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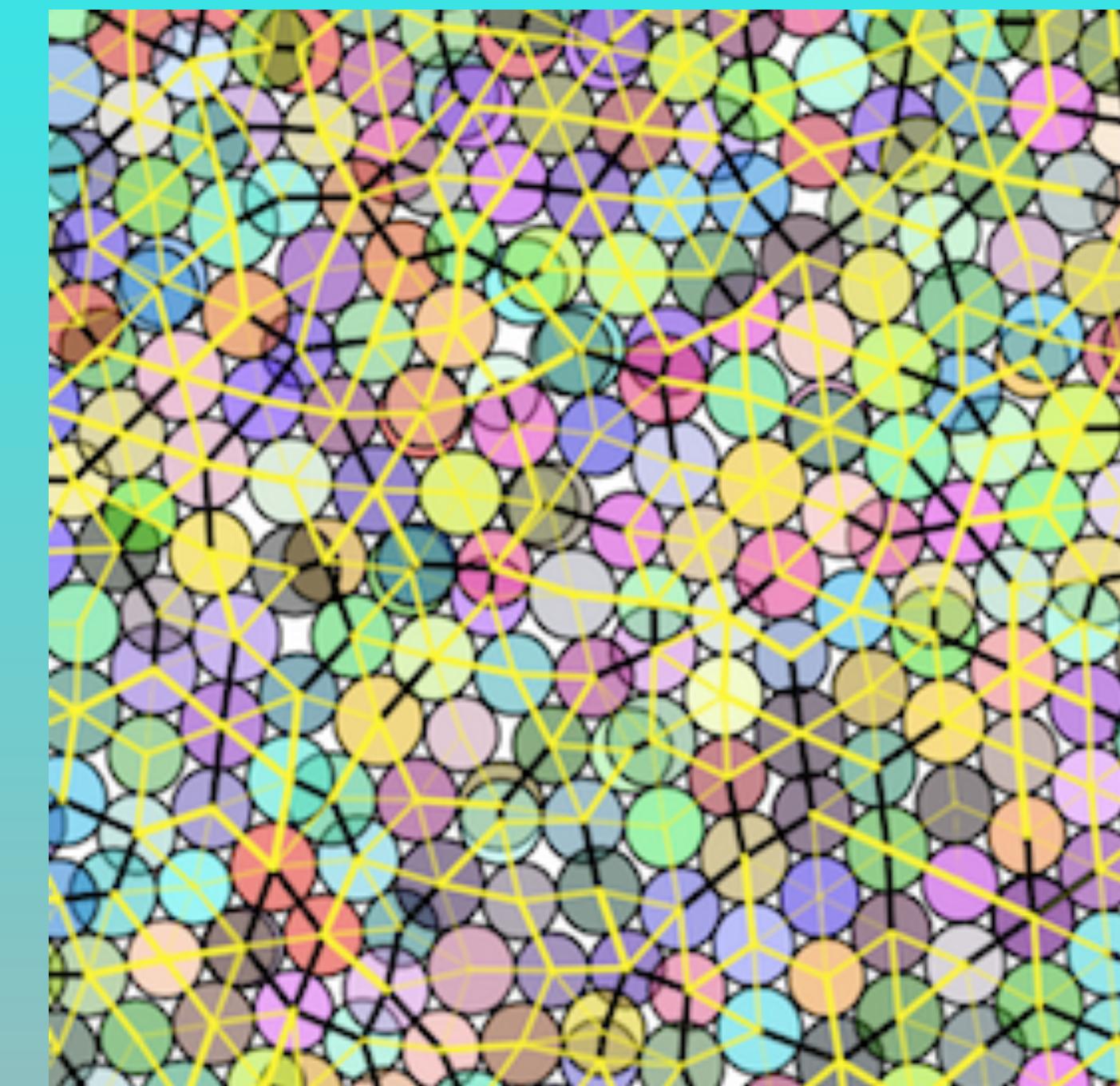
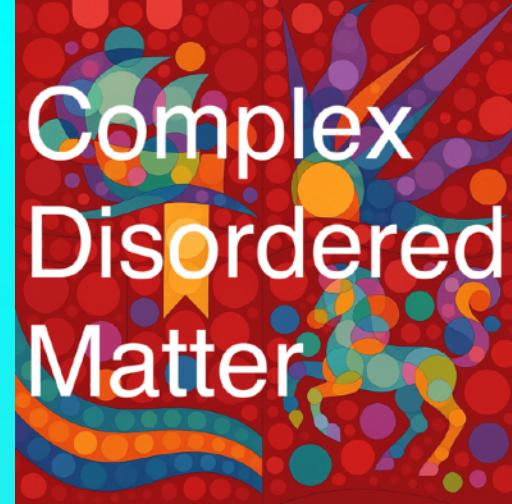
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PHYS40071: Complex Disordered Matter

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)

- Statistical Mechanics: the energy-entropy competition
- Phase Transitions and Critical Phenomena
- Metastability & 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

Assessment Breakdown

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

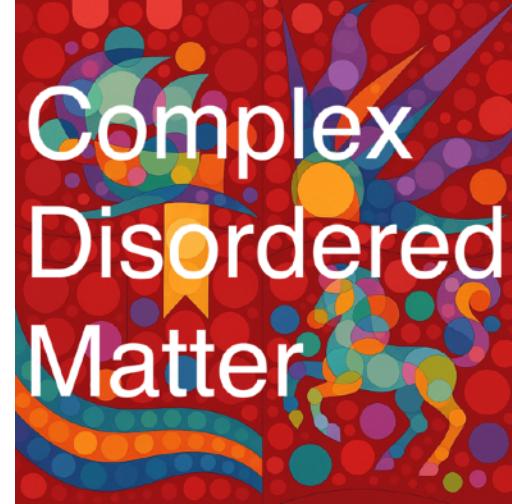
🤔 **Problem set** (20%)

📖 **Final Exam** – 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)



