

Phase transitions and critical phenomena

S. V. G. Menon
Bhabha Atomic Research Centre

Phase transitions

Stability of phases is determined by

- Competition between Energy & Entropy

Order of phase transitions

- First order (or discontinuous)
- Second order (continuous)

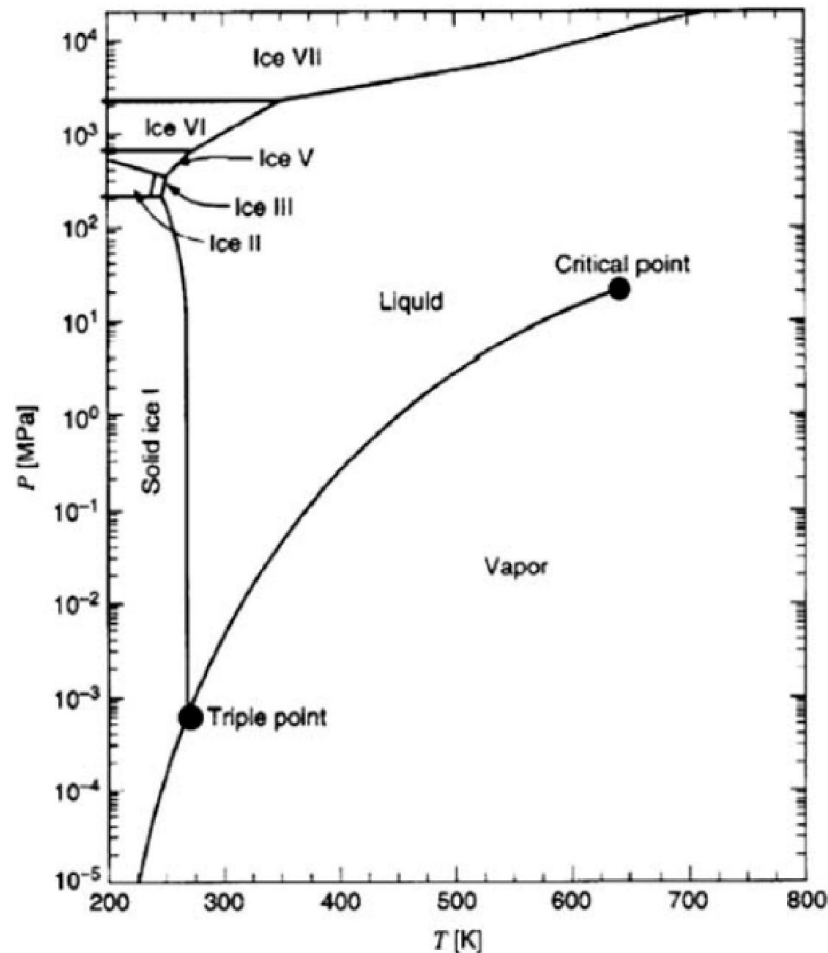
First order transitions

- First-order phase transitions are those that involve a latent heat.
- During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy.
- During this process, the temperature of the system will stay constant as heat is added: the system is in a "mixed-phase regime" in which some parts of the system have completed the transition and others have not.
- Familiar examples are the melting of ice or the boiling of water (the water does not instantly turn into water vapor, but forms a turbulence mixture of water and vapor bubbles).

