Statistical physics

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Outline

I Introduction to phase transitions and critical phenomena

1- The problems raised by phase transitions, from a statistical mechanics perspective
2- Classification of phase transitions
3- The drosophila of phase transitions
4- Order parameter and symmetry breakdown
5- Local order and correlation functions : from magnets to liquids

II First order phase transitions

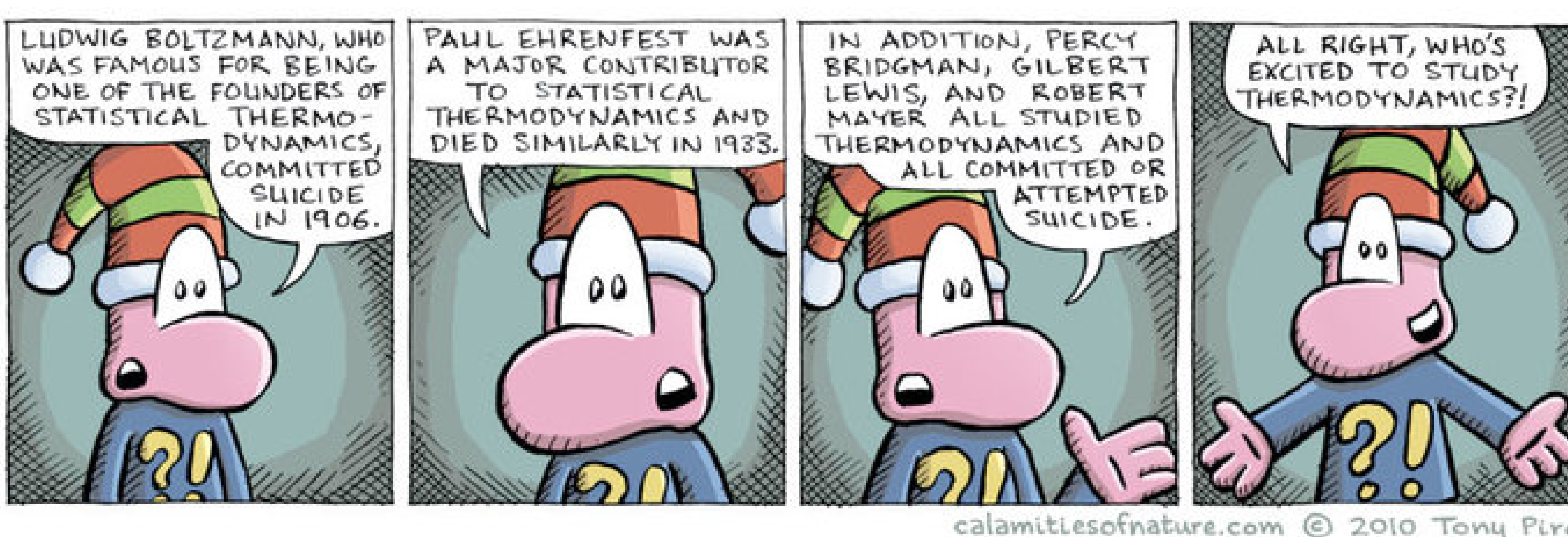
1- Unstable isotherms, double-tangent and Maxwell construction
2- Spinodal and binodal
3- Changing ensembles
4- van der Waals equation
5- The case of mixtures

III Critical phenomena : qualitative approaches

1- Weis molecular field
2- Variational mean-field
3- Critical exponents
4- Landau theory
5- Correlation functions and Ginsburg-Landau functional
6- Validity of mean-field

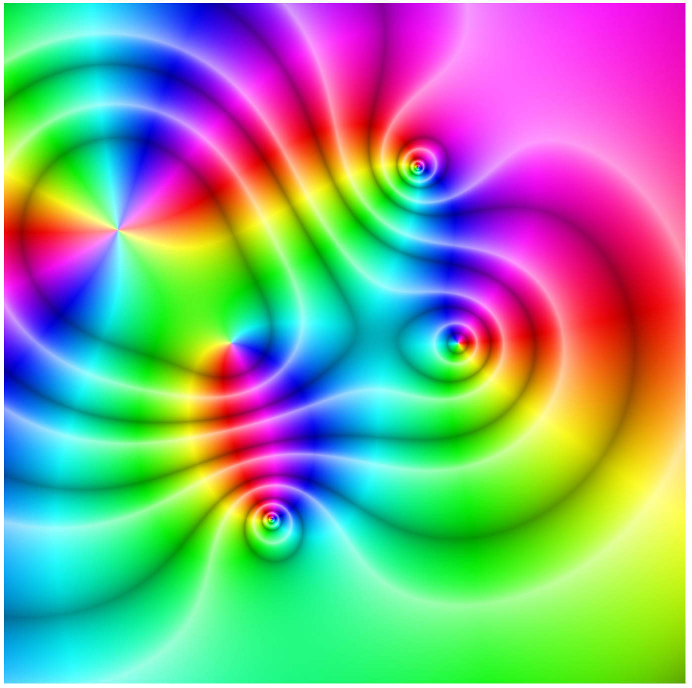
DISCLAIMER

Statistical mechanics : considered by some
as one of the most intellectually challenging subject.
Noted for a high suicide rate among founders



