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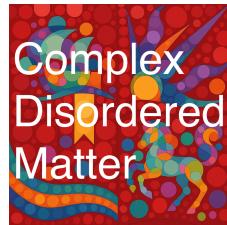


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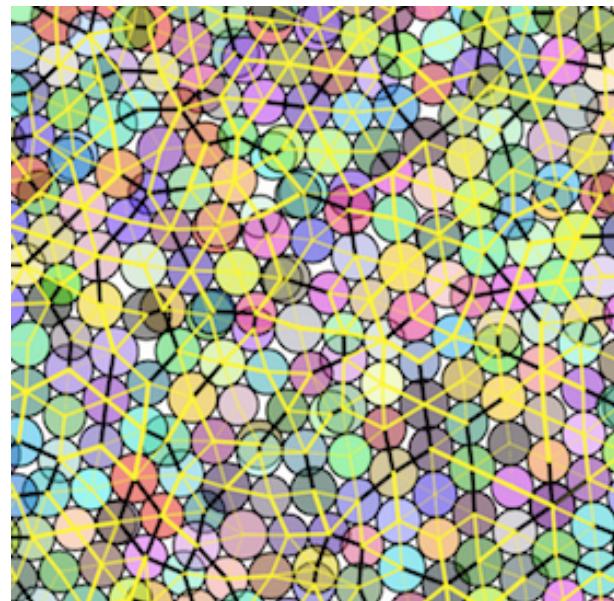


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PHYS40071: Complex Disordered Matter



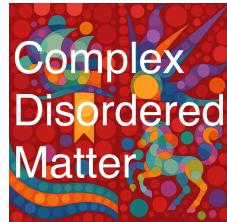
Nigel Wilding, Francesco Turci and Adrian Barnes



Welcome!

Course structure

TB 1 | 20 Credits | 3 Lectures per week + Problem Class



📌 **Unifying Concepts** (Weeks 1-5: Nigel Wilding)

- Phase transitions and critical phenomena
- Metastability and dynamics
- Stochastic processes and fluctuations

🧩 **Complex Disordered Systems** (Weeks 7-11: Francesco Turci)

- Colloids and interactions
- Polymers & Surfactants
- Liquid Crystals, Gels, Glasses
- Active Matter

🔬 **Experimental Systems & Techniques** (Weeks 5 and 11: Adrian Barnes)

- Calorimetry
- Microscopy
- Diffraction

Teaching Block 1

Weeks	Commencing	Section	Lecturer	Assessment
1 - 4	22nd Sep	Unifying Concepts	Prof. Nigel Wilding	Coursework 1: Released Monday 13th October (Week 4) 12:30, due Monday 27th October, 09:30 (Week 6). Marks and feedback returned by Fri 14th November.
5	20th Oct	Unifying Concept and Experimental Techniques	Prof. Nigel Wilding and Dr. Adrian Barnes	
6	27st Oct	<i>Consolidation Week</i>	-	
7 - 10	3rd Nov	Complex Disordered Systems	Dr. Francesco Turci	Coursework 2: Released Thursday 13th Nov 12:30 (Week 8), due Thursday 27th November, 09:30. Marks and feedback returned Friday 12th December.
11	1st Dec	Complex Disordered Systems and Experimental Techniques	Dr. Francesco Turci and Dr. Adrian Barnes	
12	8th Dec	<i>Revision Week</i>	-	
	15th Dec	Assessment Period (1 week)	-	1.5 hour examination

Each teaching week, we shall meet as follows:

Tuesdays 10:00, Room: 3.34 (Physics)	Lecture
Wednesday 11:00, Room: 3.21 (Berry theatre)	Lecture
Thursdays 12:00, Room: Fry Building G.13	Problems class
Fridays 14:00, Room: 3.21 (Berry theatre)	Lecture

Assessment Breakdown

💻 **Computational investigations** - 1 Assignment (30%)

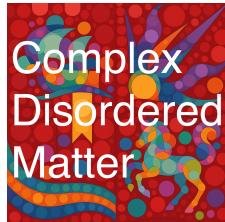
🤔 **Problem set** (20%)

📖 **90 minute exam (Dec)** – Covering all lecture material (50%)

📌 **Total: 100% Assessment** – Equally balanced between coursework and final examination.

As this is a new course, you will be provided with a mock examination paper

Delivery and format (Unifying Concepts)



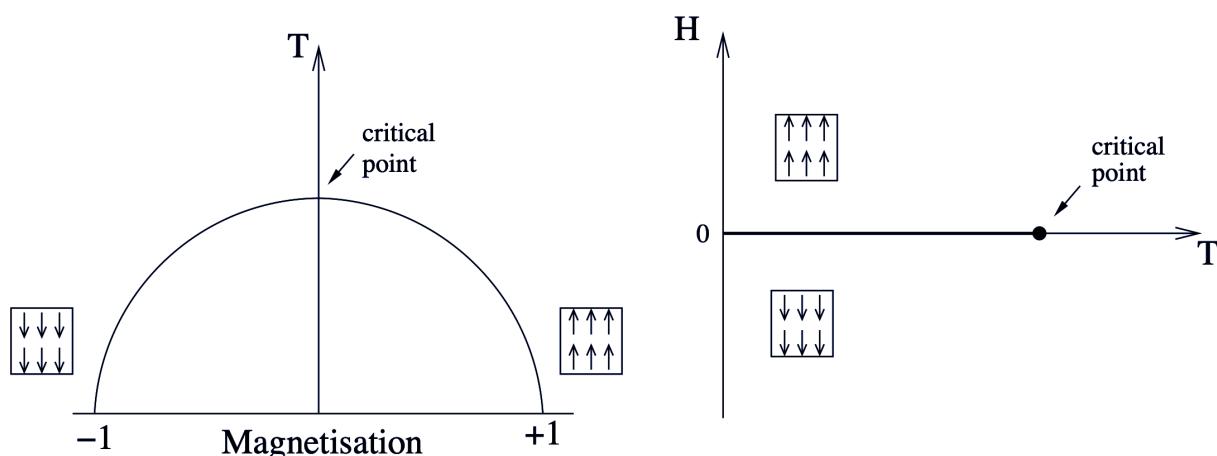
- Detailed e-notes (see Blackboard) can be viewed on a variety of devices.
- 'Traditional' lectures (Tues, Wed, Fri) in which I use slides to summarise and explain the lecture content. Questions welcome (within reason...)
- Try to read ahead in the notes, then come to lectures, listen to my explanations and then reread the notes.



