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Thermodynamics and Statistical Mechanics

- Equilibrium thermodynamics
- Phase transitions and phase equilibria
- Basic assumptions of kinetic theory

Thermodynamics V
Kinetic Theory of Gases I

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ENTROPY MAXIMUM

When 2 bodies with T_1 and T_2 are brought in thermal contact

heat flows from hot to cold body so that temperatures equilibrate

This is ☛ Second Law of thermodynamics that follows from experiment

Total entropy $\Delta S = S_1 + S_2$ in process of equilibration increases

When equilibrium is reached ΔS should attain its maximal value

Investigating behavior of total entropy near its maximum

is subject of first part of this class

HEAT EXCHANGE

Consider first simplest case in which two bodies do not exchange mass and keep their volumes unchanged

Transferred heat is the only source of the energy change

$$dU_1 = \delta Q_1 \quad \text{and} \quad dU_2 = \delta Q_2$$

Since system of two bodies is isolated from rest of the world

$$\delta Q_1 + \delta Q_2 = 0 \quad \text{and} \quad dU_1 + dU_2 = 0$$

Corresponding changes of S up to second order in transferred energy

$$dS_1 = \left(\frac{\partial S_1}{\partial U_1}\right)_V dU_1 + \frac{1}{2}\left(\frac{\partial^2 S_1}{\partial U_1^2}\right)_V (dU_1)^2 \qquad \textbf{(157)}$$

similar expression for dS_2

For derivatives ☛

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V} \qquad \textbf{(158)}$$

Eliminating $dU_2 = -dU_1$ ☛

$$dS = dS_1 + dS_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 - \frac{1}{2}\left(\frac{1}{T_1^2 C_{V_1}} + \frac{1}{T_2^2 C_{V_2}}\right)(dU_1)^2 \qquad \textbf{(159)}$$

THERMODYNAMIC STABILITY

Extremum of S corresponds to $T_1 = T_2$ ☛ thermal equilibrium

Quadratic term in (159) shows that this extremum is a maximum

provided heat capacities are positive ☛ $C_V > 0$ (160)

(160) is condition of thermodynamic stability

State with $C_V < 0$ would be unstable ☛ heat flow from hot to cold body would lead to increase of $T_2 - T_1$ instead of equilibration

For $C_V < 0$ ☛ initial state with $T_1 = T_2$
would be unstable with respect to transfer of a small amount of energy
Small fluctuation would lead to avalanche-like further transfer of energy
in same direction since temperature on receiving side would decrease

$C_P > C_V$ ☛ C_P is also positive

MORE ON THERMODYNAMIC STABILITY

(160) complements condition **(9)** of mechanical stability

☟ ☟

$C_V > 0$ $\kappa_T > 0$

At equilibrium ☛ $T_1 = T_2 = T$ **(159)** becomes

$$dS = -\frac{1}{2T^2}\left(\frac{1}{C_{V_1}} + \frac{1}{C_{V_2}}\right)(dU_1)^2 \qquad \textbf{(161)}$$

If 2nd body is much larger than 1st one ☛ it can be considered as bath

$C_{V_2} \gg C_{V_1}$ and second fraction in **(161)** can be neglected

Using $dU_1 = C_{V_1} dT_1$ and dropping index for bathed system

$$dS = -\frac{C_V}{2T^2}(dT)^2 \qquad \textbf{(162)}$$

(162) gives entropy decrease caused by deviation of system's temperature by a small amount dT from bath temperature T

GENERAL CASE OF THERMODYNAMIC EQUILIBRIUM

Consider 2 systems in contact that can exchange energy, volume, mass

Exchanging volume means there is a movable membrane between 2 bodies so that bodies can do work on each other

Exchanging mass means that this membrane is penetrable by particles

Resolving (139) for dS we obtains to first order

$$dS_1 = \frac{1}{T_1} dU_1 + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \tag{163}$$

similar expression for dS_2

We could include second-order terms like those in (157) to find extended conditions of stability

Constraints

$$dU_1 + dU_2 = 0 \qquad dV_1 + dV_2 = 0 \qquad dN_1 + dN_2 = 0 \tag{164}$$

lead to total entropy change

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 \tag{165}$$

AL QUE QUIERE CELESTE...QUE LE CUESTE

Requiring that $dS \geq 0$ in **(165)** has three consequences:

(i) Energy flows from hotter body to colder body

(ii) Body with a higher pressure expands at the expense of body with lower pressure

(iii) Particles diffuse from body with a higher chemical potential to that with the lower μ

The thermodynamic equilibrium is characterized by

$$T_1 = T_2 \qquad \text{(thermal equilibrium)} \tag{166}$$

$$P_1 = P_2 \qquad \text{(mechanical equilibrium)} \tag{167}$$

$$\mu_1 = \mu_2 \qquad \text{(diffusive equilibrium)} \tag{168}$$

COLLATERAL EFFECT

Total S must have maximum with respect to all 3 variables at equilibrium

Investigating this requires adding second-order terms to (165)

Analysis is somewhat cumbersome but the results can be figured out

Firstly ☛ condition of thermal stability (160) should be satisfied

Secondly ☛ condition of mechanical stability (9) should be satisfied

Thirdly ☛ diffusive stability condition should exist to the effect that adding particles to the system at constant volume and internal energy should increase its chemical potential