Prerequisites

- Elementary statistical mechanics
- Honest person toolbox in mathematics
    - Linear algebra
    - Probability theory
    - Complex analysis



$$f(x)=\frac{(x^2-1)(x-2-i)^2}{x^2+2+2i}$$

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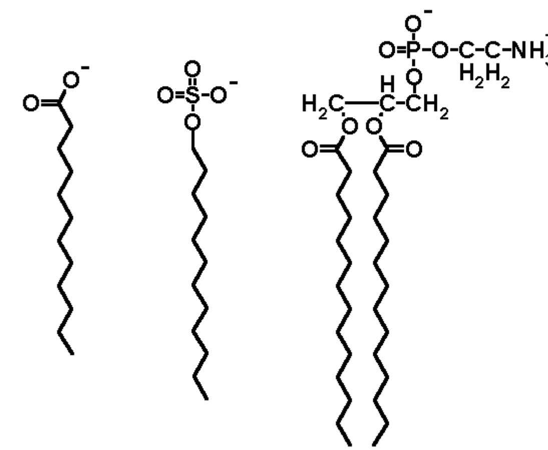
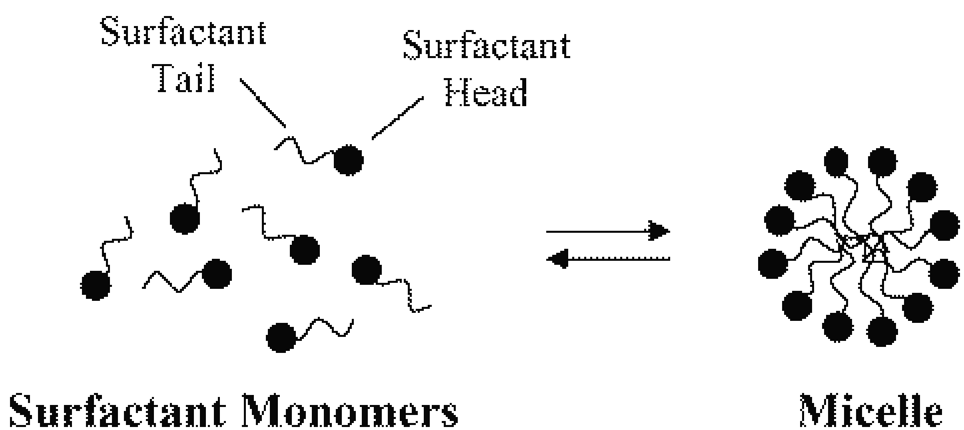
Surfactant molecules and micelle formation