- Rewriting the notes or slides to express your own understanding, or annotating a pdf copy can help wire the material into your own way of thinking.
- Problem class (Thurs) where you can try problem sets and seek help. I will go over some problems with the class. **No classes week 6.**

1. Introduction to phase behaviour

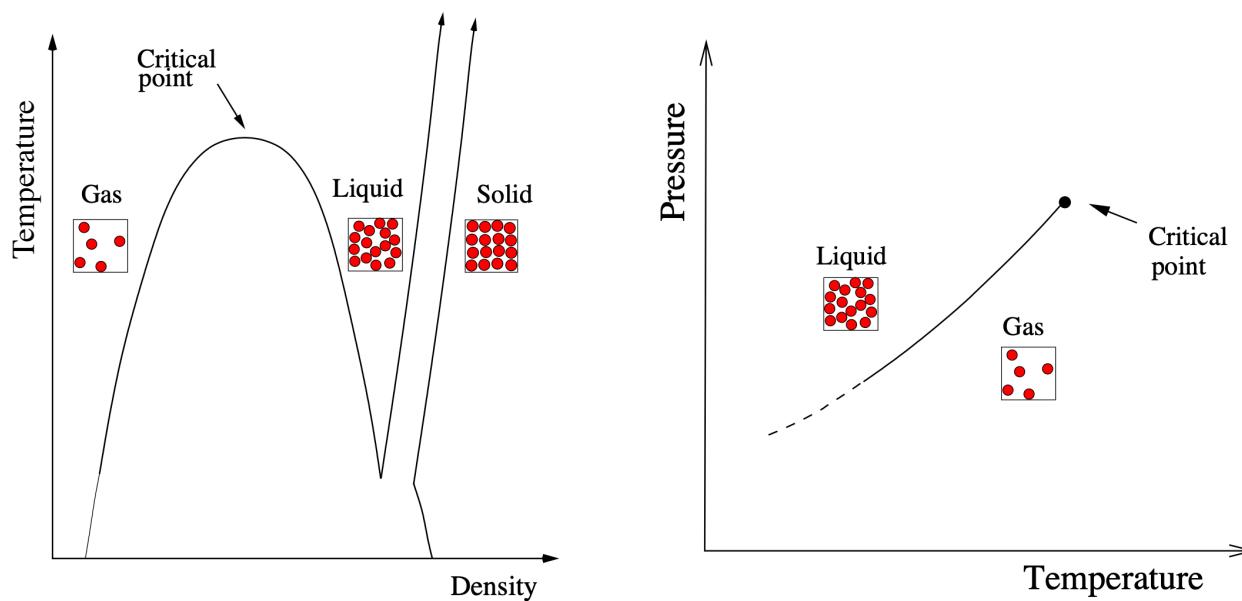
- A wide variety of physical systems undergo rearrangements of their internal constituents in response to changes in thermodynamic conditions.
- Two classic examples of systems displaying such phase transitions are the ferromagnet and fluid systems.



- As the temperature T of a ferromagnet is increased, its magnetic moment is observed to decrease smoothly, until at a certain **critical temperature**, it vanishes altogether

We define the magnetisation to be the **order parameter** of this phase transition.

- Similarly, we can induce a change of state from liquid to gas in a fluid simply by raising the temperature.



- Typically the liquid-gas transition is abrupt. However, abruptness can be reduced by applying pressure.
- At one particular p, T the jump in density at the transition vanishes. These conditions correspond to the critical point of the fluid.

- For H_2O : $T_c = 374$ K, $P_c = 218$ atm
- For CO_2 : $T_c = 304$ K, $P_c = 73$ atm
- Density difference $\rho_{liquid} - \rho_{gas}$ is the order parameter for the liquid-gas phase transition.

- Close to its critical point, a system exhibits a variety of remarkable effects known as **critical phenomena**
- Examples are the divergence (infinite values) of thermal response functions such as the specific heat and the fluid compressibility or magnetic susceptibility
- Origin of the singularities in these quantities tracable to large-length-scale co-operative effects between the microscopic constituents of the system.

- Illustration: CO_2 in a pressurised container at P_c .
- As approach $T_c = 31^\circ C$ from above, critical opalescence occurs.
- For $T < T_c$ a liquid-gas meniscus forms



- Understanding the physics of critical points is important because often one observes **quantitatively identical** critical phenomena in a range of apparently quite disparate physical systems.
- This implies a profound underlying similarity among physical systems at criticality, regardless of many aspects of their distinctive microscopic nature.
- These ideas have found formal expression in the celebrated **universality hypothesis** (see later)

2. Background concepts

- Let us denote the order parameter as Q .
- Q provides a quantitative measure of the difference between the phases coalescing at the critical point:
- Reminder: For the fluid, $Q = \rho_{liq} - \rho_{gas}$. For the ferromagnet $Q = m$, the magnetisation.

- But why should a system exhibit a phase transition at all?
- Statistical Mechanics provides the answer!

- Probability p_a that a physical system at temperature T will have a particular microscopic arrangement ('configuration' or 'state'), labelled a , of energy E_a is

$$p_a = \frac{1}{Z} e^{-E_a/k_B T}$$

- Prefactor Z^{-1} is a T -dependent constant - the partition function (recall year 2 thermal physics). Since the system must always have some specific arrangement, the sum of the probabilities p_a must be unity, implying that

$$Z = \sum_a e^{-E_a/k_B T}$$

where the sum extends over all possible microscopic arrangements.