FIRST ORDER PHASE TRANSITIONS

Results for diffusive equilibrium can be applied to phase transitions

If different phases of same substance are in contact
particles can migrate from one phase to other across phase boundary

Phase with a higher chemical potential recedes
and phase with a lower chemical potential grows

Phase boundary moves across sample
until receding phase disappears completely

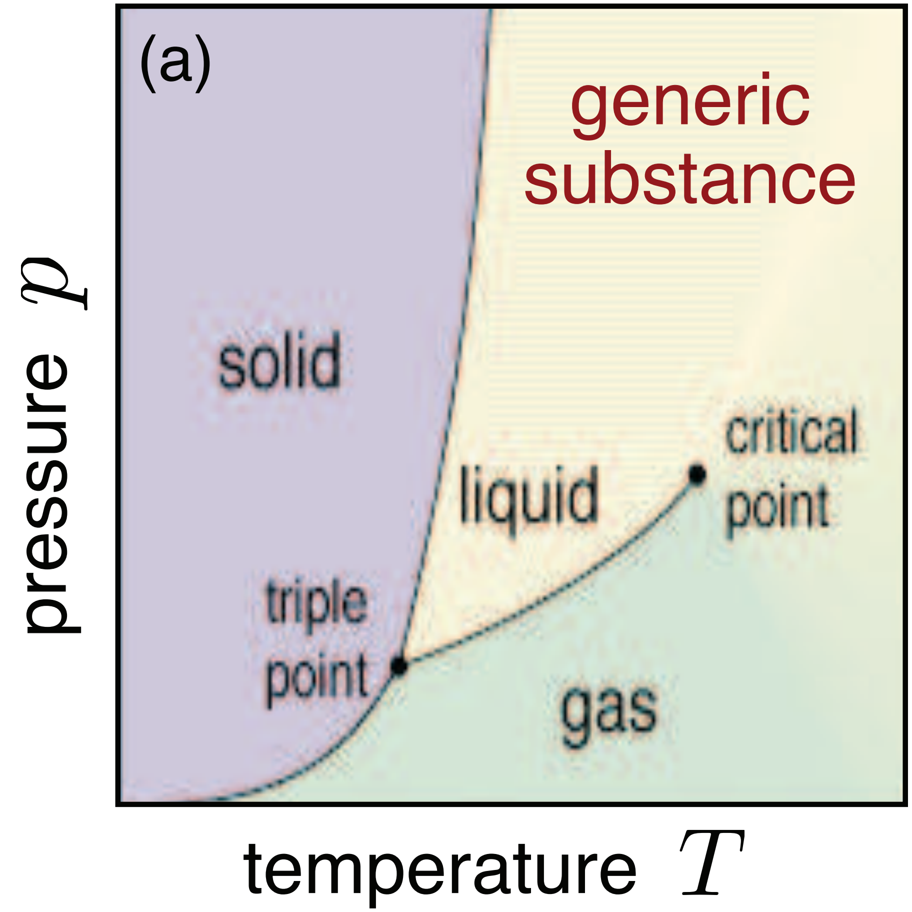
1st-oder phase transitions between phases occur at $\mu_i(P,T) = \mu_j(P,T)$
that describes lines in P,T diagram

