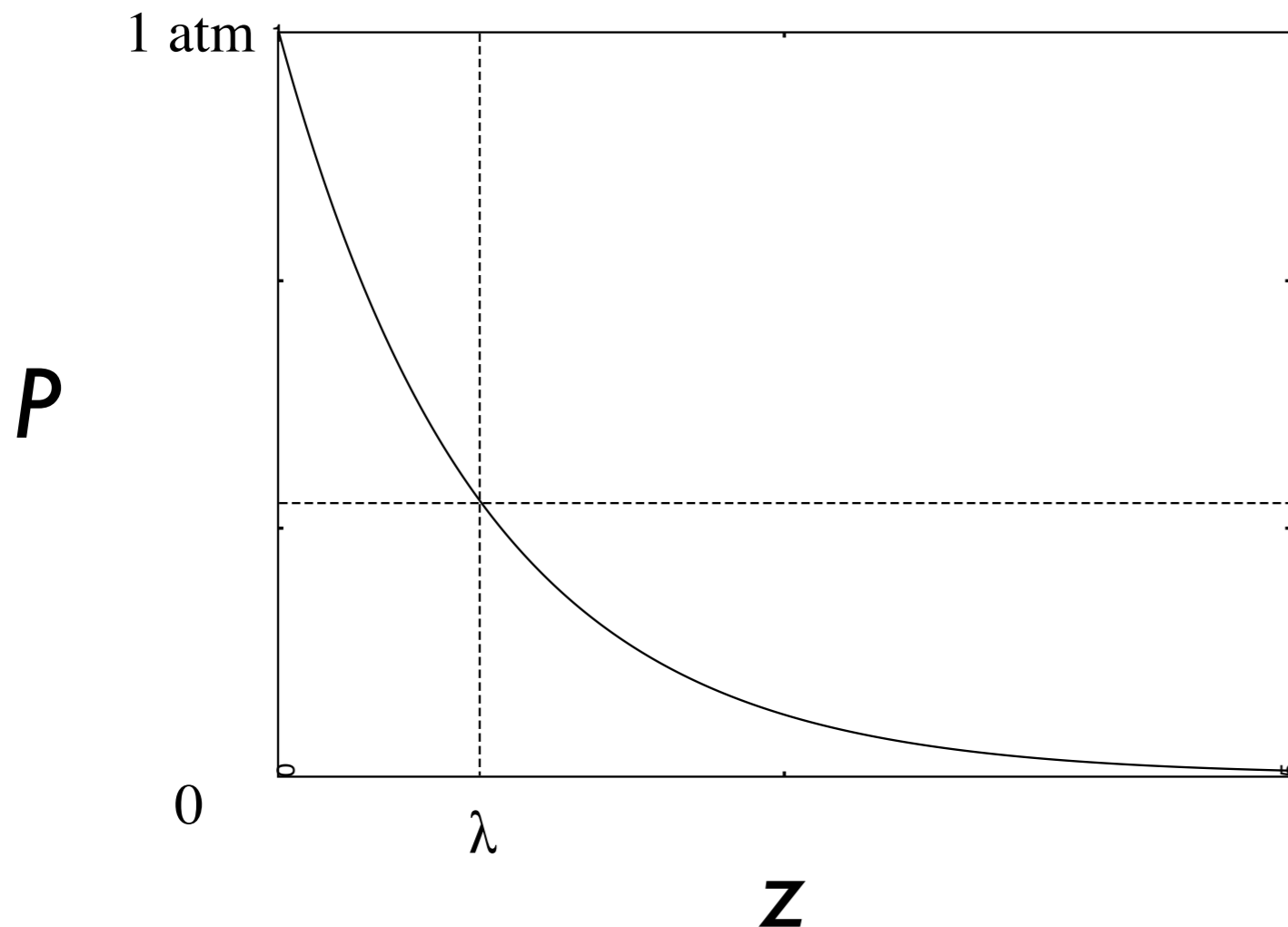
③ weight of slab ($\rho = \text{density}$)