- Expectation (ie. average) value of an observable O is given by averaging O over all the arrangements a , weighting each contribution by p_a

$$\bar{O} \equiv \langle O \rangle = \frac{1}{Z} \sum_a O_a e^{-E_a/k_B T}$$

- The order parameter is similarly a thermal average over configurations:

$$Q = \frac{1}{Z} \sum_a Q_a e^{-E_a/k_B T} \quad \dagger$$

- Consider the ferromagnetic case $Q = m$. For T very small, system will be overwhelmingly likely to be in its minimum energy arrangement (ground state) having magnetisation +1, or -1.
- For T large, enhanced prob. of ground state arrangements is insufficient to offset the fact that the sum in eq. \dagger contains a vastly greater number of arrangements in which Q_a has some intermediate value.
- In fact arrangements which have essentially zero magnetisation (equal populations of up and down spins) are by far the most numerous
- At high temperature, these disordered arrangements dominate the sum in eq. \dagger and $Q \approx 0$.

- Thus T dependence of Q results from a competition between energy-of-arrangements weighting (or simply 'energy') and the 'number of arrangements' weighting (or 'entropy').
- The critical point is that T at which the system is forced to choose amongst a number of macroscopically different sets of microscopic arrangements i.e. the finite Q arrangements and the zero Q arrangements.
- Partition function provides bridge between stat. mech and thermodynamics via

$$F = -k_B T \ln Z$$

where F is the Helmholtz free energy (see year 2, and preparatory reading).

- All thermodynamic observables, eg. Order parameter Q , specific heat C_H , susceptibility χ and compressibility κ , are obtainable as appropriate derivatives of the free energy. Eg:

$$\begin{array}{c}
 Z = \sum_a e^{-E_a/k_B T} \\
 \downarrow \\
 F = -k_B T \ln Z \\
 \swarrow \qquad \searrow \\
 \bar{E} = - \left(\frac{\partial(\beta F)}{\partial \beta} \right)_H \qquad \bar{M} = - \left(\frac{\partial F}{\partial H} \right)_T \quad (M = mN) \\
 \downarrow \qquad \qquad \qquad \downarrow \\
 C_H = \left(\frac{\partial \bar{E}}{\partial T} \right)_H \qquad \chi_T = \left(\frac{\partial m}{\partial H} \right)_T
 \end{array}$$

(Here $\beta \equiv (k_B T)^{-1}$)

Correlations

- Consider first **spatial** correlations.
- Two-point correlation function measures statistical relation between fluctuations at two spatial points
- For scalar field $\phi(\vec{R})$ eg. local density or local magnetisation, can define

$$C(r) = \langle \phi(\vec{R})\phi(\vec{R} + \vec{r}) \rangle - \langle \phi(\vec{R}) \rangle^2 \quad r = |\vec{r}| \text{ is spatial separation}$$

and the average is over configurations

Including this term gives a quantity that decays to zero

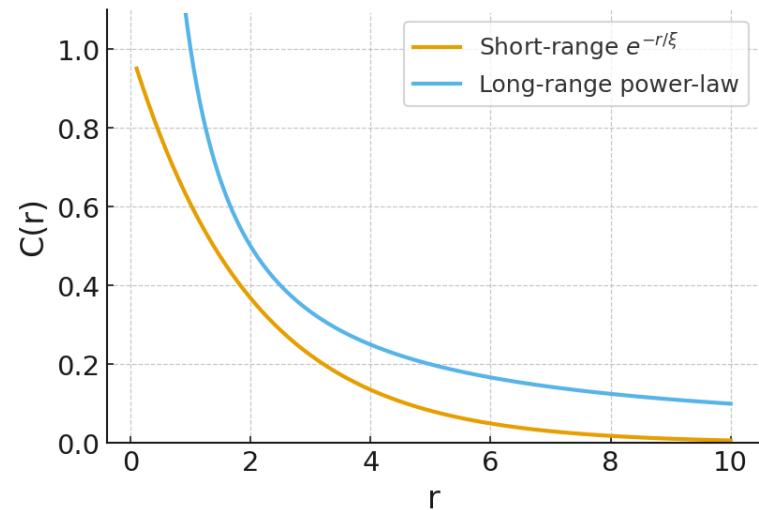
- In homogeneous/isotropic systems, $C(r)$ depends only on r and not the reference point \vec{R}

Behaviour of spatial correlations

- Correlations can be short ranged or long ranged:

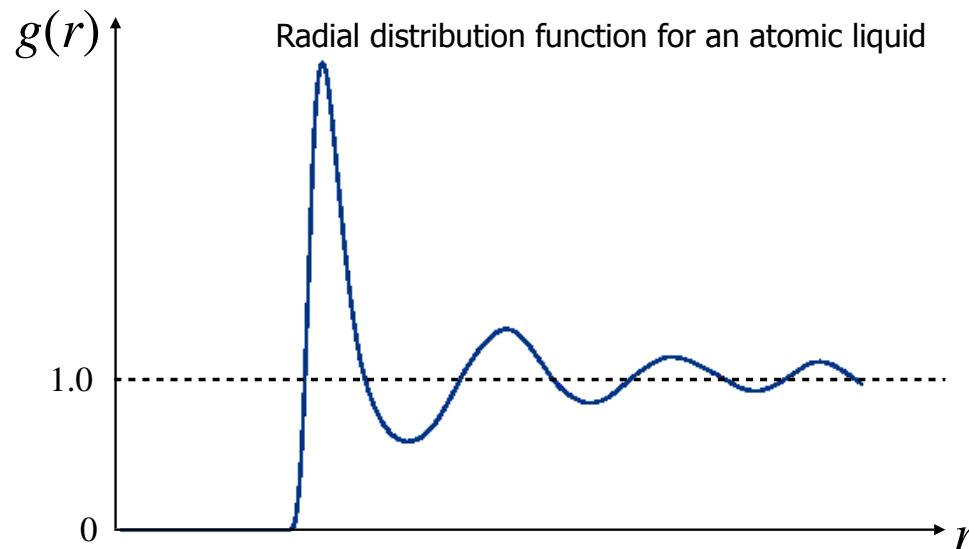
- Short-range: $C(r) \sim e^{-r/\xi}$, fast decay
- Long-range (criticality): power-law decay
 $C(r) \sim r^{-x}$

- **Correlation length ξ** sets spatial scale.