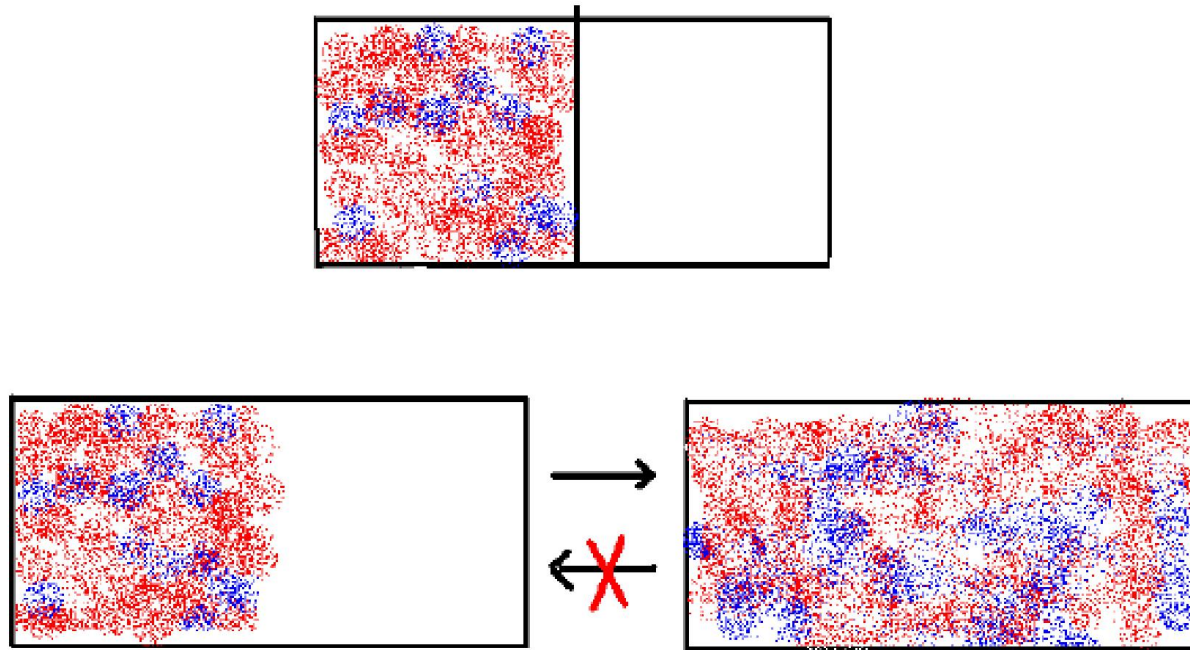
Second order transitions

- Second-order phase transitions are also called "continuous phase transitions".
- They are characterized by a divergent susceptibility, an infinite correlation length, and a power-law decay of correlations.
- Examples of second-order phase transitions are
 - ferromagnetic transition
 - liquid – vapor transition
 - superconductivity
 - super fluidity

Phase diagram of water

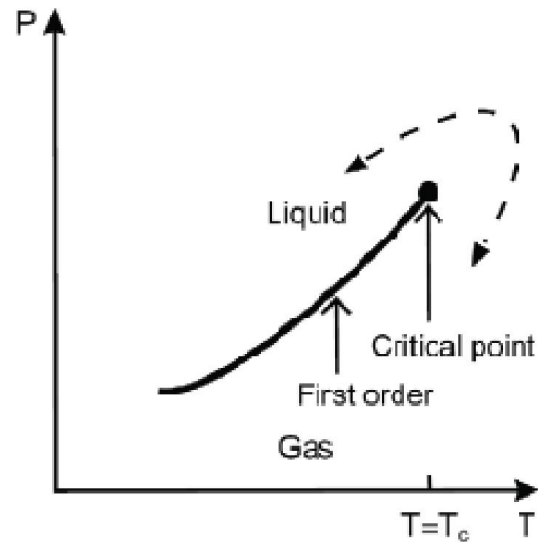
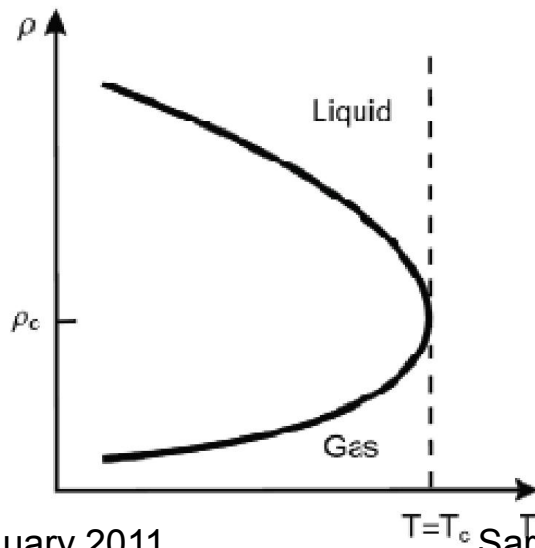
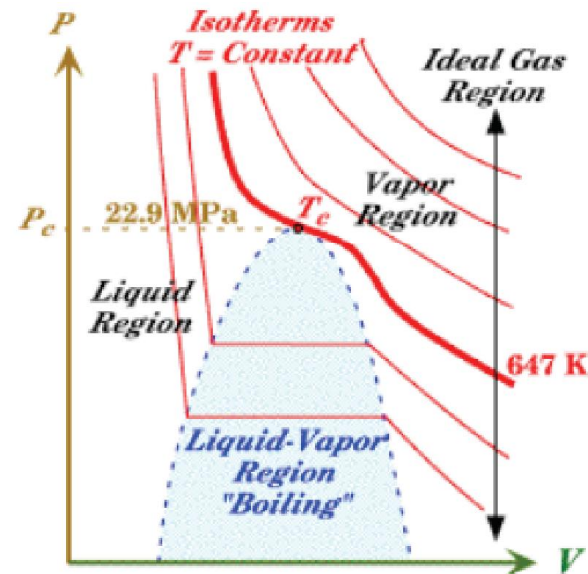