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

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

$\lambda = k_B T / mg = \text{scale length}$

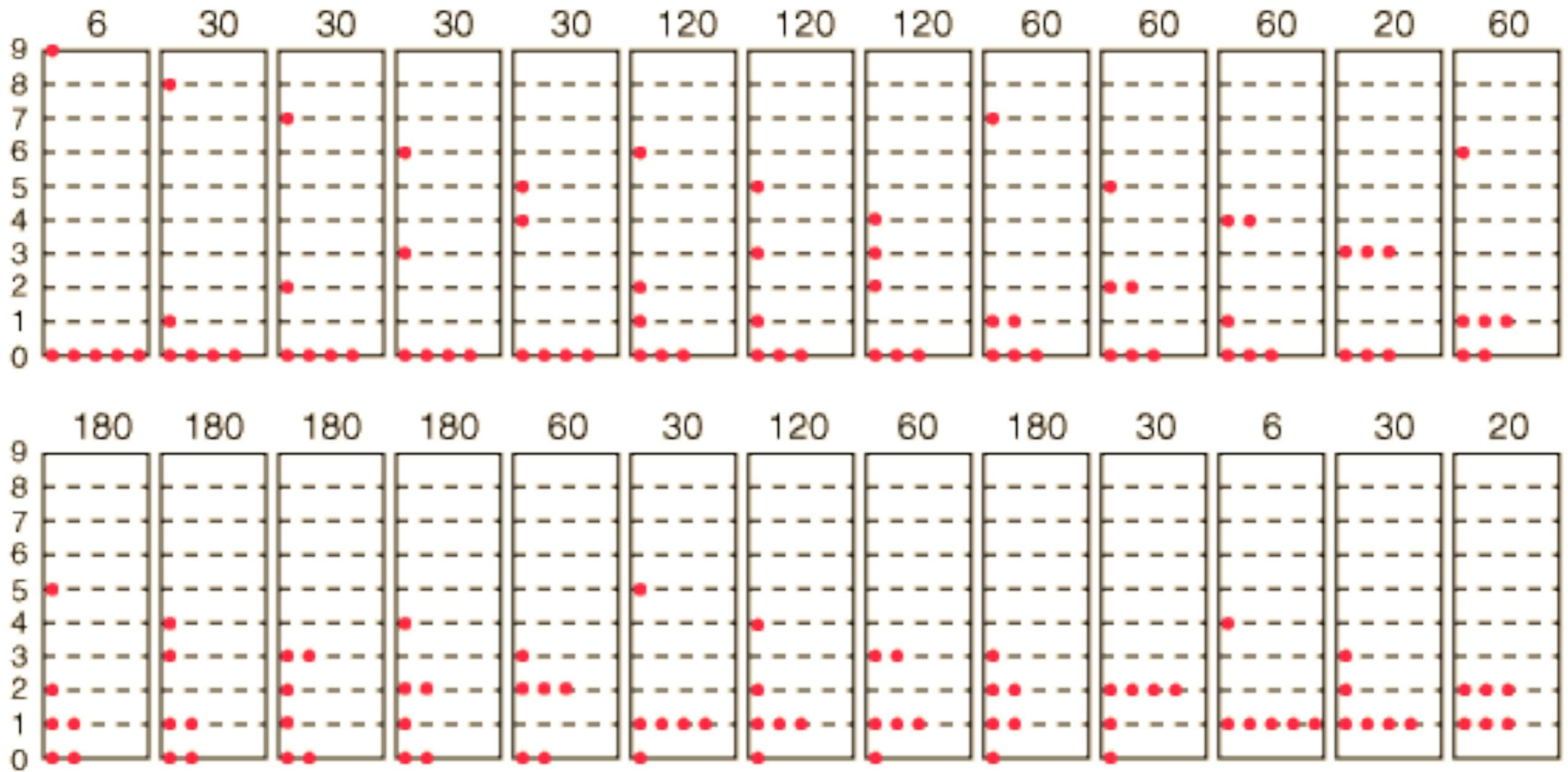
also $P = nk_B T = P_0 e^{-z/\lambda}$



$\lambda \approx 8.5 \text{ km}$, 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.



