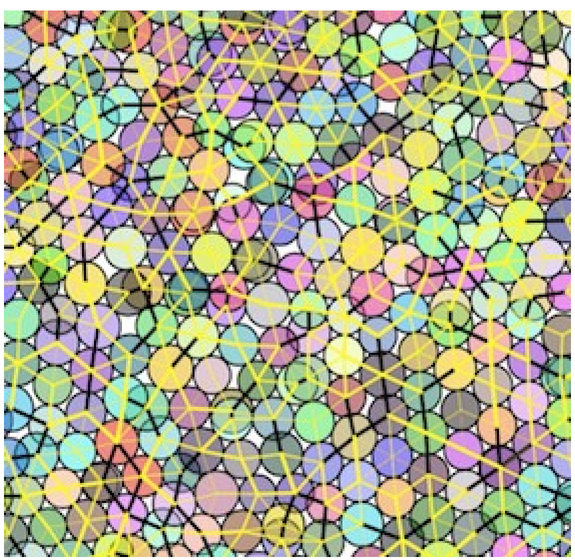
Introduction to the statistical physics of phase transitions and critical phenomena



Emmanuel Trizac
LPTMS / University Paris-Saclay

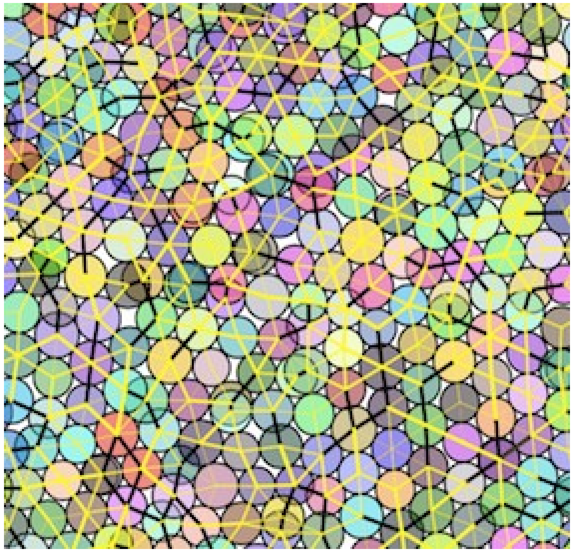
Disorder in Complex Systems @ IPa

Un Pascal → not only a unit of pressure!

Blaise Pascal

Port-Royal des Champs
15 km from IPa
8 km from St Rémy
(→ *chemin Racine*)

You registered for a school on disorder...



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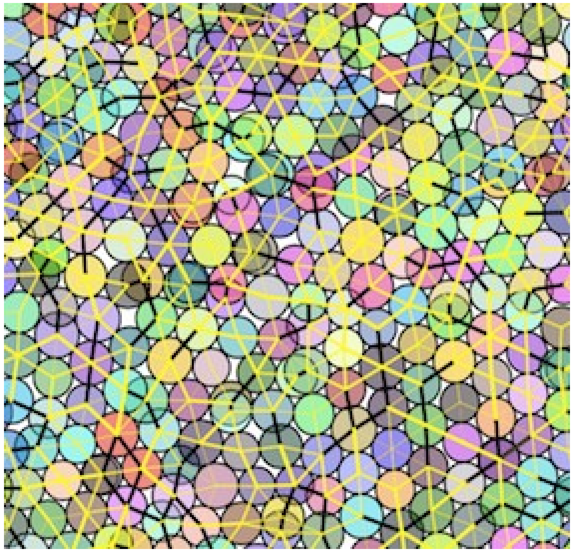


→ course deals with emergence of *order* through cooperative phenomena

J'écrirai ici mes pensées sans ordre [...]
Je ferais trop d'honneur à mon sujet, si je le traitais avec ordre
Blaise Pascal, Pensées

Statistical physics of phase transitions and critical phenomena

I Introduction

→ Classification, universality, effect of dimension, broken symmetry

II First order phase transitions

→ Unstable isotherms, double-tangent and Maxwell construction, spinodal and binodal

III Critical phenomena : qualitative approaches → mean-field

→ Variational mean-field

→ Statistical field theory / Ginzburg-Landau approach

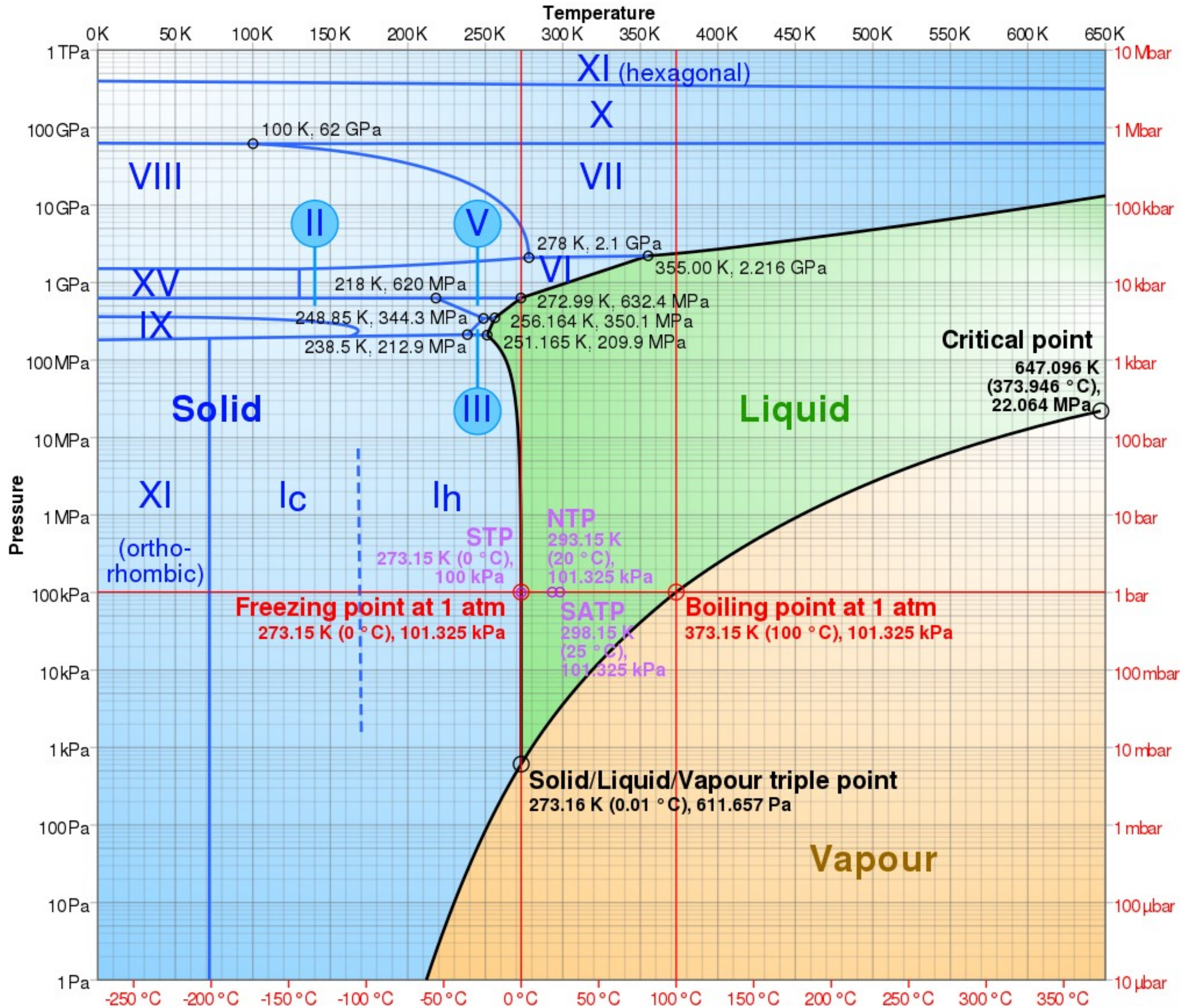
IV Beyond mean-field: fluctuations and scaling

→ Upper critical dimension

V Renormalization group ideas

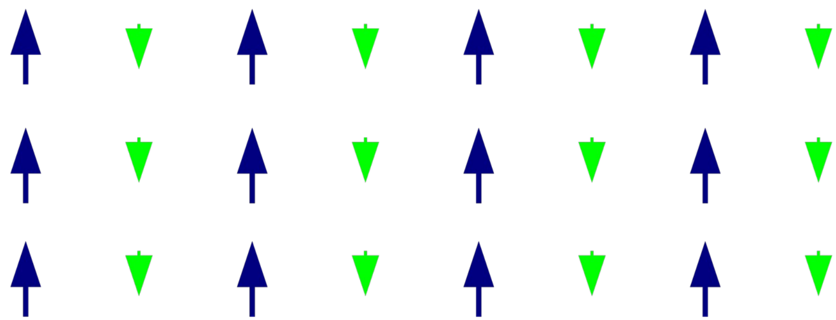
→ Take advantage from the large value of the correlation length ξ

Phase diagram of water



Ce-Sb (Cerium Antimonide)

- 14 different phases (ferrimagnetic), revealed by neutron scattering



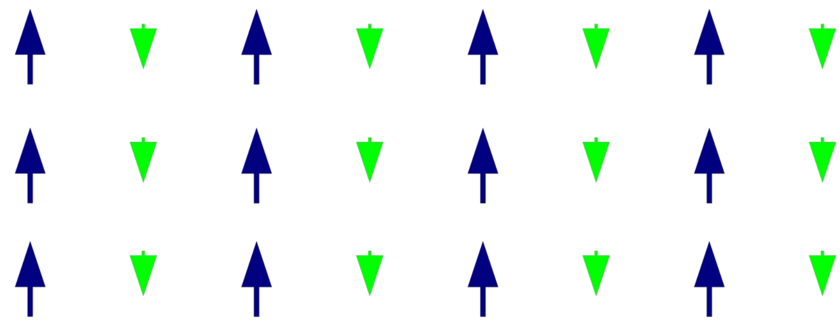
- Why the strange name *antimoine/antimonium* (against the monk)?

→ of pigs and monks?

→ unlikely: antimony used as a pill until XIXth century
eternal pill...

Ce-Sb (Cerium Antimonide)

- 14 different phases (ferrimagnetic), revealed by neutron scattering



- Why the strange name *antimoine/antimonium* (against the monk)?

→ of pigs and monks?

→ unlikely: antimony used as a pill until XIXth century

eternal pill...

although laxative!

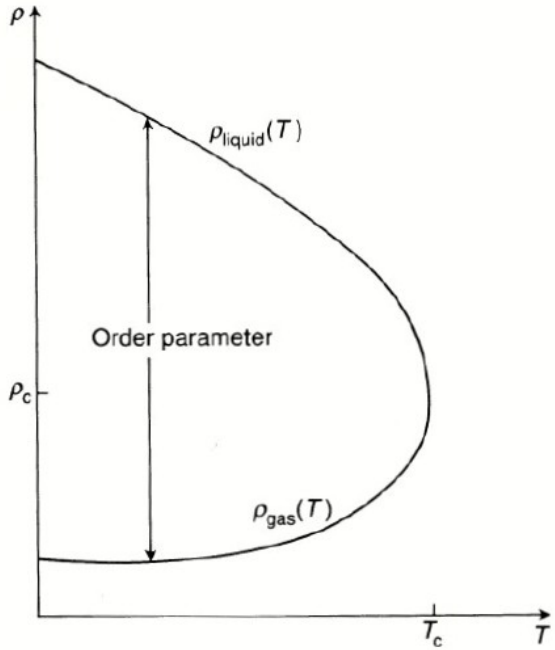
Complexity / variety of phase changes

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 ^{4}He	condensate wavefunction
superconducting[f]	Al, Nb_3Sn	ground state wavefunction
liquid crystalline[g]	rod molecules	various

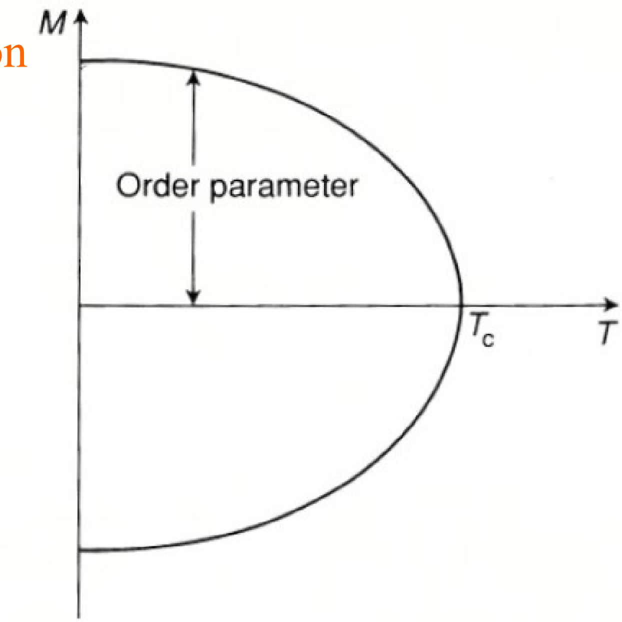
From Yeomans, *Statistical Mechanics of Phase Transitions* (Oxford)