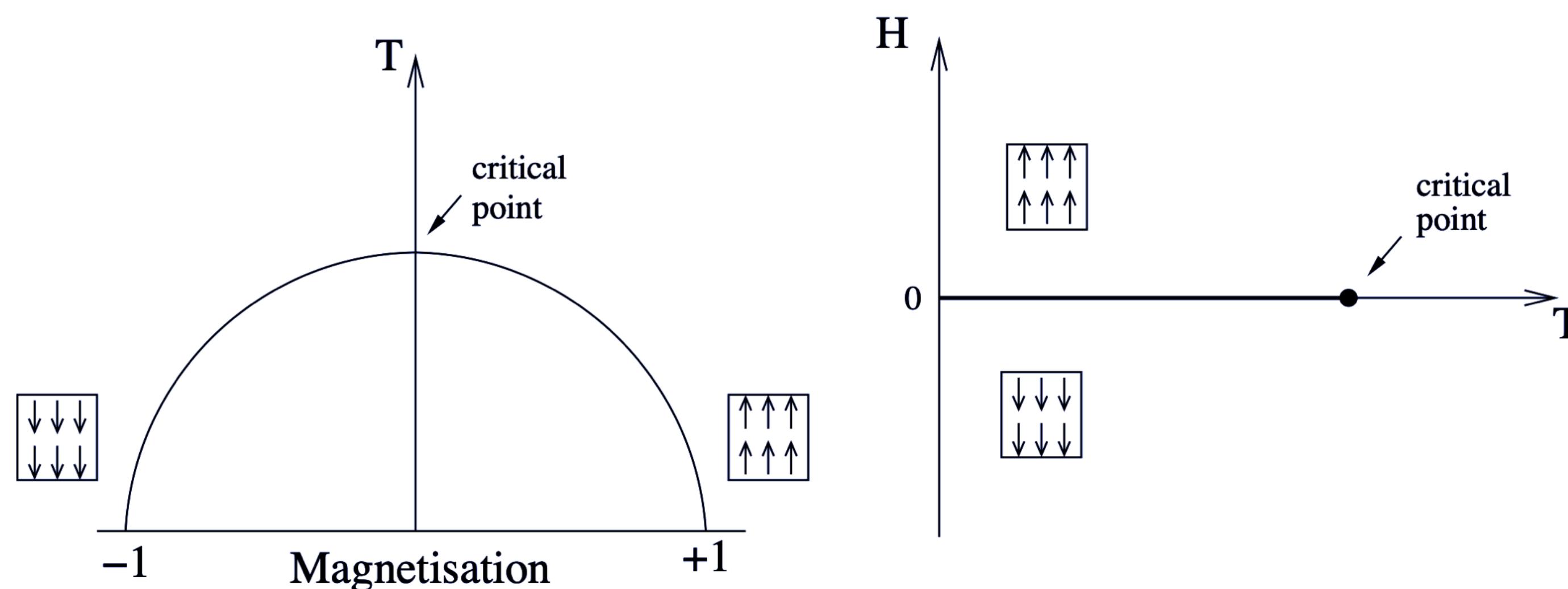
- Detailed e-notes (see Blackboard) can be viewed on a variety of devices.
- 'Traditional' lectures (Tues, Wed, Fri) in which I use slides to summarise and explain the lecture content. Questions welcome (within reason...)
- Try to read ahead in the notes, then come to lectures, listen to my explanations 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 sheets and seek help. I will go over some problems with the class. **No classes week 6.**

1. Introduction to phase behaviour

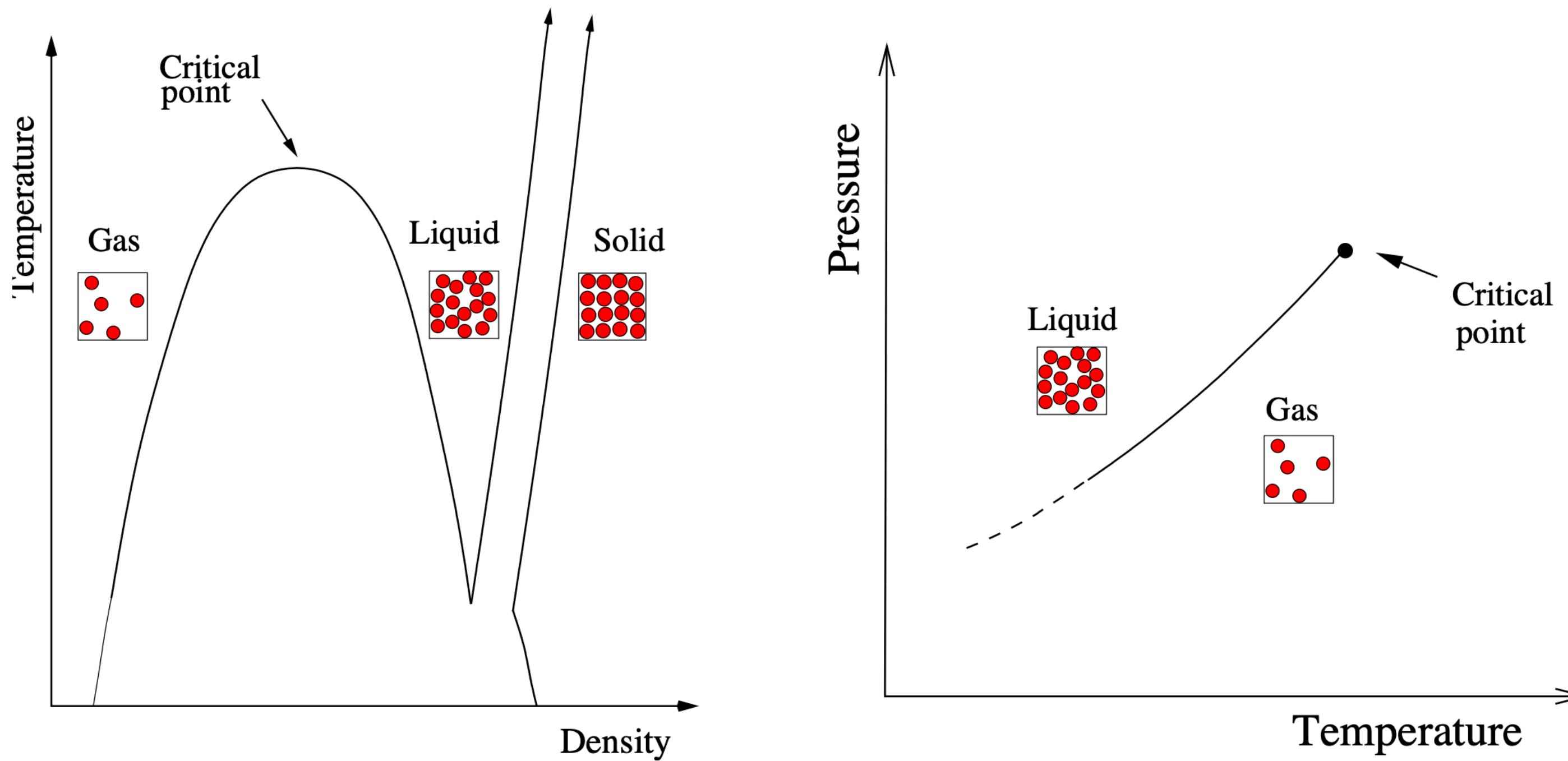
- A wide variety of physical systems undergo rearrangements of their internal constituents in response to changes in thermodynamic conditions.
- Two classic examples of systems displaying such phase transitions are the ferromagnet and fluid systems.