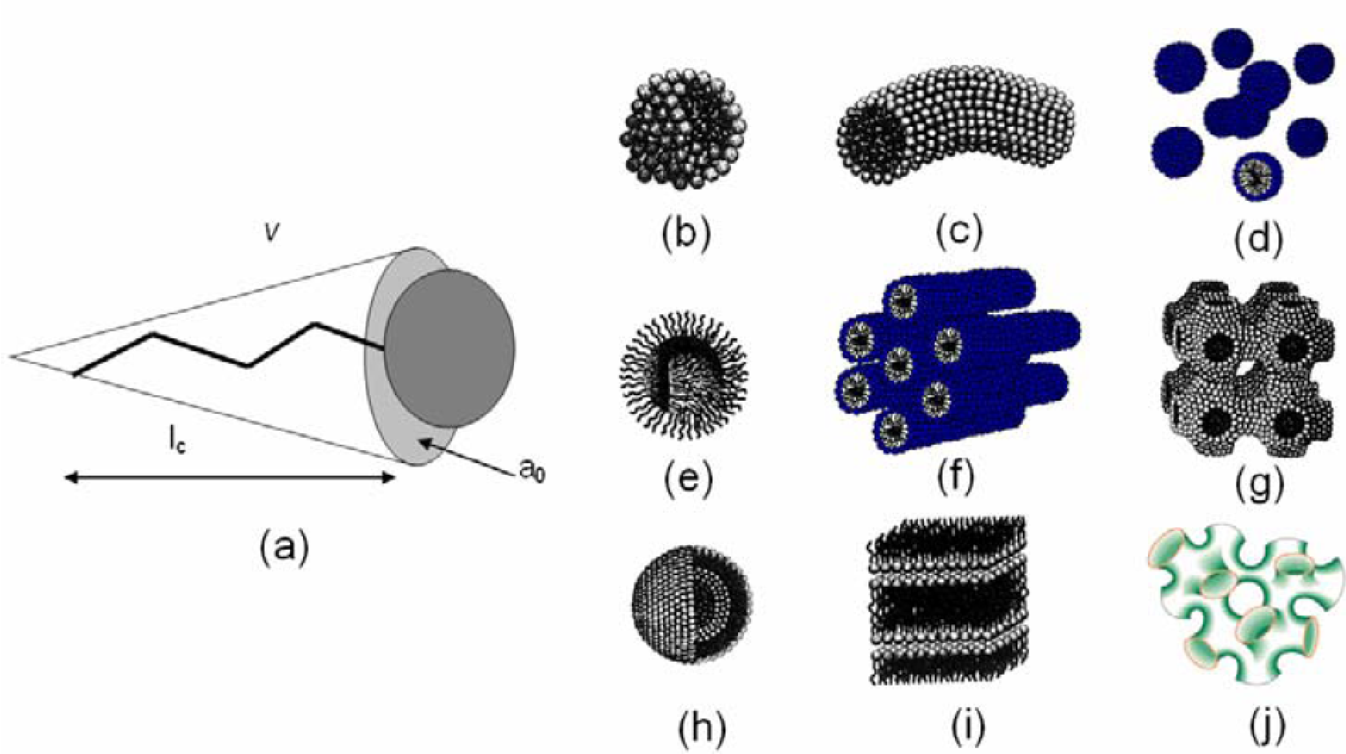


Basic mechanism



Opens for considerable richness

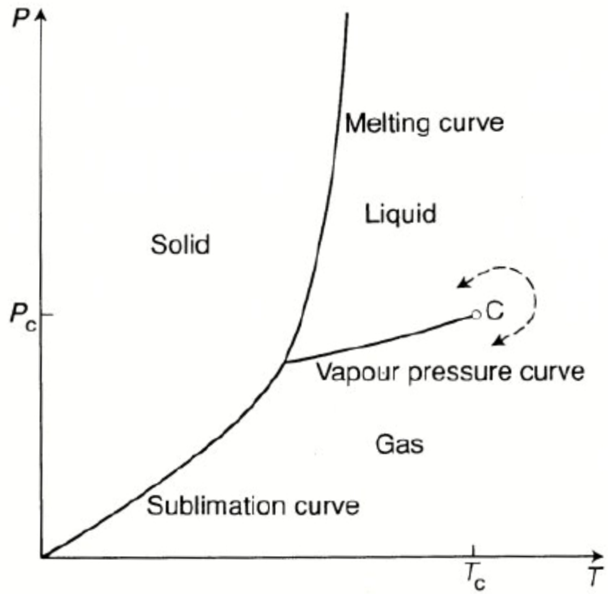
Various surfactant phases



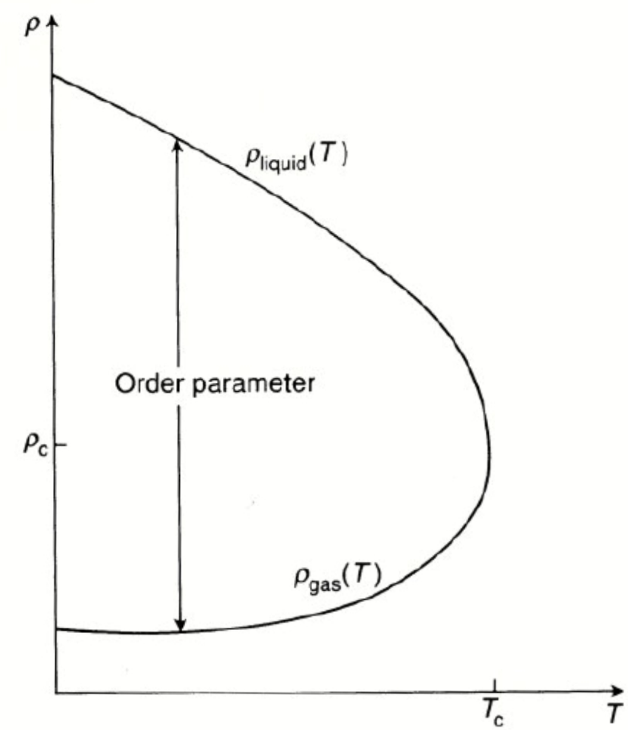
(a) An amphiphilic molecule
(b) Spherical micelle
(c) Cylindrical micelle
(d) Cubic phase
(e) Inverse micelle
(f) Hexagonal phase
(g) Bicontinuous cubic structure
(h) Vesicle
(i) Lamellar phase
(j) Sponge phase

Identify an ORDER PARAMETER

pressure



density



Complexity / variety of phase changes

Transition	Example	Order parameter
ferromagnetic[a]	Fe	magnetization
antiferromagnetic[a]	MnO	sublattice magnetization
ferrimagnetic[a]	Fe_3O_4	sublattice magnetization
structural[b]	$SrTiO_3$	atomic displacements
ferroelectric[b]	$BaTiO_3$	electric polarization
order-disorder[c]	CuZn	sublattice atomic concentration
phase separation[d]	$CCl_4+C_7F_{16}$	concentration difference
superfluid[e]	liquid ^4He	condensate wavefunction
superconducting[f]	Al, Nb_3Sn	ground state wavefunction
liquid crystalline[g]	rod molecules	various

From J. Yeomans, *Statistical mechanics of phase transitions* (Oxford)

Non spherical colloids...

