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## Outline

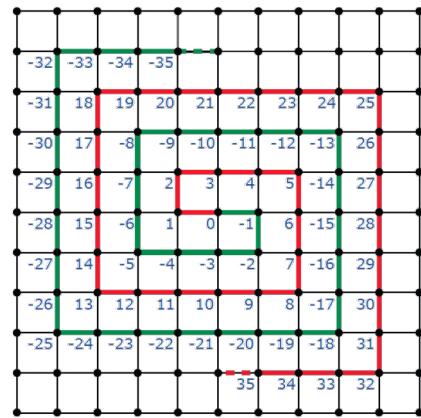
- The role of interaction's range
- The role of dimensionality
- Classification of phase transitions
- Broken symmetry
- Order parameter
- Ginzburg-Landau Theory
- Ginzburg criterion
- Scope: to point out the role of spatial dimensions and the range of interactions in a phase transition; to investigate the characteristics of different kinds of phase transitions and the consequences of a symmetry breaking phase transitions; to recognize that if the correlation length of microscopic degrees of freedom diverges at the critical point (short range interaction) there should exist a macroscopic "hydrodynamic" theory for phase transitions and their order parameters

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## The role of the interactions' range

- We showed that the one-dimensional Ising model has no finite temperature phase transition, and is disordered at any finite temperature T, but in two dimensions on the square lattice there is a finite critical temperature  $T_c$  below which there is long-ranged order
- Consider now the construction depicted in figure, where the sites s of a two-dimensional square lattice are mapped onto those of a linear chain
- Clearly we can obtain a one-to-one mapping between the sites of a two-dimensional square lattice and those of a one-dimensional chain. That is, the two-dimensional square lattice Ising model may be written as a one-dimensional Ising model



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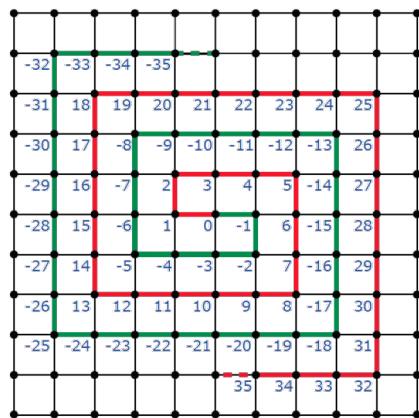
- That is:

$$H = -\frac{J}{2} \sum_{\langle i,j \rangle_{n.n.}}^{\text{square lattice}} \sigma_i \sigma_j = -\sum_{i,j}^{\text{linear chain}} J_{i,j} \sigma_i \sigma_j$$

How can this be consistent with the results we have just proven?

- The point is that the interaction along the linear chain is long-ranged. This is apparent from inspecting the site labels in figure
- With each turn of the concentric spirals in the figure, the range of the interaction increases
- It is the long-ranged nature of the interactions on our artificial one-dimensional chain which spoils our previous energy-entropy argument, because now the domain walls themselves interact via a long-ranged potential.

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## Validity and Accuracy of MFA

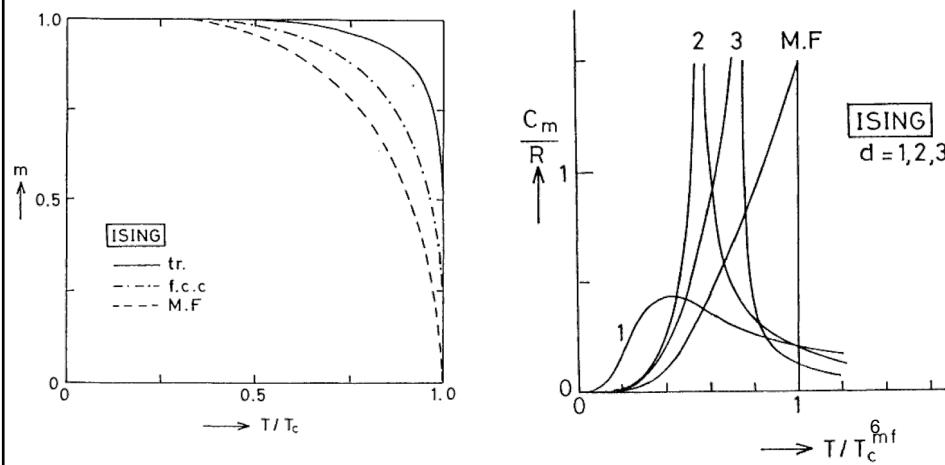
- First of all, let us compare the transition temperature,  $T_c$ , and the energy per spin at the critical point,  $u_c$ , of the Ising model on various different  $d$ -dimensional lattices with the corresponding predictions of the mean-field theory
- For this purpose, we present them in the form of  $k_B T_c / (n_{nn} J)$  and  $-(u_c/u_0)$  in the table, where  $u_0 = -n_{nn} J/2$  is the energy per spin at  $T = 0$
- Clearly, mean-field theory makes a completely wrong prediction in  $d = 1$
- However, the mean-field estimate of  $T_c$ , as well as that of  $u_c$ , improves in accuracy with the increase of space dimensionality

Lattice	$d$	$n_{nn}$	$k_B T_c / J n_{nn}$	$-u_c/u_0$
LinearChain	1	2	0	1
Honeycomb	2	3	0.5062	0.7698
Square	2	4	0.5673	0.7071
Triangular	2	6	0.6068	0.6667
Diamond	3	4	0.6761	0.4370
SimpleCubic	3	6	0.7519	0.3308
B.C.C.	3	8	0.7942	0.2732
F.C.C.	3	12	0.8163	0.2475
Mean - field	—	—	1	0

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## Validity and Accuracy of MFA

- In fact, when the thermostatic quantities, like magnetization and specific heat, are plotted as functions of  $T/T_c$  we find that the curve is closer to the corresponding mean-field prediction in higher dimension



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## MFA vs “exact” results

- We can compare also the results for the **critical exponents** obtained for the  $d$ -dimensional Ising model in the mean field approximation with the exact result for the 2D Ising model and the (Monte Carlo) numerical estimations for the 3D Ising model

	Mean-field	Ising $d = 2$	Ising $d = 3$
$(n, d)$		(1,2)	(1,3)
Specific heat	$\alpha$	0 (disc.)	$0 (\log)$
Order parameter	$\beta$	$1/2$	$1/8$
Susceptibility	$\gamma$	1	$7/4$
Order parameter ( $T_c$ )	$\delta$	3	?
Correlation length	$\nu$	$1/2$	1
			$0.119 \pm .006$
			$0.326 \pm .004$
			$1.239 \pm .003$
			$4.80 \pm .05$
			$0.627 \pm .002$

- Thus, again, we find that the **mean-field** approximation **yields better estimates for higher  $d$** . In  $d = 2$  there is substantial difference between the exact values of the critical exponents and the corresponding mean-field estimates

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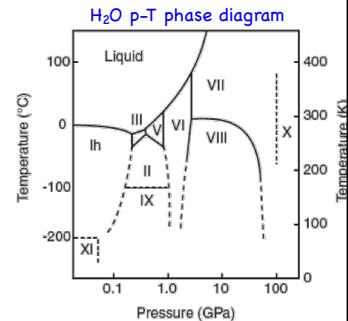
## Role of dimensionality

- The Mean Field approximation becomes exact in the limit as the number of interacting neighbours  $n_{nn} \rightarrow \infty$
- This is the case when the **range of interaction goes to infinity** or if **the spatial dimension is high**. In both cases, a site “feels” contributions from many neighbours and therefore the fluctuations average out or become even irrelevant
- If  $m$  is the order parameter of the system, then mean field theory requires that the fluctuations in the order parameter are much smaller than the actual value of the order parameter near the critical point. **Quantitatively, this means that  $\langle (\delta m)^2 \rangle \ll \langle m \rangle^2$** . This is the **Ginzburg criterion**. For Ising systems, they become irrelevant in  $d > 4$ .
- At low  $d$ , the MFA must be used with caution. Not only that it predicts wrong critical exponents, its predictions are even qualitatively wrong sometimes. As we have seen, it predicts long-range order and finite critical temperature for the 1D Ising model

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## Phase transitions

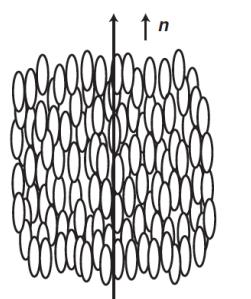
- Any substance of fixed chemical composition, water  $H_2O$ , for example, can exist in homogeneous forms whose properties can be distinguished, called **states or phases**
- Water exists as a gas, a liquid, or a solid, ice. These three **phases (states) of matter** differ in density, heat capacity, optical and mechanical properties etc.
- In general, for the same solid or liquid substance, several **distinct arrangements** of the atoms, molecules, or particles associated with them can be observed and will correspond to different properties of the solid or liquid, and thus to different phases
- Experiments thus demonstrate **phase transitions** or **changes of state**. These phase transitions are **not always induced by modification of atomic or molecular arrangements** (for example: ferromagnetism and superconductivity which corresponds to the modification of electronic properties).