- 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.

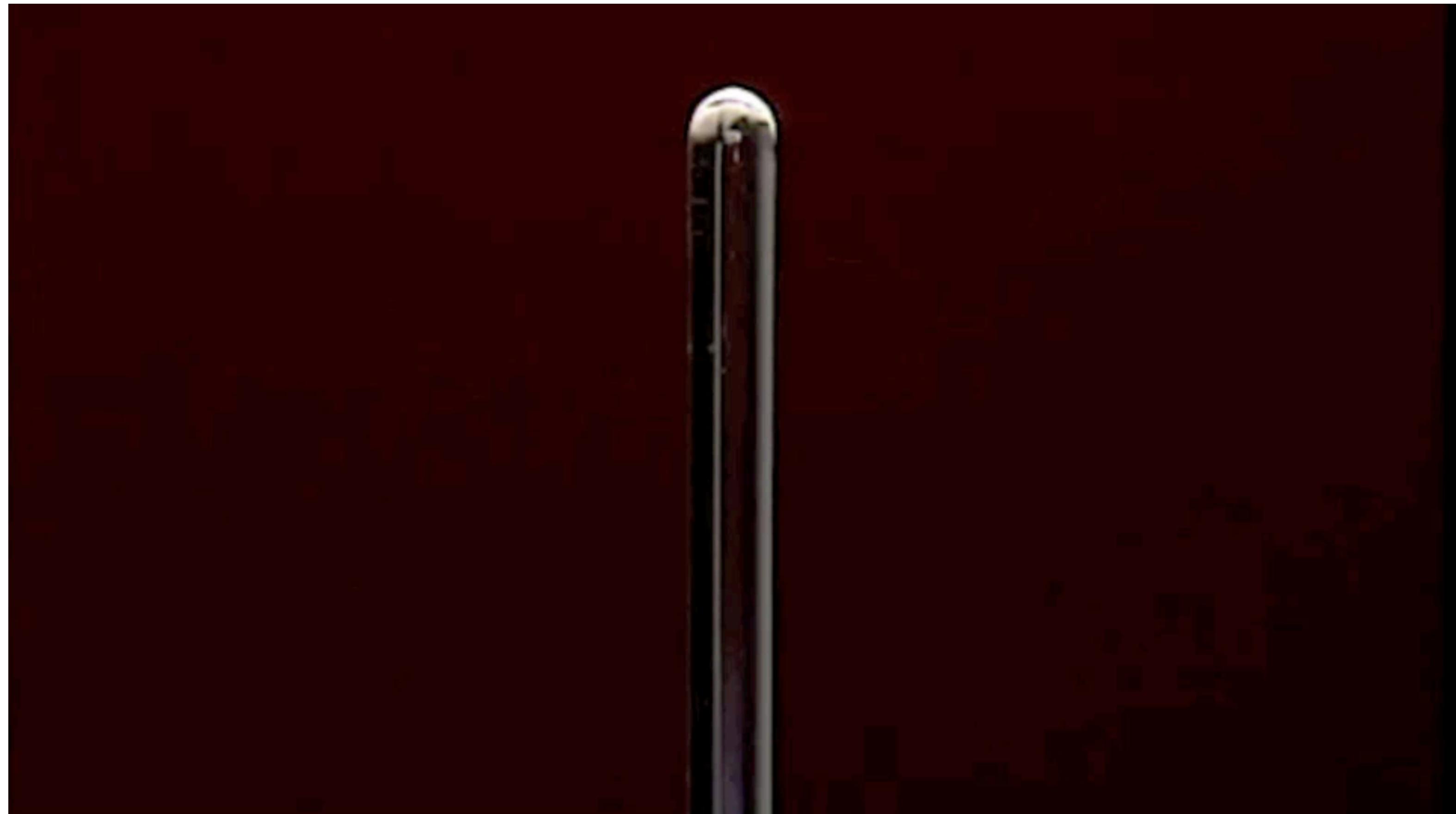


- Typically the liquid-gas transition is abrupt. However, abruptness can be reduced by applying pressure.
- At one particular p, T the jump in density at the transition vanishes. These conditions correspond to the critical point of the fluid.