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

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

Lecture 6

- Gas molecules constantly colliding, mean free path, $\lambda = 1/(\sqrt{2}n\pi d^2)$

- 1D Maxwellian distribution function

$$f(v_x) dv_x = A \exp\left(-\frac{1}{2}mv_x^2/k_B T\right) dv_x$$

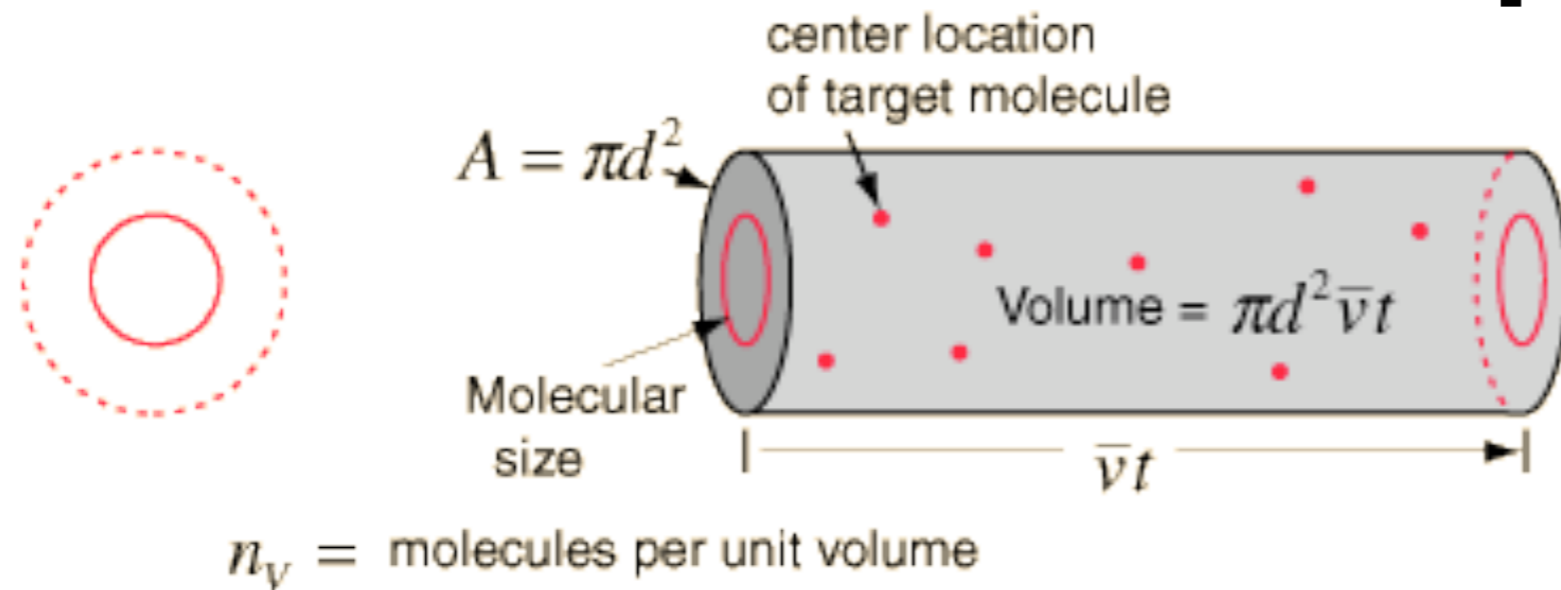