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- A **phase transition** is induced by acting from the outside to modify **state variables** characterizing the system: temperature, pressure, volume, magnetic or electric field, etc.
- Normally, if we slightly modify the state variables of a thermodynamic system, properties change with continuity
- This is not always true: it is common experience that, under certain conditions, a **small change in the state variables induces drastic changes in the properties**; for example, liquid boiling, solid fusion, paramagnetic-ferromagnetic state-change
- A phase transition occurs when a phase becomes unstable in the given **thermodynamic conditions**. We have learned that under fixed experimental condition there is a particular thermodynamic potential which characterizes the **equilibrium**: the stable phase corresponds to the **minimum** of the respective **thermodynamic potential** (Enthalpy: constant  $\{N,p,S\}$ , Helmholtz free energy: constant  $\{N,V,T\}$ , Gibbs free energy: constant  $\{N,p,T\}$ , Grand potential: constant  $\{\mu,V,T\}$ , etc.)



Molecules in a nematic liquid crystal tends to be aligned along a particular direction

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## Latent heat...

- In general, a transition is manifested by a series of associated physical events. For most of them, the transition is accompanied by **latent heat** and **discontinuity of a state variable** characterizing each phase (for example density in the case of a solid→liquid transition).
- Latent heat is a quantity of heat, and thus of energy, that must be supplied in order to change from one phase to the other phase, even without changing p or T
- Consider a container with a **liquid at fixed pressure**, as we slowly increase its temperature. When the system first reaches the liquid-gas transition at  $T=T_v$ , a small bubble of gas will form at the top; by supplying heat without a further increase of T, this bubble will gradually grow, inflating and filling the container
- At constant  $\{N,p,T\}$  we characterize the equilibrium phase with the **Gibbs free energy**:

$$G(N, p, T) = U - TS + pV$$

whichever state minimizes G, it wins.

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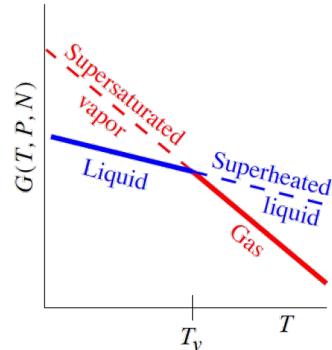
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## ... difference in entropies

- The Euler relation  $E=TS-pV+\mu N$  tells us that  $G=\mu N$ . So, the state with the **lower chemical potential will be favored**, and the **phase transition will occur when  $\mu_{liq} = \mu_{gas}$** .
- That makes sense; at a **liquid-vapor boundary**, one can **exchange energy, volume, or particles**. Energy will exchange until the temperatures are equal, volume will exchange until the pressures are equal, and then **particles will move from liquid to gas until the chemical potentials are equal**.
- Varying the temperature at fixed pressure and number of particles, we have

$$\left( \frac{\partial G}{\partial T} \right)_{N,P} = -S$$

- At the phase boundary, the two free energies agree. The difference in slopes of the two lines is given by the **difference in entropies** between the liquid and the gas



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## First order phase transitions

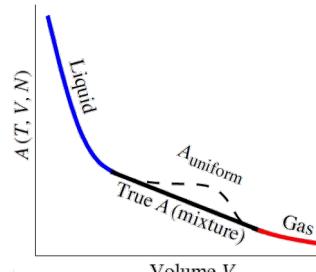
- The thermodynamic definition of the entropy  $dS = dQ/T$  tells us that the entropy difference is given by the latent heat over the transition temperature. This entropy difference is, in general, connected to a difference in "order" (phase space volume) among the two phases
- The fact that the Gibbs free energy has a kink at the phase transition reflects the jump in the entropy between liquid and gas; abrupt phase transitions will have jumps in the first derivatives of their free energies. This led early workers in the field to term these transitions **first-order phase transitions**
- The physical quantities which show discontinuity are extensive (**S** and **V** in our specific example (liquid  $\rightarrow$  gas), **M** in the ferromagnetic case)
- The relevant thermodynamic potentials to observe such jumps in their first derivatives are those expressed in terms of the conjugated intensive variables [ $G(N,p,T)$  in our example]

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- Thermodynamic potentials which have the relevant extensive quantity as independent variable [ $A(N,V,T)$  in our example] show a first order transition with a rectilinear segment. In our liquid  $\rightarrow$  gas transition

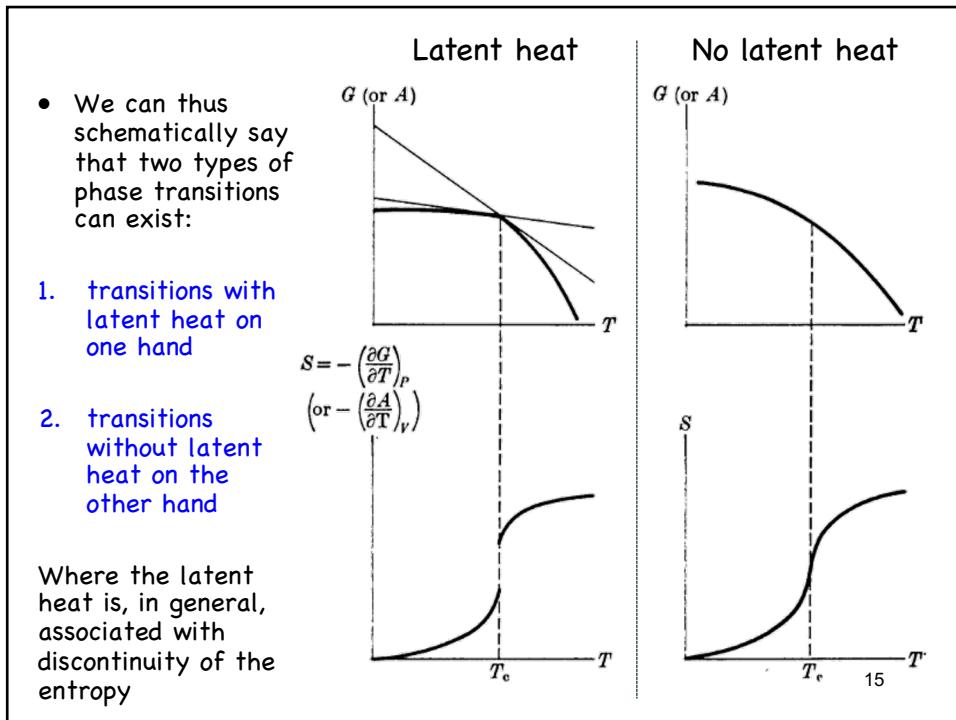
$$P = - \left( \frac{\partial A}{\partial V} \right)_{N,T} = \text{const.} \quad V_{\text{liq.}} < V < V_{\text{sol.}}$$