- 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

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

- It follows that the order parameter is:
$$Q = \frac{1}{Z} \sum_a Q_a e^{-E_a/k_B T} \quad \dagger$$
- Now consider the ferromagnetic case $Q = m$. For T very small, system will be overwhelmingly likely to be in its minimum energy arrangements (ground states) 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:

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

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:

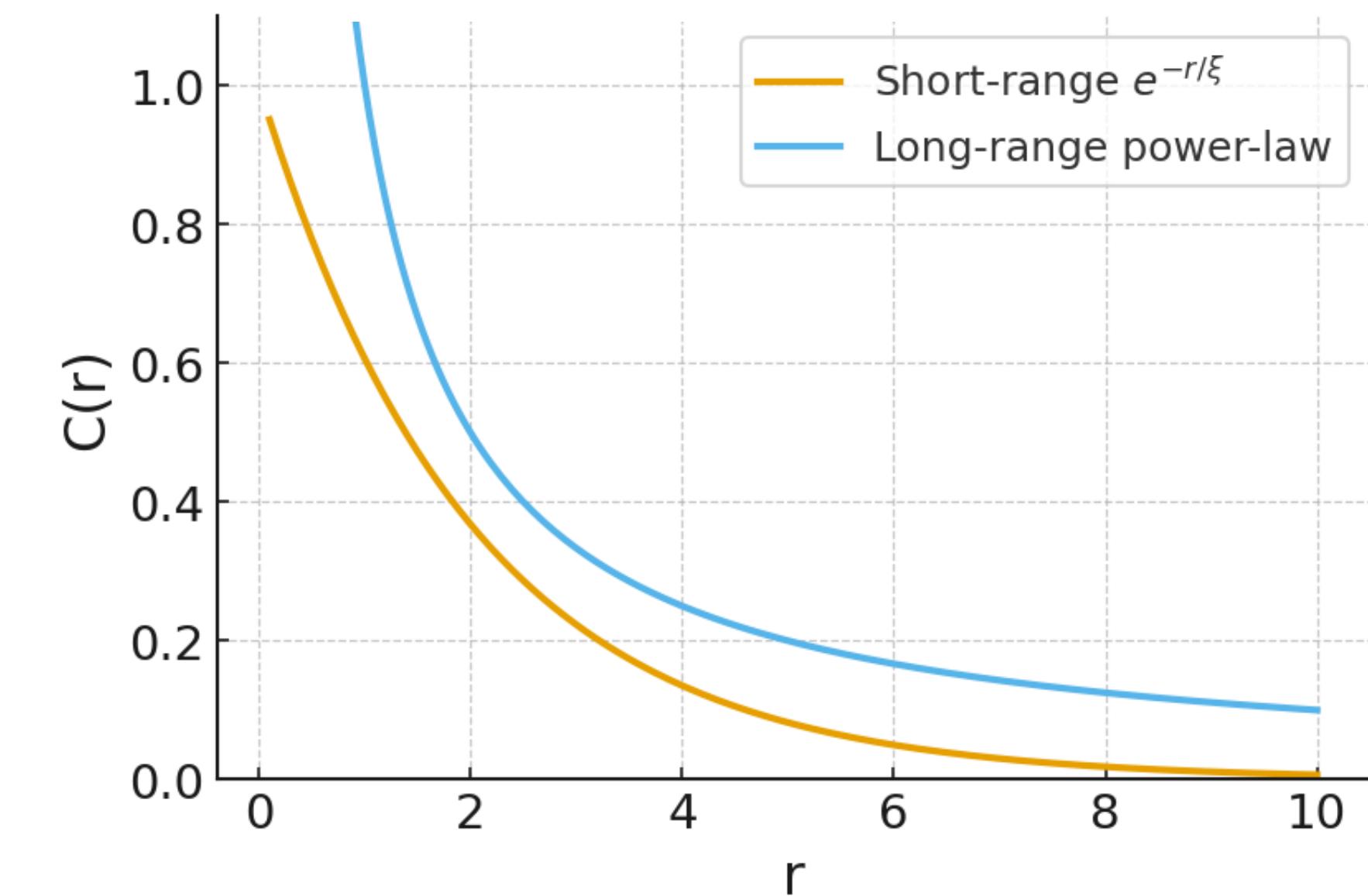
$$C(r) = \langle \phi(\vec{R})\phi(\vec{R} + \vec{r}) \rangle - \langle \phi(\vec{R}) \rangle^2 \quad r = |\vec{r}| \text{ is spatial separation}$$

and the average is over configurations

- In homogeneous/isotropic systems, $C(r)$ depends only on r .