Some systems are equivalent
Magnets (⟺liquids) as prototypical examples

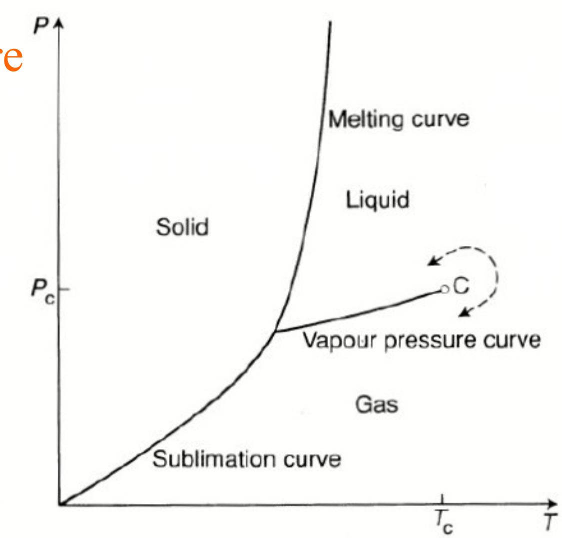
density



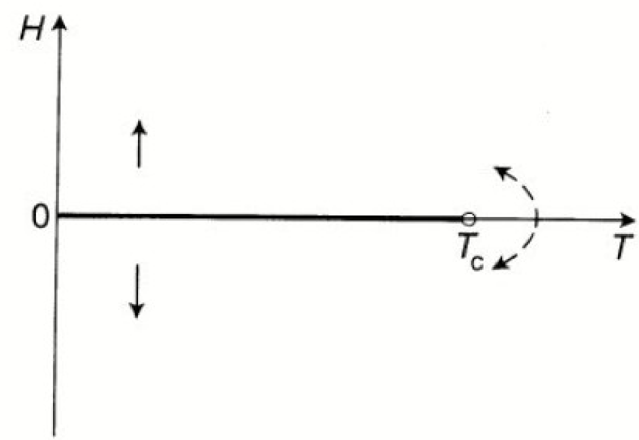
magnetization



pressure

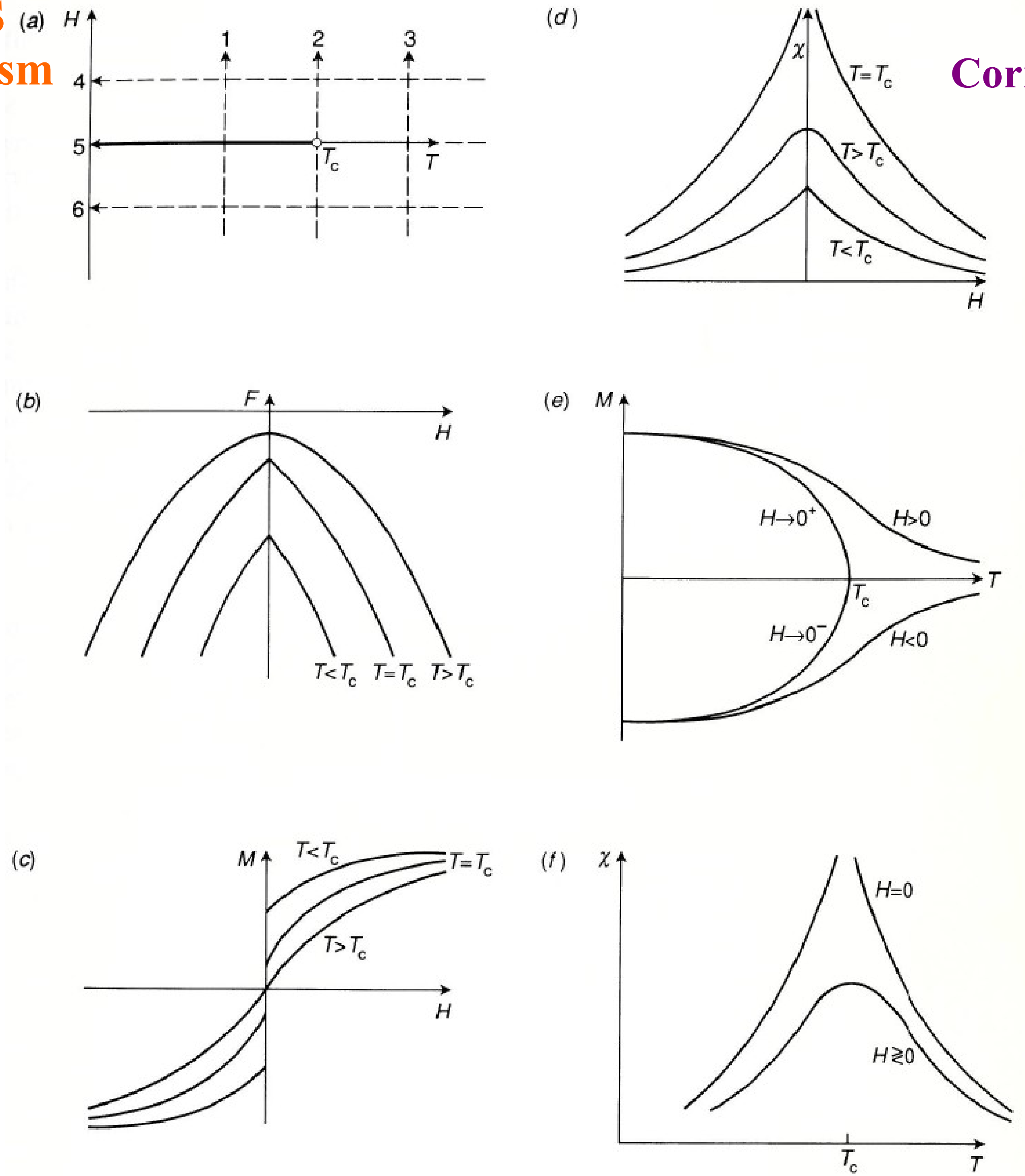


magnetic field



MAGNETS
Ferromagnetism

Correlation length diverges



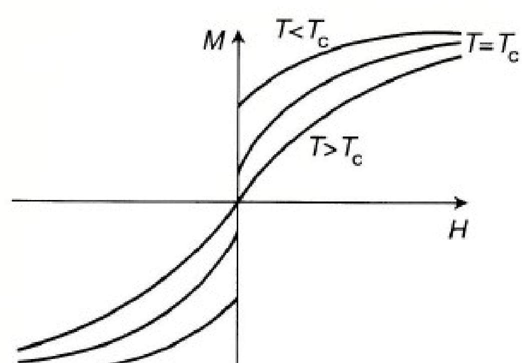
- Abundance/complexity
- Identify an order parameter ↔ free energy derivative

$$M = -\left(\frac{\partial F}{\partial B}\right)_T$$

- Onsager's *singular* legacy

Lars Onsager
(1903-1976)

- Singularity absent in a finite system…
  → consider the thermodynamic limit



Chapter 1

Introduction to phase transitions and critical phenomena

1- Problems raised by phase transitions, from a stat mech 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

Characterization of 2nd order transitions → critical exponents

fluids

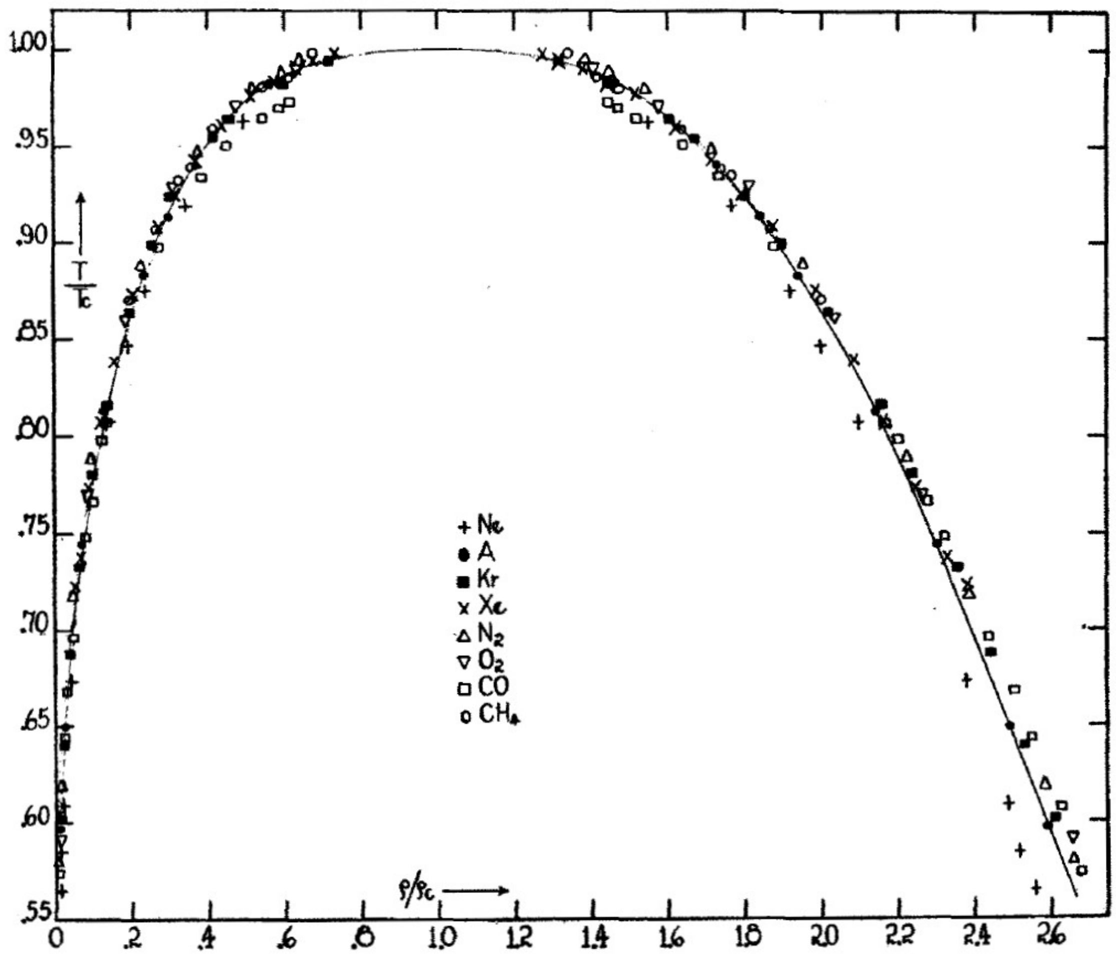
Specific heat at constant volume V_c	$C_V \sim \mid t \mid^{-\alpha}$
Liquid–gas density difference	$(\rho_l - \rho_g) \sim (-t)^\beta$
Isothermal compressibility	$\kappa_T \sim \mid t \mid^{-\gamma}$
Critical isotherm $(t = 0)$	$P - P_c \sim \mid \rho - \rho_c \mid^\delta \operatorname{sgn}(\rho - \rho_c)$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

From Yeomans, *Statistical Mechanics of Phase Transitions* (Oxford)

Why are critical exponents interesting ?
→ several layers of universality



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

Corresponding states for liquid-gas transition

	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 : $\beta = 1/8$

Different universality classes

Universality class	Symmetry of order parameter	α	β	γ	δ	ν	η	Physical examples
2-d Ising	2-component scalar	0 (log)	1/8	7/4	15	1	1/4	some adsorbed mono e.g. H on Fe
3-d Ising	2-component scalar	0.10	0.33	1.24	4.8	0.63	0.04	phase separation, flu order-disorder e.g. β
3-d X-Y	2-dimensional vector	0.01	0.34	1.30	4.8	0.66	0.04	superfluids, supercon
3-d Heisenberg	3-dimensional vector	−0.12	0.36	1.39	4.8	0.71	0.04	isotropic magnets
mean-field		0 (dis.)	1/2	1	3	1/2	0	
2-d Potts, q=3	q-component scalar	1/3	1/9	13/9	14	5/6	4/15	some adsorbed mono
q=4		2/3	1/12	7/6	15	2/3	1/4	e.g. Kr on graphite

→ define the *O(n)* model

→ existence of scaling relations, eg $\nu d = 2 - \alpha$

Chapter

1

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Ernst Ising (1900-1998)

Why a transition ?

energy ↔ entropy competition…

against

Why a transition ?

Often energy $\leftrightarrow$ entropy competition…

but not always

Non spherical colloids...