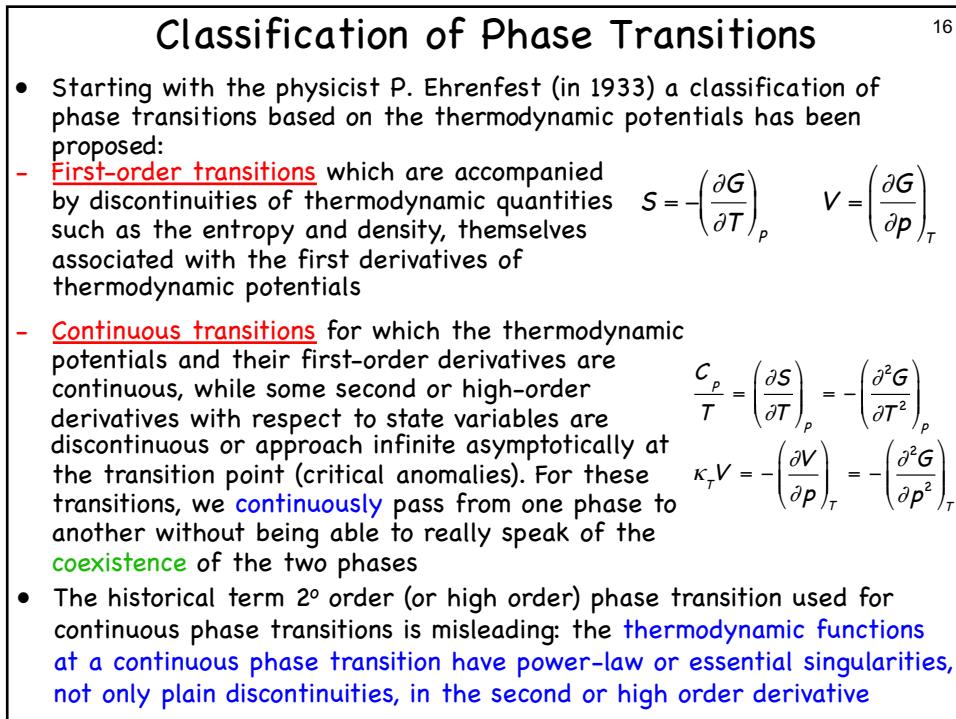
- we have **phase coexistence**: the system is in spontaneous heterogeneous state
- It has also been observed that an entire series of phase transitions takes place with no latent heat... or discontinuity of state variables (for example the **critical point** in the liquid/gas transition, or the **Curie point** in the ferromagnetic/paramagnetic transition)
- At all points of the liquid-vapor coexistence curve, with the exception of the terminal point (critical point), latent heat and discontinuity of density are simultaneously observed in the transition. At the critical point, on the contrary, we have learned that one continuously passes from the liquid phase to the gas phase; anyway **critical anomalies** are present

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## Some examples of phase transitions

- Solid  $\leftrightarrow$  Liquid (first order)
- Liquid  $\leftrightarrow$  Gas (first order, critical point)
- Phase separation in multi-components fluids (first order, critical point)
- Normal liquid  $\leftrightarrow$  Superfluid (critical point)
- Paramagnetic  $\leftrightarrow$  Ferromagnetic (first order, critical point)
- Normal metal  $\leftrightarrow$  Superconductor (critical point)
- Structural phase transition in crystals (in general, first order)
  
- Connected physical phenomena:
  - Static equilibrium (thermodynamic properties, spatial correlations)
  - Dynamic equilibrium (transport properties, space-temporal correlations)
  - Non equilibrium phenomena (nucleation, metastability)
  
- Until now we have discussed mainly static equilibrium phenomena in the liquid  $\leftrightarrow$  gas and in the paramagnetic  $\leftrightarrow$  ferromagnetic phase transitions

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## Symmetries in the model

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- In general the Hamiltonian,  $H$ , of a system possess some symmetries, i.e. there exists some transformations which leave unchanged  $H$ . Some examples:
  1. Simple substance with pair interaction  $\hat{H} = \hat{K} + \frac{1}{2} \sum_{i \neq j}^N v(\hat{\vec{r}}_i - \hat{\vec{r}}_j)$   
where  $K$  is the kinetic energy operator.  
If we assume periodic boundary conditions, this Hamiltonian is invariant for a generic translation  $R$ :  
$$\hat{T}_R \hat{H} = \hat{H}$$
  2. Ferromagnetic Ising model without external magnetic field:  
$$\hat{H} = -\frac{1}{2} \sum_{i,j \in n.n.} J s_i s_j \quad s_i = \pm 1 \quad J > 0$$
  
the Hamiltonian is invariant under spins-inversion:  $\hat{I} \hat{H} = \hat{H} \quad \hat{I} s_i = -s_i$
  3. Ferromagnetic Heisenberg model without external magnetic field:  
$$\hat{H} = -\frac{1}{2} \sum_{i,j \in n.n.} J \hat{\vec{s}}_i \cdot \hat{\vec{s}}_j \quad J > 0$$
  
this Hamiltonian is invariant for spin-rotations:  $\hat{R}(\theta, \varphi) \hat{H} = \hat{H} \quad \forall (\theta, \varphi)$

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## Spontaneous broken symmetry

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- Question: macroscopic physical properties will show the same symmetries present in the Hamiltonian?
- This is not always true! ... and phase transitions are responsible of this fact
- For certain values of the state variables, for example at high temperature, this is true; but there are regions of the phase diagram where macroscopic physical properties posses lower symmetry respect to the Hamiltonian  $\Rightarrow$  spontaneous broken symmetry. For example:
  - A. 1) a system in the fluid phase is uniform; local average values of any quantity are independent from the position; this is the same invariance which the Hamiltonian possess.  
2) At low T, we know that a crystalline solid is formed (apart from liquid Helium!); if  $\{R_i\}$  represent the equilibrium positions of the particles, given that the system is no more uniform, its properties are invariant only for  $T(R_i)$  translations and no more for a generic translation  $T(R)$ : system symmetry is lower than Hamiltonian symmetry

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- B. 1) At high temperature the ferromagnetic Ising model is found in the disordered paramagnetic phase, thus the system is invariant under the transformation which reverts all the spins  
2) At low T, we have seen that the system possess spontaneous magnetization; thus the system is no more invariant under the inversion of all the spins  $\Rightarrow$  spontaneous symmetry breaking
- C. 1) At high temperature even the Heisenberg model is found in the disordered paramagnetic state  
2) Even in this case at low temperature there is spontaneous magnetization, the spins points, on average, in a specific direction; contrarily to the Hamiltonian, the system is no more invariant under rotation  $\Rightarrow$  spontaneous symmetry breaking
- Warning: not all phase transitions are associated with a spontaneous symmetry breaking; one example is the liquid-gas transition
- It is safe to say, though, that if the two materials have different symmetries, they realize different phases

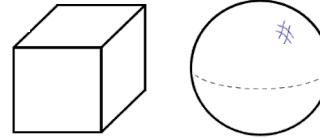
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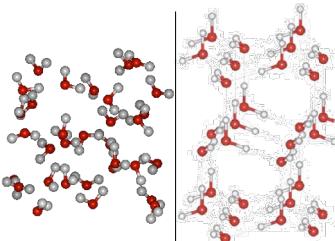
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## Identify the broken symmetry

- Which is more symmetric a cube or a sphere?  
Clearly, the sphere: One can rotate the cube by 90° in various directions and not change its appearance, but one can rotate the sphere by any angle and keep it unchanged.