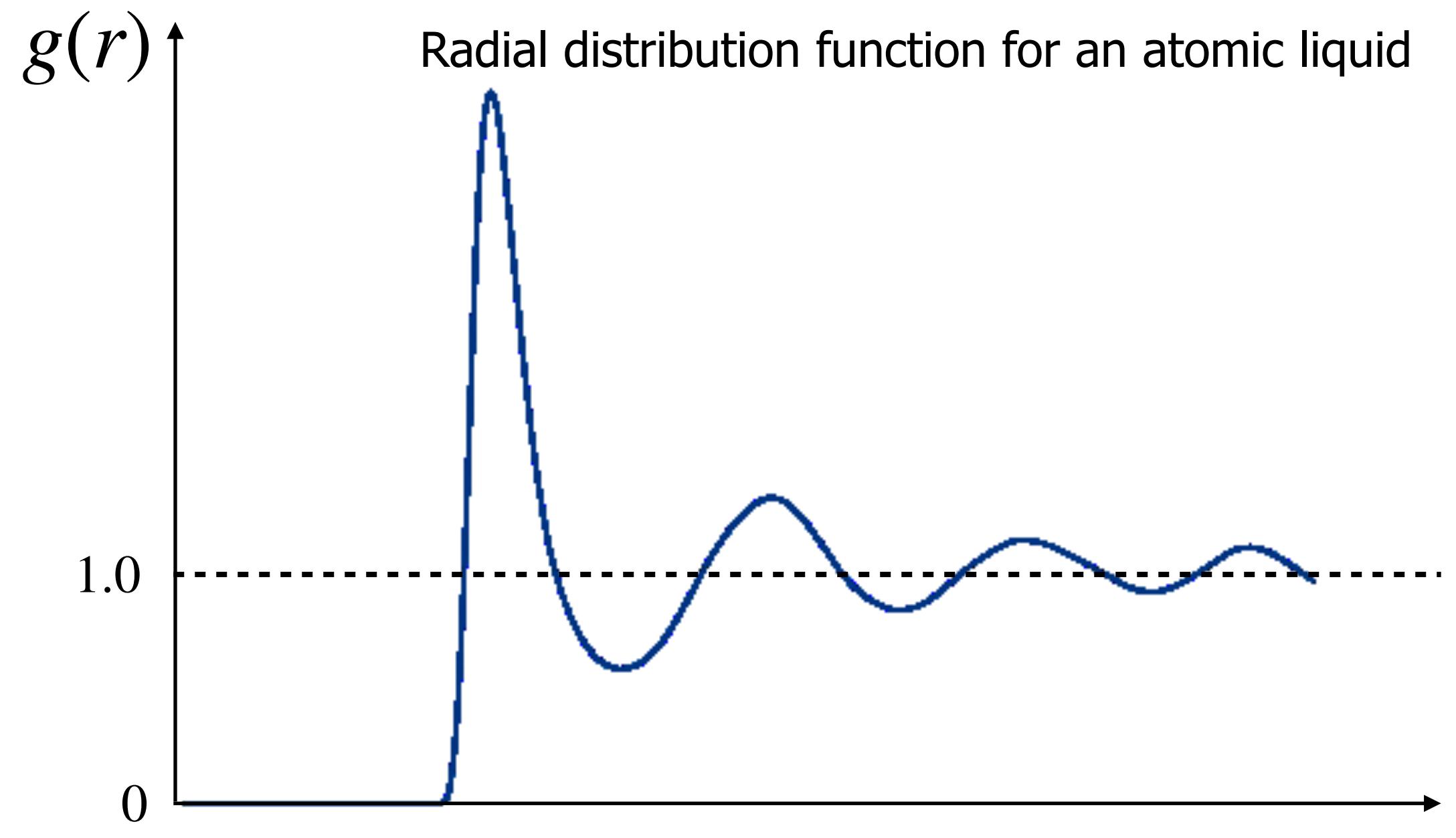
Behaviour of spatial correlations

- 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.

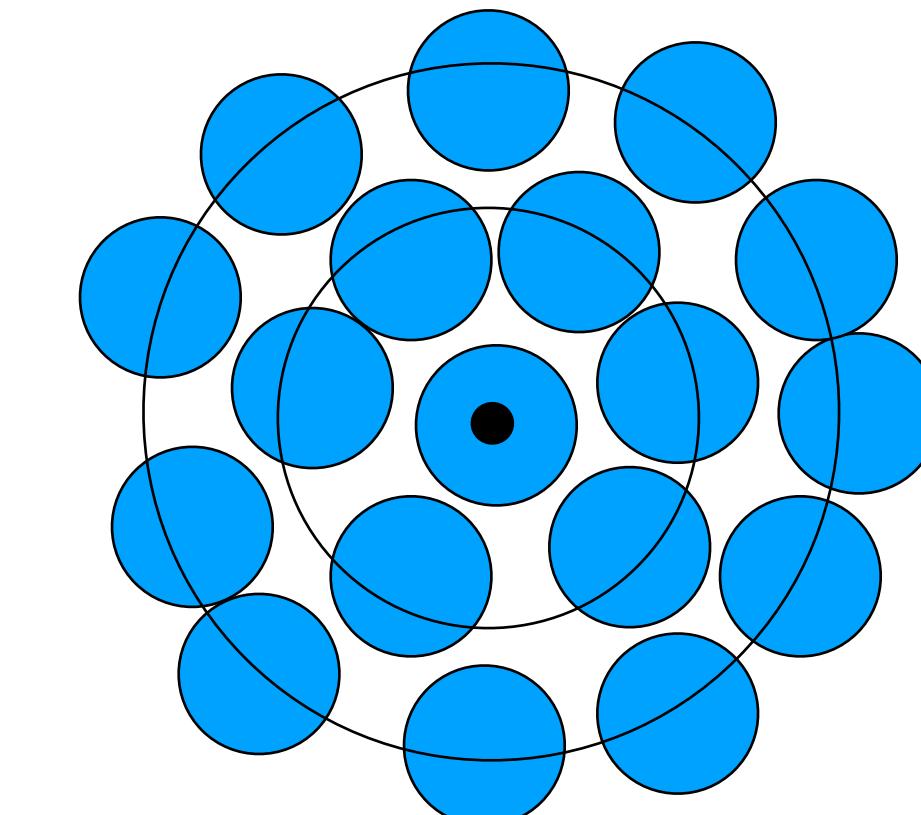


Pair Correlation Function (a.k.a radial distribution function)

- $g(r) = \text{probability of finding particle at distance } r \text{ relative to ideal gas.}$
- It is related to density correlations via: $g(r) = \frac{1}{\rho^2} \langle \rho(0)\rho(r) \rangle$