What is entropy



The probability of going from left to right is overwhelming, but that of going in the other way is practically zero

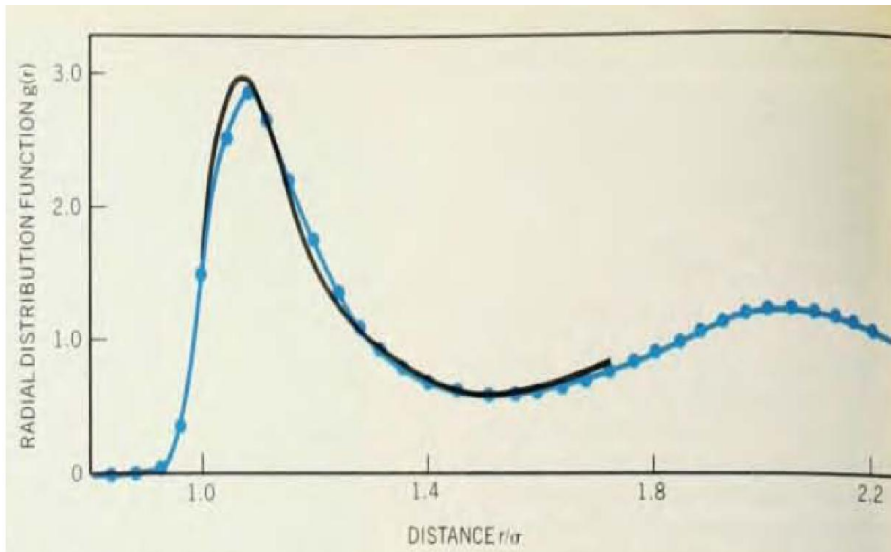
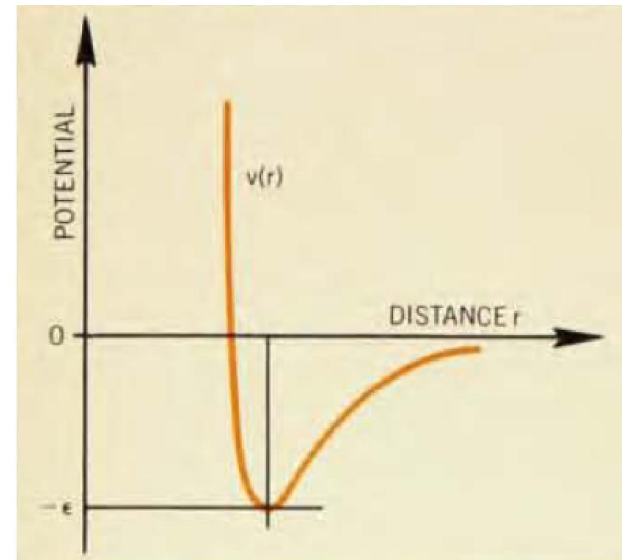
Phase diagram of fluids