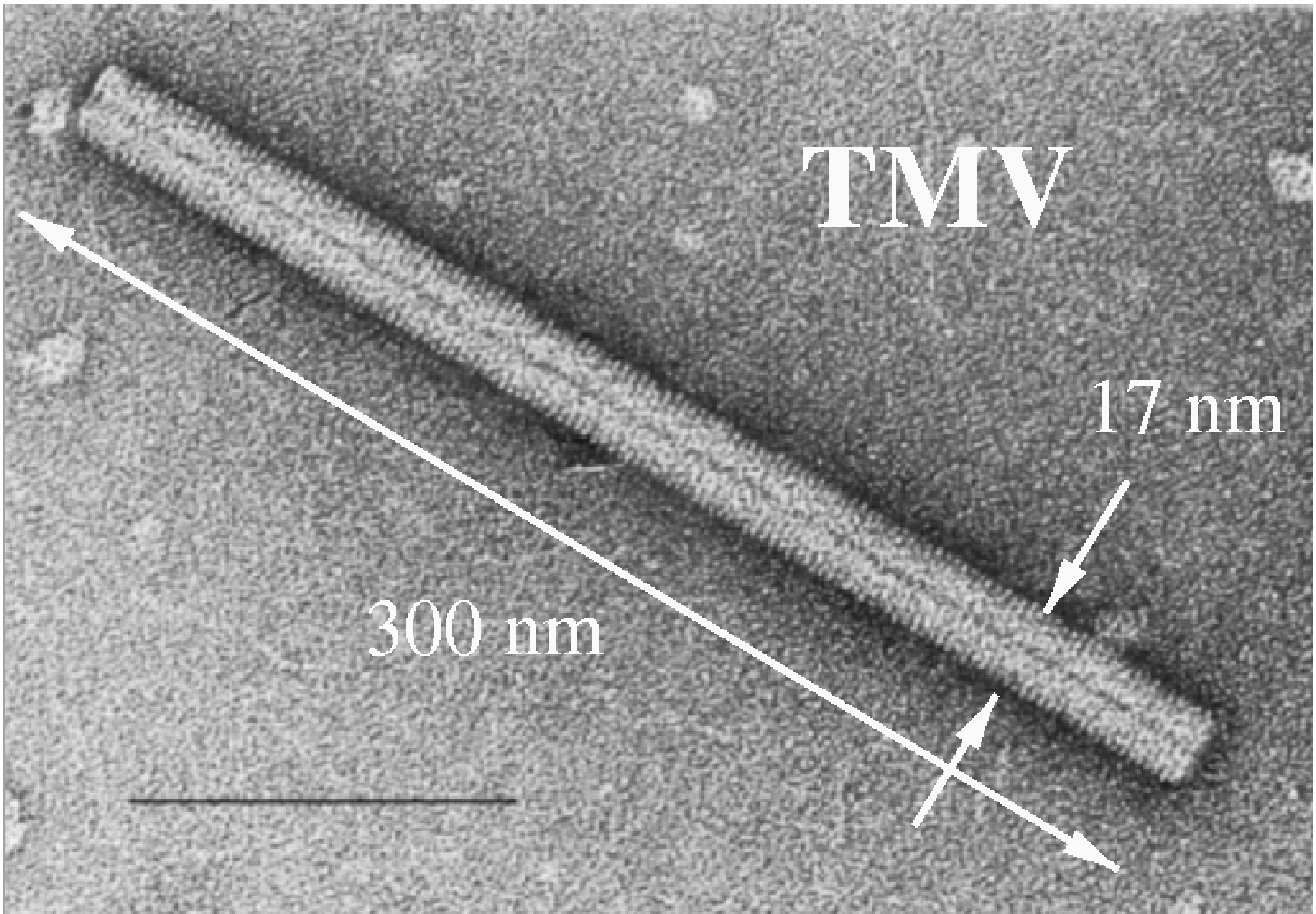
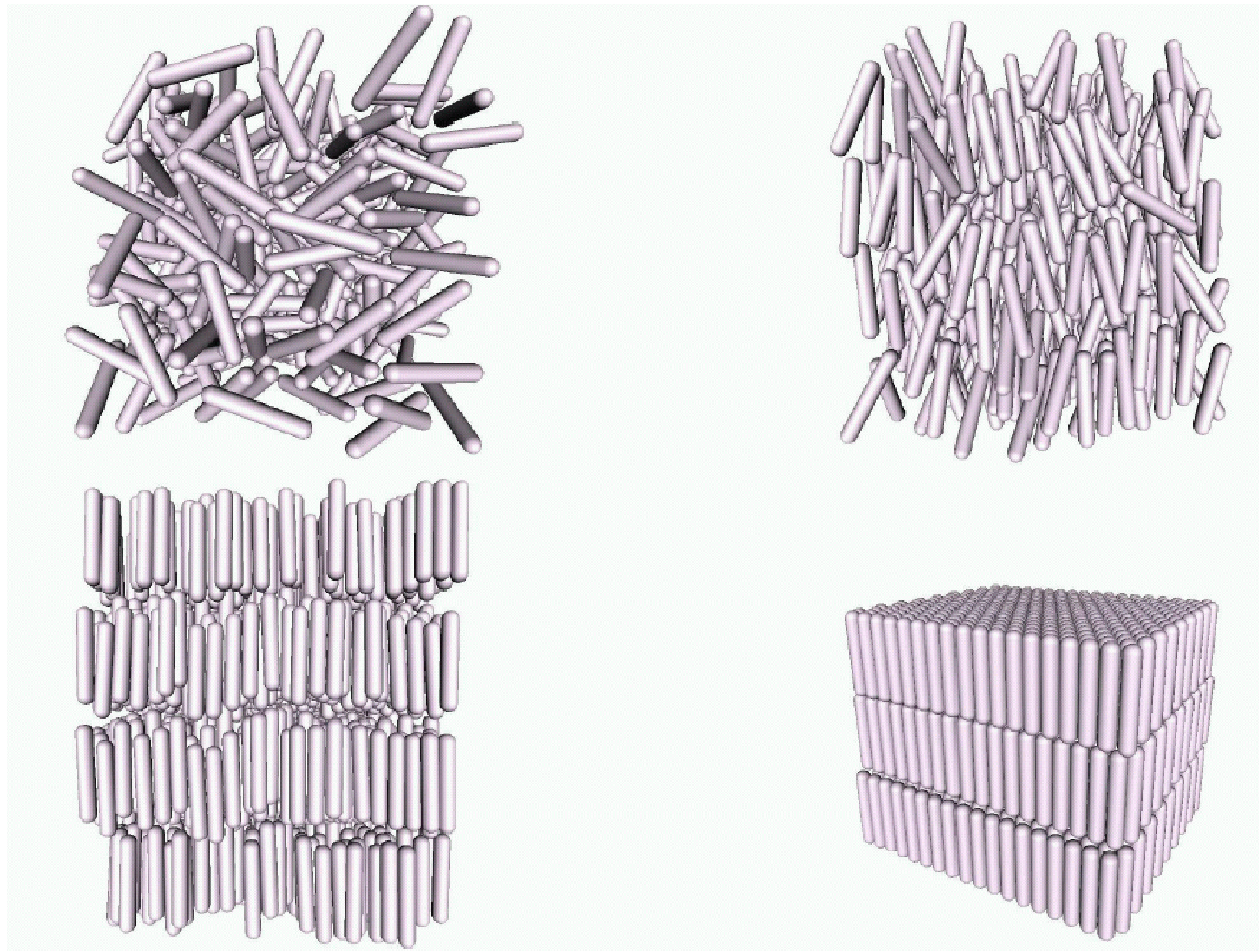