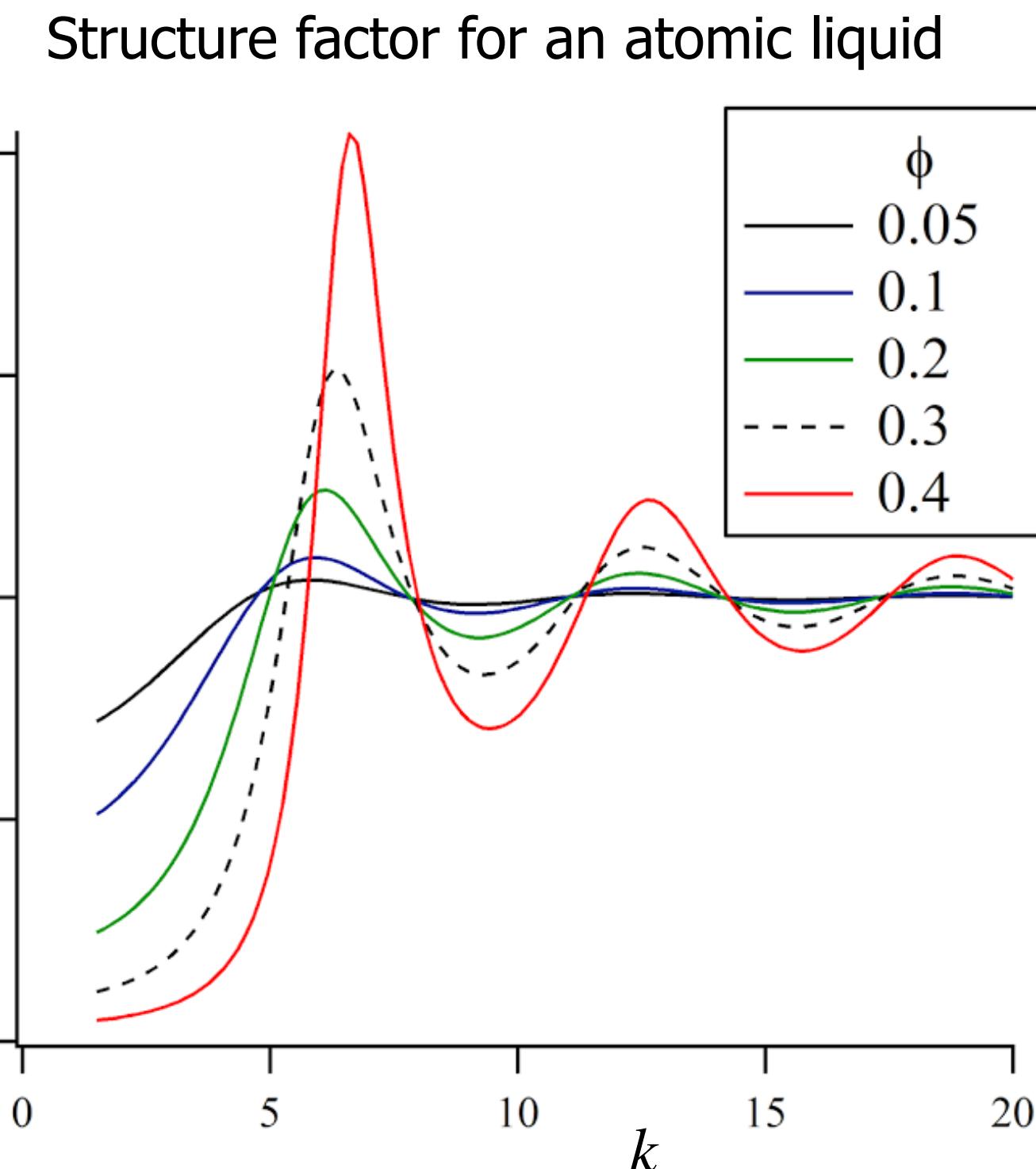
- At large r correlation die out, ie.
$$g(r) \rightarrow 1 \quad \text{as } r \rightarrow \infty$$



- 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 is the scattering wave vector (often also written as q)
- Measured in scattering experiments (see lecture 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:

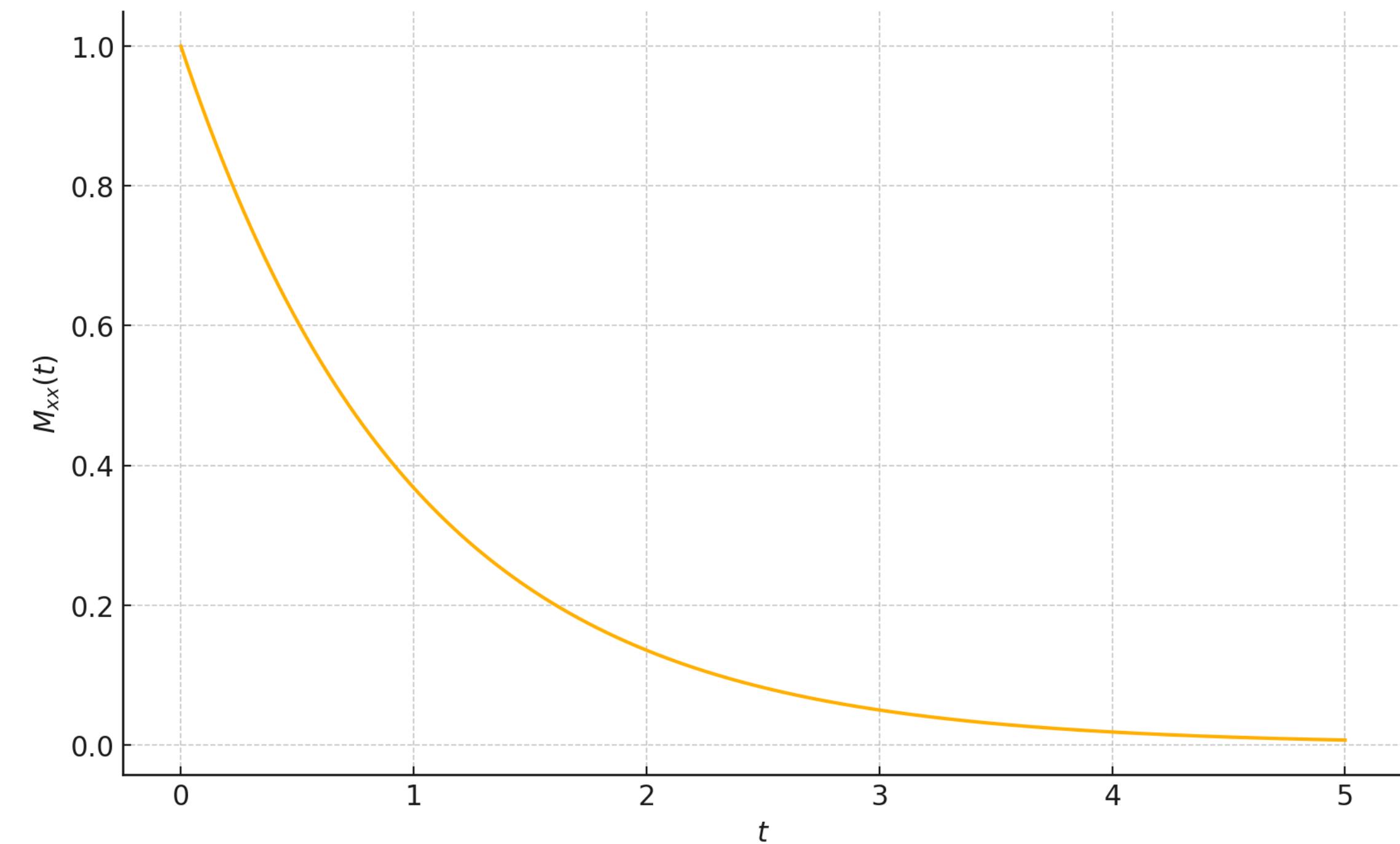
$$\langle x(\tau)x(\tau + t) \rangle$$

- In equilibrium: $\langle x(\tau)x(\tau + t) \rangle = M_{xx}(t)$

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 .