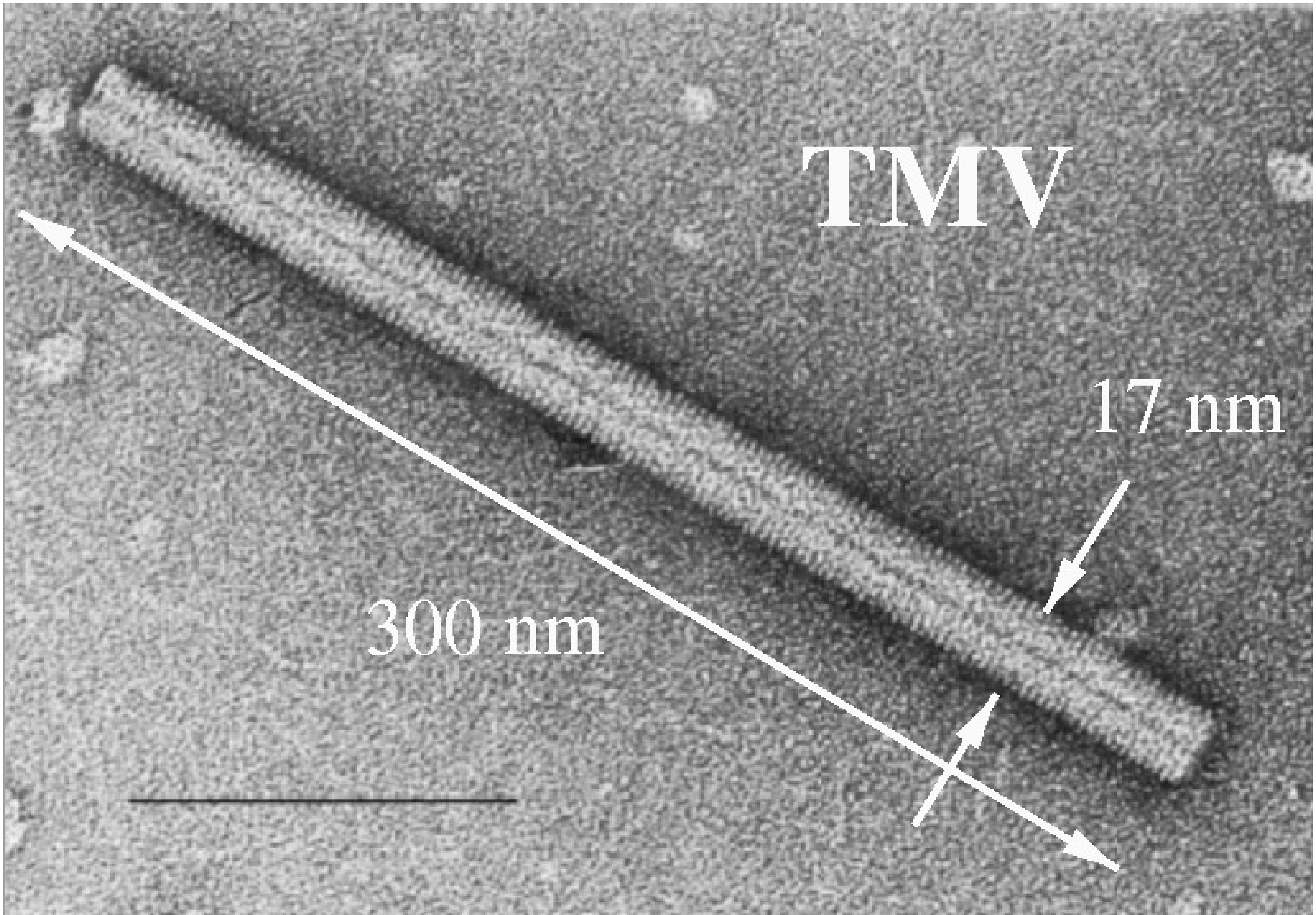
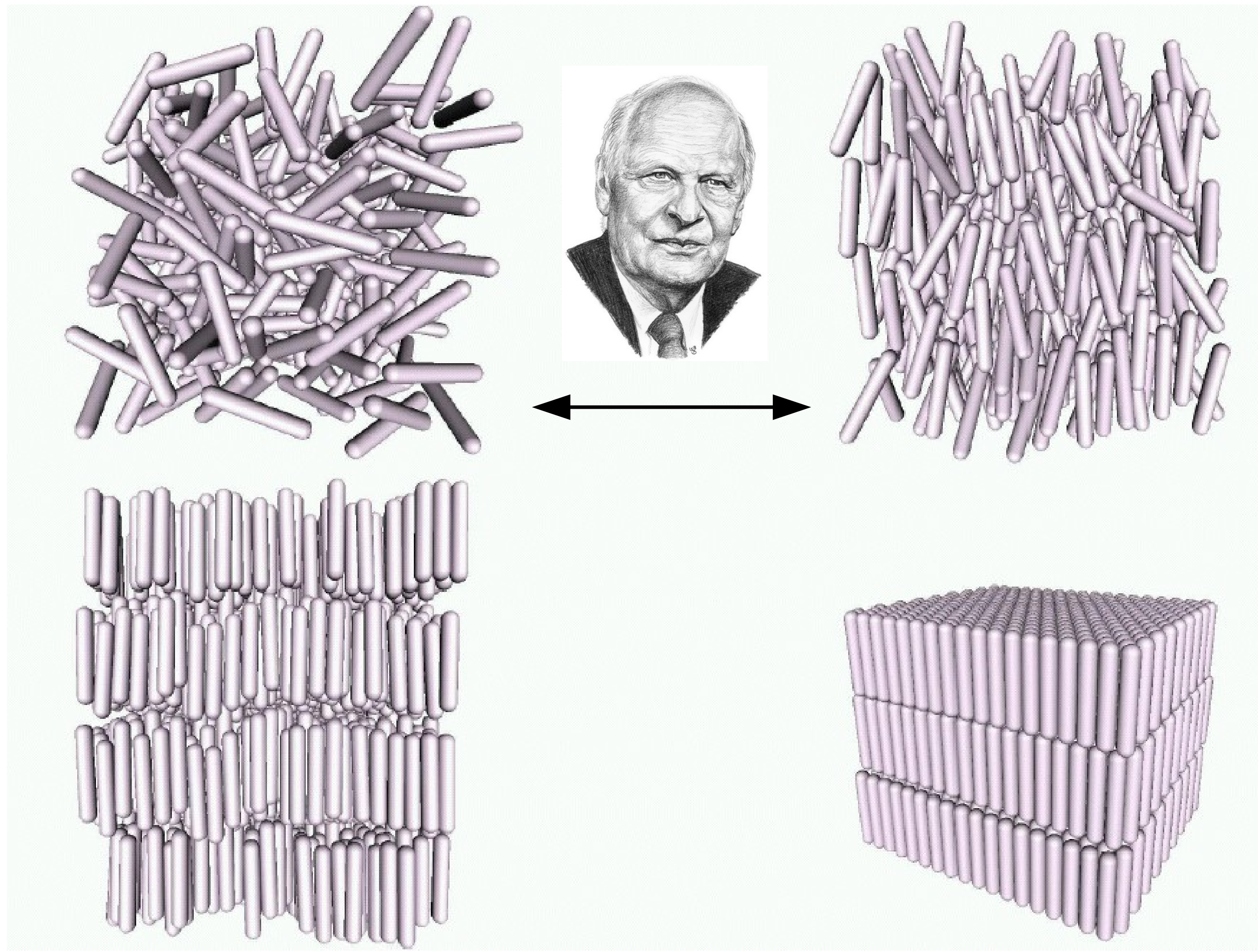


Image from the International Committee on Taxonomy of Viruses database

Phase behaviour of hard sphero-cylinders

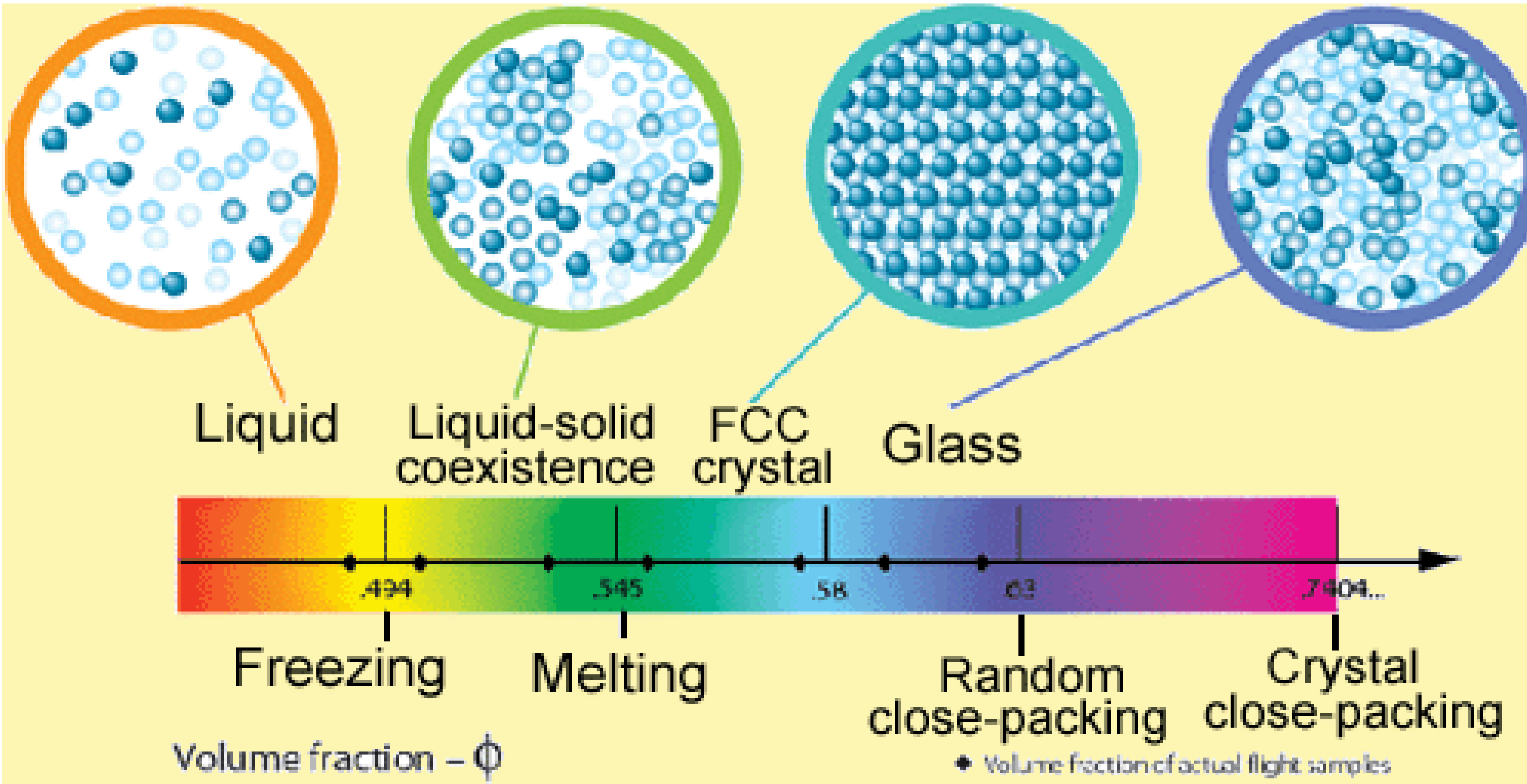


P. Bolhuis, 1996

The dark hand of entropy

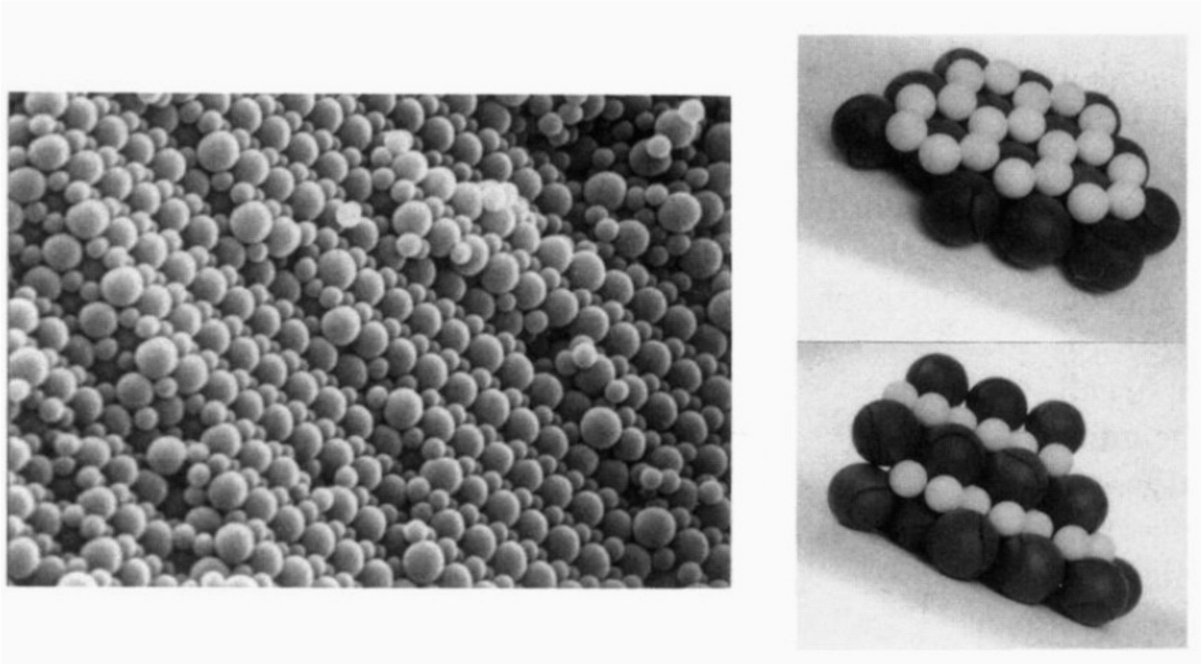
10 fundamental stamps...

The dark hand of entropy



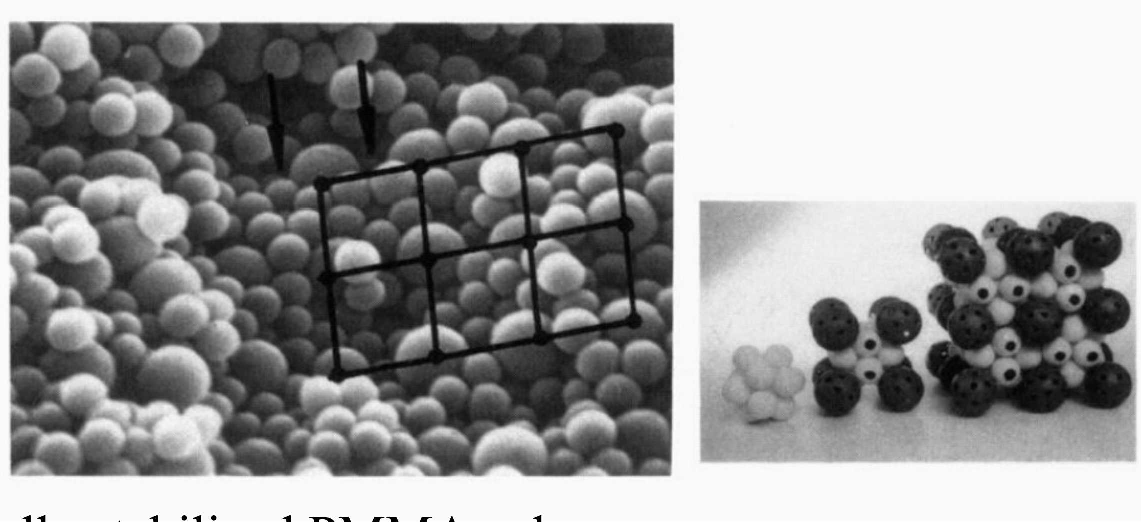
Entropic phase transition for hard spheres (NASA experiment)

Entropic phase transition for binary mixtures...