Image from the International Committee on Taxonomy of Viruses database

Phase behaviour of hard sphero-cylinders



P. Bolhuis, 1996

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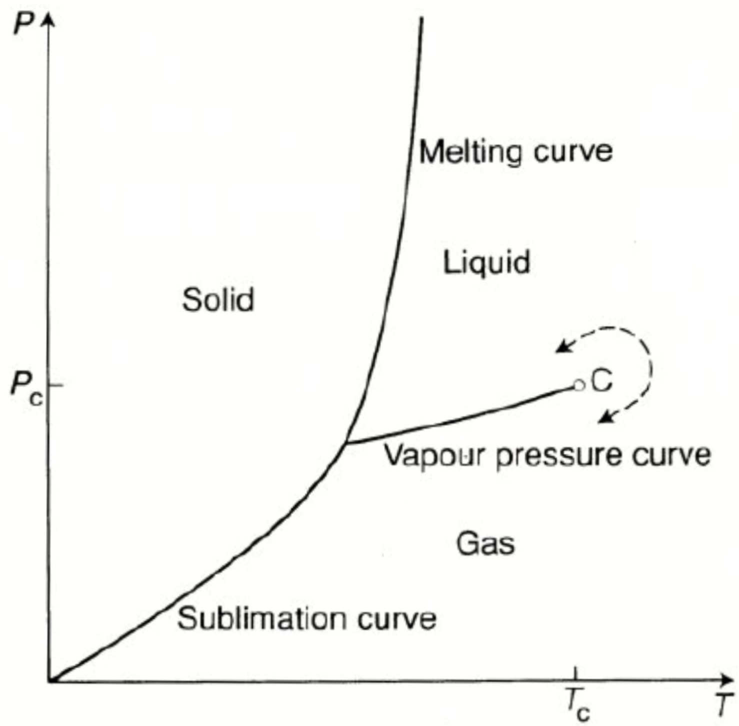
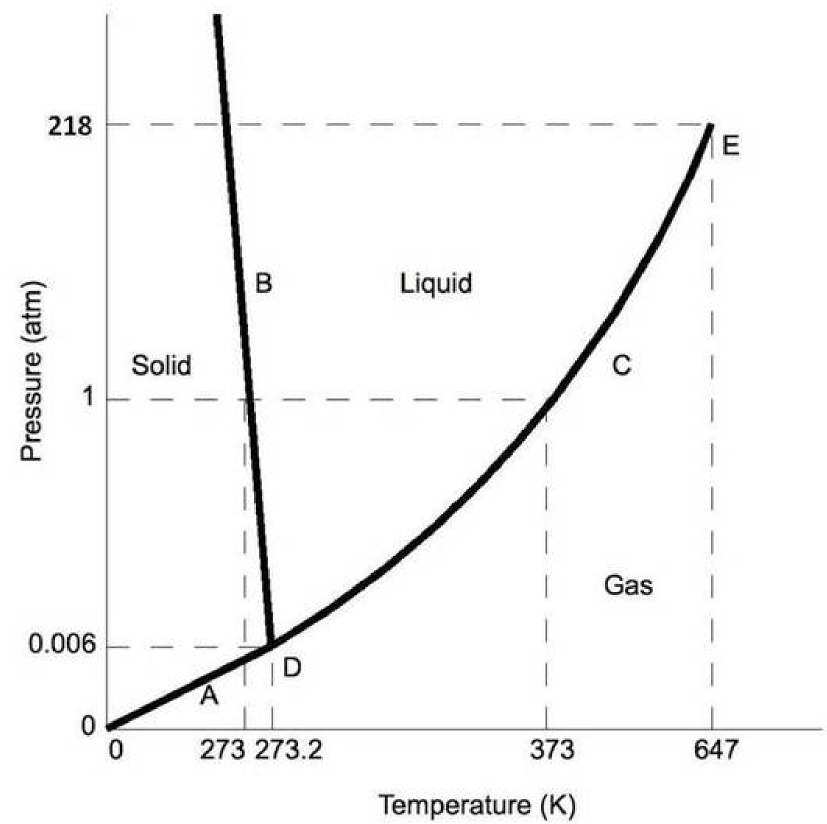
Examples and exceptions