H_2O

Simple model of fluid

- van der Waals equation
 - $P = RT / (V-b) - a / V^2$

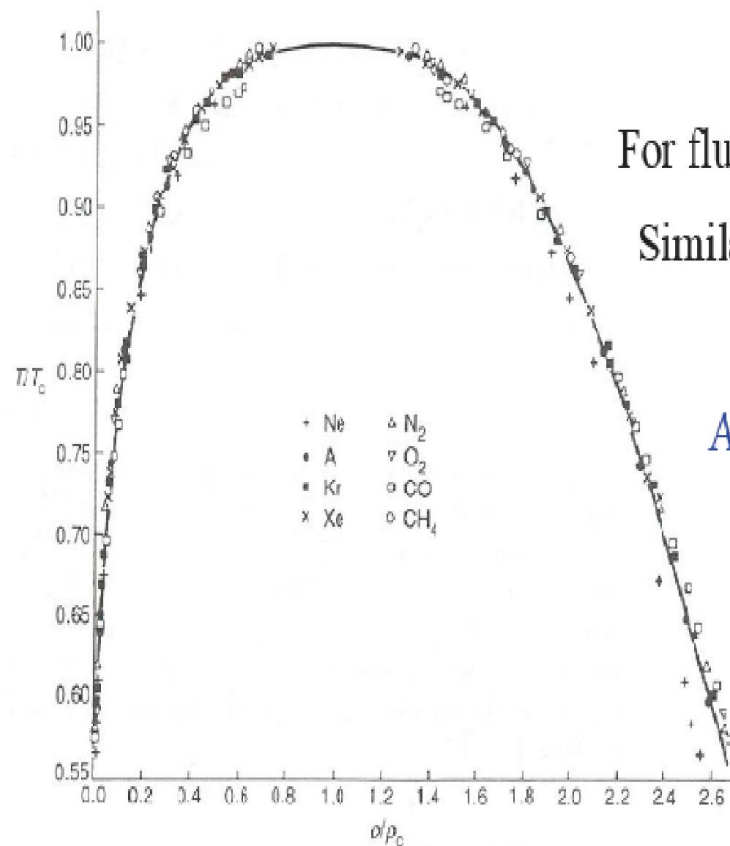


Lennard-Jones fluid
at critical point

Universal behavior in fluids

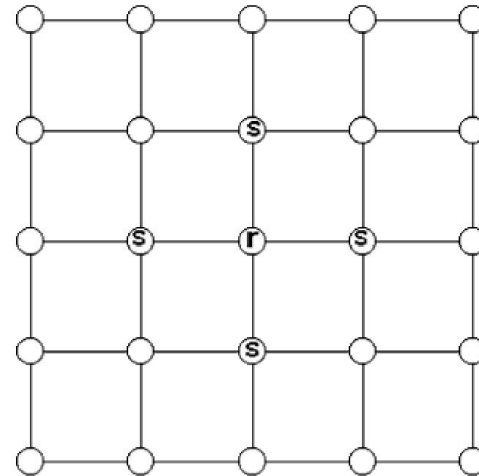
Phase diagram
in scaled
variables

Universal curve



Simple models

- Ising model
- Weiss theory



$$-H/T = K \sum_{nn} \sigma_r \sigma_s + h \sum_r \sigma_r$$

Gibbs Theory

Probability of occurrence of a configuration

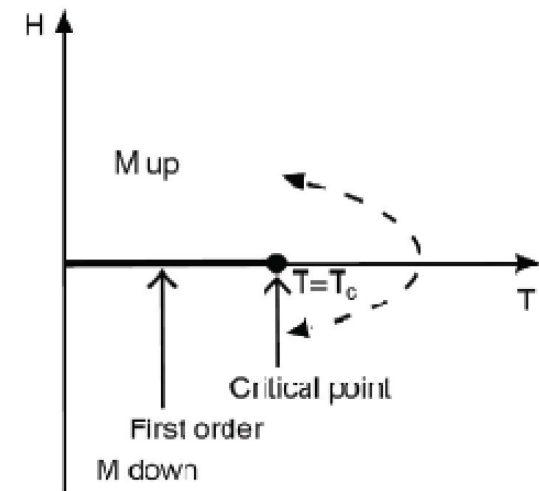
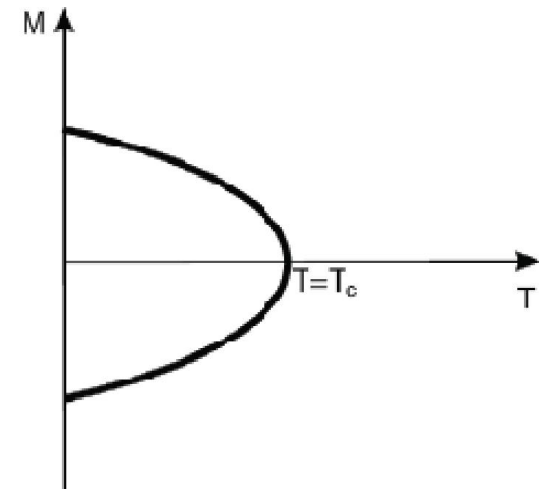
$$\rho(c) = e^{-H(c)/T} / Z,$$

Partition function and free energy

$$Z = e^{-F/T} = \sum_c e^{-H(c)/T}$$

Phase diagram of magnets

P. Curie, Ann. Chem. Phys. 5, 289 (1895).
P. Weiss, J. Phys. 6, 661 (1907). use very similar mean field theory arguments to derive properties of paramagnetic to ferromagnetic transition. This is followed by a host of mean field calculations mostly used to describe many different kinds of phase transitions, with many different kinds of order.