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

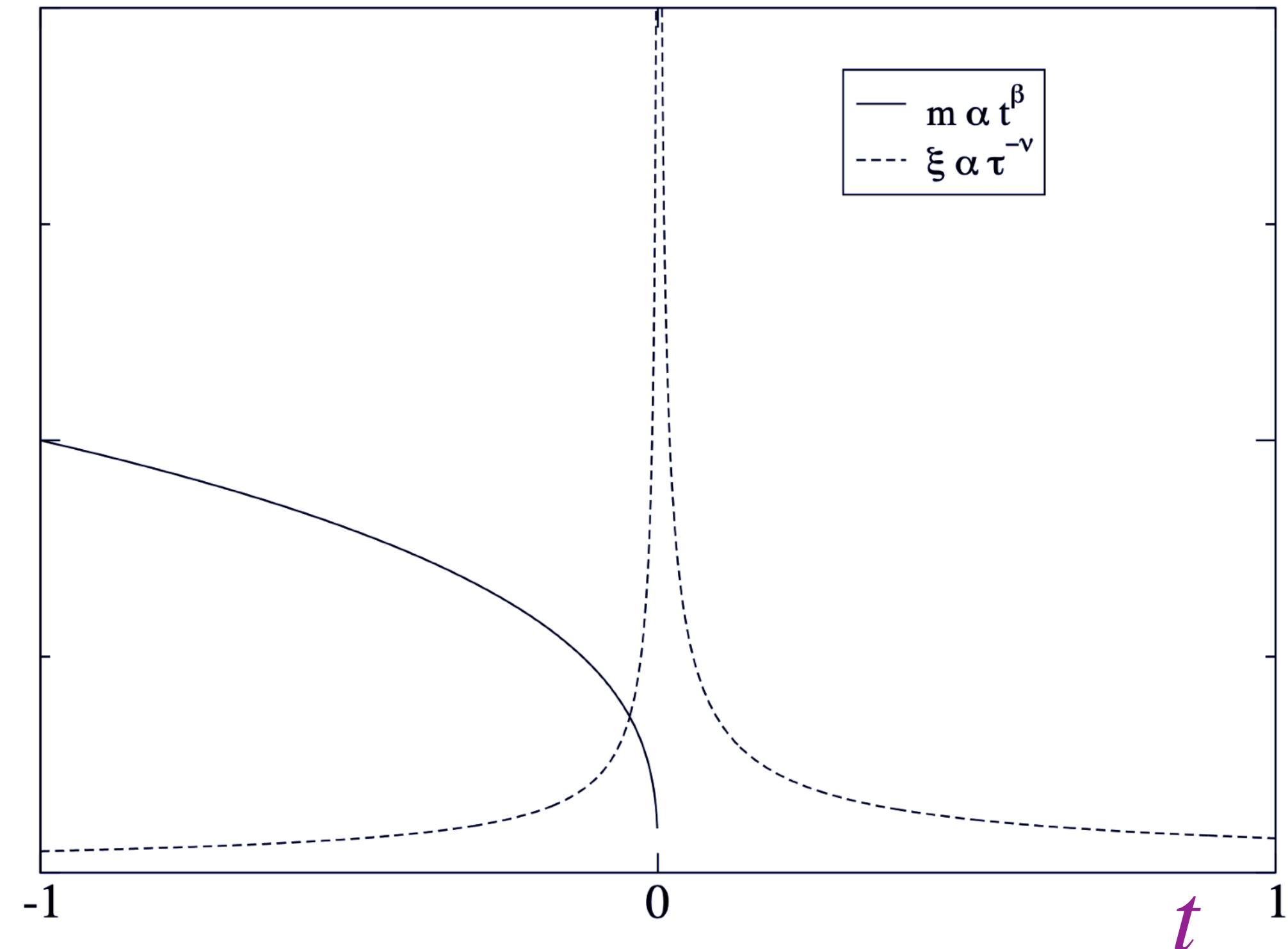
- Similar power law behaviour is found for the order parameter Q which vanishes in a singular fashion (it has infinite gradient) as $T \rightarrow T_c^-$

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

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.