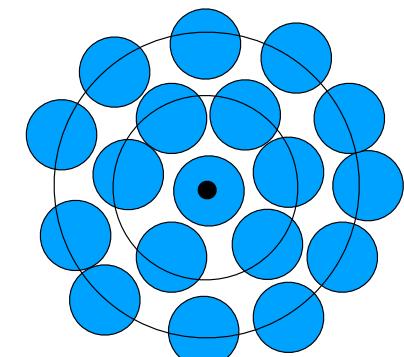


Example: pair correlation function of a fluid (a.k.a radial distribution function)

- For a fluid $\phi(\vec{R}) = \rho(\vec{R})$, the local number density
- $g(r) = \text{probability of finding particle at distance } r = |\vec{r}| \text{ relative to ideal gas.}$
- It is related to density correlations via: $g(r) = \frac{1}{\rho^2} \langle \rho(0)\rho(r) \rangle = 1 + C(r)/\rho^2$



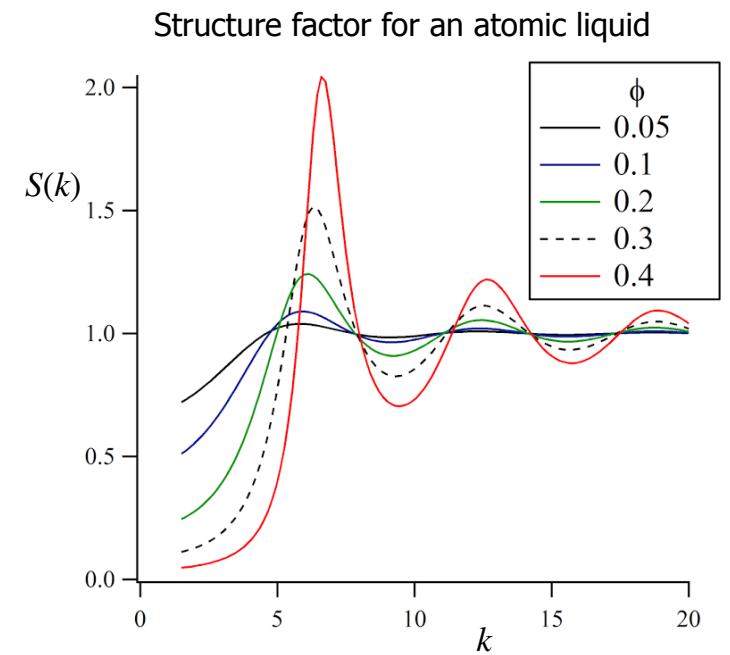
- At large r correlation die out, ie.
$$g(r) \rightarrow 1 \quad \text{as } r \rightarrow \infty$$



- Peaks in $g(r)$ indicate ordering (e.g. shells in liquids).

Structure Factor $S(k)$

- Fourier transform of correlations: $S(k) = \int d^3r e^{i\vec{k}\cdot\vec{r}} C(r)$
 $k = \frac{2\pi}{\lambda}$ is the scattering wave vector (often also written as q)
- Measured in scattering experiments (see lectures by A. Barnes). Connects real-space correlations with momentum-space
- Peaks in $S(k)$ = characteristic length scales.
- Near criticality: divergence at small k (long-range fluctuations)
- For short ranged correlations, decay of $S(k)$ has a Lorentzian form.
- For long ranged correlations, decay has a power law form (see notes)



Temporal correlations

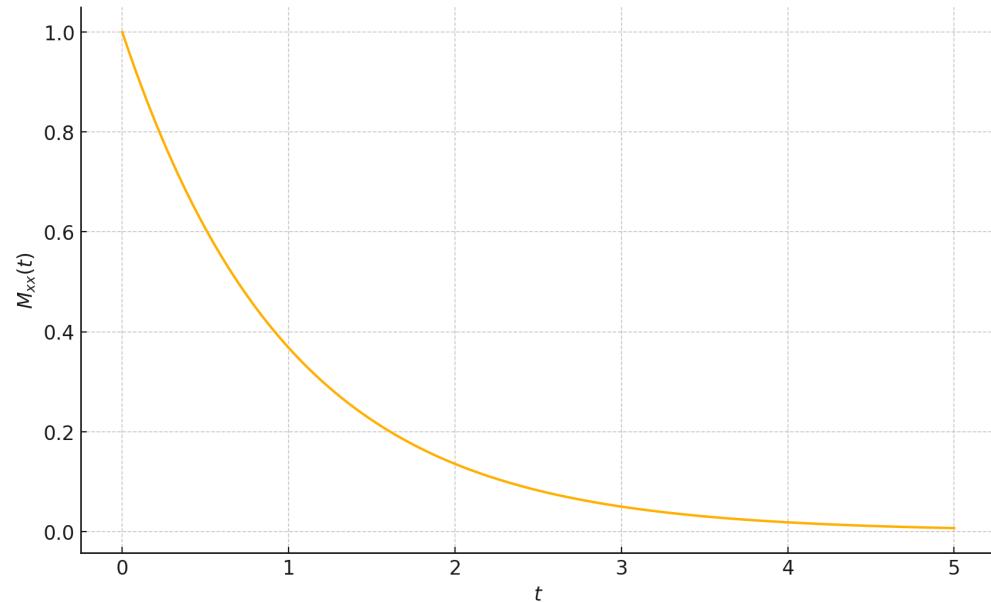
- Consider a thermodynamic variable x with zero mean that fluctuates over time.
- Temporal correlations are characterized by the two-time correlation function:

$$\langle x(\tau)x(\tau + t) \rangle$$

- In **equilibrium**: $\langle x(\tau)x(\tau + t) \rangle = M_{xx}(t)$ i.e only depends on t not on τ
- Typically (away from criticality):

$$M_{xx}(t) \sim \exp(-t/t_c)$$

ie. memory of fluctuations fades exponentially with correlation time t_c



3. The approach to criticality

- Approach to criticality is characterised by the divergence of various thermodynamic observables.
- Eg. in a ferromagnet near T_c , C_H and χ_T are singular functions, diverging as some power of the **reduced temperature** $t \equiv (T - T_c)/T_c$

$$\chi \equiv \frac{\partial m}{\partial h} \propto t^{-\gamma} \quad C_H \equiv \frac{\partial E}{\partial T} \propto t^{-\alpha}$$

- Recall that the correlation length ξ , measuring the distance over which fluctuations of the magnetic moments are correlated. This diverges with an exponent ν .

$$\xi \propto t^{-\nu} \quad (T > T_c, H = 0)$$

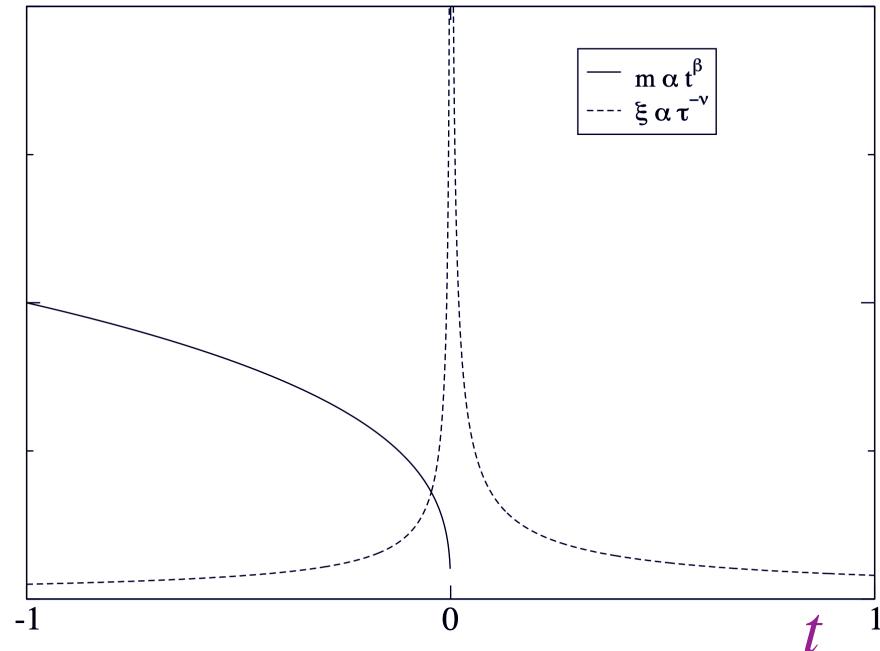
- Similar power law behaviour is found for the order parameter Q which vanishes in a singular fashion (it has infinite gradient) as $T \rightarrow T_c^-$

$$m \propto t^\beta \quad (T < T_c, H = 0)$$

And as a function of magnetic field:

$$m \propto h^{1/\delta} \quad (T = T_c, H > 0)$$

with $h \equiv (H - H_c)/H_c$ the reduced magnetic field.



- $\gamma, \alpha, \nu, \beta$ are known as **critical exponents**. They control the rate at which the associated observables change on the approach to criticality.

- Remarkably, similar power laws occurs in many qualitatively distinct systems near their critical point (eg, fluid, polymer solutions, magnets, electrolytes, traffic jams, sandpiles, financial markets).
- To obtain the corresponding power law relationships simply substitute the analogous thermodynamic quantities in to the above equations. eg.

$$\rho_{liq} - \rho_{gas} \sim t^\beta; \quad \kappa \sim t^{-\gamma}$$

- Even more remarkable is the experimental observation that the values of the critical exponents for a whole range of fluids and magnets (and indeed many other systems with critical points) are **identical**.
- This is the celebrated phenomenon of universality. It implies a deep similarity between systems at their critical points.

4. Ising model

- We can use simple models to probe the properties of the critical region.
- Simplest is the 2d spin- $\frac{1}{2}$ Ising model, which comprises a lattice of N magnetic moments or 'spins' on an infinite plane.
- Each spin can take two values, +1 ('up' spins) or -1 ('down' spins) and interacts with its nearest neighbours via the Hamiltonian

$$\mathcal{H}_I = - J \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i \quad J > 0$$

- The order parameter is simply the average magnetisation: $m = \frac{1}{N} \langle \sum_i s_i \rangle$

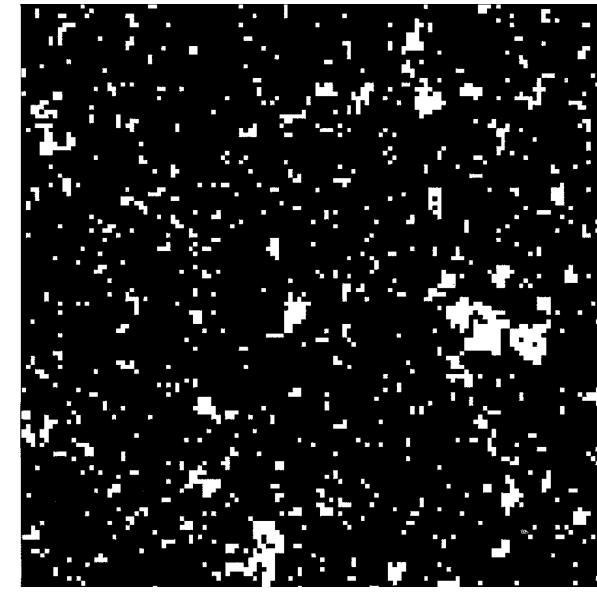
- At low temperatures for which there is little thermal disorder, there is a preponderance of aligned spins and hence a net spontaneous magnetic moment $|m| \approx 1$
- As T is raised, thermal disorder increases until at T_c , entropy drives the system through a continuous phase transition to a disordered spin arrangement with $|m| = 0$.
- These trends are visible in configurational snapshots from computer simulations of the 2D Ising model.