Generic case

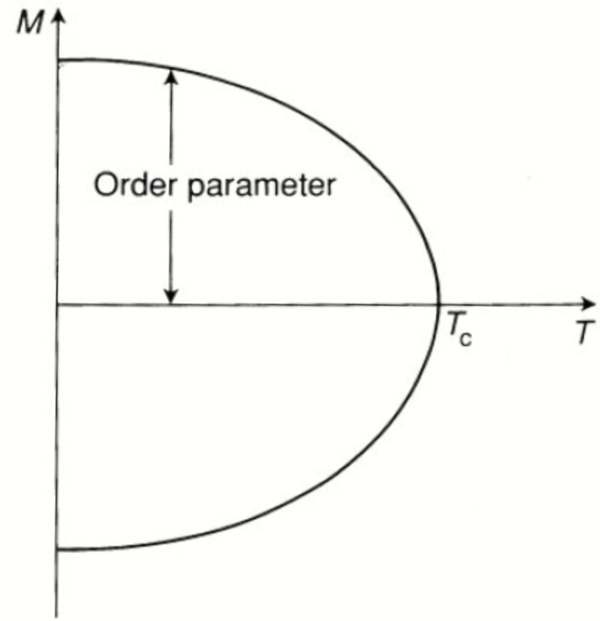
$$\frac{dP}{dT}(coex)=\frac{1}{T}\frac{L_{liq\rightarrow gas}}{v_{gas}-v_{liq}}$$

Water

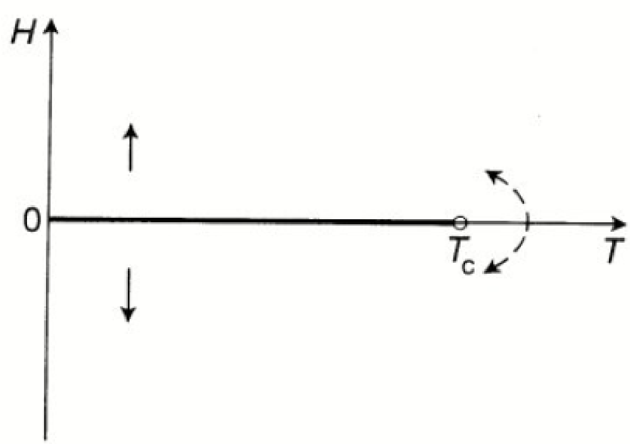


What about magnets ?