- Maxwell-Boltzmann speed distribution

$$f(v) dv = A^3 \exp(-\alpha v^2) 4\pi v^2 dv$$

- Most probable speed, $v_{mp} = (2k_B T/m)^{\frac{1}{2}}$

- $\langle v \rangle = \int_0^\infty v f(v) dv = (8k_B T/\pi m)^{\frac{1}{2}}$

Mean-free path



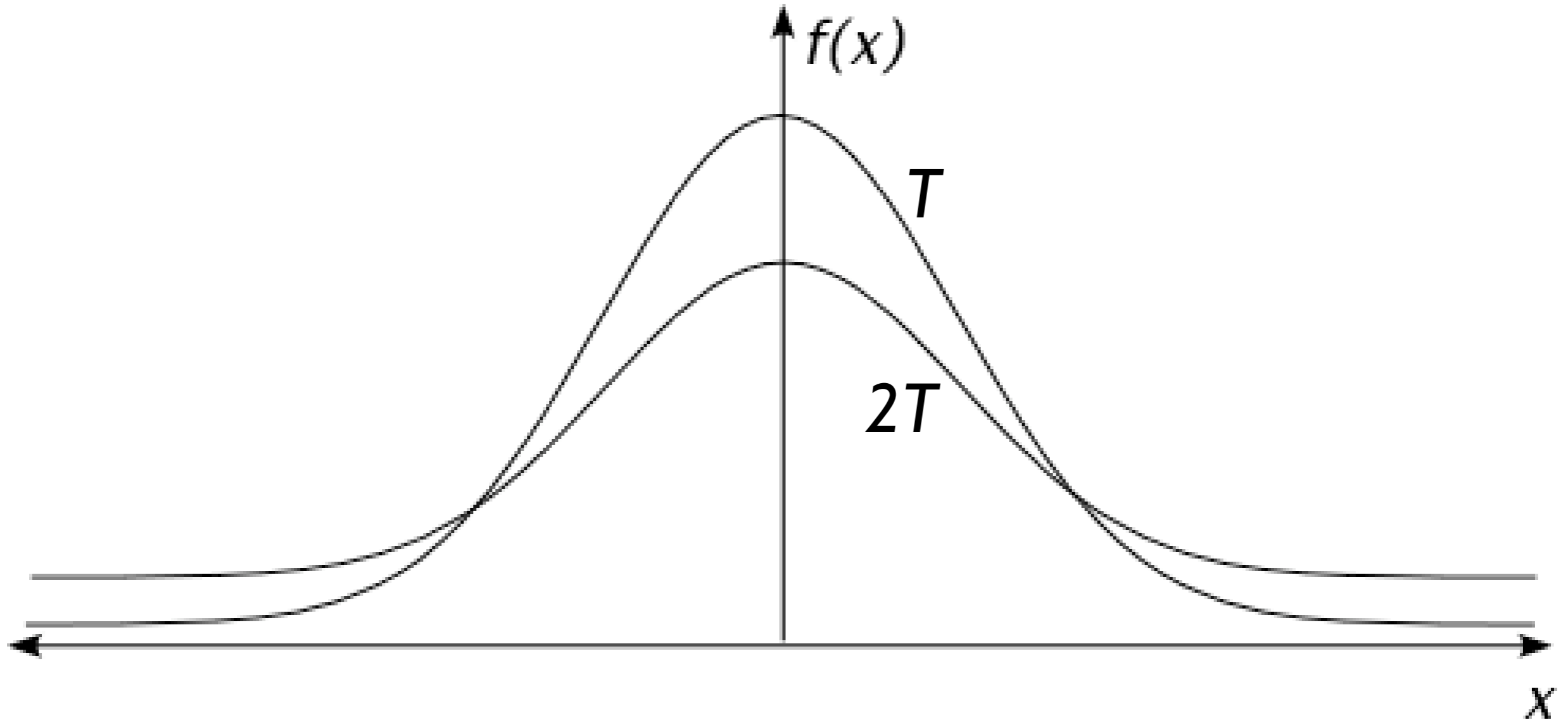
In time t , volume swept out by a particle with the mean velocity \bar{v} is,