Phases are labeled by discrete variables i

1 for solid 2 for liquid and 3 for a gas

THERMODYNAMIC PHASE DIAGRAMS

Typical thermodynamic phase diagram of $P - V - T$ system



triple point ☛ 3 phase coexistence

Solid lines delineate boundaries between distinct thermodynamic phases

Along these lines we have coexistence of 2 phases

and thermodynamic potentials are singular

P-V-T SURFACES

Equation of state for single component system may be written as

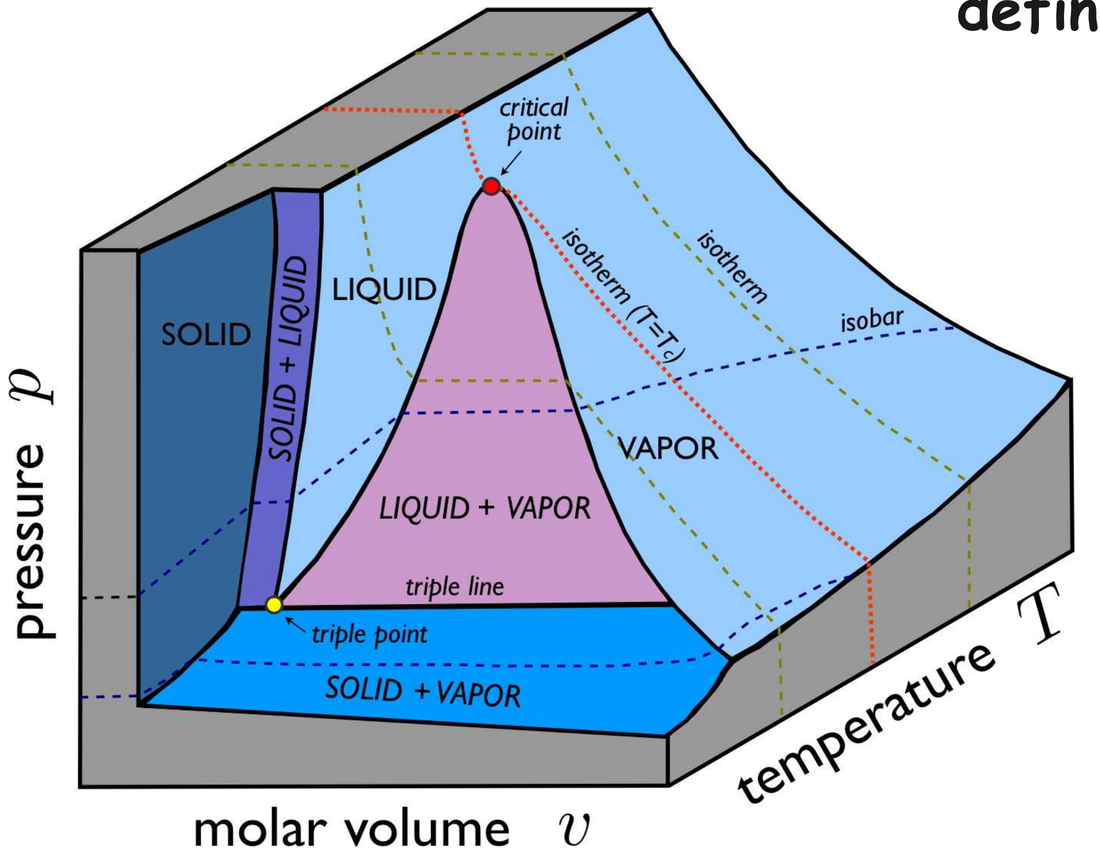
$$f(P, V, T) = 0$$

This may in principle be inverted to yield

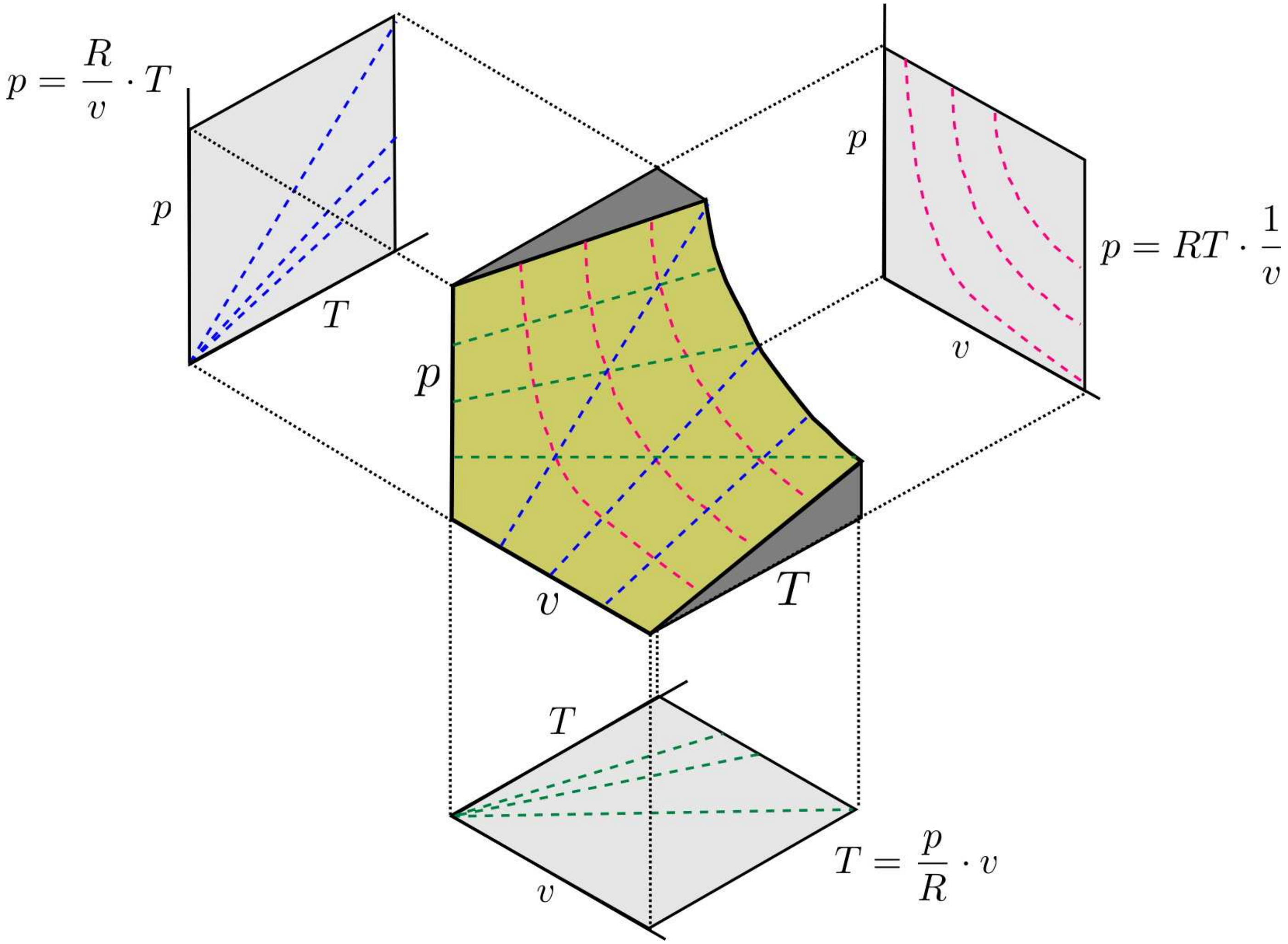
$$P = P(V, T) \qquad V = V(T, P) \qquad T = T(P, V)$$