AB_2 super-structure
also observed in gem opals

AB_{13} super-structure
also observed in gem opals



System : sterically stabilized PMMA spheres
P. Bartlett, R. Ottewill, P. Pusey, *Phys. Rev. Lett.* **68**, 3801 (1992)

Back to Ising model

- *d=1:* transfer matrix formalism

- *d=2:* Peierls + Onsager's exact solution

- *d=3*: renormalization group treatment

THE RENORMALIZATION GROUP AND CRITICAL PHENOMENA

Nobel lecture, 8 December 1982

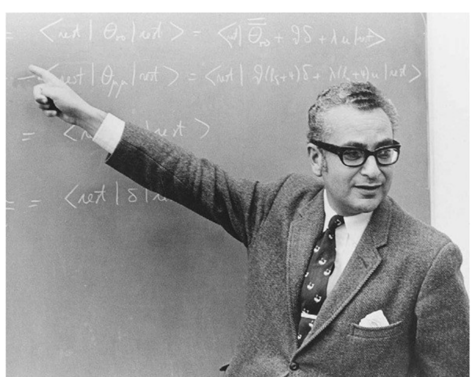
by

KENNETH G. WILSON

Laboratory of Nuclear Studies, Cornell University,
Ithaca, New York 14853

When I entered graduate school, I had carried out the instructions given to me by my father and had knocked on both Murray Gell-Mann's and Feynman's doors, and asked them what they were currently doing. Murray wrote down the partition function for the three dimensional Ising model and said it would be nice if I could solve it (at least that is how I remember the conversation). Feynman's answer was "nothing". Later, Jon Mathews explained some of

Nobel 1969

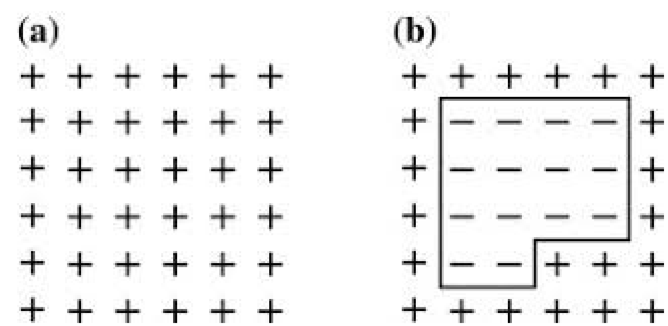


Nobel 1965

One and higher dimension
Where does the difference come from ?

d=1

d=2 (and larger)

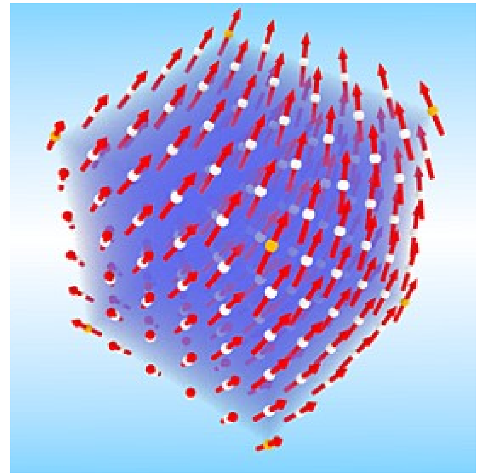


→ In 1d, the energetic cost of fluctuations is too small
Entropy dominates, fluctuations proliferate

→ no phase transition

→ notion of lower critical dimension : $d_{lower} = 1$ for usual Ising

Back to the *O(n)* model with *n>1*: the physics of spin waves



The Mermin Wagner theorem

No phase transition with continuous symmetry in one and two dimensions

Chapter 1

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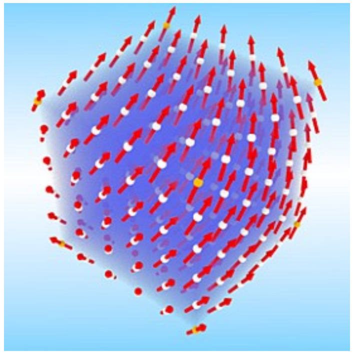
Conclusion of chapter

- Phase transition ↔ discontinuity or singularity in free energy derivative
- No phase transition in a finite system
  (so… what about computer simulations? → see the tutorial on Binder cumulants)
- Phase transition means long range order…
  although the correlation function is short range outside T_c
- Correlation length diverges at T_c : microscopic details no longer matter
  → universality → renormalization group treatment
- Notion of lower critical dimension :
  1 for discrete spins, 2 in continuous case (Mermin Wagner)

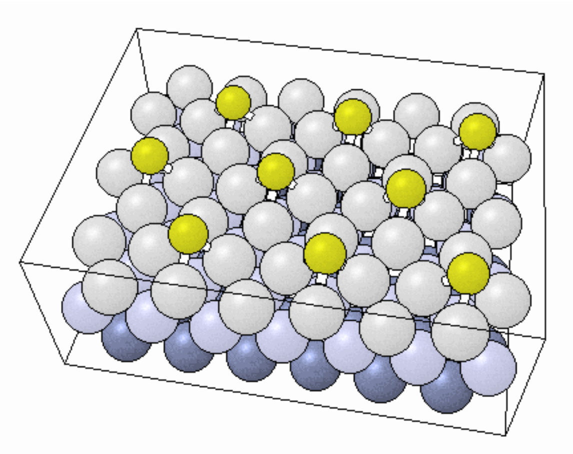
Goldstone modes
destabilize order



Beyond universality, Ising also important through isomorphism of models

- Binary alloys
- Lattice gas model, for liquid/gas transition ; or adsorption of H onto iron

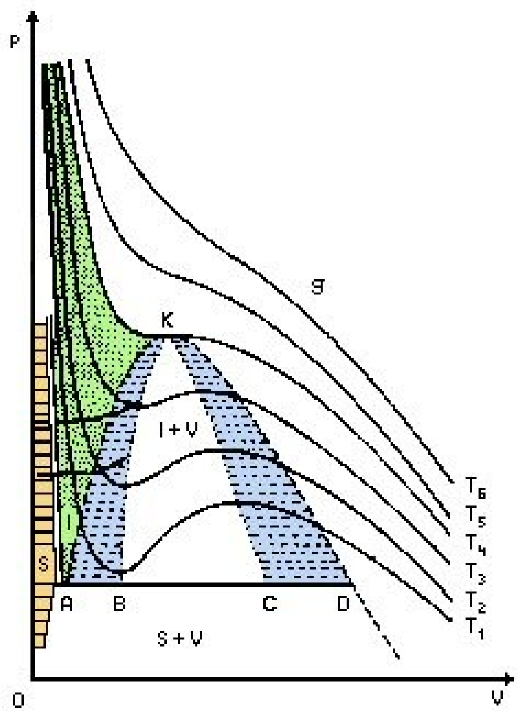
Fe surface (110)

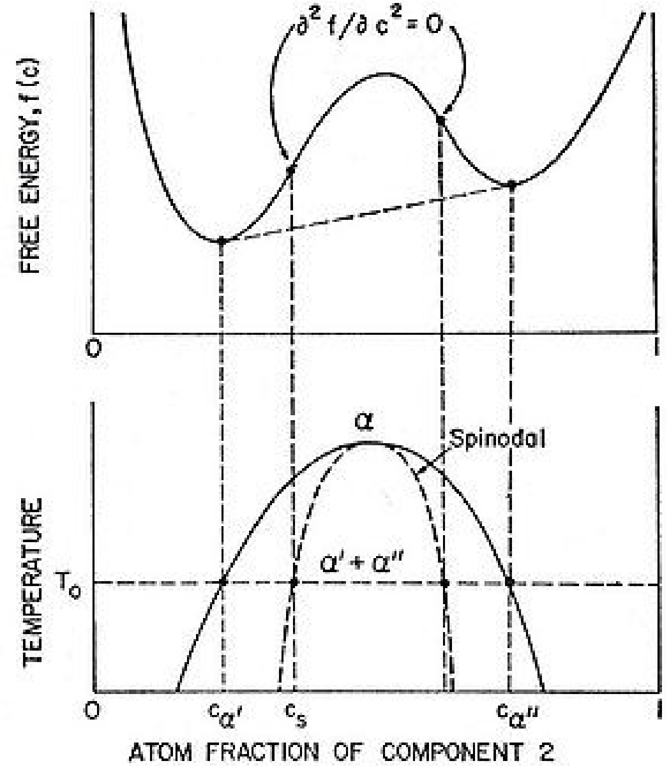


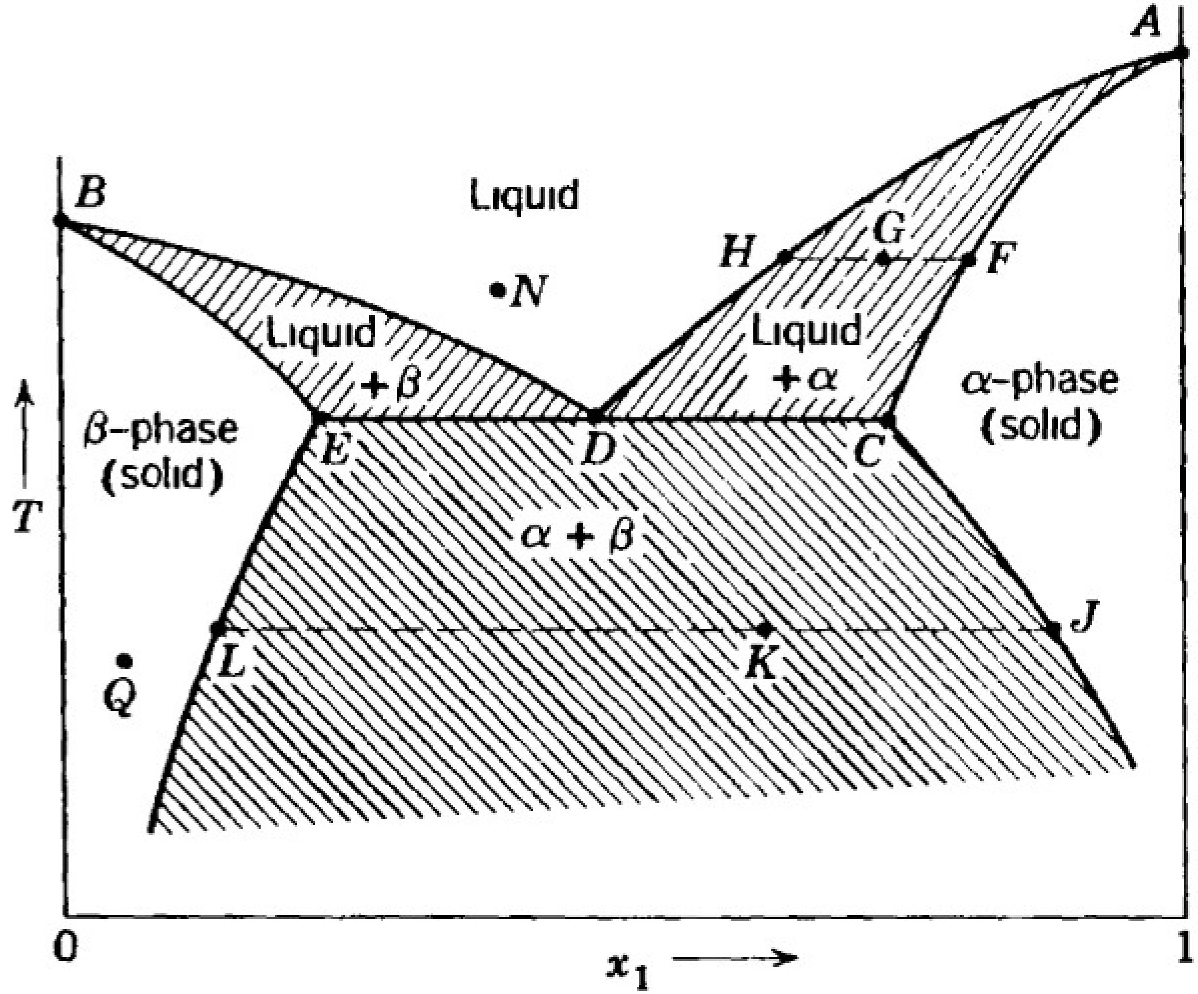
- Fads/herds and hypes (*effets de mode*)
- Neuronal activity
- Protein folding,
- Bird flocking…