$$V = \pi d^2 \bar{v} t$$

and no. of particles in this volume (which thus equals number of collisions) is,

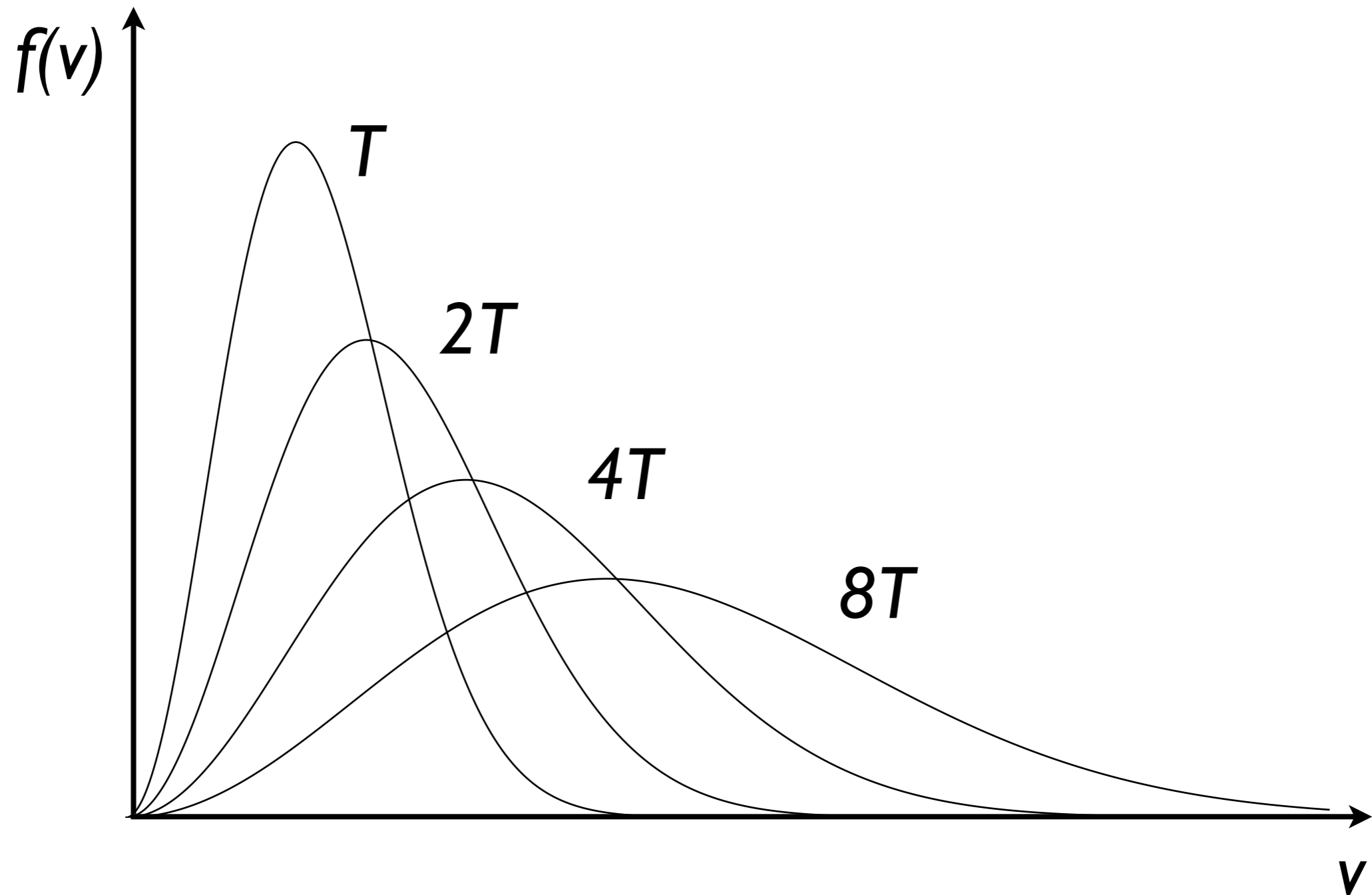
$$N_{coll} = n \pi d^2 \bar{v} t$$

1 dimensional Maxwellian



Most probable $v_x = 0$

Most probable speed, $v_{mp} = (2k_B T/m)^{\frac{1}{2}}$



NB particles with very low speeds v unfavoured due to reduction in **density of states** at small v