$T = 1.2T_c$



$T = T_c$



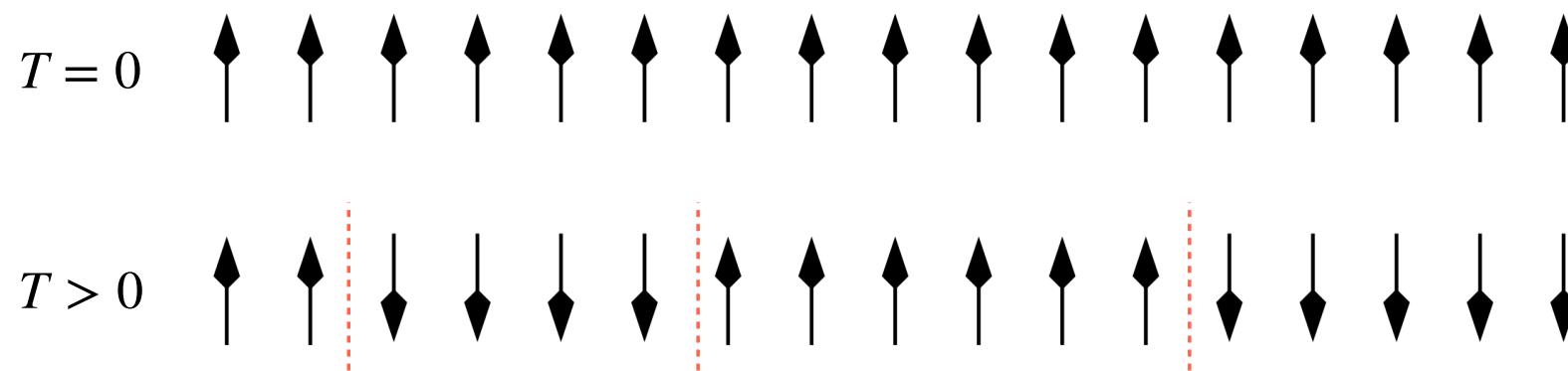
$T = 0.95T_c$

- Although each spin interacts only with its nearest neighbours, the phase transition occurs due to cooperative effects among a large number of spins.
- In the neighbourhood of the transition temperature these cooperative effects engender fluctuations that can extend over all length-scales from the lattice spacing up to the correlation length.

- Despite its simplicity, critical point universality implies that critical exponents of Ising model are same as those of real magnets.
- Ising model therefore provides a simple, yet quantitatively accurate representation of the critical properties of a whole range of real magnetic (and indeed fluid) systems.
- This universal feature of the model is largely responsible for its ubiquity in the field of critical phenomena.

Exact Solutions: the 1D Ising chain

- Why is the 2D Ising model the simplest to exhibit a phase transition? What happens in 1D?
- In fact there is no phase transition in 1D for $T > 0$.
- Consider the ground state of a 1D Ising chain and a state with various "domain walls" dividing spin-up and spin-down regions



- Transform from a spin representation to a domain wall representation.

- Domain walls can occur on the bonds of the lattice of which there are $N - 1$. If a wall is present, the energy cost is $\Delta = 2J$.
- A configuration can be specified by stating whether or not there is a domain wall on each bond.
- Presence of a domain wall on one bond doesn't affect likelihood of domain wall on neighbouring bond (as long as $H = 0$). Thus domain walls are **independent**
- Partition functions from independent contributions multiply.
- Hence the partition function of system is $Z = Z_1^{N-1}$, where for a single domain wall,

$$Z_1 = e^{\beta J} + e^{\beta(J-\Delta)} = e^{\beta J}(1 + e^{-\beta\Delta}) \quad \beta \equiv \frac{1}{k_B T}$$

So free energy density

$$\beta f \equiv \beta F/(N - 1) = -\ln Z_1 = -\beta J - \ln(1 + e^{-\beta\Delta})$$

- Second term arises from the entropy of the domain wall population and since it is negative for all $T > 0$, the free energy is lowered by having domain walls, ie the system is always disordered.

More general 1D spin systems

- For a 1-d assembly of N spins each having m discrete energy states, and in the presence of a magnetic field H , possible to get free energy via the **transfer matrix method**.
- Let us start by assuming that the assembly has cyclic boundary conditions, then the total energy of configuration $\{s\}$ is

$$\begin{aligned}\mathcal{H}(\{s\}) &= - \sum_{i=1}^N (Js_i s_{i+1} + Hs_i) \\ &= - \sum_{i=1}^N (Js_i s_{i+1} + H(s_i + s_{i+1})/2) \\ &= \sum_{i=1}^N E(s_i, s_{i+1})\end{aligned}$$

where we have defined $E(s_i, s_{i+1}) = - Js_i s_{i+1} - H(s_i + s_{i+1})/2$.

Partition function may be written

$$\begin{aligned}
 Z_N &= \sum_{\{s\}} \exp(-\beta \mathcal{H}(\{s\})) \\
 &= \sum_{\{s\}} \exp(-\beta [E(s_1, s_2) + E(s_2, s_3) + \dots + E(s_N, s_1)]) \\
 &= \sum_{\{s\}} \exp(-\beta E(s_1, s_2)) \exp(-\beta E(s_2, s_3)) \dots \exp(-\beta E(s_N, s_1)) \\
 &= \sum_{i,j,\dots,l=1}^m V_{ij} V_{jk} \dots V_{li} \quad \ddagger
 \end{aligned}$$

where the $V_{ij} = \exp(-\beta E_{ij})$ are elements of an $m \times m$ matrix \mathbf{V} , known as the transfer matrix.