Single constraint $f(P, V, T)$ on 3 state variables

defines surface in $\{P, V, T\}$ space



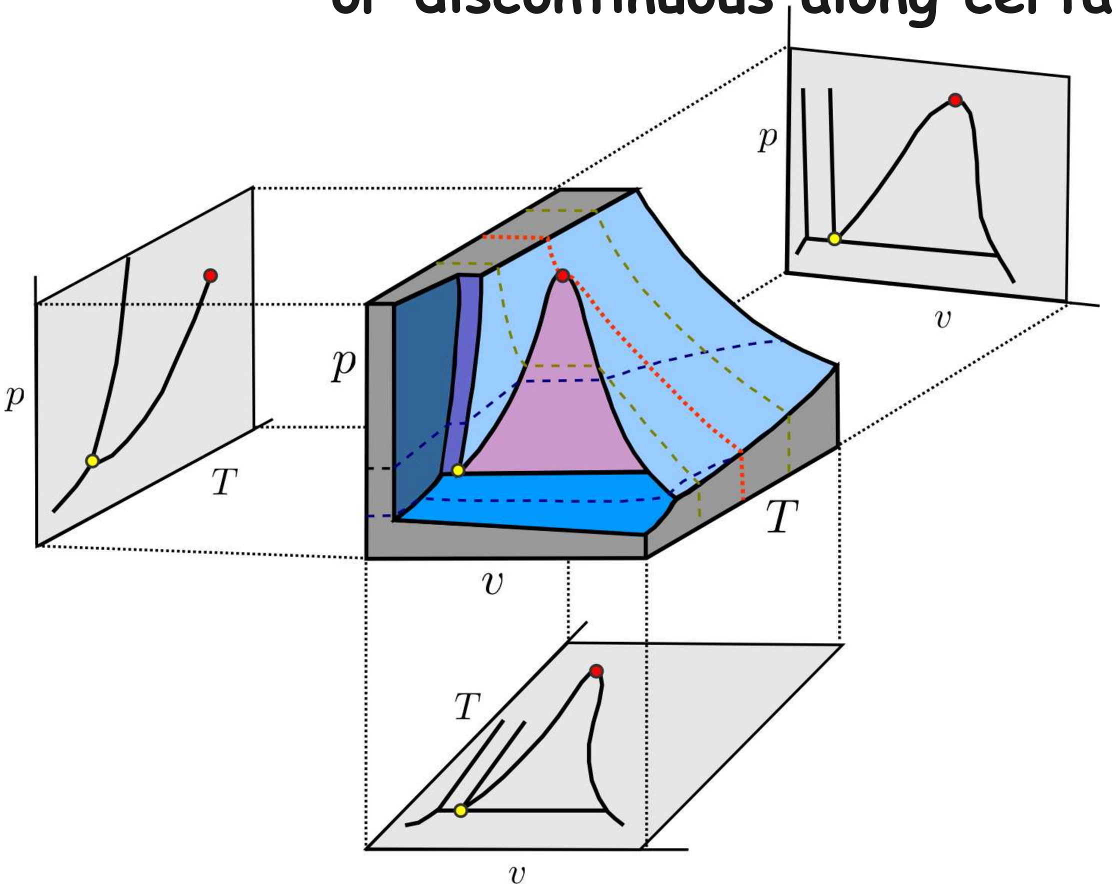
P-V-T SURFACE OF IDEAL GAS



Surface $P(v,T) = RT/v$ corresponding to ideal gas equation of state and its projections onto $(P,T), (P,v), (T,v)$ planes