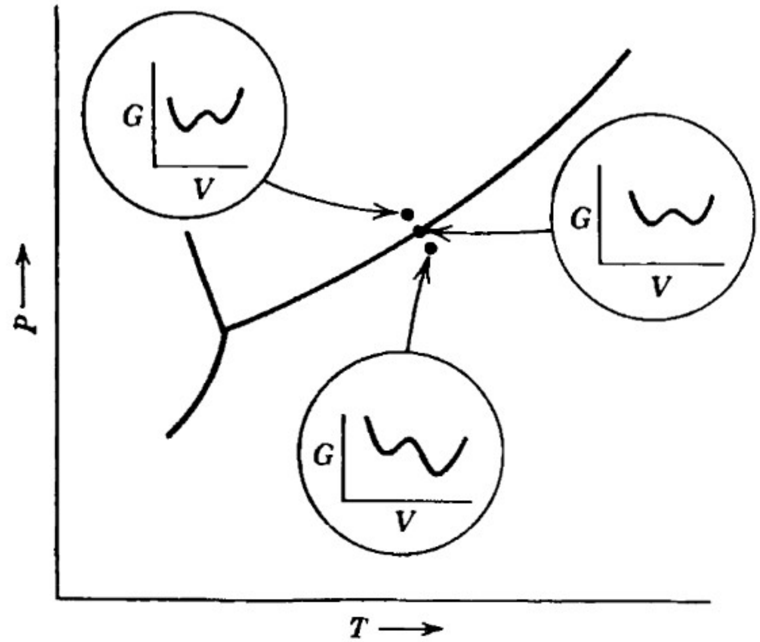
  and much more

Spinodal and binodal






A
B
Liquid
G
H
F
N
Liquid
+ β
Liquid
+ α
α-phase
(solid)
β-phase
(solid)
E
D
C
T
α + β
J
L
K
Q
0
1
x_1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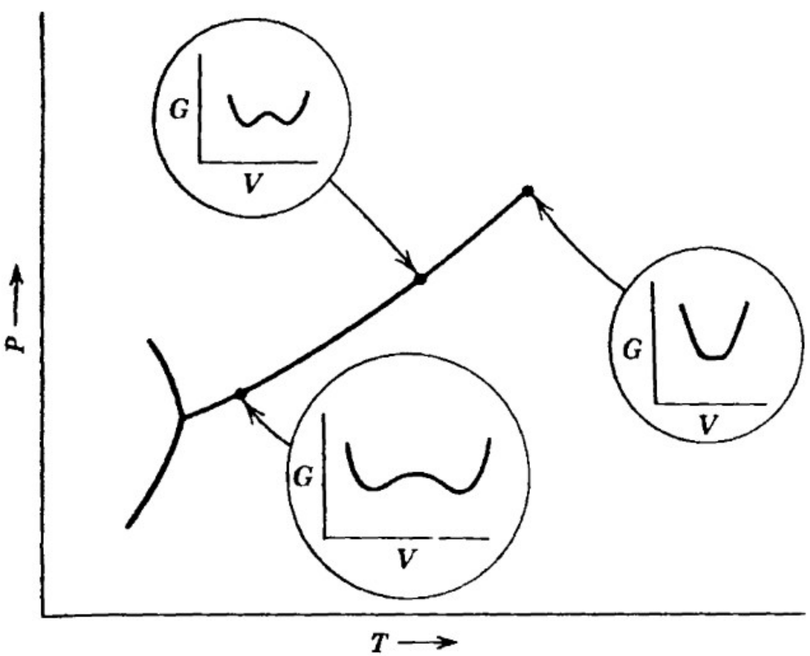
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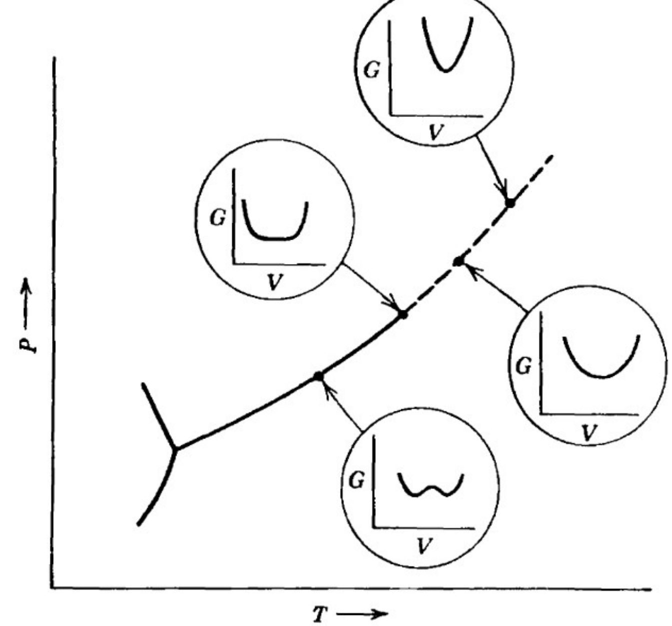
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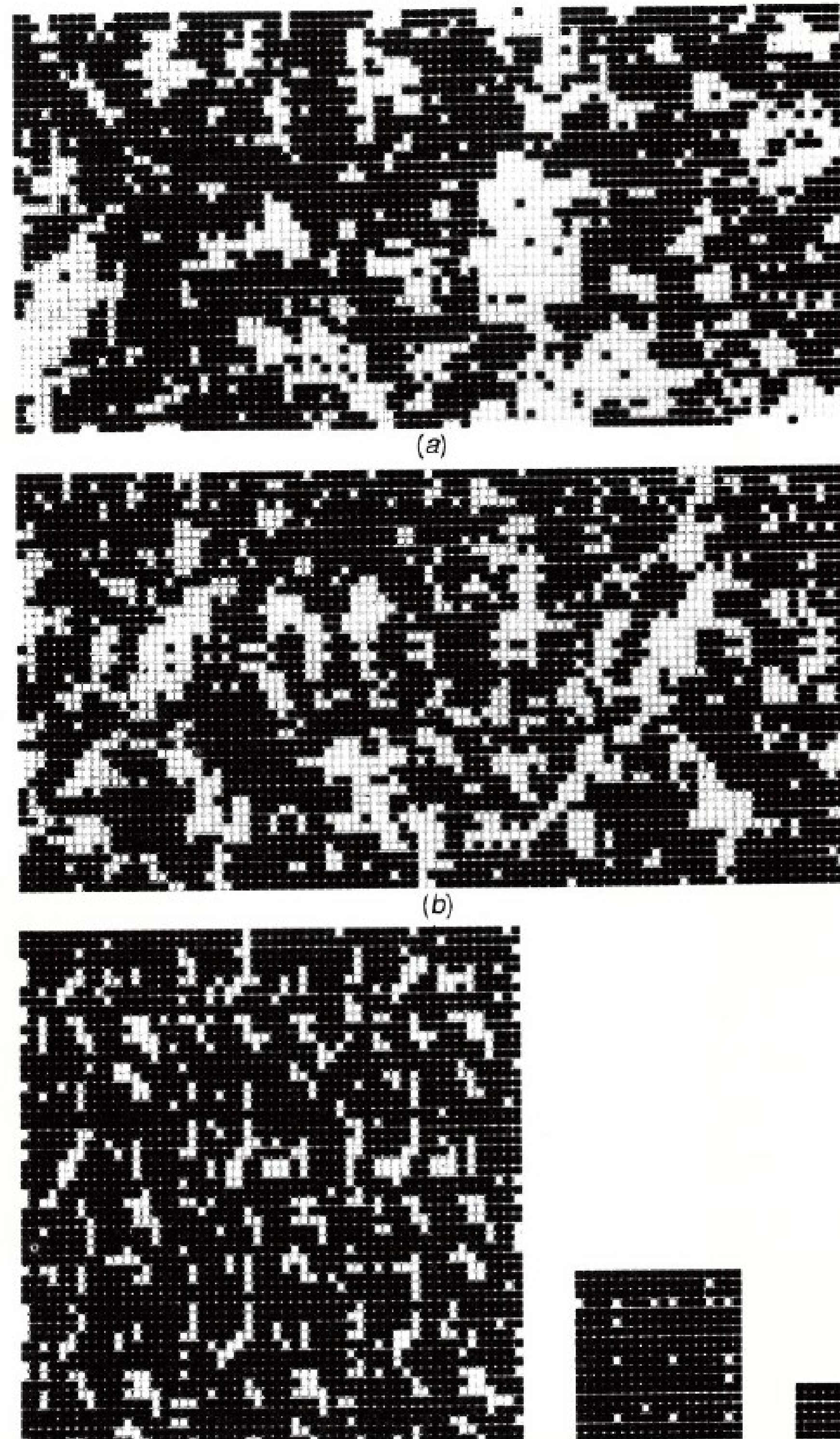
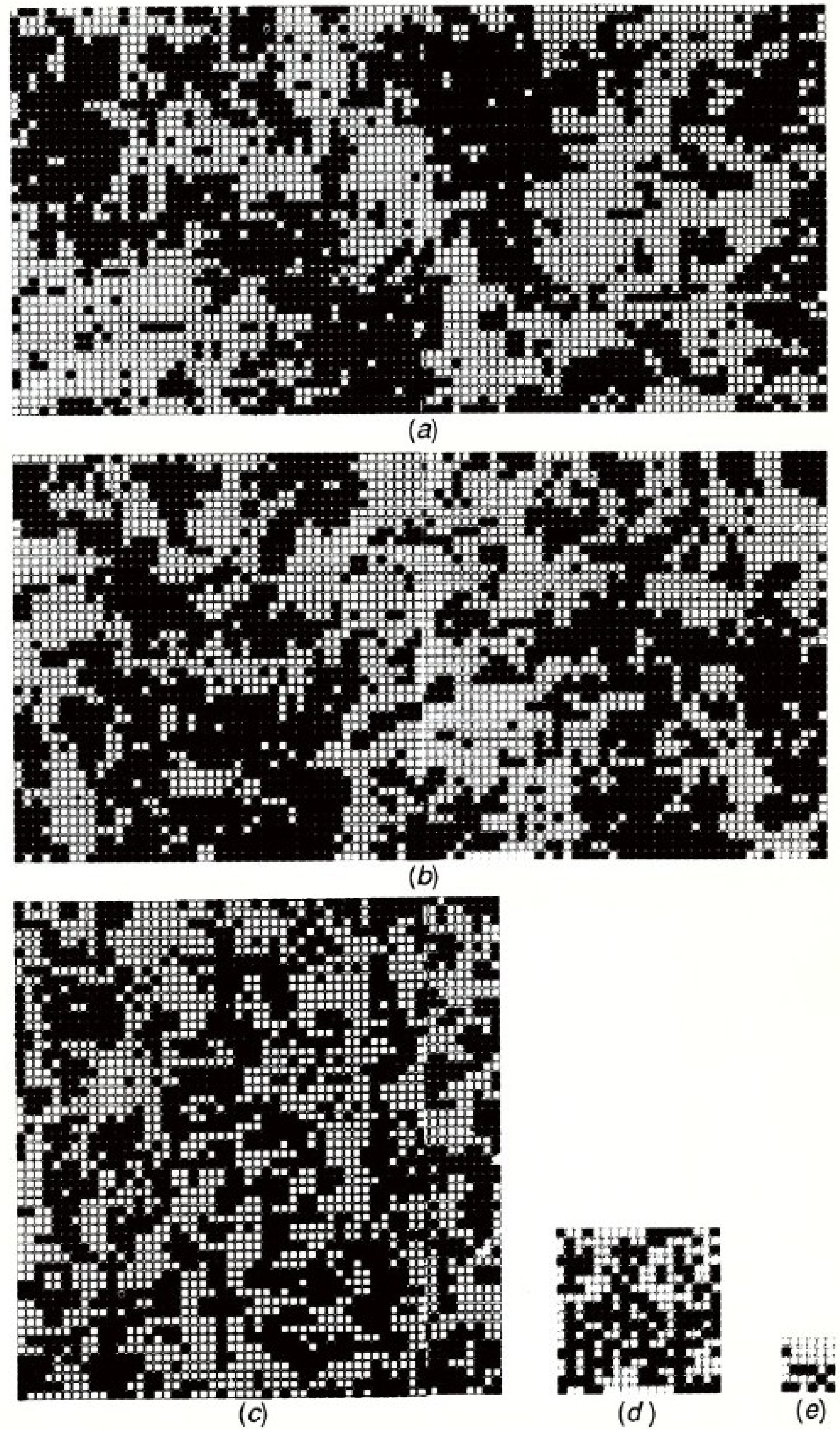
$T=1.22\ T_c$