Lecture 7

- Mean square velocity,

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = (3k_B T/m)$$

- Mean-kinetic energy of particle

$$\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$$

- Kinetic energy due to single degree of freedom

$$\langle \frac{1}{2} m v_x^2 \rangle = \frac{1}{2} k_B T$$

- Implies each degree of freedom contributes $\frac{1}{2} k_B T$

- *Equipartition theorem* : $U = \frac{1}{2} n d N k_B T$

- *For diatomic gases, also 2 rotation and 2 vibrational degrees of freedom, but QM effects mean at room temp, vibrational degrees are “frozen out”*

Lecture 8

- * Types of bonding, ionic, covalent, metal & Van der Waals

- * For VW potential is given by,

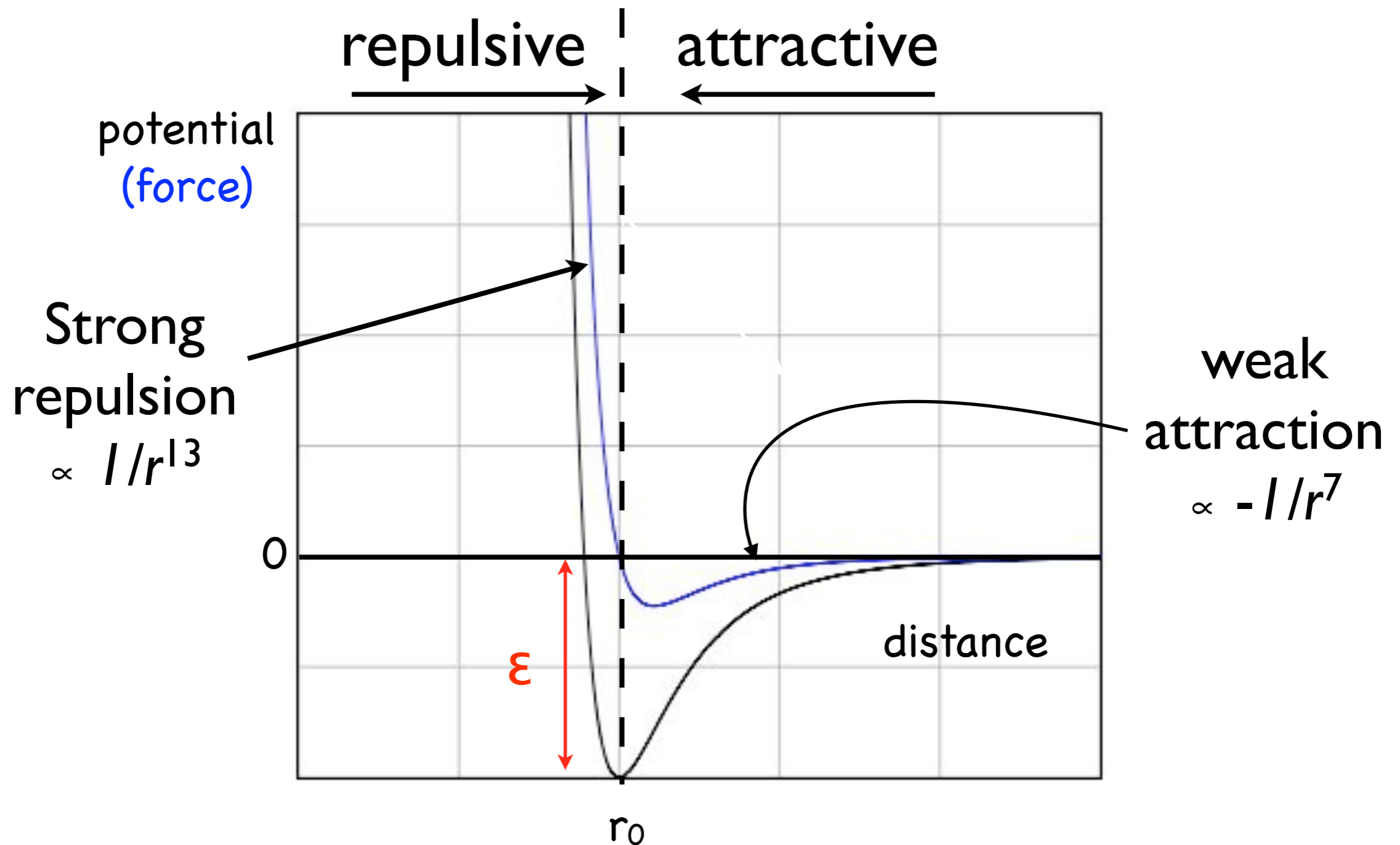
$$U = \epsilon \left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6$$