- Transpires that the sum over the product of matrix elements in \ddagger is the trace of \mathbf{V}^N , given by the sum of its eigenvalues:-

$$Z_N = \lambda_1^N + \lambda_2^N + \dots + \lambda_m^N$$

- As $N \rightarrow \infty$, largest eigenvalue λ_1 dominates since $(\lambda_2/\lambda_1)^N$ vanishes. Consequently $Z_N = \lambda_1^N$
- Specializing to the case of the simple Ising model, the transfer matrix takes the form

$$\mathbf{V}(H) = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}$$

- This matrix has two eigenvalues which can be readily calculated in the usual fashion. They are

$$\lambda_{\pm} = e^{\beta J} \cosh(\beta H) \pm \sqrt{e^{2\beta J} \sinh^2 \beta H + e^{-2\beta J}}$$

- Hence the free energy per spin $f = -k_B T \ln \lambda_+$ is

$$f = -k_B T \ln \left[e^{\beta J} \cosh(\beta H) + \sqrt{e^{2\beta J} \sinh^2 \beta H + e^{-2\beta J}} \right]$$

5. Mean field theory

- The critical behaviour of most model systems cannot be found analytically.
- A few exceptions: eg. 2D Ising model (but not the 3D) have been solved
 $(\beta = \frac{1}{8}, \nu = 1, \gamma = \frac{7}{4}, T_c = -2J/\ln(\sqrt{2} - 1) \approx 2.269J)$
- But such solutions provide little insight into the essential nature of criticality.
- When an exact solution is elusive, can try to make simplifying assumptions to calculate critical behaviour. Mean field theory is such an approximation scheme.

- Look for a mean field expression for the free energy of the Ising model. Write

$$s_i = \langle s_i \rangle + (s_i - \langle s_i \rangle) = m + (s_i - m) = m + \delta s_i$$

- Then

$$\begin{aligned} \mathcal{H}_I &= -J \sum_{\langle i,j \rangle} [m + (s_i - m)][m + (s_j - m)] - H \sum_i s_i \\ &= -J \sum_{\langle i,j \rangle} [m^2 + m(s_i - m) + m(s_j - m) + \delta s_i \delta s_j] - H \sum_i s_i \\ &= -J \sum_i (qms_i - qm^2/2) - H \sum_i s_i - J \sum_{\langle i,j \rangle} \delta s_i \delta s_j \end{aligned}$$

where the sum $\sum_{\langle i,j \rangle}$ over bonds of a quantity which independent of s_j is just $q/2$ times that quantity, with q the lattice coordination.

- Now the mean field approximation is to ignore the last term giving

$$\mathcal{H}_{mf} = - \sum_i H_{mf} s_i + NqJm^2/2 \quad \text{where } H_{mf} \equiv Jqm + H$$

- It follows that the partition function is

$$Z = Z(1)^N = e^{-\beta qJm^2N/2} [2 \cosh(\beta(qJm + H))]^N$$

so the free energy is

$$F(m) = NJqm^2/2 - Nk_B T \ln[2 \cosh(\beta(qJm + H))]$$

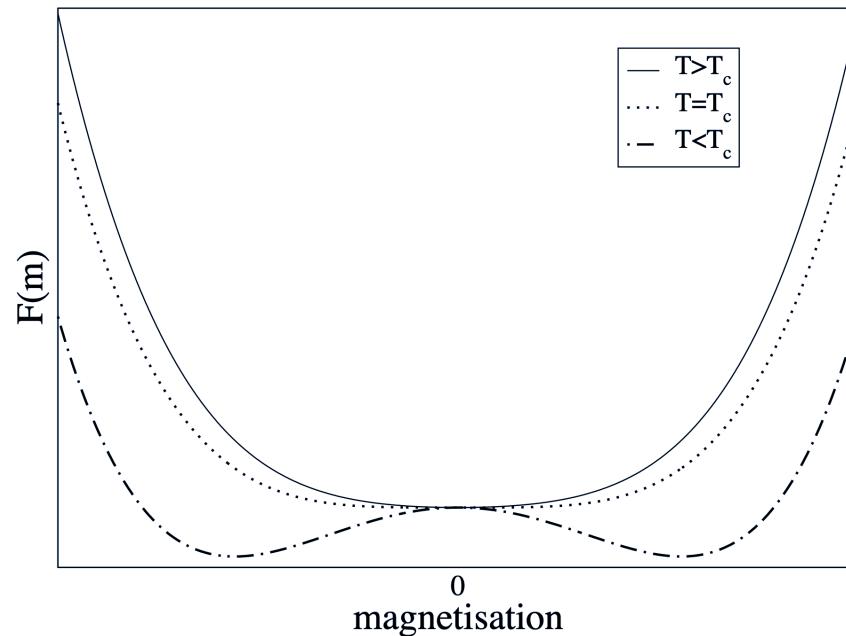
- From which the magnetisation follows as

$$m = -\frac{1}{N} \frac{\partial F}{\partial H} = \tanh(\beta(qJm + H))$$

- To find $m(H, T)$, we must numerically solve this last equation self consistently.

Spontaneous symmetry breaking

- Mean field method reveals what is happening in the Ising model near the critical temperature T_c
- Plot $\beta F(m)/N$ vs T for $H = 0$:
- For $H = 0$, $F(m)$ is symmetric in m . At high T , entropy dominates \rightarrow single minimum in $F(m)$ at $m = 0$.