$T=0.99\ T_c$

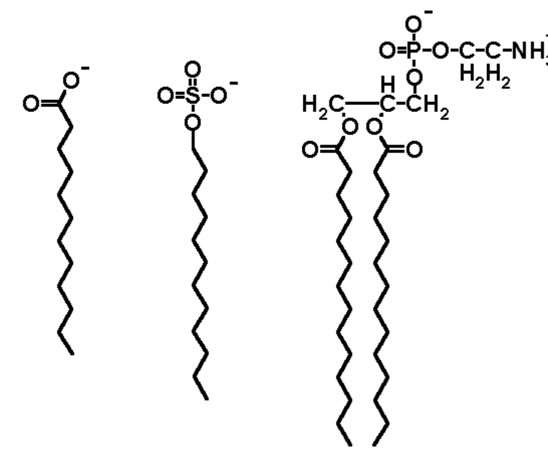


$T = T_c$

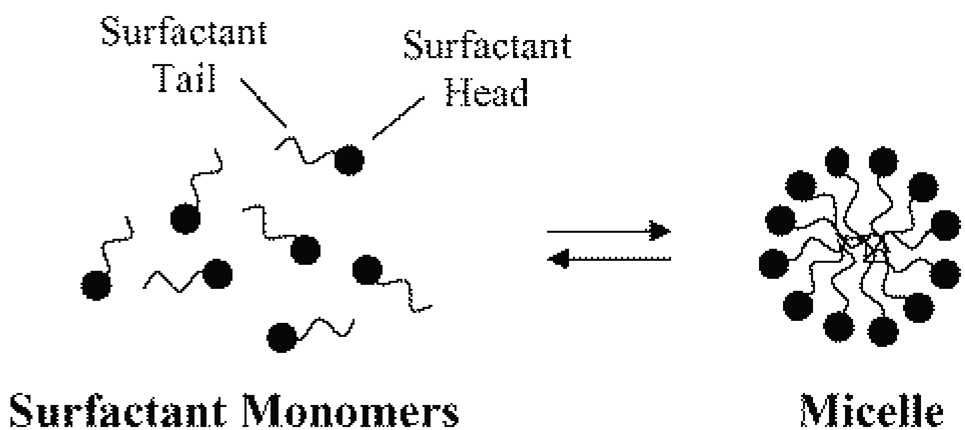


Backup slides

Surfactant molecules and micelle formation

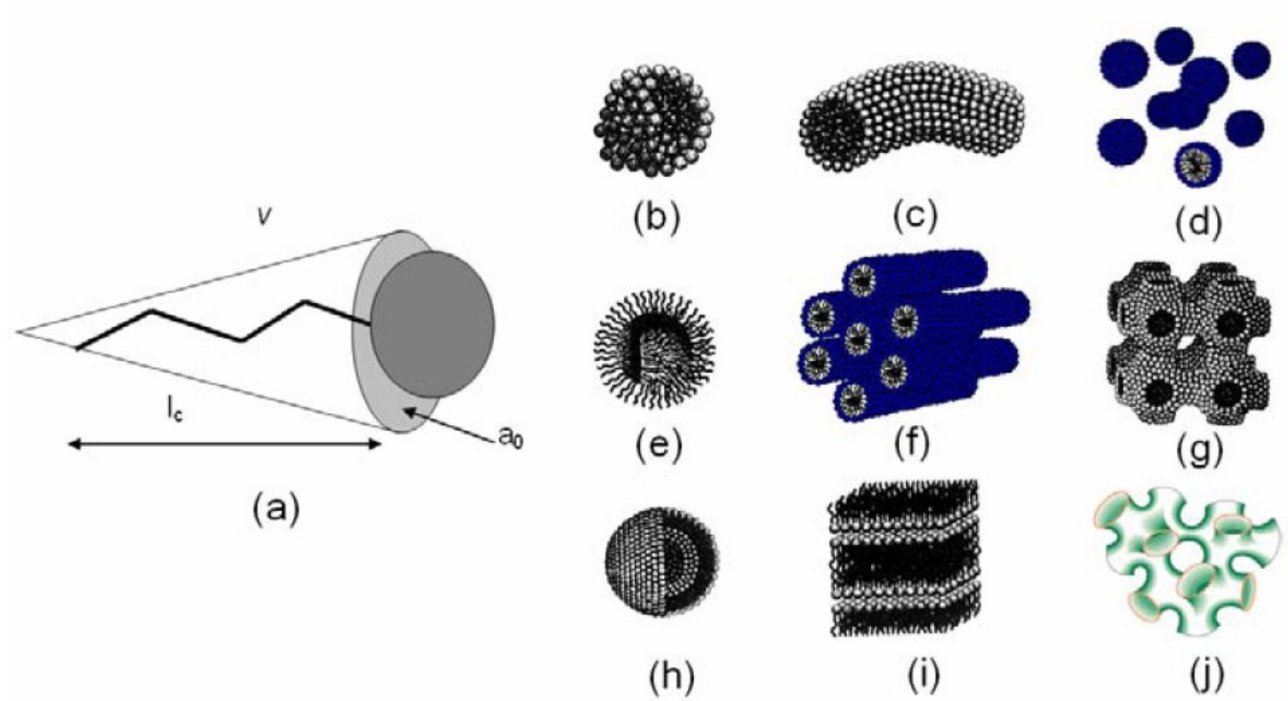


Basic mechanism



Opens for considerable richness

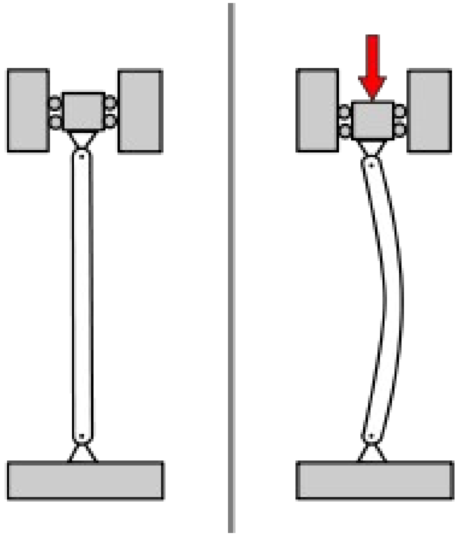
Various surfactant phases



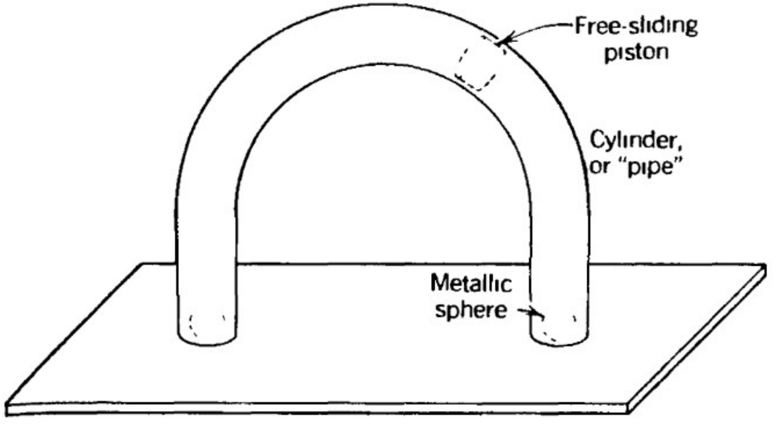
(a) An amphiphilic molecule
(b) Spherical micelle
(c) Cylindrical micelle
(d) Cubic phase
(e) Inverse micelle
(f) Hexagonal phase
(g) Bicontinuous cubic structure
(h) Vesicle
(i) Lamellar phase
(j) Sponge phase

a whole zoo

Mechanical symmetry breakdown



Buckling



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- Ising model: why ?
4- Order parameter and symmetry breakdown
5- Local order and correlation functions

II First order phase transitions *(mostly treated as a tutorial)*
1- Unstable isotherms, double-tangent and Maxwell construction
2- Spinodal and binodal

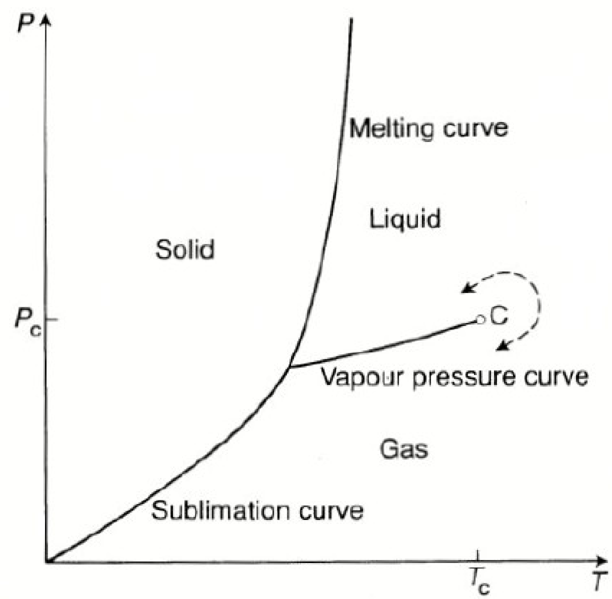
III Critical phenomena : qualitative approaches
1- Weiss molecular field
2- Variational mean-field and critical exponents
4- Landau theory
5- Correlation functions and Ginsburg-Landau functional

IV Beyond mean-field: fluctuations and scaling
1- Fluctuations
  What do mean-field practitioners really do ?
  Fluctuation correction to the saddle-point
  Ginzburg criterion, crossover behaviour
  Scattering and fluctuations: measure of structure factors
2- The scaling hypothesis: life with a large correlation length
  Homogeneity and scaling relations
  Finite size scaling: turning a drawback into an advantage

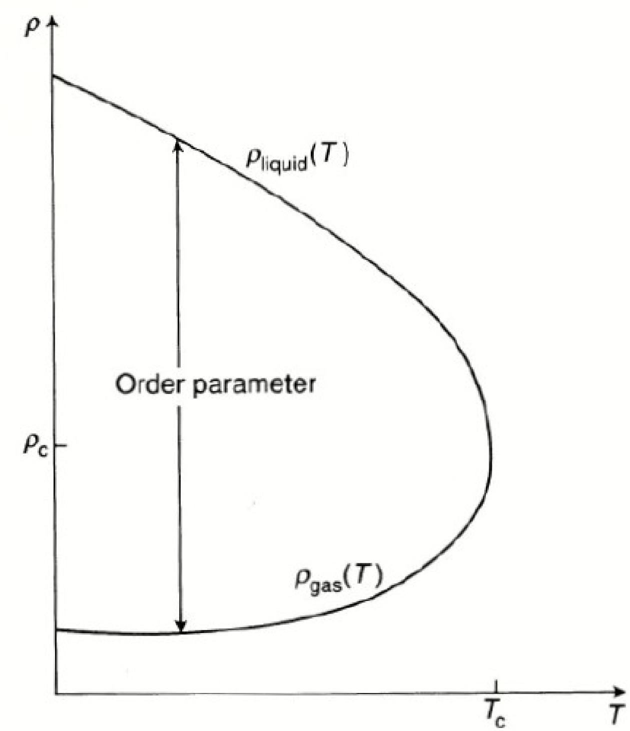
V Renormalisation group ideas
1- What are the problems ?
2- Definition of a renormalisation group transformation
3- Fixed points and universality
4- Scale invariance, critical exponents