- Which state is more symmetric water or ice?  
Naively, the ice looks much more symmetric; regular arrangements of atoms forming a lattice structure. Ice has a discrete rotational and translational symmetry. The water looks irregular and disorganized. On the other hand, if one rotated by an arbitrary angle, it would still look like water! Water is not a snapshot; it is better to think of it as a combination (or ensemble) of all possible snapshots. Water as a phase has complete rotational and translational symmetry



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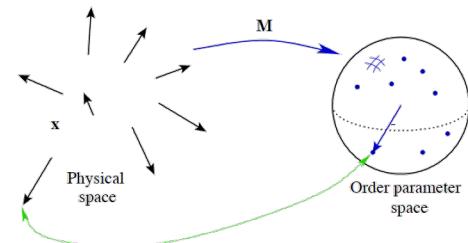
## The order parameter

- A symmetry-breaking transition transforms a disordered (more symmetric) state into an ordered (less symmetric) medium, or an ordered medium into a medium with a more intricate form of order
- A phase transition in a macroscopic system affects an enormous number of degree of freedom. A rationale **macroscopic theory** should contain, however, only a **minimal number of relevant variables**.
- Thermodynamics uses a limited set of macroscopic variables characterizing the state of the physical system; even this may be excessive if we want to grasp the single most important feature and to give a quantitative **measure of order that emerges as a result of a symmetry-breaking transition**.
- Landau has coined for this purpose the term **order parameter**. Order parameter can mean different things in different circumstances. It can be associated with various physical variables or their combinations; it can be a mathematical object of various kind: **real or complex, scalar or vector, depending on the symmetry of the ordered phase**

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- The widely used appellation “parameter” is, however, inadequate; it is, in fact, a **field variable**. In a spatially extended continuous medium, the **order parameter may vary in space and time on a macroscopic scale far exceeding the scale of any microscopic structure that may exist in the medium, or the scale of statistical fluctuations** The important variables are thus combined into an “order parameter field”.
- In figure we see the order parameter field for a magnet. By becoming magnetized, the system at each position  $r = (x, y, z)$  have a finite magnetization  $M(r)$ . This material has broken the rotational symmetry
- The order parameter  $M$  labels which of the various broken symmetry directions the material has chosen **locally**
- Usually, the material has lowest free energy when the order parameter field is uniform, i.e., when the symmetry is broken in the same way throughout space. In practice, though, the material often does not break symmetry uniformly.



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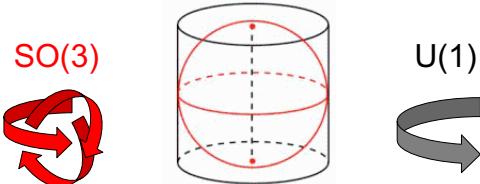
## Broken symmetries and group theory

- From a group-theoretical point of view, “**broken symmetry**” means that below the transition the **equilibrium state of the system is no longer invariant under the full group of symmetry transformation  $G$** , as it was above the transition
- Certain symmetries are “broken”, such that this state is now only **invariant under a subgroup  $H$  of the full group  $G$  of symmetry transformation**
- While the group  $H$  describes the remaining symmetries of the order parameter, the **coset (or factor) space  $R$  (formally  $R=G/H$ ) characterizes the broken symmetries**, i.e. those transformations that change the ground state perceptibly (although they leave the energy invariant, because the corresponding states are degenerate with respect to the energy)
- Example 1: Ferromagnet.** The order parameter is given by the magnetization  $M$  a real three-component vector. Above the transition the spin system is invariant under arbitrary **global rotations in the 3D spin space**, i.e.  $G=SO(3)$  (Special Orthogonal group)

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- Below the Curie temperature  $T_c$  the spins are aligned along the preferred direction of the Magnetization  $\mathbf{M}$ . Now the ground state is invariant only under rotation about the axis parallel to  $\mathbf{M}$ . This remaining symmetry corresponds to the group of transformations  $U(1)$ , (Unitary group) i.e.  $H=U(1)$ . The broken symmetry is  $R=SO(3)/U(1)$



- Example 2: BCS superconductor or superfluid  $^4\text{He}$ . Here the order parameter is given by a single complex parameter  $\psi=\psi_0 e^{i\theta}$ , with amplitude  $\psi_0$  and phase ("gauge")  $\theta$ . Above  $T_c$  the system is invariant under arbitrary change of the phase. This invariance is equivalent to a  $U(1)$  symmetry, i.e.  $G=U(1)$  the group of rotations about a single axis. Below  $T_c$  a particular value of  $\theta$  is spontaneously preferred hence the  $U(1)$  symmetry is completely broken:  $H=\text{identity}$
- This discussion, somewhat formal, speak about really important physical phenomena, in some cases intuitively well known!

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## Ginzburg-Landau-Onsager mean field theory

- In contrast to the Van der Waals-Weiss formulation of mean-field theory, the Landau formulation by passes the main difficulty of statistical mechanics, namely, that of calculating the partition function from the given microscopic Hamiltonian of the system
- Landau theory is a **phenomenological theory**; establishing the occurrence of a phase transition in any particular system, which is described by a given microscopic Hamiltonian, is not the aim of this formalism.
- At the phenomenological level, the existence of a phase transition in a system is considered as the **starting point of the Landau theory**.
- The advantage of this kind of approach [Landau (1937–1941), Onsager (1949) and Ginzburg-Landau (1950)] is that it does not require us to describe in any detailed fashion the microscopic structure of the medium: it is enough to use its symmetry properties to derive the equations of motion on the large "hydrodynamic" scale; the detailed microscopic structure affects only coefficients rather than the general form of these equations

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- There are **three main ingredients** of the phenomenological Landau theory of symmetry-breaking transitions in equilibrium systems:

1. First, one has to **identify the appropriate order parameter**,  $\Psi$ , for the phase transition under investigation. An **uniform order parameter** is the ingredient of the premier **Landau theory**;  $\Psi=\Psi(\mathbf{r})$  in the **Ginzburg-Landau** version of the theory. We can speak therefore of the **order parameter field**  $\Psi(\mathbf{r})$  over  $d$ -dimensional real space (or space-time). The medium is **uniform** if the value of  $\Psi$  is everywhere constant; it is **disordered** if  $\Psi=0$ , and **ordered** otherwise. A disordered state is necessarily uniform, but an ordered one may be not
1. The second ingredient is the assumption that a **free energy density**,  $f$ , which is a function of the order parameter, its spatial derivatives (obviously only in the Ginzburg-Landau version) and the temperature, **can adequately define the preferred state of the system** by reaching a minimum in the equilibrium state:  

$$f(\Psi(\vec{r}), T)$$
2. Then the third ingredient is the hypothesis that **in the vicinity of the transition point, where  $\Psi$  is small, the free energy density,  $f$ , can be expanded in terms of the order parameter**

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- $f$  can be constructed out of **symmetry considerations** alone, so that the same form would be **applicable to a variety of physical systems**. The simplest model-free-energy-densities can be constructed by combining the lowest order terms that posses the required symmetries.
- If one intends to construct a theory where the order would emerge spontaneously "out of nothing", rather than being brought in by design,  $f$  should not favour any particular state of broken symmetry. Therefore the simplest term in  $f(\Psi, T)$  is a "**potential**" term,  $V(\Psi, T)$ , which **should be invariant to applicable symmetry transformations of the order-parameter-space**
- The other necessary terms should include derivatives of the order parameter field. These terms should discourage spatial in-homogeneities. Without these terms, arbitrarily discontinuous (certainly non-physical) fields would not be ruled out. The lowest order "**kinetic**" term will include only the first derivatives
- The **simplest example** is a **local** Ginzburg-Landau  $f(\Psi, T)$  dependent on a **real scalar order parameter**  $\Psi(\mathbf{r})$  :

$$f(\Psi, T) = \left[ \frac{1}{2} |\vec{\nabla} \Psi(\vec{r})|^2 + V(\Psi(\vec{r})) \right]$$