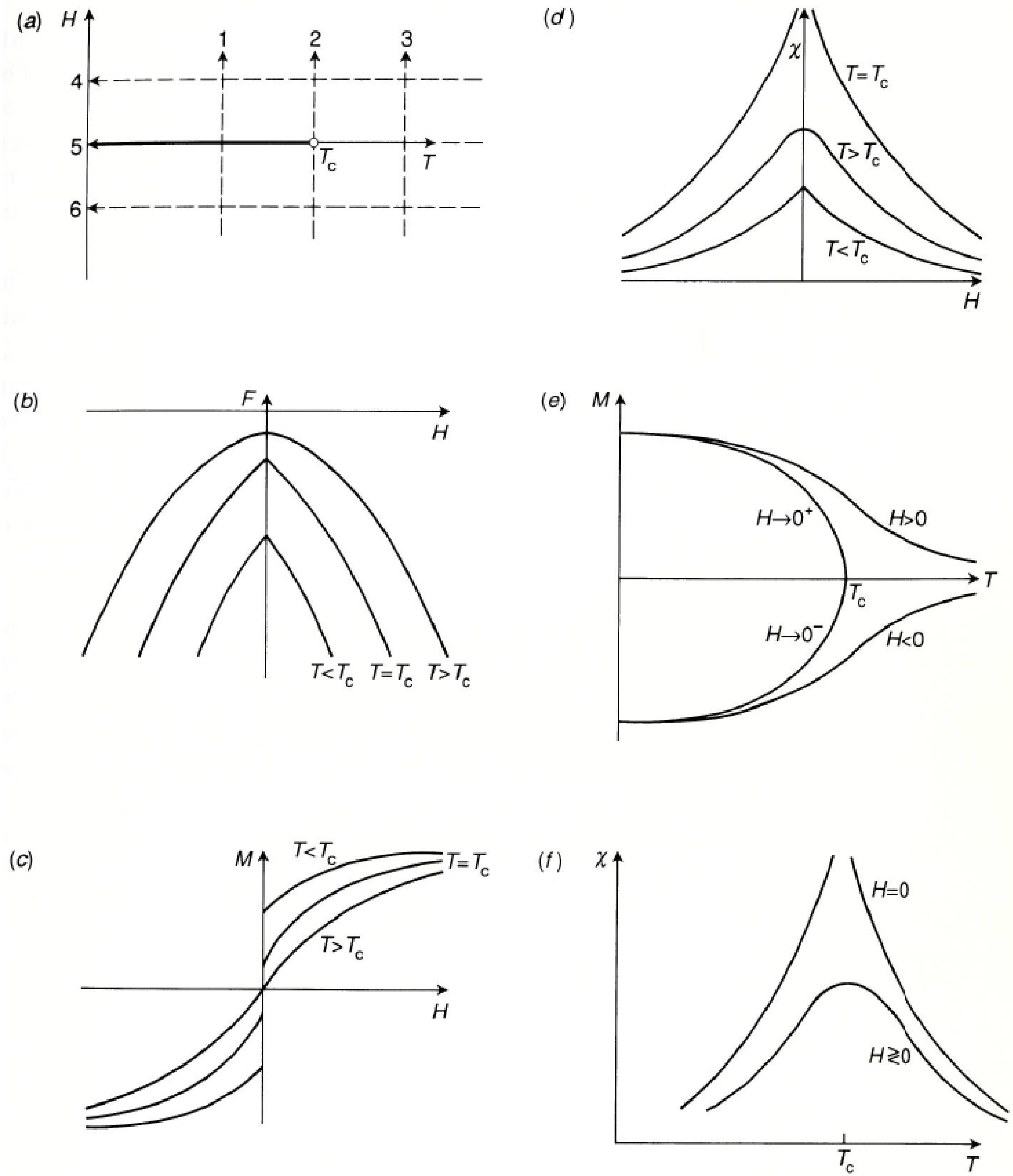
magnetization



magnetic field



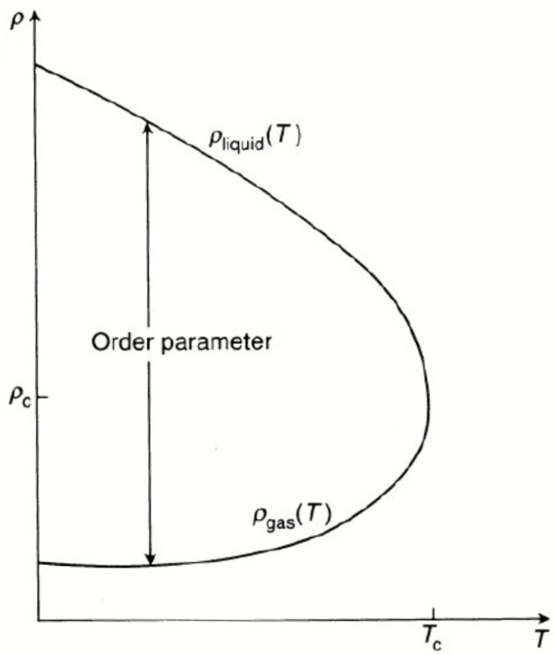
MAGNETS



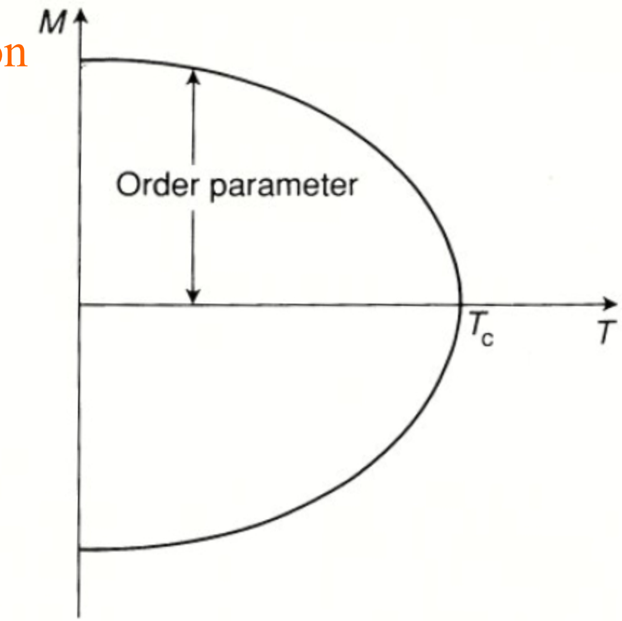
(a)
H
T
T_c
1
2
3
4
5
6
(b)
F
H
$T<T_c$
$T=T_c$
$T>T_c$
(c)
M
H
$T<T_c$
$T=T_c$
$T>T_c$
(d)
χ
H
$T=T_c$
$T>T_c$
$T<T_c$
(e)
M
T
T_c
$H \to 0^+$
$H>0$
$H \to 0^-$
$H<0$
(f)
χ
T
T_c
$H=0$
$H \gtrless 0$

Analogy between magnets and liquids ?