Identify an ORDER PARAMETER

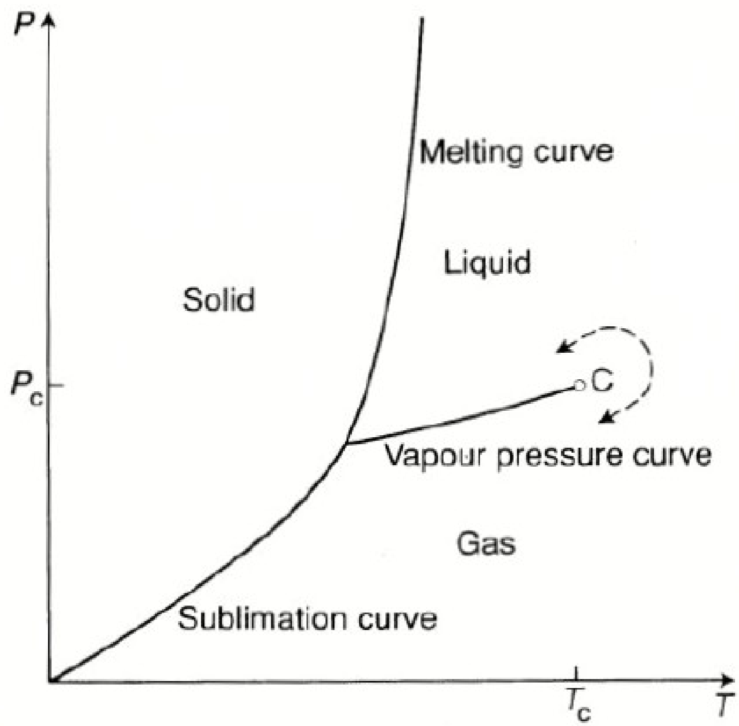
pressure



density



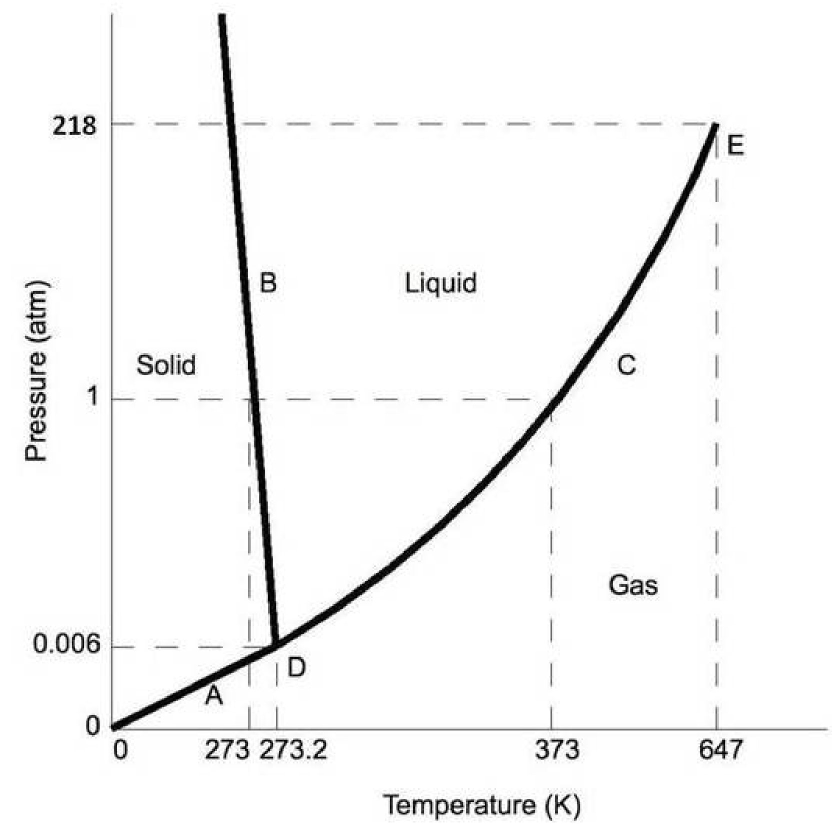
Examples and exceptions



Generic case

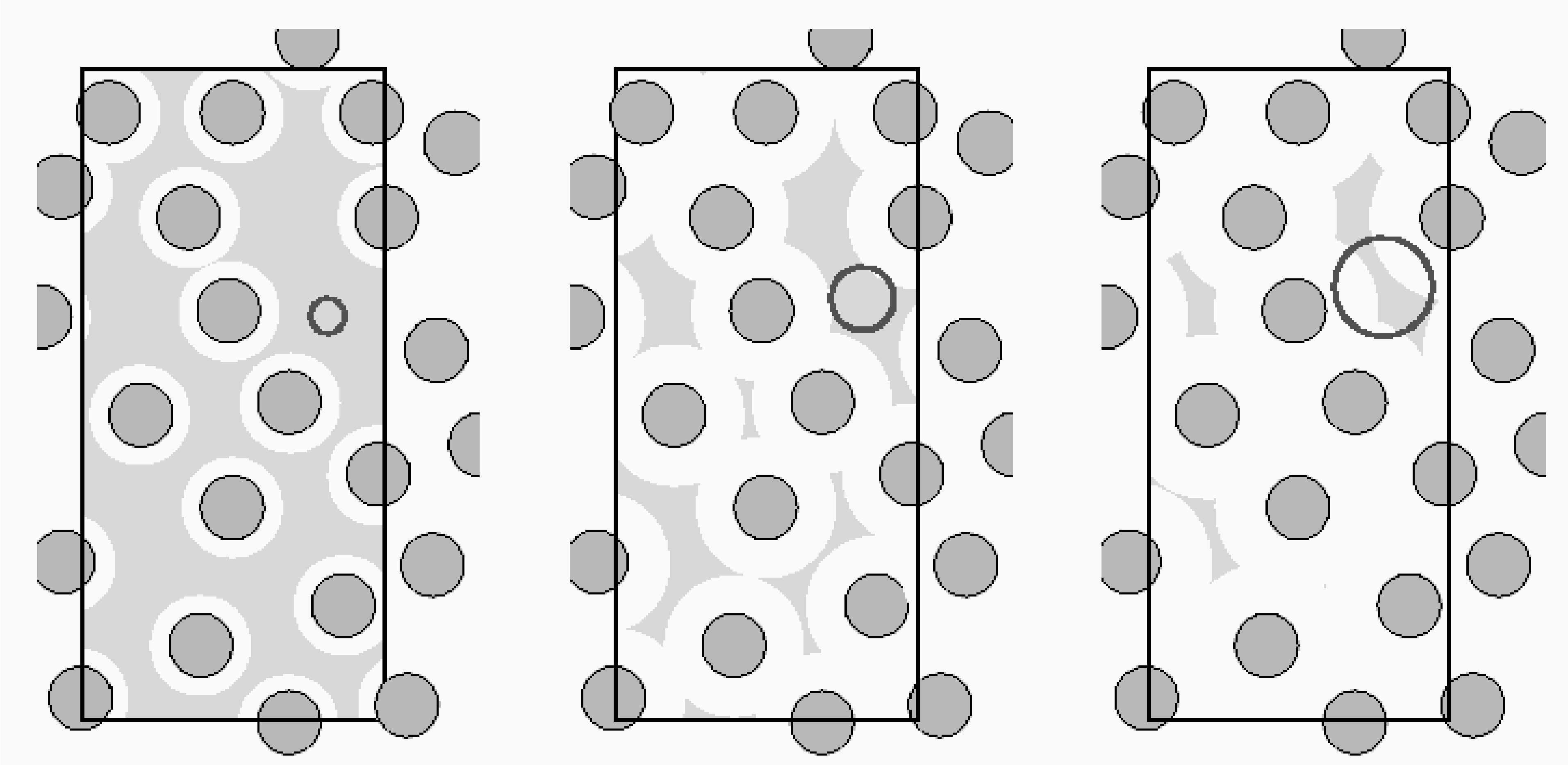
$$\frac{dP}{dT}(coex) = \frac{1}{T}\frac{L_{liq \rightarrow gas}}{v_{gas} - v_{liq}}$$

Water



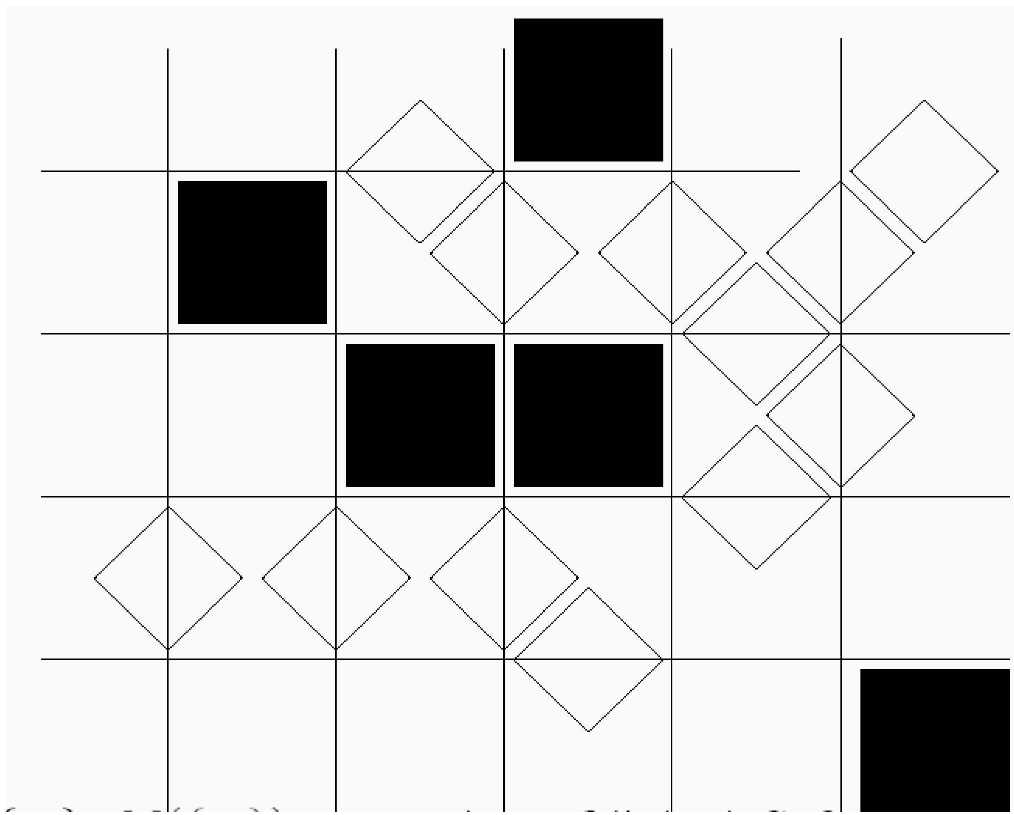
The excluded volume

Increasing the size of a tagged particle



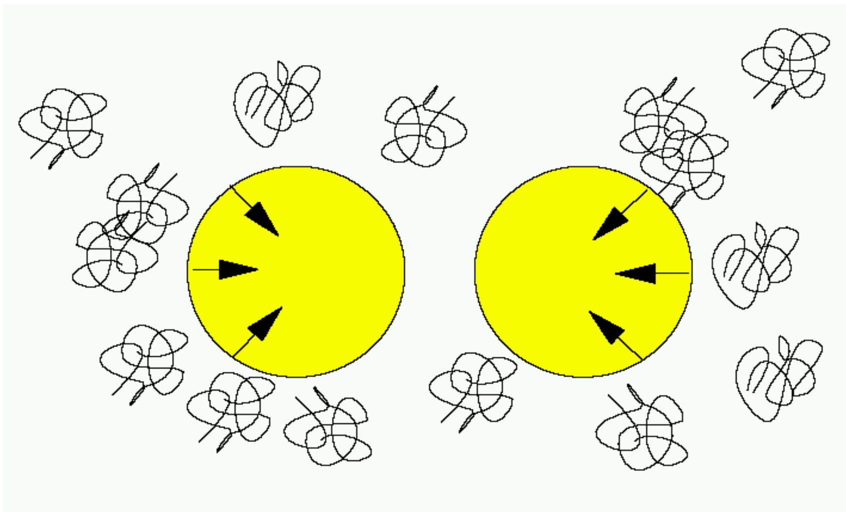
after Barrat/Hansen

Depletion forces: an exactly solvable lattice model



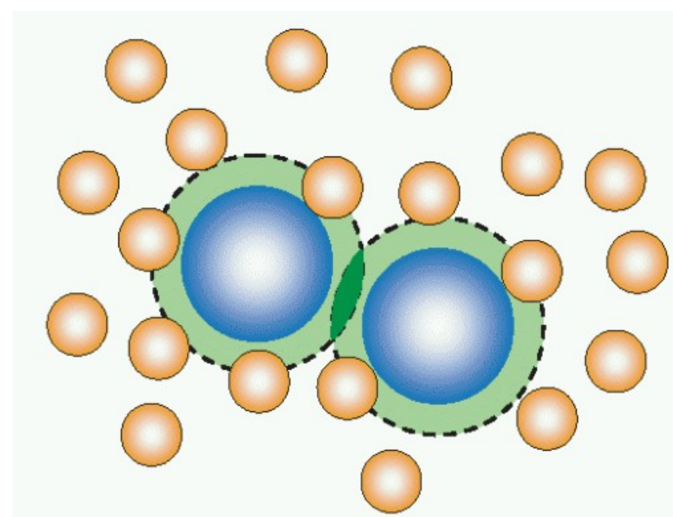
Frenkel and Louis, *Phys. Rev. Lett.* **68**, 3363 (1992)