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## Local order parameter

- In fact, we shall consider now a **spatially non-uniform order parameter**, for example, arising from an in-homogeneous external field
- This is the Ginzburg-Landau generalization of the Landau-theory, which was historically introduced to study the normal-metal/superconductor phase transition (2003 Nobel prize: Ginzburg, Abrikosov, Leggett)
- Anyway, even in the absence of an external field, it is useful to consider spatially non-uniform order parameter  $\Psi(\mathbf{r})$  to gain a deep insight into the physical meaning of the Landau free energy and to appreciate its fundamental importance in the field theoretic formulations of statistical mechanics.
- Suppose we divide the Ising spin system into **blocks** of linear size  $L$ . We define the **local magnetization**  $m_L(\mathbf{r})$  within each block centered at  $\mathbf{r}$  by the relation

$$m_L(\vec{r}) = \frac{1}{N_L(\vec{r})} \sum_{i \in \vec{r}} \sigma_i$$

where  $N_L(\mathbf{r})$  is the number of spins in the block centered at  $\mathbf{r}$       29

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- Thus  $\mathbf{r}$  does not refer to any specific single lattice site but to a block (or cell) of volume  $L^d$  (where  $d$  is the dimensionality of the system) centered around  $\mathbf{r}$ . Therefore,  $m_L(\mathbf{r})$  is the local order parameter and, in the general notation, can be denoted by  $\Psi(\mathbf{r})$ .
- Being  $a$  the lattice constant of the lattice, If  $a \ll L$  there will be large number of spins within each block and  $m_L(\mathbf{r})$  will vary smoothly over space
- This process of replacing the microscopic description by a description in terms of coarser variables is called "**coarse-graining**". Although coarse-grained magnetization is not unique and depends on  $L$ , we do not need to choose any specific value of  $L$  for explaining the conceptual framework under consideration.
- If  $f(m_L(\mathbf{r}))$  is the free energy of the block centered around  $\mathbf{r}$  corresponding to the specific local magnetization  $m_L(\mathbf{r})$  then, at first sight, it may appear that the total Landau free energy  $F$  should be  $F = \sum_{\mathbf{r}} f(m_L(\mathbf{r}))$ , but this would be wrong...

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- ... because it does not take into account the free energy cost of maintaining different local magnetizations in adjacent cells
- Using the fact that  $m_L(\vec{r})$  varies slowly in space, the **total free energy** corresponding to the particular order parameter profile  $\{m_L(\vec{r})\}$  is approximately

$$F\left(\{m_L(\vec{r})\}, T\right) = \sum_{\vec{r}} \left[ f(m_L(\vec{r}), T) + \frac{c}{2} |\vec{\nabla} m_L(\vec{r})|^2 \right]$$

- where  $c > 0$ , and

$$f(m_L(\vec{r}), T) = a_0(T) + \frac{1}{2} a_2(T) m_L^2(\vec{r}) + \frac{1}{3} a_3(T) m_L^3(\vec{r}) + \frac{1}{4} a_4(T) m_L^4(\vec{r}) + \dots$$

- By construction,  $m_L(\vec{r})$  varies slowly and smoothly in space and has **no Fourier component corresponding to the wavelength smaller than  $L$**
- Thus, in general, for a system (not necessarily a magnetic system) with a scalar order parameter, Landau-Ginzburg free energy functional is given by

$$F(\Psi(\vec{r}), T) = \int d^d \vec{r} \left[ \frac{c}{2} |\vec{\nabla} \Psi(\vec{r})|^2 + a_0(T) + \frac{1}{2} a_2(T) \Psi^2(\vec{r}) + \frac{1}{3} a_3(T) \Psi^3(\vec{r}) + \frac{1}{4} a_4(T) \Psi^4(\vec{r}) + \dots \right]$$

## Continuous phase transitions

- We consider the case of a **uniform order parameter** (Landau theory).
- We begin with the discussion for a system like a uniaxial magnet whose free energy density  $f(\Psi, T)$  has the symmetry

$$f(\Psi, T) = f(-\Psi, T)$$

- For such a system the coefficients of the odd powers of  $\Psi$  in the "potential" term must all vanish simultaneously at all  $T$ :

$$f(\Psi, T) = \frac{1}{2} a_2(T) \Psi^2 + \frac{1}{4} a_4(T) \Psi^4$$

with  $a_4(T) > 0$  ;

- here we have assumed also that all higher order even terms can be neglected. In absence of an external magnetic field, the locations of the **extrema** of  $f(\Psi, T)$  are given by

$$\frac{\partial}{\partial \Psi} f(\Psi, T) = 0 = a_2(T) \Psi + a_4(T) \Psi^3$$

- Whose solutions are:

$$\Psi = 0 \quad \Psi = \pm \sqrt{-a_2(T)/a_4(T)}$$

- Clearly, the two solution on the right are purely imaginary if both  $a_2(T)$  and  $a_4(T)$  are positive; in that case  $\Psi=0$  is the only allowed real solution.
- If  $a_4(T)$  remains positive at all  $T$  (it must!) then, in order to have a non-vanishing real order parameter in equilibrium,  $a_2(T)$  must be negative in that temperature regime. In this scenario,  $a_2(T_C)=0$  would determine the transition temperature  $T_c$
- In order to examine the validity of this scenario let us calculate the second derivative

$$\frac{\partial^2}{\partial \Psi^2} f(\Psi, T) = a_2(T) + 3a_4(T)\Psi^2 = \begin{cases} a_2(T) & \text{if } \Psi = 0 \\ -2a_2(T) & \text{if } \Psi = \pm \sqrt{-a_2(T)/a_4(T)} \end{cases}$$

- Now, to describe a phase transition in our uniaxial magnet we assume  $a_2(T)>0$  for  $T>T_c$  and  $a_2(T)<0$  for  $T<T_c$  while  $a_2(T)=0$  at  $T=T_c$

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- The situation is that depicted in this figure:

- $\Psi=0$  corresponds to the minimum of  $f(\Psi, T)$  at  $T>T_c$  and a maximum of  $f(\Psi, T)$  at  $T<T_c$  whereas the solutions

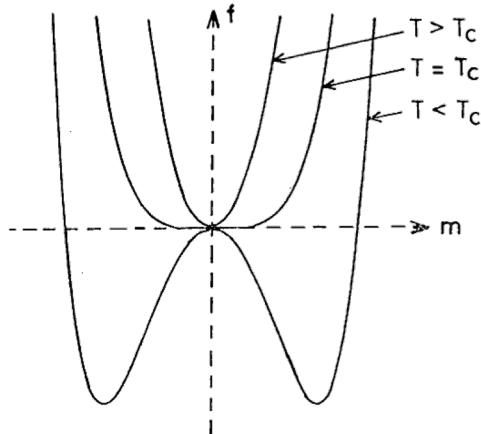
$$\Psi = \pm \sqrt{-a_2(T)/a_4(T)}$$

are the two degenerate equilibrium values of the order parameter in this temperature range

- Our discussion so far has been restricted to the situations where the external magnetic field  $h=0$ . However, if  $h\neq 0$ , the equilibrium value of  $\Psi$  is given by the equation

$$h = \frac{\partial f}{\partial \Psi} = a_2(T)\Psi + a_4(T)\Psi^3$$

being  $h$  conjugated to the order parameter  $\Psi$



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## Critical Exponents in Landau Theory

- Assuming the expansion coefficients to be smooth functions of T and expanding  $a_4(T)$  around  $T_c$  we have

$$a_4(T) = a_4(T_c) + (T - T_c) \left( \frac{da_4}{dT} \right)_{T_c} + \dots \approx a_4(T_c)$$

- where we suppose that the temperature-dependence of  $a_4(T)$  near  $T_c$  is so weak that it can be well approximated as a positive constant, namely,  $a_4(T_c)$
- On the other hand, because of the requirement that  $a_2(T_c)=0$ , the Taylor expansion for  $a_2(T)$  implies that, at temperatures close enough to  $T_c$

$$a_2(T) = \bar{a}_2(T - T_c)$$

where  $\bar{a}_2$  is a temperature-independent coefficient.