**Mean field
theory
predictions
not accurate
near T_c**

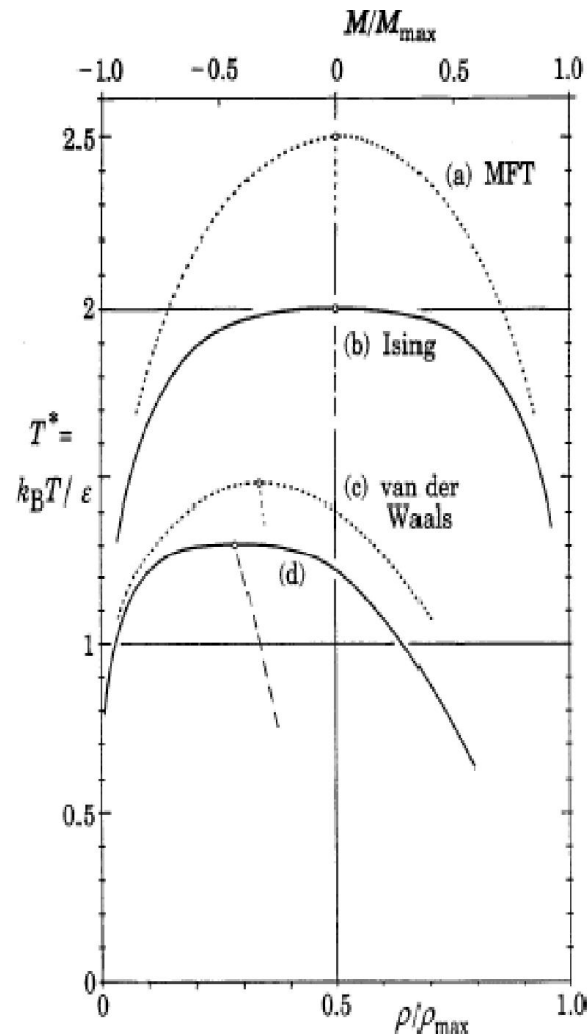
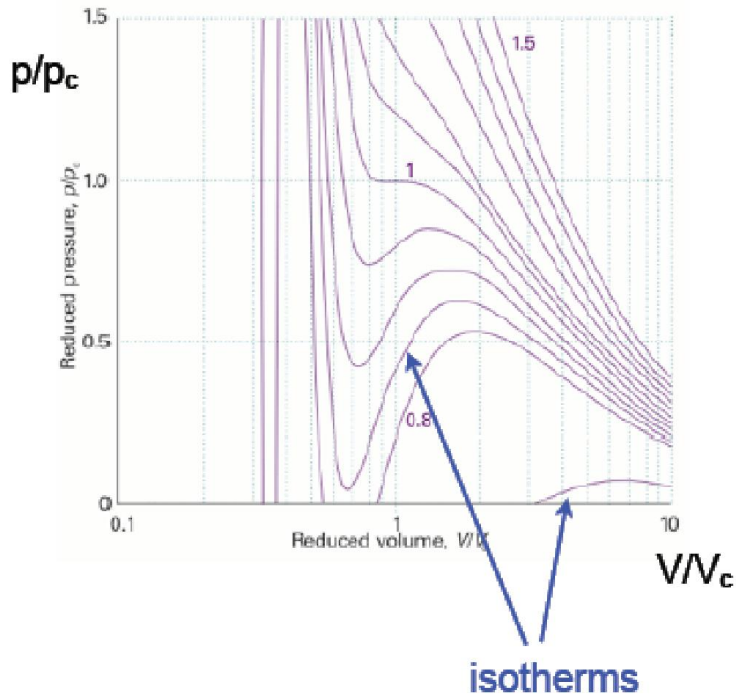
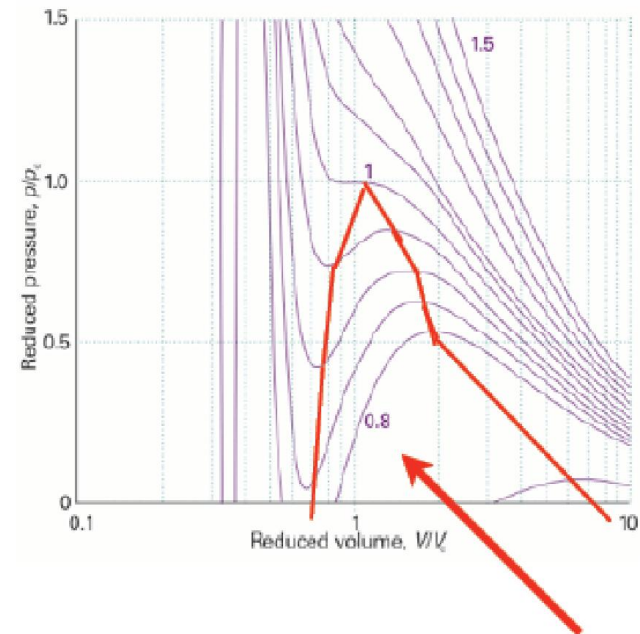


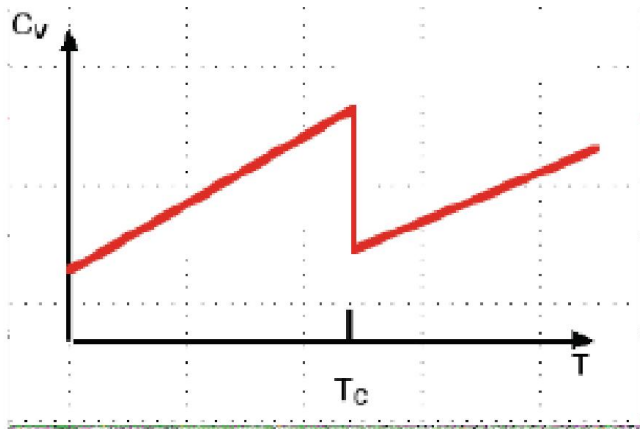
FIG. 1. Temperature vs. magnetization and density coexistence curves (temperature, T) and corresponding magnetization plots (magnetization vs. T). The solid curves, (b) and (d), represent (semiquantitatively) modern theory, while the dotted curves, (a) and (c), illustrate the corresponding predictions (mean-field theory and van der Waals approximation). The small open circles are located at the critical points, where the coexistence curves are parabolic through the origin. The critical temperature, T_c , and the critical density, ρ_c , are parameters particular to each system; they vary widely in magnitude.