P-V-T SURFACE OF REAL GASES

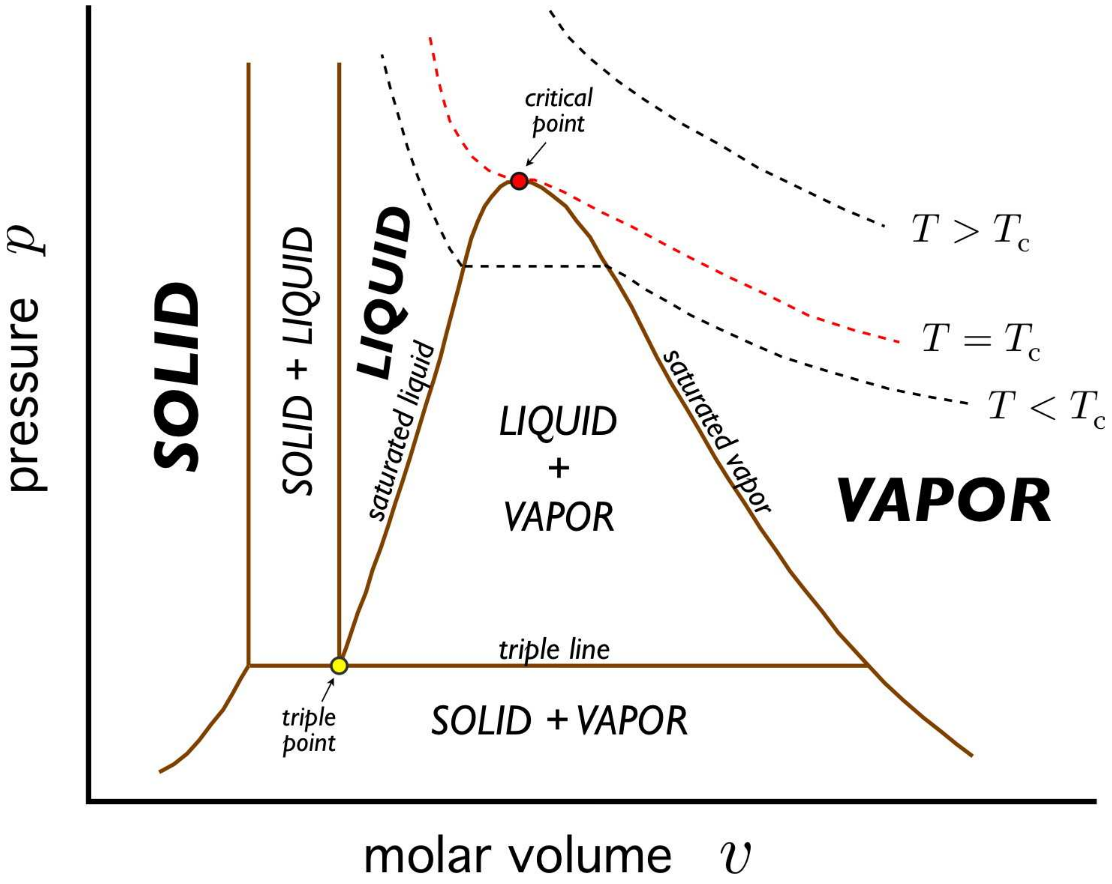
Real $P - v - T$ surfaces are much richer than that for ideal gas because real systems undergo phase transitions in which thermodynamic properties are singular or discontinuous along certain curves on $P - v - T$ surface



High temperature isotherms resemble those of ideal gas but as one cools below T_c isotherms become singular

@ $T = T_c$ isotherm $P = P(v, T_c)$ becomes perfectly horizontal @ $v = v_c$ which is critical molar volume