- The expression for  $f(\Psi, T)$  can be written as

$$f(\Psi, T) \underset{T=T_c}{\approx} \frac{1}{2} \bar{a}_2 T_c \left( \frac{T}{T_c} - 1 \right) \Psi^2 + \frac{1}{4} a_4(T_c) \Psi^4$$

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- From  $\partial f / \partial \Psi = h$  we get  $\bar{a}_2 T_c \left( \frac{T}{T_c} - 1 \right) \Psi + a_4(T_c) \Psi^3 - h = 0$
- Exponent  $\beta$ :** putting  $h=0$  we get  $\Psi \approx \left( 1 - \frac{T}{T_c} \right)^{\beta}$   $\beta = \frac{1}{2}$
- Exponent  $\delta$ :** putting  $T=T_c$  we get  $\Psi \approx h^{1/\delta}$   $\delta = 3$
- Exponent  $\gamma$ :** Taking derivative with respect to  $h$  we get

$$\bar{a}_2 T_c \left( \frac{T}{T_c} - 1 \right) \frac{\partial \Psi}{\partial h} + 3a_4(T_c) \Psi^2 \frac{\partial \Psi}{\partial h} - 1 = 0$$

$$\Rightarrow \chi = \frac{\partial \Psi}{\partial h} = \frac{1}{\bar{a}_2 T_c \left( \frac{T}{T_c} - 1 \right) + 3a_4(T_c) \Psi^2} \xrightarrow[\Psi=0]{T \rightarrow T_c} \frac{1}{\bar{a}_2 (T - T_c)} \Rightarrow \gamma = 1$$

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- **Exponent  $\alpha$ :** Using the solutions for the order parameter in absence of the external field,  $\Psi=0$  for  $T>T_c$  and  $\Psi=\pm\sqrt{[-a_2(T)/a_4(T)]}$  for  $T<T_c$ , we have

$$f(\Psi, T) = \frac{1}{2} a_2(T) \Psi^2 + \frac{1}{4} a_4(T) \Psi^4 = \begin{cases} 0 & T > T_c \\ -a_2^2(T)/4a_4(T) & T < T_c \end{cases}$$

- Therefore the specific heat possess a discontinuity at  $T_c$

$$C_V = -T \frac{\partial^2 f}{\partial T^2} = \begin{cases} 0 & T > T_c \\ -T_c \frac{\partial^2}{\partial T^2} \left[ -\frac{a_2^2(T-T_c)^2}{4a_4(T_c)} \right] = \frac{a_2^2 T_c}{2a_4(T_c)} & T \approx T_c \end{cases}$$

So, in the Landau theory:  $\alpha=0$

- Thus, we find that the numerical values of all the critical exponents in the Landau theory are identical to those of the corresponding exponents in the Mean Field Approximation
- Indeed, Landau theory is a phenomenological generalization of the mean-field theory in the neighbourhood of the critical point. In contrast to mean field theory, Landau theory does not predict the location of the critical point, i.e., it cannot predict  $T_c$

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## Equilibrium local order parameter

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- In the presence of an external field  $h(\vec{r})$ , the local order parameter at equilibrium, if non-zero, will be not uniform and could be obtained from the expression of  $F$  via functional derivative

$$h(\vec{r}) = \frac{\delta F(\Psi(\vec{r}), T)}{\delta \Psi(\vec{r})} = -c \nabla^2 \Psi(\vec{r}) + a_2(T) \Psi(\vec{r}) + a_3(T) \Psi^2(\vec{r}) + a_4(T) \Psi^3(\vec{r}) + \dots$$

- Equivalently, one could change the “statistical ensemble” and work with the Landau-Ginzburg “Gibbs free energy” functional

$$G(h(\vec{r}), T) = F - \int d^d \vec{r} h(\vec{r}) \Psi(\vec{r})$$

- and the equilibrium local order parameter is obtained from:  $\Psi(\vec{r}) = -\frac{\delta G(h(\vec{r}), T)}{\delta h(\vec{r})}$
- One can compute also the order parameter susceptibility:

$$\left. \frac{\delta \Psi(\vec{r})}{\delta h(\vec{r}')} \right|_T = \chi_T(\vec{r} - \vec{r}')$$

- Note therefore that:  $\chi_T(\vec{r} - \vec{r}') = \left. \frac{\delta \Psi(\vec{r})}{\delta h(\vec{r}')} \right|_T = -\frac{\delta^2 G}{\delta h(\vec{r}') \delta h(\vec{r})}$

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## Two-Point Correlation Function

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- Assuming this last free energy can be written as  $G(h(\vec{r}), T) = -k_B T \ln[Z(h(\vec{r}))]$  we have:

$$\chi_T(\vec{r} - \vec{r}') = -\frac{\delta^2 G}{\delta h(\vec{r}) \delta h(\vec{r}')} = k_B T \frac{\delta}{\delta h(\vec{r}')} \left[ \frac{1}{Z} \frac{\delta Z}{\delta h(\vec{r})} \right] = k_B T \left[ \frac{1}{Z} \frac{\delta^2 Z}{\delta h(\vec{r}') \delta h(\vec{r})} - \frac{1}{Z} \frac{\delta Z}{\delta h(\vec{r})} \frac{1}{Z} \frac{\delta Z}{\delta h(\vec{r}')} \right]$$

- It turns out that we can write:

$$\chi_T(\vec{r}, \vec{r}') = \frac{1}{k_B T} \left[ \langle \Psi(\vec{r}) \Psi(\vec{r}') \rangle - \langle \Psi(\vec{r}) \rangle \langle \Psi(\vec{r}') \rangle \right] = \frac{1}{k_B T} G(\vec{r}, \vec{r}')$$

i.e. the order parameter susceptibility is connected with a **two-point correlation function** (fluctuation-dissipation theorem).

- Let's go on with the "Helmholtz free energy" functional for a system with the **symmetry** for the local free energy  $f(\Psi, T) = f(-\Psi, T)$ , and for which all terms higher than  $\Psi^4$ -term can be neglected
- Taking the functional derivative of  $F$  with respect to  $\Psi$  we get

$$-c\nabla^2\Psi(\vec{r}) + a_2(T)\Psi(\vec{r}) + a_4(T)\Psi^3(\vec{r}) = h(\vec{r})$$

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- Next, taking the functional derivative of both sides of this equation with respect to  $h(\vec{r}')$  we get

$$\left[ -c\nabla^2 + a_2(T) + 3a_4(T)\Psi^2(\vec{r}) \right] \chi_T(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

- Where we have used that  $\frac{\delta h(\vec{r})}{\delta h(\vec{r}')} = \delta(\vec{r} - \vec{r}')$
- Using the previous relation among  $\chi(\vec{r}, \vec{r}')$  and  $G(\vec{r}, \vec{r}')$  we thus obtain:

$$\boxed{\left[ -c\nabla^2 + a_2(T) + 3a_4(T)\Psi^2(\vec{r}) \right] G(\vec{r}, \vec{r}') = k_B T \delta(\vec{r} - \vec{r}')}}$$

- At  $T > T_C$  where  $\Psi = 0$  this equation reduces to

$$\left[ -\nabla^2 + \xi_{>}^{-2} \right] G(\vec{r}, \vec{r}') = \frac{k_B T}{c} \delta(\vec{r} - \vec{r}') \quad \left( \xi_{>} = \sqrt{\frac{c}{a_2(T)}} \right)$$

- On the other and for  $T < T_C$  we have  $\Psi = \pm \sqrt{-a_2(T)/a_4(T)}$   
(with this substitution we are consistent: we consider correlations for spontaneous fluctuations/linear response of the uniform order parameter) and thus

$$40 \quad \left[ -\nabla^2 + \xi_{<}^{-2} \right] G(\vec{r}, \vec{r}') = \frac{k_B T}{c} \delta(\vec{r} - \vec{r}') \quad \left( \xi_{<} = \sqrt{-\frac{c}{2a_2(T)}} \right)$$

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- Note that by assuming the usual  $T$  dependence of the coefficient  $a_2(T)$

$$a_2(T) = \bar{a}_2 \cdot (T - T_c) \quad \bar{a}_2 = \text{const.} > 0$$

- We obtain that both  $\xi_s$  and  $\xi_c$  diverges as  $|T-T_c|^{-1/2}$

- Thus, both above and below  $T_c$  the two-point correlation function  $G$  satisfy the differential equation

$$\left[ -\nabla^2 + \xi^{-2} \right] G(\vec{r}, \vec{r}') = \frac{k_B T}{c} \delta(\vec{r} - \vec{r}')$$