Unphysical behavior

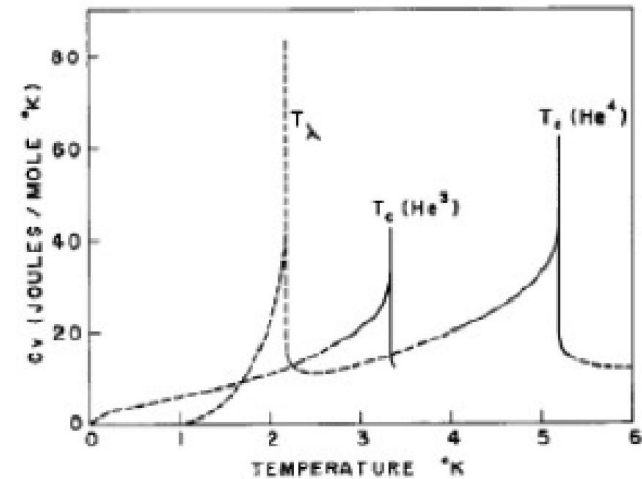


Red delimits region of absolute (mechanical) instability, where theory must be wrong.

MFT shows discontinuity near T_c



Specific heat variation
according to van der Waals



Divergence found in experiments

Critical behavior

Specific descriptors of critical region:

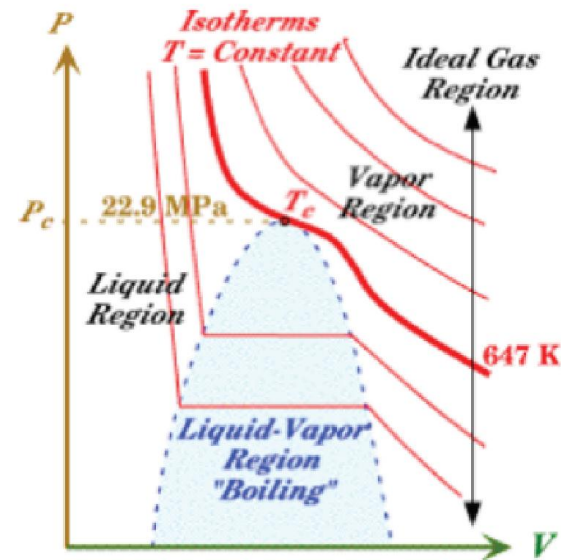
look for dependence on $t = T - T_c$, $h = p - p_c$

quantity	formula	value (MFT)	value* d=2	value d=3
compressibility (opalescence)	$t^{-\gamma}$	$\gamma = 1$	15/8	1.33
coherence length, ξ	$a t^{-\nu}$	$\nu = 0.5$	1	0.62
jump in density	$(-t)^\beta$	$\beta = 1/2$	1/8	0.34
density dependence on pressure	$\rho - \rho_c \sim h^{1/\delta}$	$\delta = 3$	15	4.3

* Onsager solution, Ising model

Phase Transitions: today's view

- thermodynamic phase transitions involve singularities, and infinities arising (almost always) from unbounded numbers of particles
- these infinities appear in thermodynamic derivatives which is caused by a coherence length (correlation length) that diverges*
- in practice coherence length describes spatial extent of fluctuations that look like regions of two phases intermixed, e.g. drops of vapor in liquid or drops of liquid in vapor.



The approximate theories of stat mech (e.g. MFT's) must be improved near critical point.