PROJECTION OF THE P-V-T SURFACE

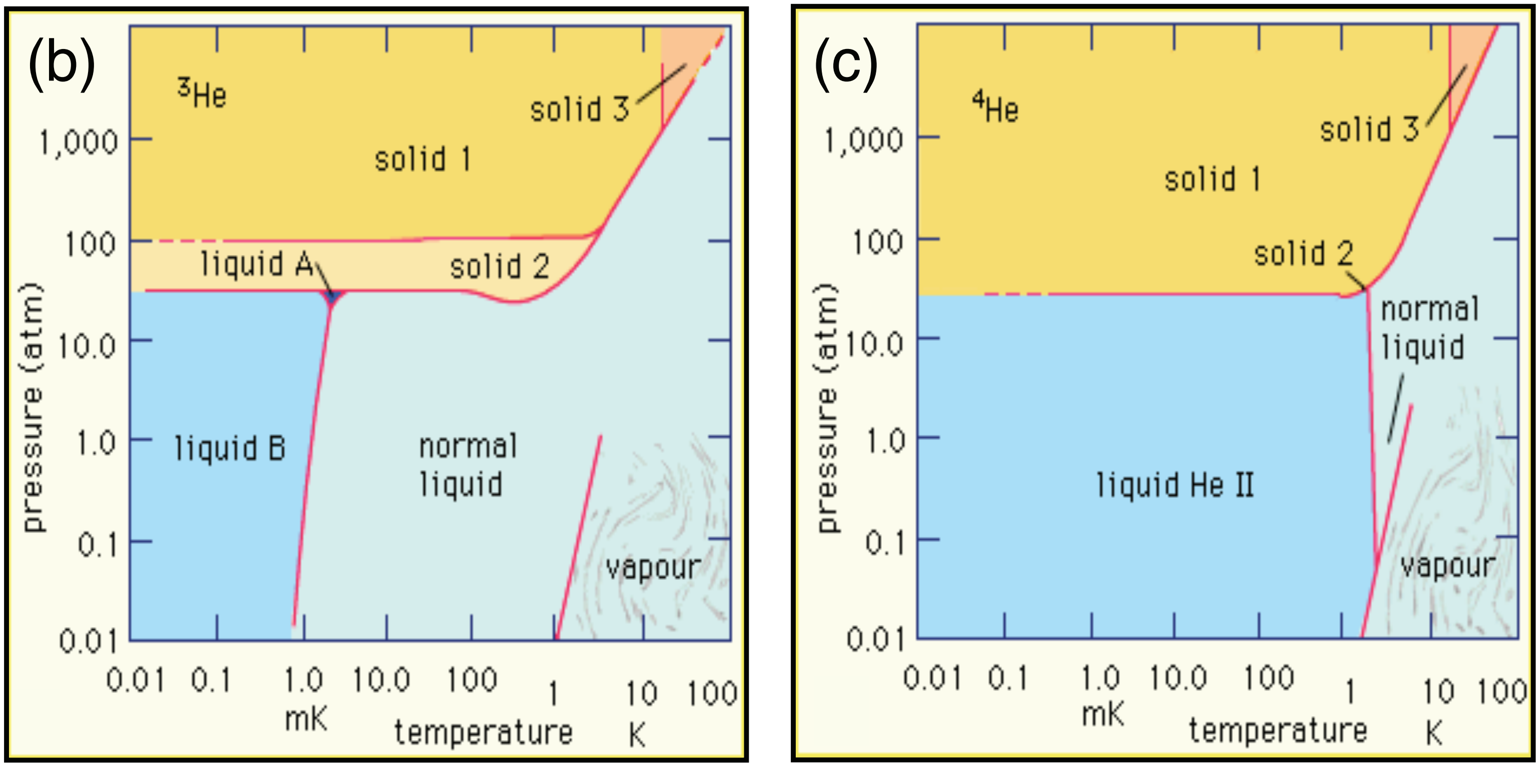


$$\lim_{T\to T_C} \kappa_T = \lim_{T\to T_c} -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \infty$$

Below T_c isotherms have a flat portion corresponding to a two-phase region where liquid and vapor coexist

WHAT A DIFFERENCE A NEUTRON MAKES!

Phase diagrams for ^{3}He and ^{4}He



^{3}He ^{4}He

Only difference between these two atoms is a neutron:

(2p + 1n + 2e) in ^{3}He versus (2p + 2n + 2e) in ^{4}He

As we shall learn when we study mechanical statistics
this extra neutron makes all the difference
because ^{3}He is a fermion while ^{4}He is a boson

SECOND ORDER PHASE TRANSITIONS

Phases are described by order parameter η
that is zero in one of phases and nonzero in other phase

Most of second-order transitions are controlled by temperature

High-temperature (symmetric) phase ☛ $\eta = 0$

For $T < T_c$ ☛ $\eta \propto (T_c - T)^\beta$ with $\beta > 0$

For chemical potential in form $\mu(\eta)$

there are boundaries between regions with different values of η
which are associated to different values of μ

Particles migrate from phase with higher μ to that with lower μ

spatial boundary between phases moves to reach equilibrium state

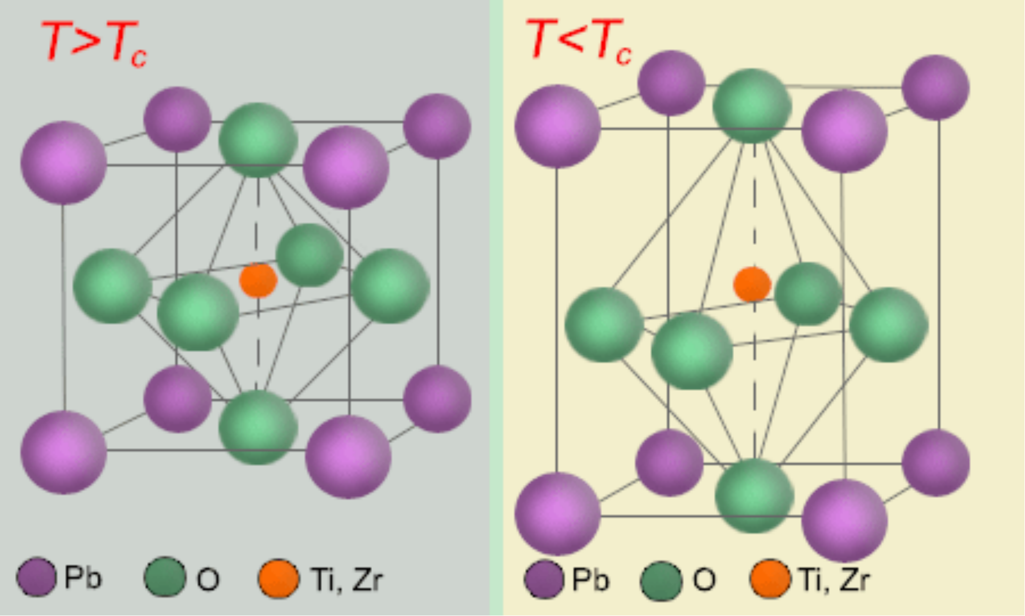
Since η can change continuously

it can adjust in uniform way without any phase boundaries
decreasing its chemical potential everywhere

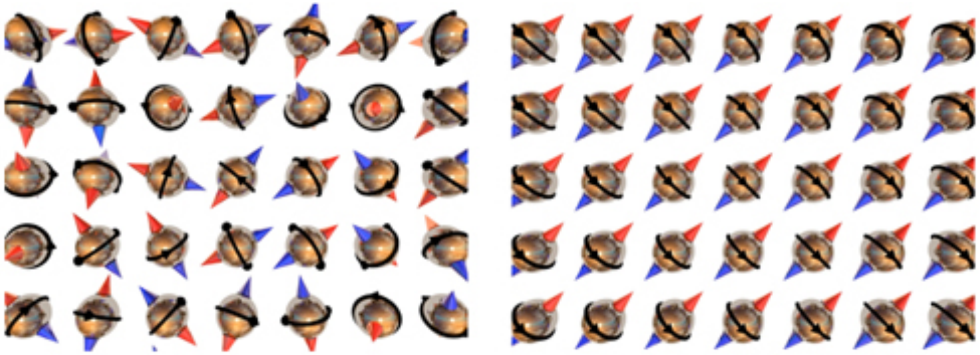
SMART MATERIALS

Tetragonal phase expands more rapidly in 2 directions than the 3rd one becomes cubic phase that expands uniformly in 3 directions as T is raised