Sphere-sphere depletion potential

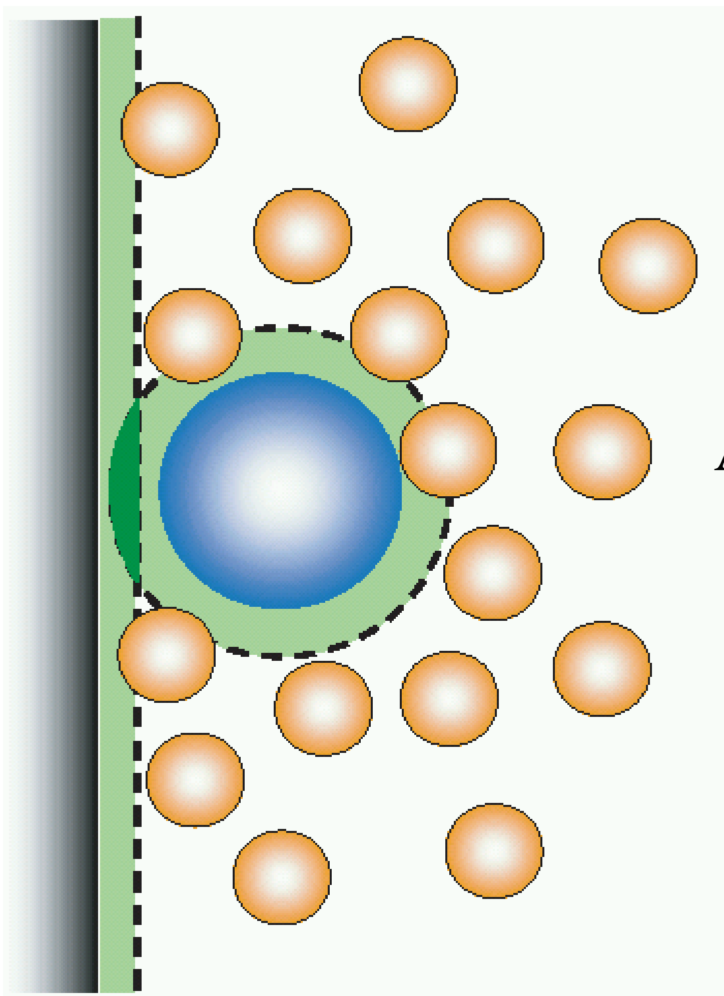


Colloid-polymer mixture

Mechanical and entropic interpretations fully coincide

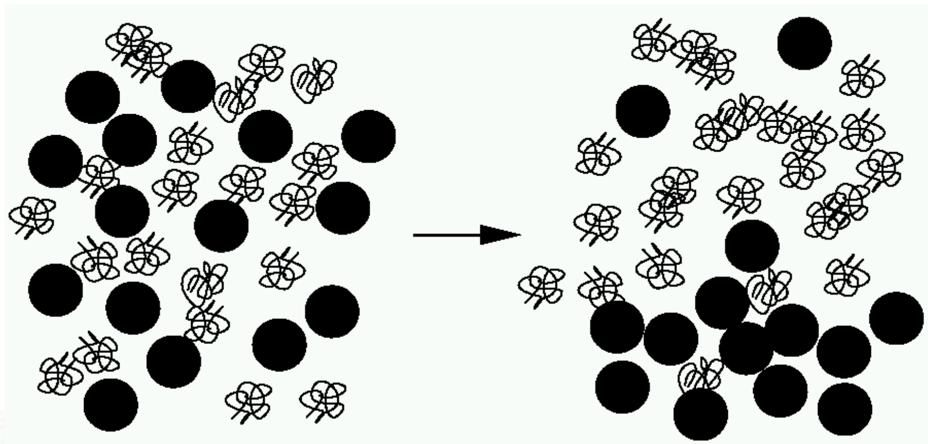


Sphere-plane depletion potential

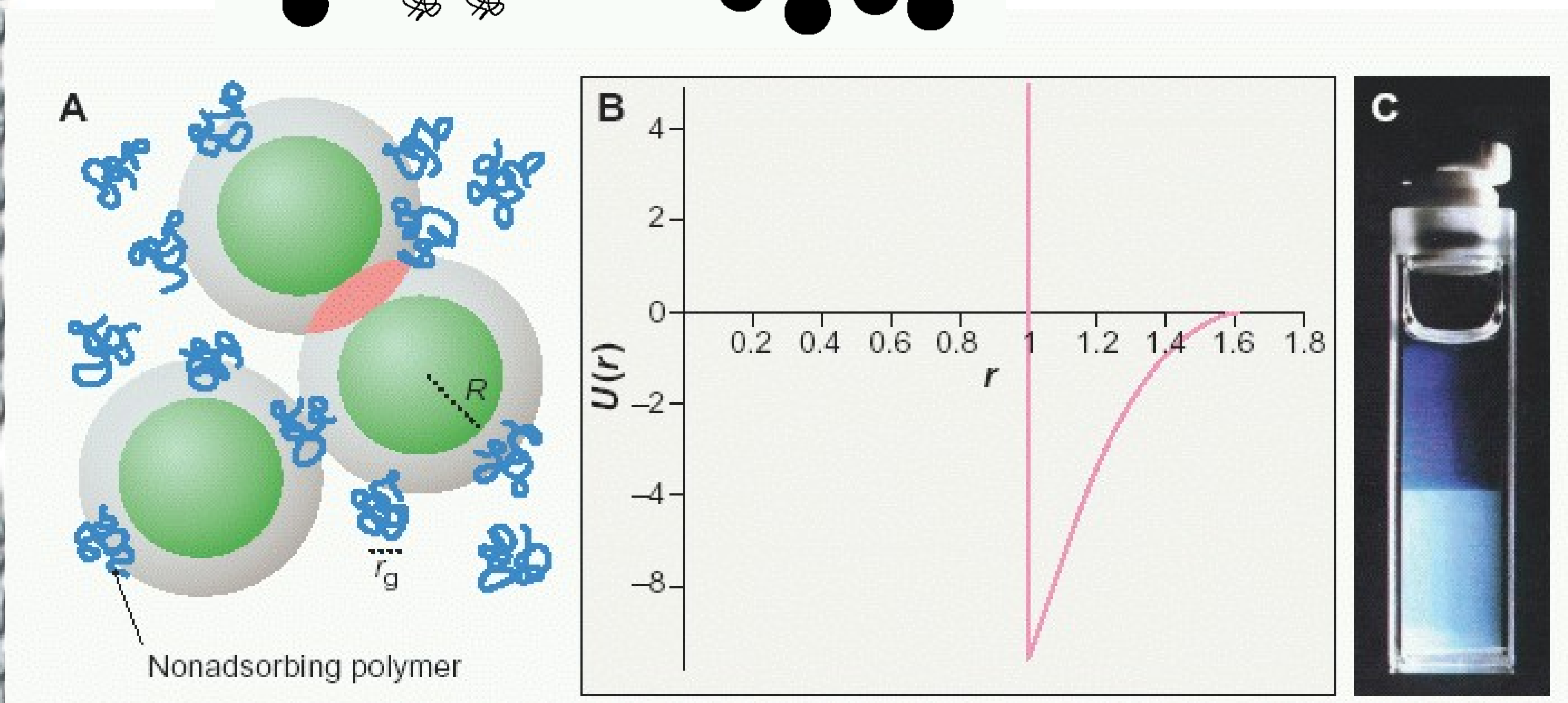


Again... uncompensated pressure
overlap of exclusion zones

Polymer induced flocculation



expected mechanism



PMMA spheres (70 nm) + polystyrene

Chapter 2

Chapter 1

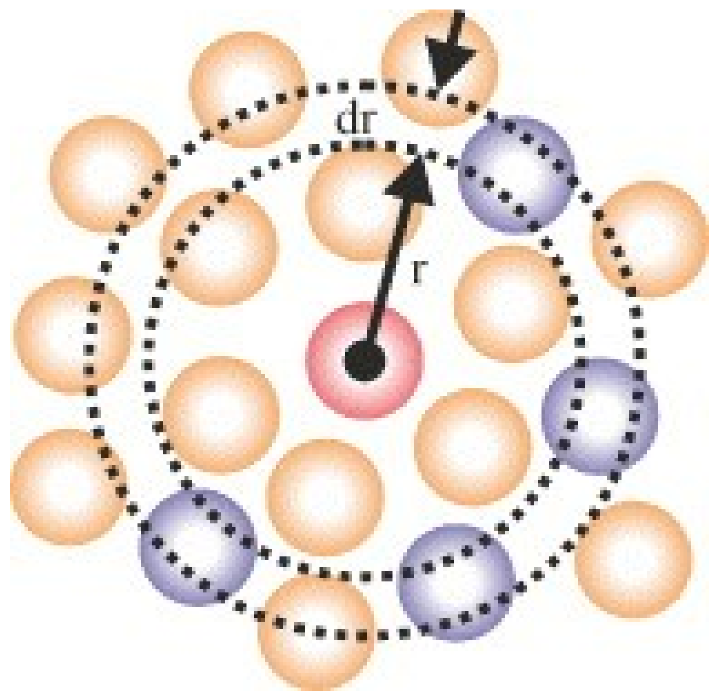
Chapter 3

Chapter 5

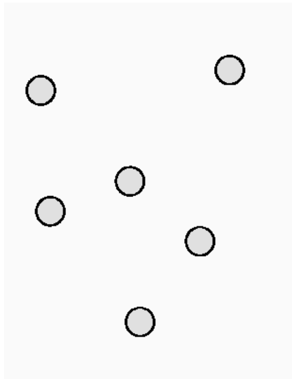
Chapter 7

Chapter 6

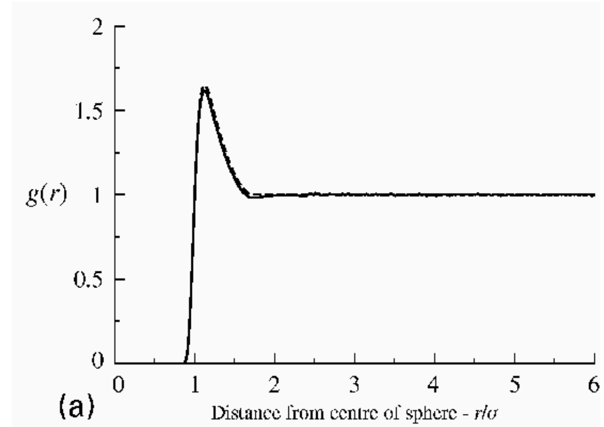
The pair correlation function *g(r)*

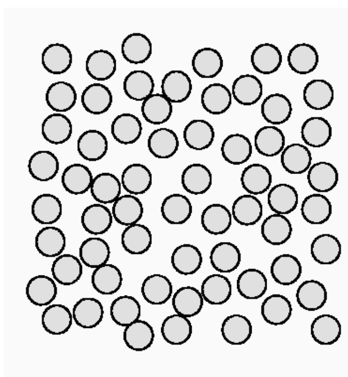


For a Lennard-Jones fluid

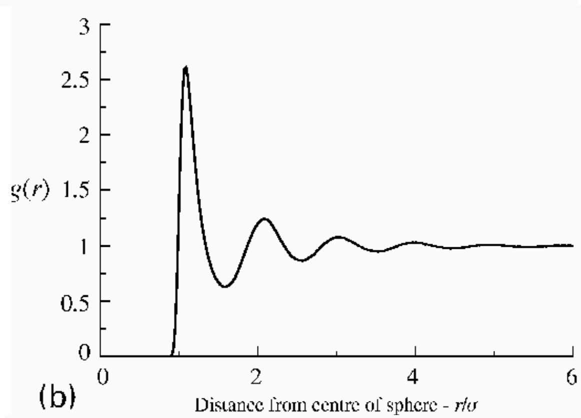


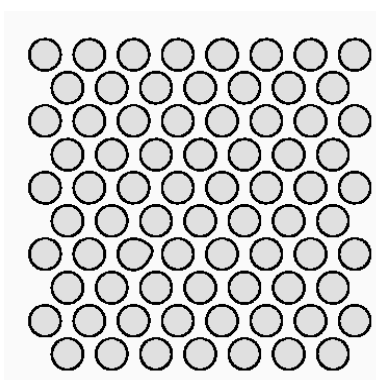
Gas



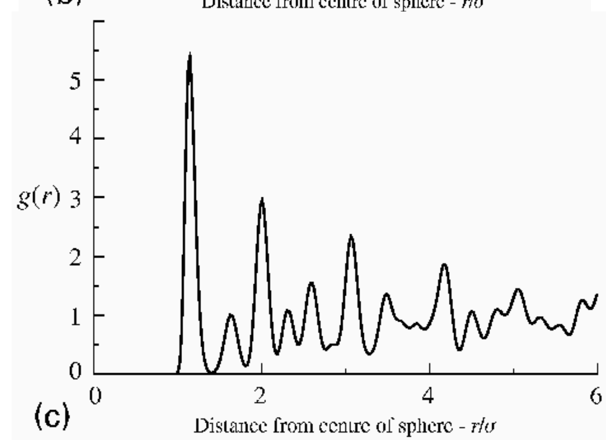


Liquid



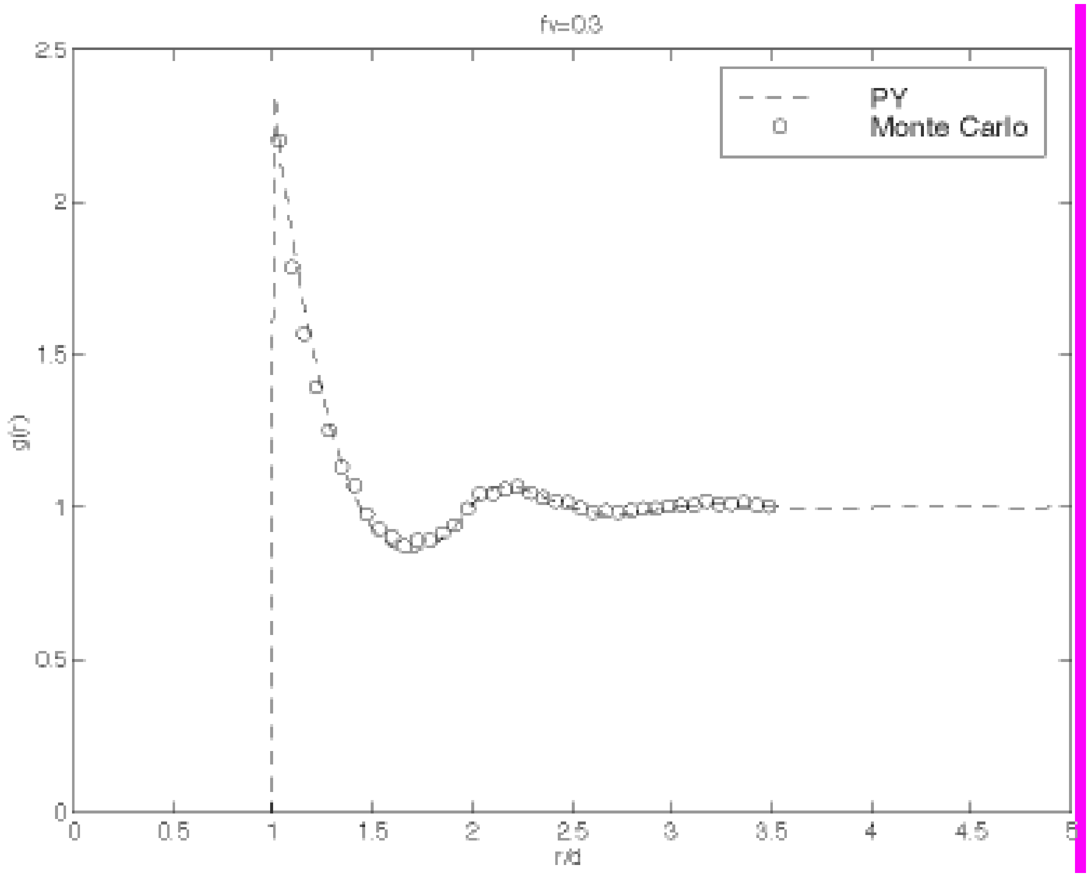


Solid



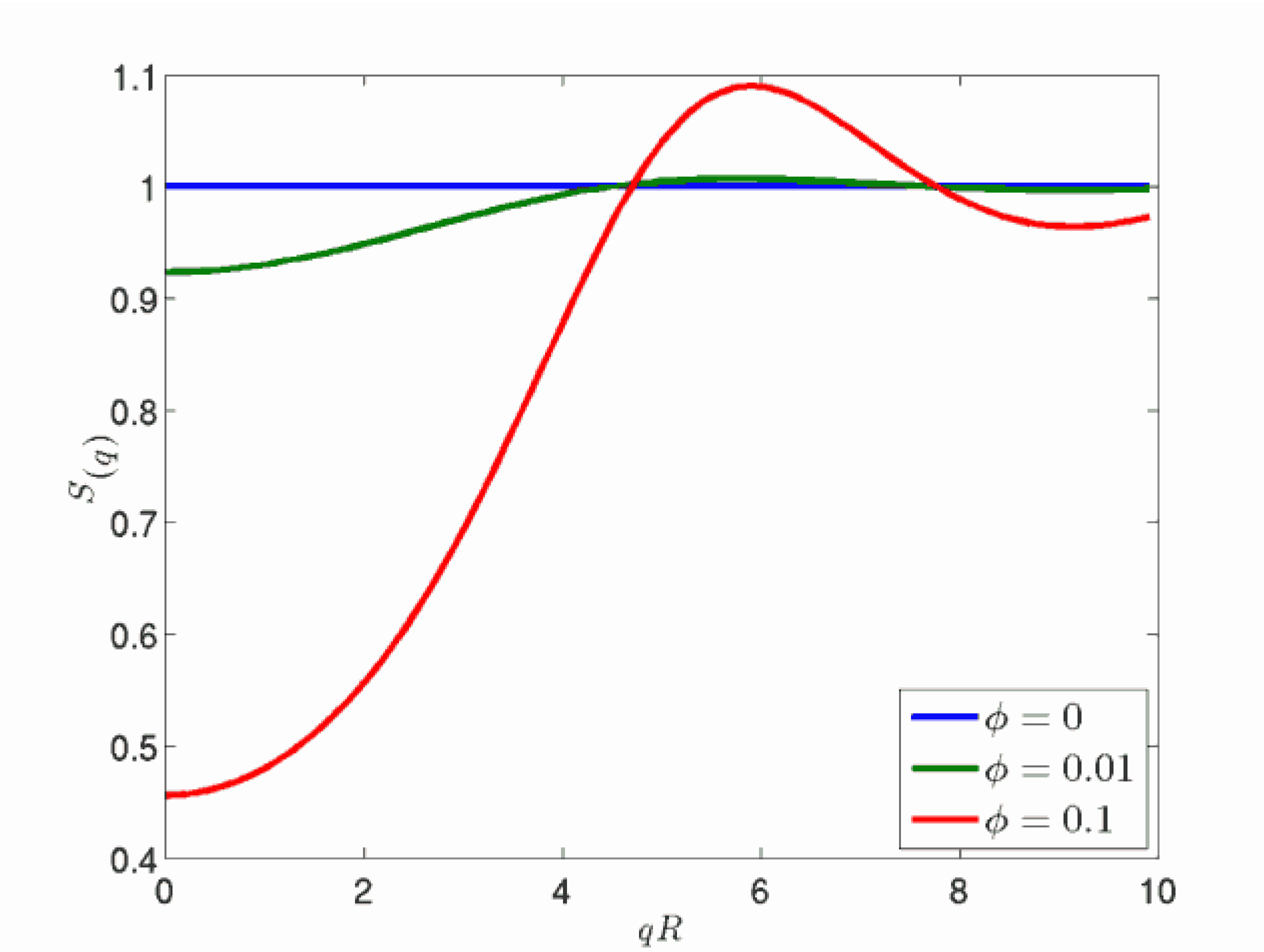
From Barrat/Hansen, *Basic concepts for simple and complex fluids* (2003)

The pair distribution function



Hard spheres ; maximum at contact

Structure factor *S(k)*



Hard spheres