- Assuming that we are studying correlations in the spontaneous fluctuations of the (thus uniform!) order parameter we have that  $G=G(|\vec{r}-\vec{r}'|)$ , so, taking the Fourier transform of both sides of this equation we get

$$\hat{G}(k) = \frac{k_B T}{c} \frac{1}{k^2 + \xi^{-2}} \quad \text{Ornstein-Zernike structure factor}$$

- We will see that the Fourier transform of the two-points correlation function (unless for a delta contribution) is the static structure factor

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- We can anti-transform to obtain  $G(|\vec{r}-\vec{r}'|)$ :

$$G(|\vec{r} - \vec{r}'|) = \frac{k_B T}{(2\pi)^d c} \int_{-\infty}^{\infty} dk_1 \cdots \int_{-\infty}^{\infty} dk_d \frac{e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}}{k^2 + \xi^{-2}}$$

- The result depends on the dimensionality  $d$ . When  $d>2$  and  $|\vec{r}-\vec{r}'| \approx \xi$  or greater, it turns out that

$$G(|\vec{r} - \vec{r}'|) = \text{cost.} \frac{e^{-|\vec{r} - \vec{r}'|/\xi}}{|\vec{r} - \vec{r}'|^{d-2}} \quad \text{Ornstein-Zernike correlation function}$$

- This expression makes clear the physical meaning of  $\xi$ : near the critical point the correlations decay exponentially on a scale comparable with  $\xi$ , it is the correlation length
- As we have seen,  $\xi$  diverges at the critical point as  $|T-T_c|^{-1/2}$ ; thus  $v=1/2$ , one again in agreement with the Mean Field result previously obtained for the Ising model correlation function
- We know however that the Mean Field approximation, and Landau Theory are inadequate near the critical point, at least for  $d=1, 2$  and 3. Why?

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## Ginzburg criterion

- The Mean field approximation corresponds to neglect the fluctuations of the order parameter. This is a good approximation only if

$$\frac{\langle \Psi(\vec{r})\Psi(\vec{r}') \rangle - \Psi(\vec{r})\Psi(\vec{r}')}{\Psi^2(\vec{r})} = \frac{G(\vec{r} - \vec{r}')}{\Psi^2(\vec{r})} \underset{|\vec{r}-\vec{r}'| \approx \xi}{\ll} 1$$

- We now know that  $G(|\vec{r} - \vec{r}'|) = \text{cost.} \frac{e^{-|\vec{r} - \vec{r}'|/\xi}}{|\vec{r} - \vec{r}'|^{d-2}} \underset{|\vec{r} - \vec{r}'| \approx \xi}{\approx} \frac{1}{\xi^{d-2}} \approx \left| \frac{T - T_c}{T_c} \right|^{\frac{d-2}{2}}$
- Thus, we obtain: 
$$\left| \frac{G(\vec{r} - \vec{r}')}{\Psi^2(\vec{r})} \right|_{|\vec{r}-\vec{r}'| \approx \xi} \approx \left| \frac{T - T_c}{T_c} \right|^{\frac{d-2-1}{2}} = \left| \frac{T - T_c}{T_c} \right|^{\frac{d-4}{2}} \quad \left[ \Psi \approx \left( 1 - \frac{T}{T_c} \right)^{1/2} \right]$$
- Conclusion:** only for  $d > 4$  fluctuations are negligible when  $T \rightarrow T_c$ . For  $d < 4$  the theory is not consistent because fluctuations diverges for  $T \rightarrow T_c$ . For  $d=4$  we should expect that fluctuations are small, it is the **critical dimension** for the Ginzburg-Landau theory here investigated

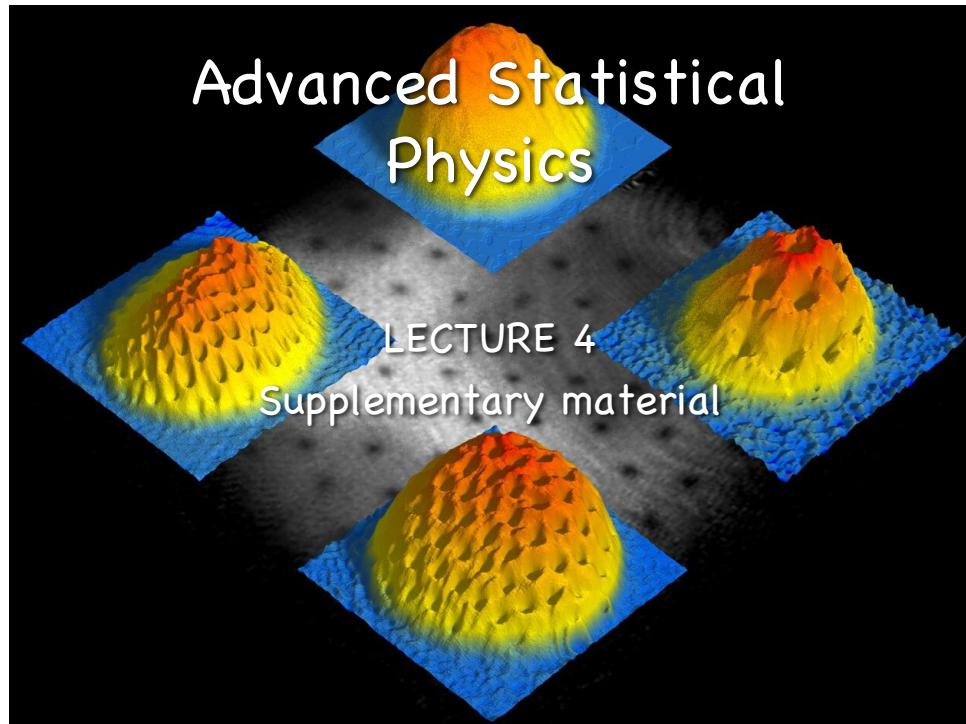
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## Lecture 4: Suggested books

- L. Peliti, "Appunti di meccanica statistica", Bollati Boringhieri
- K. Huang, "Statistical Mechanics", II edition, Wiley
- R. Piazza "Note di Fisica Statistica" Springer
- R. K. Pathria, "Statistical mechanics", II ed., Oxford

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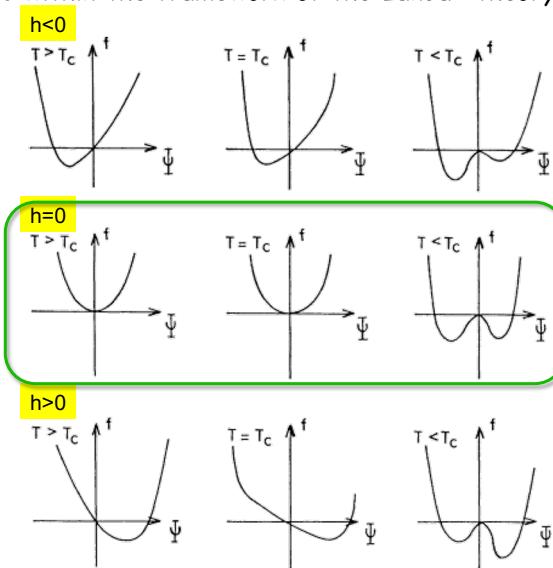
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## First Order Phase Transitions