- * Atoms in a lattice vibrate, vibrations are particle like (phonons) and can carry heat. Frequency given by,

$$\omega_E = \left(\frac{144\epsilon}{mr_0^2} \right)^{1/2}$$

- * Solids expand with increasing T , $\Delta L = L_0 \alpha T$
- * Molar heat capacity of solid given by $C_{vm} = 3R$ at room temperatures, but phonons frozen out at low T

Lennard-Jones potential: $U = \frac{A}{r^{12}} - \frac{B}{r^6}$



rewrite in terms of r_0 and ϵ : $U = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]$

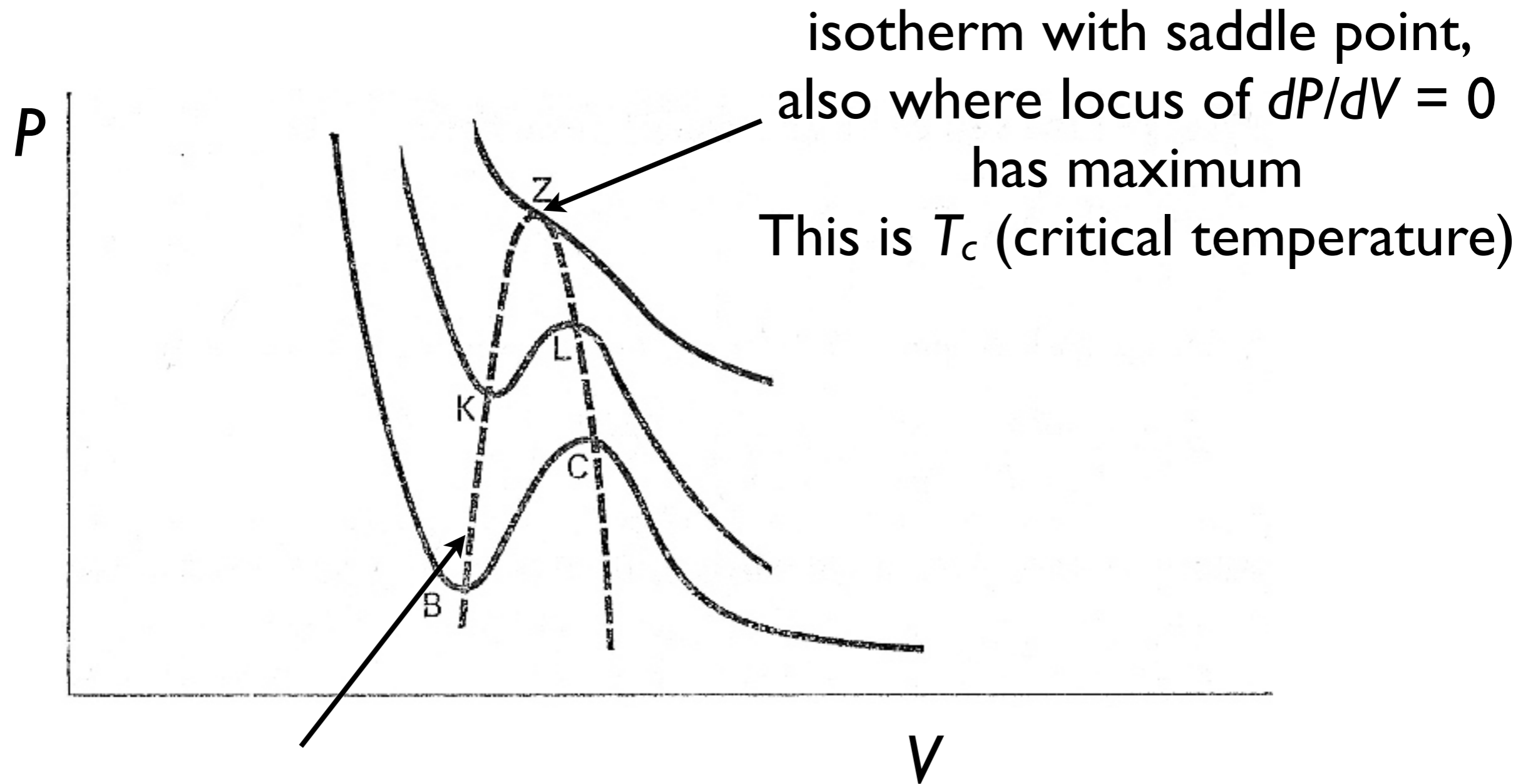
Lecture 9

- Van der Waal's equation for real gas:

$$(P + a(N^2/V^2))(V - Nb) = Nk_B T$$

- Effective volume of particles $b \approx 4V_m$
(V_m = molecular volume)
- Isotherms cubic curves on PV diagram
- Above T_c (critical temperature) no turning points -
gas and liquid phases indistinguishable
- Internal energy for VW gas, $U = (3/2)Nk_B T - aN^2/V$
- Joule-Kelvin process, $(3/2)Nk_B T - aN^2/V =$
constant, basis of gas liquification.

van der Waal isotherms