* This divergence makes extended similarity theorem work

05 January 2011

Sardar Patel University Lecture

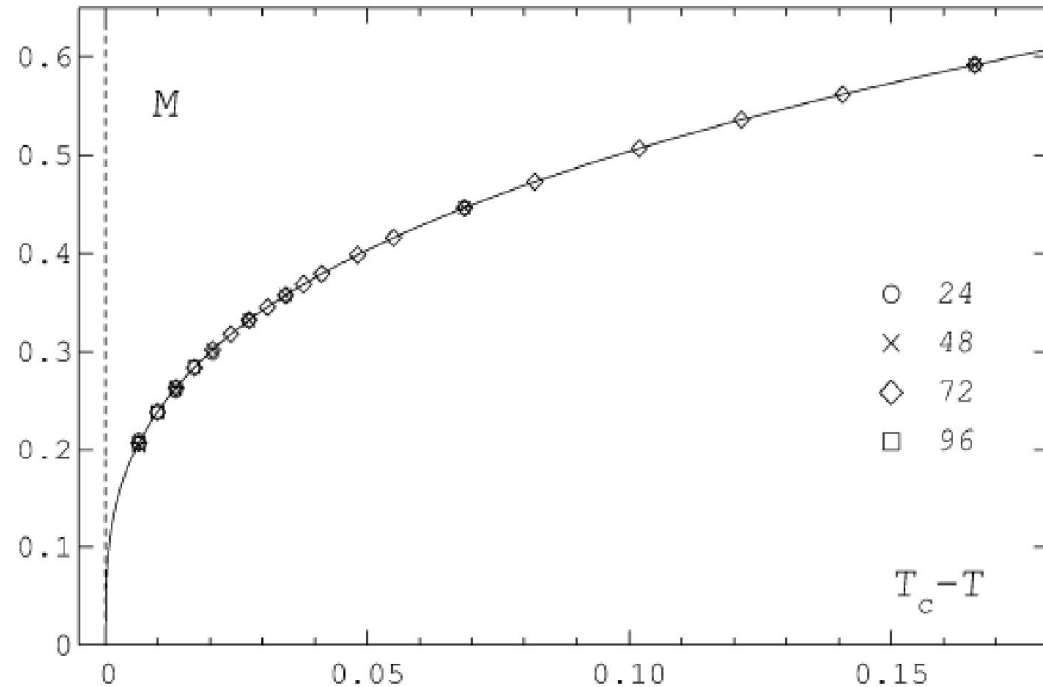
11

Order parameters

- Order parameter is a quantity which is 0 in one phase (above critical point) and non-zero in the other.
- An order parameter is a measure of the degree of order in a system. It characterizes the onset of order at the phase transition.
- Order parameter susceptibility will usually diverge approaching the critical point.
- For a ferromagnetic system undergoing a phase transition, the order parameter is the net magnetization.
- There is symmetry breaking in the ferromagnetic phase as the direction of magnetization is spontaneously chosen below the Curie point.
- For solid-liquid or liquid-gas transitions, order parameter is the density.

Computer simulations

- Computer simulations of ISING model
- Metropolis method
 - Start with a configuration
 - Generate a new configuration by randomly flipping a spin
 - Accept it if energy is reduced
 - if energy is increased accept it with probability $\exp(-\Delta E/k_B T)$
 - Calculate average quantities
 - $M = \Sigma_c M_c$



$$-H/T = K \sum_{nn} \sigma_r \sigma_s + h \sum_r \sigma_r$$

Complex molecular ordering



Mean Field Theory's application to electrodynamics of continuous media

In van der Waals MFT, a particle is affected by the average field produced by particles around it. A good and accurate example of MFT is the electrodynamics of continuous media: described by **E,D,B,H** fields.

Fields produced externally to material are **D,H**

Fields **E,B** include, in addition, averaged effects of charges and currents within material.

This kind of mean field theory is usually very accurate because electrodynamics includes long-ranged forces and many charges. It fails in nanoscopic materials.

Thank You