- As T is lowered, there comes a point ($T = T_c$) where the curvature of $F(m)$ at the origin changes sign; ie.

$$\frac{\partial^2 F}{\partial m^2} = 0$$

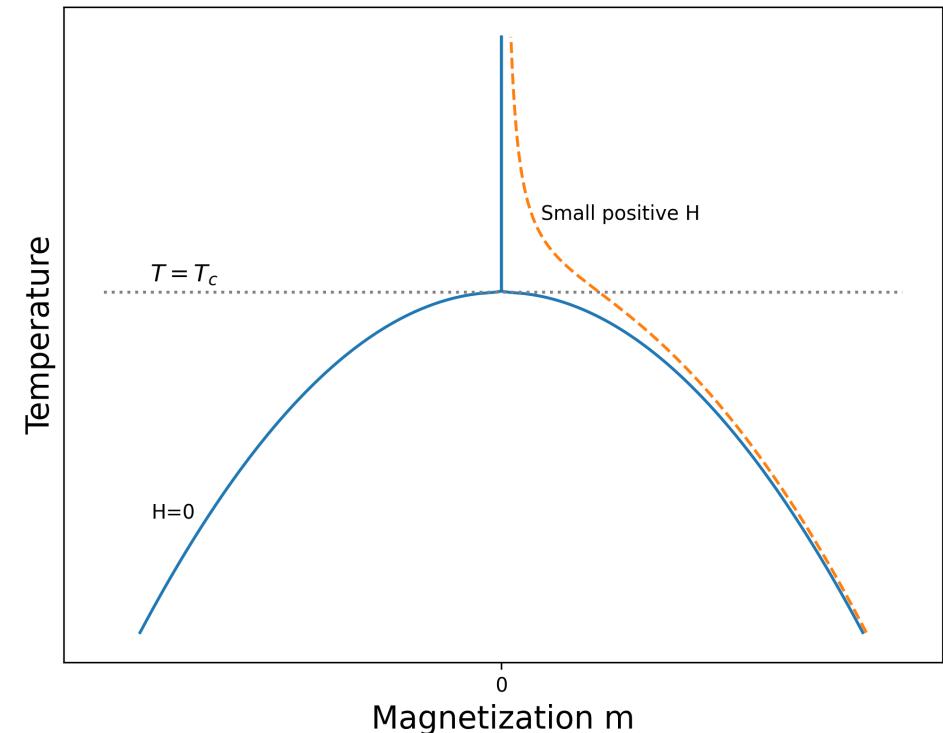
- At lower temperature: two minima at nonzero $m = \pm m^*$, where the equilibrium magnetisation m^* is the positive root (calculated explicitly below) of

$$m^* = \tanh(\beta J q m^*) = \tanh\left(\frac{m^* T_c}{T}\right)$$

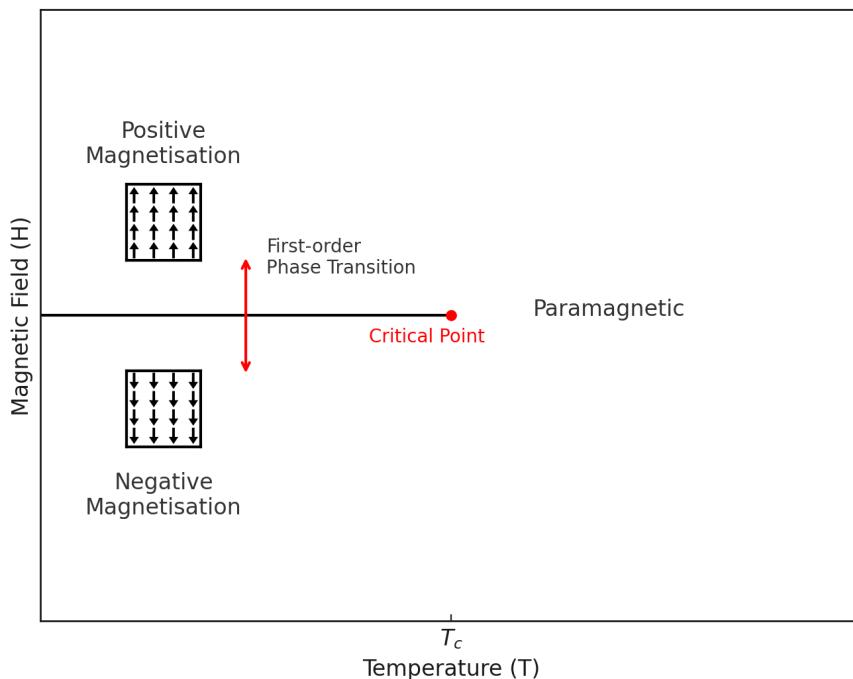
- $m^* = 0$ which remains a root of this equation, is clearly an unstable point for $T < T_c$ (since F has a maximum there).
- This is an example of spontaneous symmetry breaking: Pair of ferromagnetic states (spins mostly up, or spins mostly down) which - by symmetry - have the same free energy, lower than the unmagnetized state.

Phase diagram

- The resulting zero-field magnetisation curve:
- Sudden change of behaviour at T_c (continuous phase transition).
- For $T < T_c$, arbitrary which of the two roots $\pm m^*$ is chosen; typically it will be different in different parts of the sample (giving macroscopic ``magnetic domains'').
- Picture is qualitatively modified by a magnetic field H . Then there is always a finite magnetization, even for $T \gg T_c$ (no phase transition).



- Sit below T_c with $H > 0$ and gradually reduce H so that it becomes negative. Observe very sudden change of behaviour at $H = 0$: the equilibrium state jumps discontinuously from $m = m^*$ to $m = -m^*$.



- This is called a **first order phase transition**.

First order transition: magnetisation (or similar order parameter) depends discontinuously on other variables such as H or T

Continuous transition (criticality): Change of functional form, but no discontinuity in m ; typically, however, $(\partial m / \partial T)_H$ (or similar) is either discontinuous, or diverges.

- We say that the phase diagram of the magnet in the H, T plane shows a line of first order phase transitions, terminating at a continuous transition, which is the critical point.