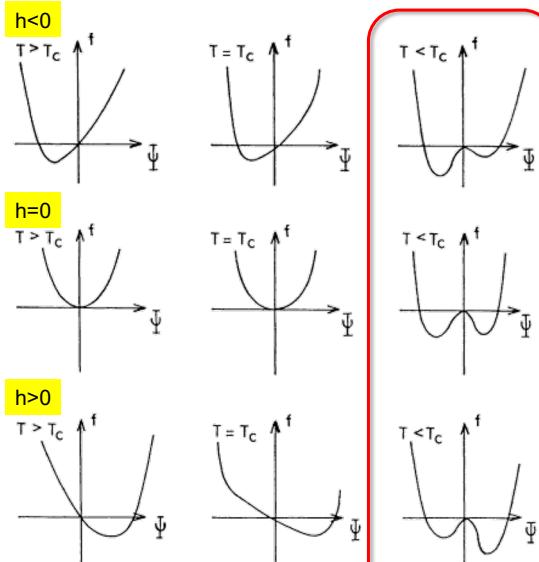
- We shall demonstrate three different mechanisms of the occurrence of first order phase transitions within the framework of the Landau theory
- (1) **Field driven transition:**
  - Let us sketch  $f(\Psi, T)$  for different signs of  $h$
- If  $h=0$  and we decrease  $T$  starting from  $T>T_c$  to  $T<T_c$  we find that the order parameter, which is zero above  $T_c$ , becomes nonzero as  $T$  crosses  $T_c$  and increases continuously with the further decrease of  $T$ . This is an example of **continuous phase transition**



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- On the other hand, if keeping  $T$  fixed at some value  $T < T_c$  we increase  $h$  gradually from a negative value to a positive value **the order parameter changes discontinuously** at  $h=0$  as we go from  $h=0^-$  to  $h=0^+$
- This is an example of **field-driven**, rather than temperature-driven, **first order phase transition**
- this phenomenon is the analog of boiling of water at  $100^\circ C$  by reducing the pressure rather than by increasing the temperature.



$$\left[ \Psi = m = -\frac{1}{V} \left( \frac{\partial A}{\partial h} \right)_T = -\left( \frac{\partial f}{\partial h} \right)_T \right] \quad 47$$

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## (2) T-driven transition:

- Next, let us demonstrate how a **first order phase transition** can take place in the Landau theory, in the **absence of  $h$** , with the variation of temperature.
- Suppose, for system under consideration, that  $f(\Psi, T) \neq f(-\Psi, T)$
- so that the  $\Psi^3$ -term in the Landau free energy cannot be dropped (in absence of  $h$ , the linear term is absent to ensure the stability of the higher symmetry phase). In this case, retaining up to the  $\Psi^4$ -term, the Landau free energy density is given by

$$f(\Psi, T) = \frac{1}{2} a_2(T) \Psi^2 + \frac{1}{3} a_3(T) \Psi^3 + \frac{1}{4} a_4(T) \Psi^4 \quad \text{with } a_3(T) < 0$$

- Now, searching for the extrema  $\frac{\partial f}{\partial \Psi} = 0 = a_2(T)\Psi + a_3(T)\Psi^2 + a_4(T)\Psi^3$
- and the solutions of equation are

$$\Psi = 0 \quad \text{and} \quad \Psi = \frac{-a_3(T) \pm \sqrt{a_3^2(T) - 4a_2(T)a_4(T)}}{2a_4(T)} = \Psi_{\pm}$$

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- The temperature  $T_c$  is still defined as the temperature at which the coefficient  $a_2$  vanishes (but the subscript does not mean "critical"!)
- At sufficiently high temperature (much above  $T_c$ ), the non-zero solutions are complex and  $\Psi=0$  is the only allowed physical solution. But, as  $T$  decreases, and approaches  $T_c$  from above, the solutions  $\Psi_{\pm}$  become real at a temperature  $T_r$  such that
- Moreover, assuming  $a_2$  to be given by

$$a_2(T) = \bar{a}_2 \cdot (T - T_c) \quad \bar{a}_2 = \text{const.} > 0$$

- we conclude that the non-zero solutions  $\Psi_{\pm}$  are real at  $T < T_r$  where

$$T_r = T_c + \frac{a_3^2(T_r)}{4a_4(T_r)\bar{a}_2}$$

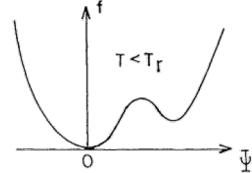
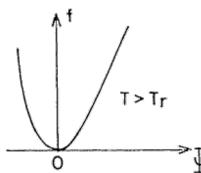
- Since both  $\bar{a}_2$  and  $a_4$  have been assumed positive,  $T_r > T_c$
- Therefore, the solutions become real above  $T_c$ . However, this does not necessarily mean that either of these non-zero solutions corresponds to the stable equilibrium at  $T < T_r$

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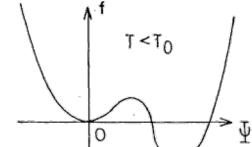
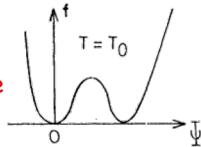
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- In fact, being  $T_0$  the temperature at which the two minima of  $f$ , located at  $\Psi=0$  and  $\Psi=\Psi_+$ , are equally deep, in the temperature range  $T_0 < T < T_r$ ,  $\Psi_-$  corresponds to a maximum of  $f$

- Thus, stable equilibrium corresponds to  $\Psi=0$  in the temperature range  $T > T_0$  and to  $\Psi=\Psi_+$  in the temperature range  $T < T_0$



- Because of a discontinuous change of the order parameter, at  $T_0$ , the phase transition is first order



- The transition from the isotropic phase to the nematic phase of liquid crystals is an example of such first order phase transitions.

- The conditions  $f(\Psi_+, T_0) = f(0, T_0)$  imply

$$T_0 = \dots = T_c + \frac{10}{9} \frac{a_3^2(T_0)}{a_4(T_0)\bar{a}_2} > T_c$$

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(3) T-driven transition; symmetric case:

- There is yet another mechanism of temperature-driven first order transitions in the Landau theory. Suppose, only even terms are allowed by the symmetry of the system but  $a_4(T)<0$ . Then, stability requires inclusion of the  $\Psi^6$ -term with the coefficient  $a_6(T)>0$

- In this case,

$$f(\Psi, T) = \frac{1}{2} a_2(T) \Psi^2 + \frac{1}{4} a_4(T) \Psi^4 + \frac{1}{6} a_6(T) \Psi^6$$

- In order to show the first order transition at a temperature, say,  $T=T_*$ , we need to argue that there are solutions  $\Psi_* \neq 0$ , in addition to  $\Psi=0$ , such that

$$f(\Psi_*, T_*) = \frac{1}{2} a_2(T_*) \Psi_*^2 + \frac{1}{4} a_4(T_*) \Psi_*^4 + \frac{1}{6} a_6(T_*) \Psi_*^6 = 0$$

$$\frac{\partial f(\Psi_*, T_*)}{\partial \Psi} = a_2(T_*) \Psi_* + a_4(T_*) \Psi_*^3 + a_6(T_*) \Psi_*^5 = 0$$

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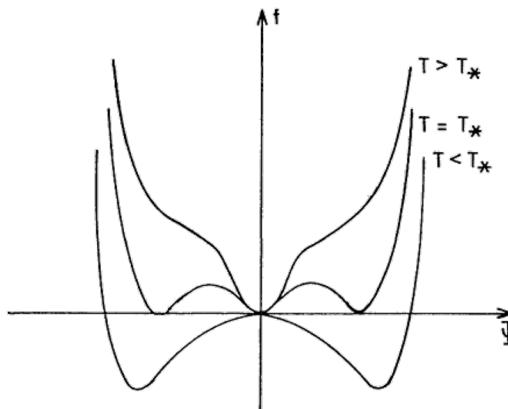
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- Eliminating  $a_2(T_*)$  we get

$$\Psi_* = \pm \sqrt{-\frac{3}{4} \frac{a_4^*(T_*)}{a_6^*(T_*)}}$$

- which are real solution ( $a_4(T)<0$  &  $a_6(T)>0$ )

- In other words, when cooled gradually from a high temperature, a first order phase transition can occur in this system at  $T_*$ , where the order parameter changes discontinuously from  $\Psi=0$  to  $\Psi=\pm\Psi_*$



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