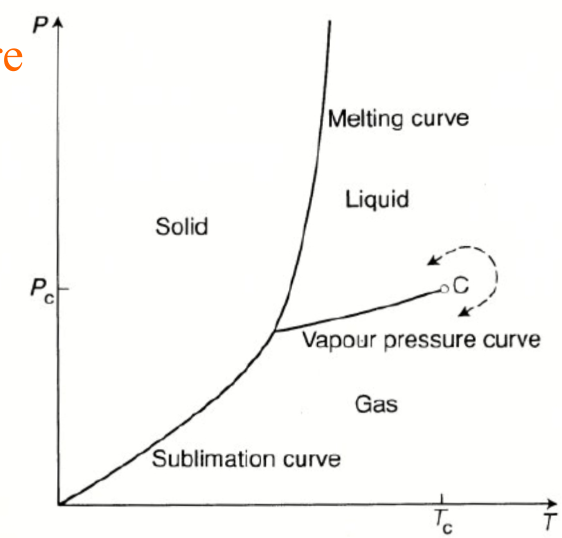
density



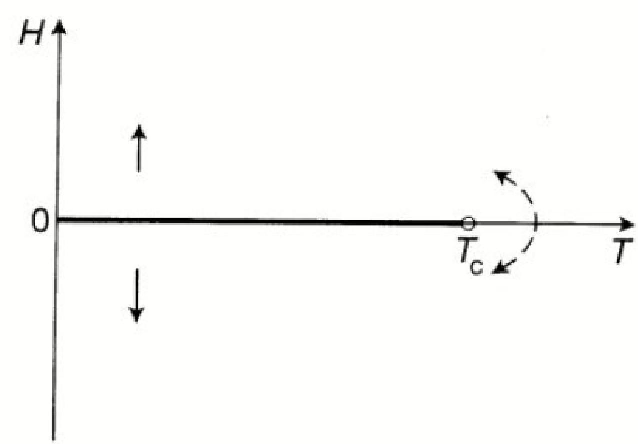
magnetization



pressure



magnetic field



Definition of critical exponents

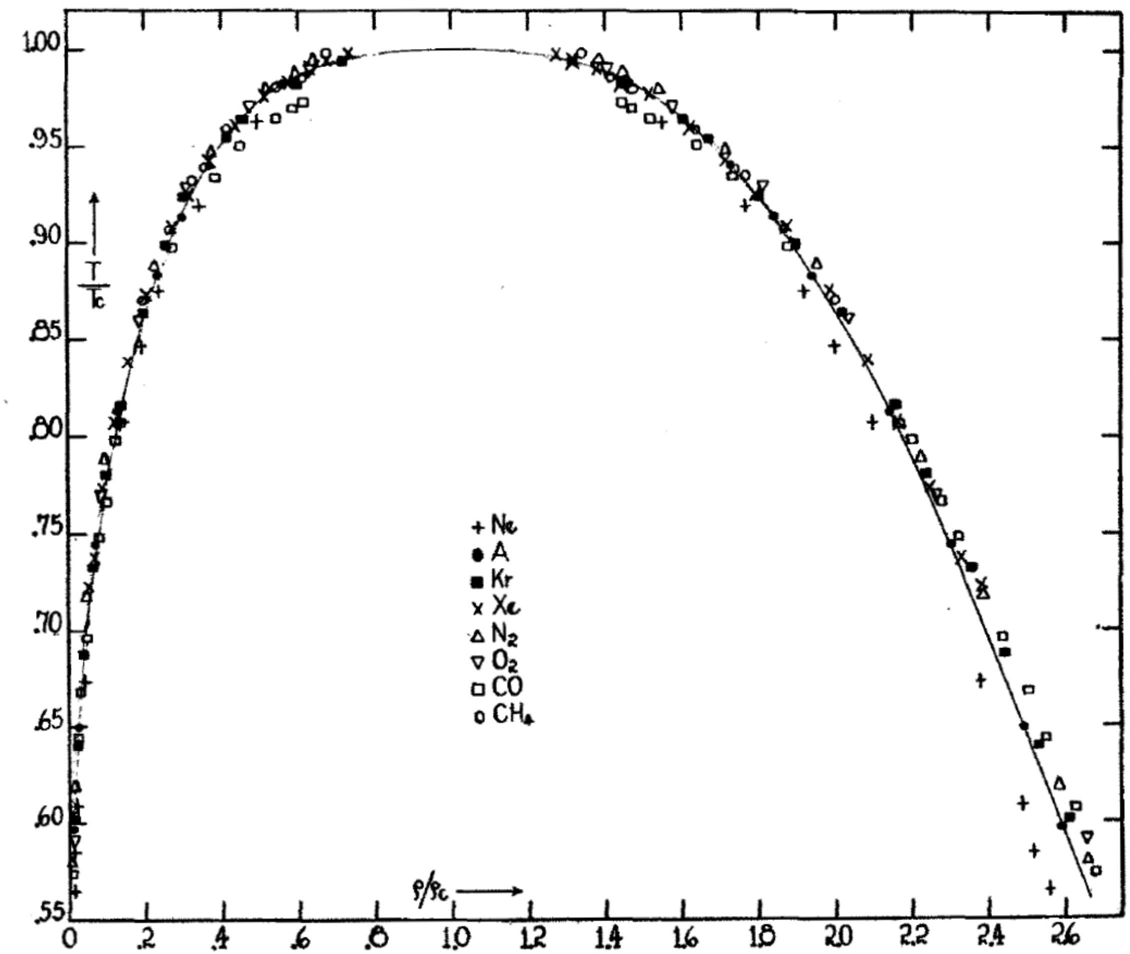
fluids

Specific heat at constant volume V_c	$C_V \sim \mid t \mid^{-\alpha}$
Liquid–gas density difference	$(\rho_l - \rho_g) \sim (-t)^\beta$
Isothermal compressibility	$\kappa_T \sim \mid t \mid^{-\gamma}$
Critical isotherm $(t = 0)$	$P - P_c \sim \mid \rho - \rho_c \mid^\delta \operatorname{sgn}(\rho - \rho_c)$
Correlation length	$\xi \sim \mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

magnets

Zero-field specific heat	$C_H \sim \mid t \mid^{-\alpha}$
Zero-field magnetization	$M \sim (-t)^\beta$
Zero-field isothermal susceptibility	$\chi_T \sim \mid t \mid^{-\gamma}$
Critical isotherm $(t = 0)$	$H \sim \mid M \mid^\delta \operatorname{sgn}(M)$
Correlation length	$\xi \sim \mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

Why are critical exponents interesting ?
→ several layers of universality



Corresponding states for liquid-gas transition

E. A. Guggenheim,
J. Chem. Phys. 13, 253 (1945)

	T_c (K)	P_c (atm)
Ne	45	26
Ar	150	48
Kr	209	54
Xe	290	58
N_2	126	33
O_2	154	50
CO	133	34
CH_4	190	45

There is more to universality

- Liquid-gas transition: $\beta \sim 0.33$
- Magnets with uniaxial anisotropy (MnF_2): $\beta \sim 0.33$
- Phase separation in binary mixture (CCl_4+C_7F_{16}): $\beta \sim 0.33$
- 3d Ising model on cubic lattice, fcc etc…: $\beta \sim 0.33$
- ...

→ all belong to the same ***universality class***

What matters is space dimension + symmetry of order parameter
e.g. for Ising in 2D : $\beta = 1/8$

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