locus of points for
which $dP/dV = 0$

Lecture 10

- Archimedes Principle $\rho g V_{disp} = \text{buoyancy}$

- Continuity $\mathbf{u}_1 \cdot \mathbf{A}_1 = \mathbf{u}_2 \cdot \mathbf{A}_2$

- Bernoulli's equation

$$P_1 + \frac{1}{2}\rho u_1^2 + \rho h_1 g = P_2 + \frac{1}{2}\rho u_2^2 + \rho h_2 g$$

- Fluid equation of motion -Navier-Stokes Eqn

$$\rho \left(\frac{\partial u}{\partial t} + u \cdot \nabla u \right) = -\nabla P + \rho \eta \nabla^2 u$$

- Turbulence arises at high Reynolds Number

$$Re = \frac{v_s L}{\eta}$$

Lecture 11

- Bose-Einstein fluids: ultracold state of matter; exhibit superfluidity, infinite heat conduction, quantum effect

- Degeneracy for $T_c \lesssim \frac{h^2}{3mk_B} n^{2/3}$

- ✱ Plasmas: superhot state of matter; fluid like but with strong interparticle force; exhibit collective effects:

- ✱ Debye shielding

- ✱ plasma waves.

$$\lambda_d = \left(\frac{\epsilon_0 k_B T}{ne^2} \right)^{1/2}$$
$$\omega_p = \left(\frac{ne^2}{\epsilon_0 m} \right)^{1/2}$$