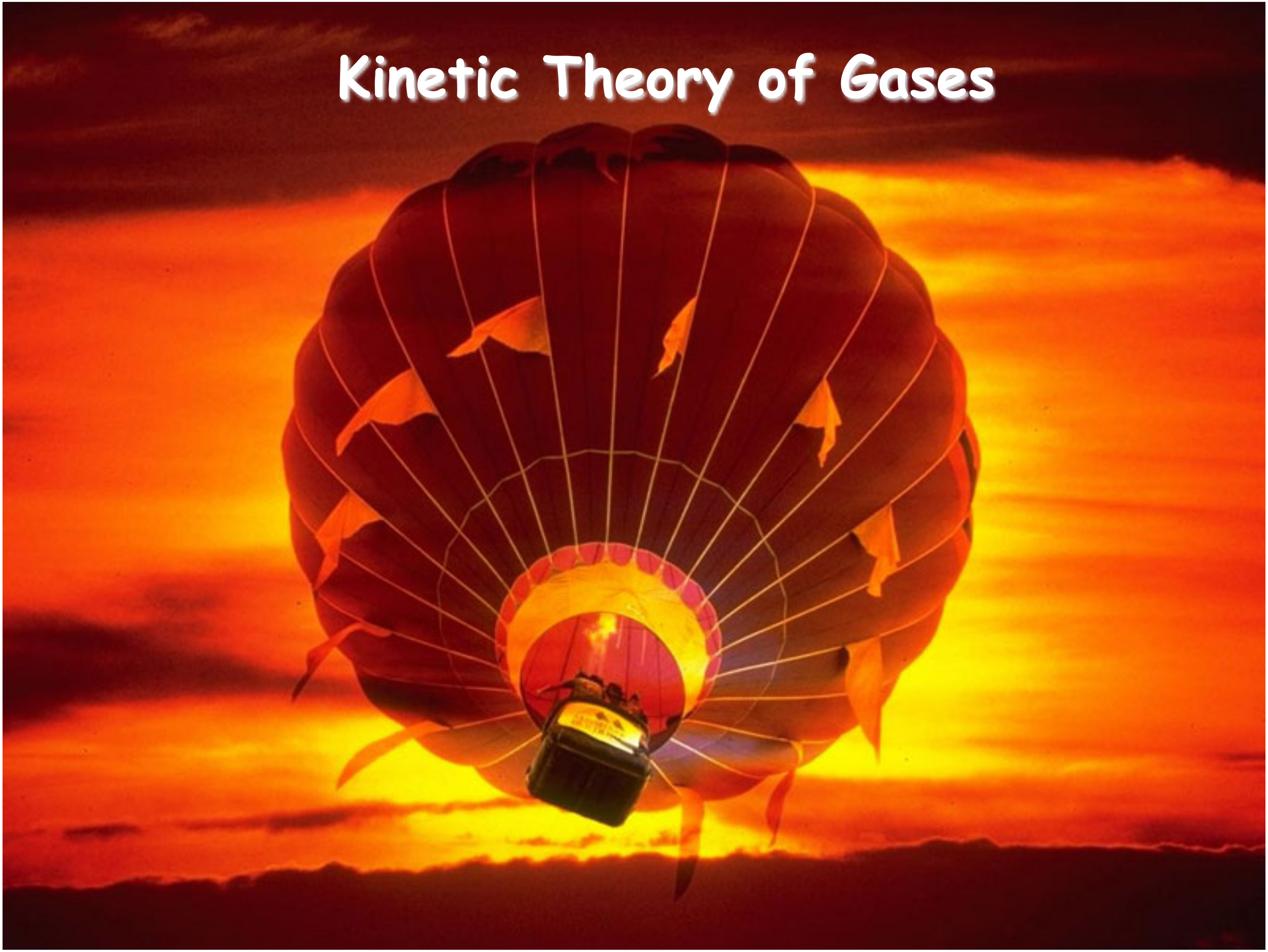
There is no rearrangement of atoms at transition temperature



Ferromagnetic ordering below the Curie point



Kinetic Theory of Gases



BASIC ASSUMPTIONS OF THE MOLECULAR THEORY

There are about 10^{19} molecules in $1\ \mathrm{cm}^3$ at normal conditions

Because of large number of particles
impacts of individual particles on walls merge into time-independent pressure

Characteristic distance between molecules largely exceeds molecular size
and typical radius of intermolecular forces

This assumption allows to consider gas as ideal
with internal energy dominated by kinetic energy of molecules

In describing equilibrium properties of ideal gas
collisions between molecules can be neglected

Molecules are uniformly distributed within container

Directions of velocities of molecules are also uniformly distributed

CHARACTERISTIC LENGTHS OF GAS

Concentration of molecules n is defined by

total number of molecules

$$n \equiv \frac{N}{V} \tag{1}$$

volume of container

Characteristic distance r_0 between molecules can be estimated as

$$r_0 = \frac{1}{n^{\frac{1}{3}}} \tag{2}$$

Let a be radius of molecule ☛ assumption (2) requires $a \ll r_0$

There are also long-range attractive forces between molecules

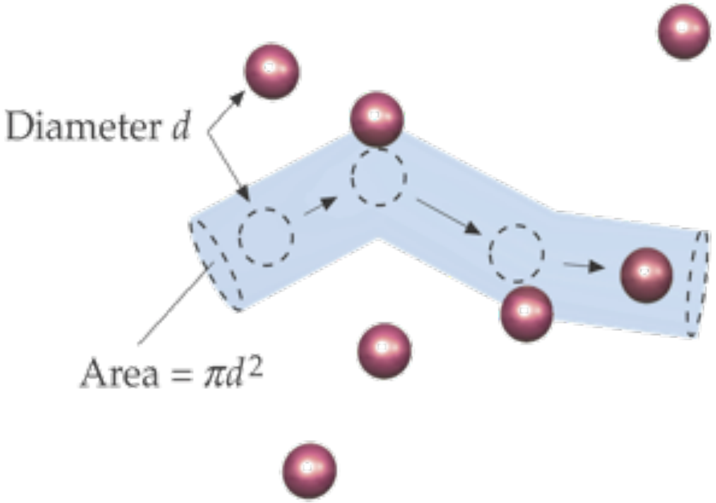
but they are weak and do not essentially deviate molecular trajectories

if temperature is high enough and gas is ideal

MEAN FREE PATH

mean free path ☛ typical distance l travel by molecules before colliding

Considering other molecules as non-moving ☛



molecule under consideration will hit (on average) other molecules

that are within cylinder of height l and cross-section $\sigma = \pi(2a)^2$

Volume σl of this cylinder ☛ volume per molecule $1/n$

$$l = \frac{1}{\sigma n} \sim \frac{1}{a^2 n} = \left(\frac{r_0}{a}\right)^2 r_0 \gg r_0 \gg a \qquad (3)$$

VELOCITY DISTRIBUTION FUNCTIONS

Distribution of molecules in space is practically uniform,

Distribution in space of velocities (v_x, v_y, v_z) is nontrivial

Introduce the distribution function $G\ (v_x, v_y, v_z)$ via

$$dN = NG(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z \qquad (4)$$

☟

number of molecules with velocities within elementary volume ☟

$$dv_x\, dv_y\, dv_z \equiv d^3v \equiv dv \quad (5)$$

around velocity vector specified by its components ☛ (v_x, v_y, v_z)

Integration over the whole velocity space gives total number of molecules N

$G\ (v_x, v_y, v_z)$ ☛ satisfies normalization condition ☟

$$1 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_x\, dv_y\, dv_z\, G(v_x, v_y, v_z) \qquad (6)$$

DISTRIBUTION FUNCTION OF MOLECULAR SPEEDS

Since directions of molecular velocities are distributed uniformly

$G\ (v_z, v_y, v_z)$ depends only on absolute value of the velocity ☛ the speed

$$v\ =\ \sqrt{v_z^2\ +\ v_y^2\ +\ v_z^2} \qquad (7)$$

Using expression for elementary volume in spherical coordinates

$$d^3v\ =\ dv\ \times vd\theta\ \times\ v\ \sin\,\theta d\varphi\ =\ v^2\,dv\ \sin\,\theta d\theta d\varphi \qquad (8)$$

(4) becomes ☛ $dN\ =\ N\,G\,(v)v^2\,dv d\Omega$ ☟ (9)

$$d\Omega\ \equiv\ \sin\ \theta d\theta d\varphi \qquad (10)$$

Using area of a sphere of unit radius

$$\int_{\rm sphere} d\Omega\ =\ \int_0^\pi\ d\theta\ \sin\ \theta\ \int_0^{2\pi}\ d\varphi\ =\ 2\pi\ \int_{-1}^1\ \underset{☟}{dx}\ =\ 4\pi \qquad (11)$$

$$(x \equiv\ \cos\ \theta)$$

number of molecules within spherical shell becomes

$$dN\ =\ NG(v)\,4\pi v^2 dv\ =\ N\,f(v)dv \qquad (12)$$

distribution function over molecular speeds ☛ $f(v)\ =\ 4\pi v^2G(v)$ (13)

normalization ☛ $1\ =\ \int_0^\infty\ dv\,f(v)$ (14)

AVERAGE, MEAN SQUARE AND RMS SPEEDS

(9) can be rewritten in terms of $f(v)$ as

$$dN = N\, f(v) dv\, \frac{d\Omega}{4\pi} \tag{15}$$

average speed

$$\bar{v} = \int_0^\infty dv\, v\, f(v) \tag{16}$$

mean square speed

$$\bar{v^2} = \int_0^\infty dv\, v^2\, f(v) \tag{17}$$

root mean square or **rms** speed

$$v_{\rm rms} = \sqrt{\bar{v^2}} \tag{18}$$