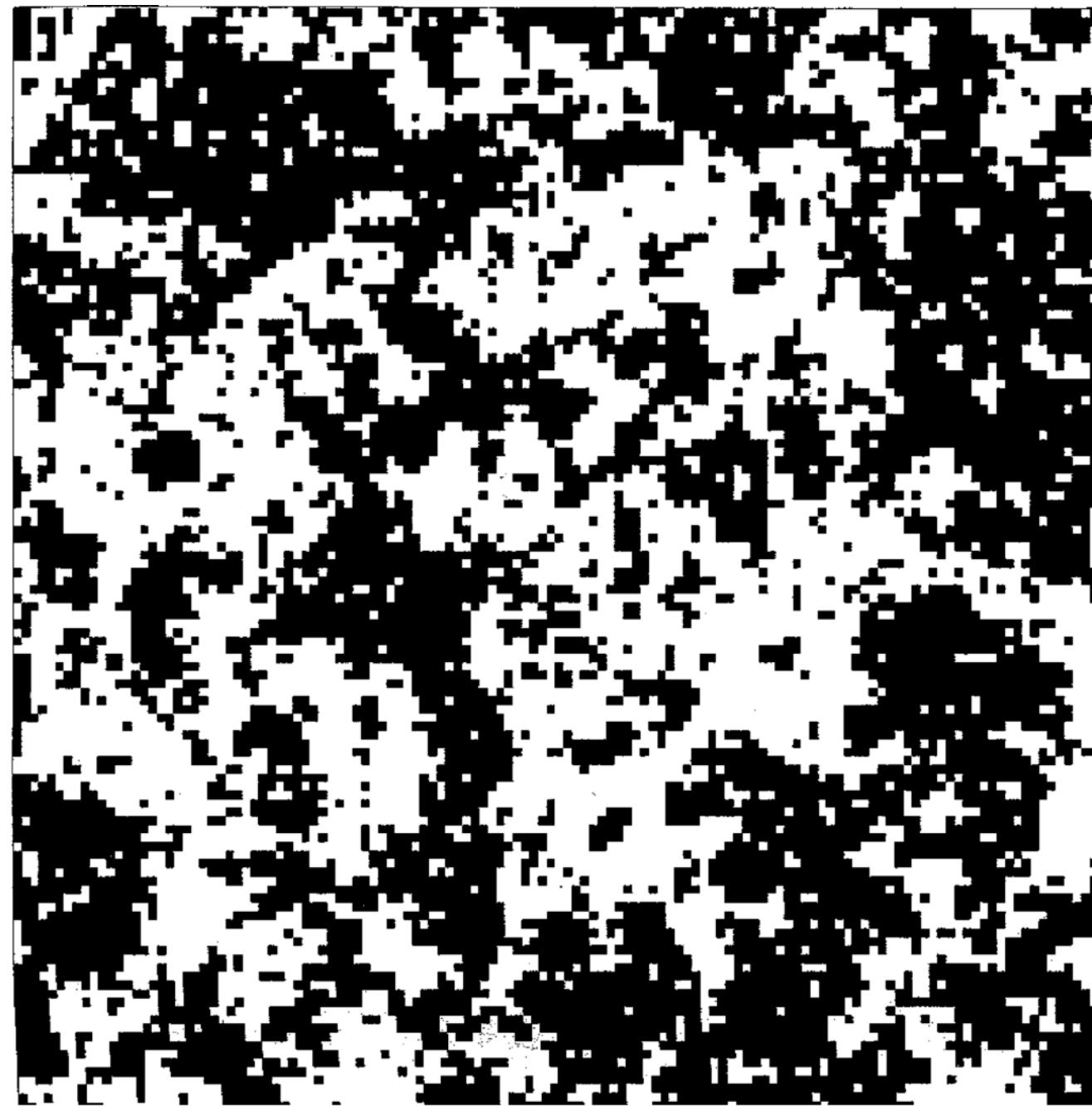
4. Ising model

- We can use simple models to probe the properties of the critical region.
- Simplest is the 2d spin $\text{spin-}\frac{1}{2}$ 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

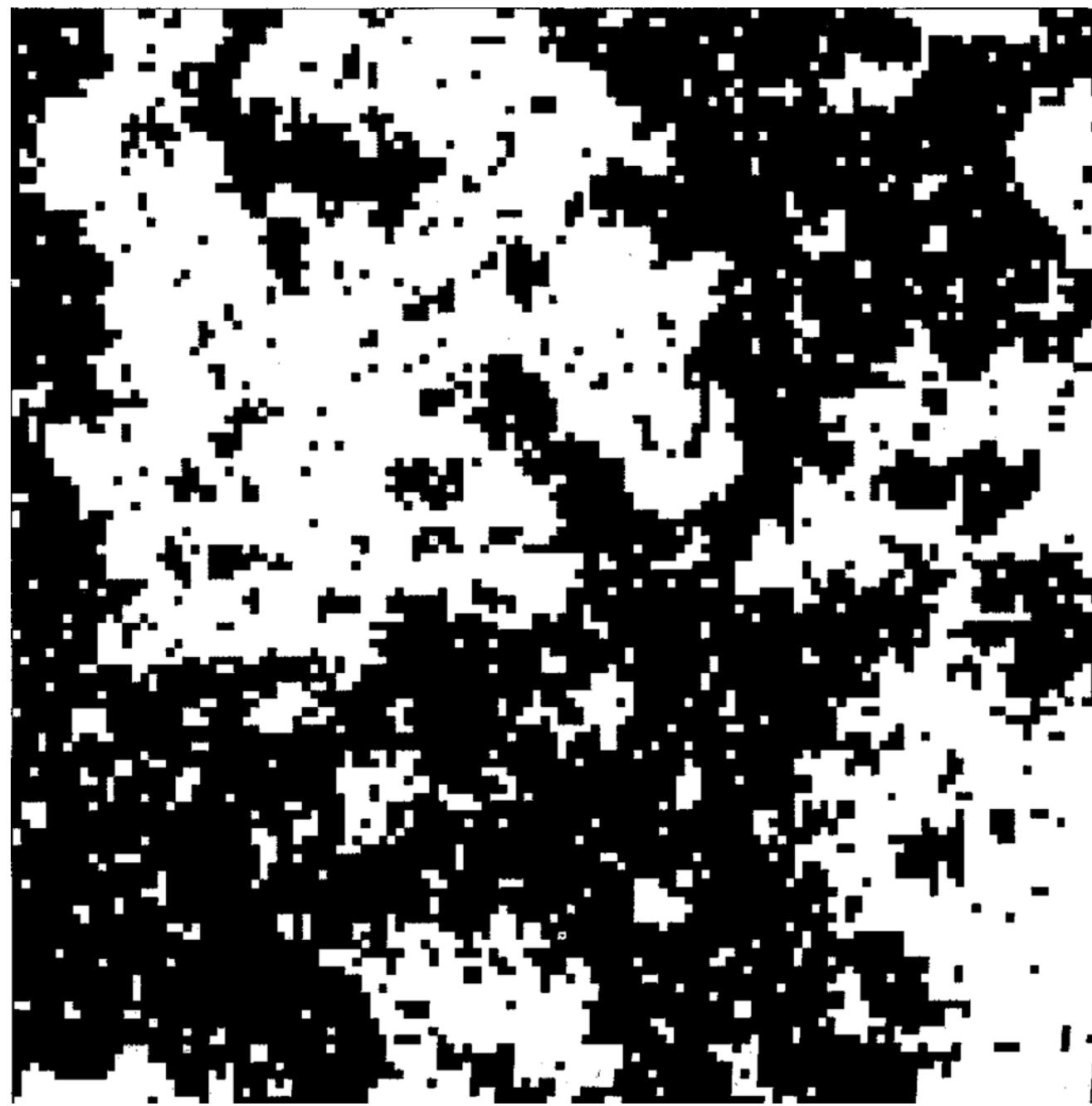
$$\mathcal{H}_I = - J \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i$$

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

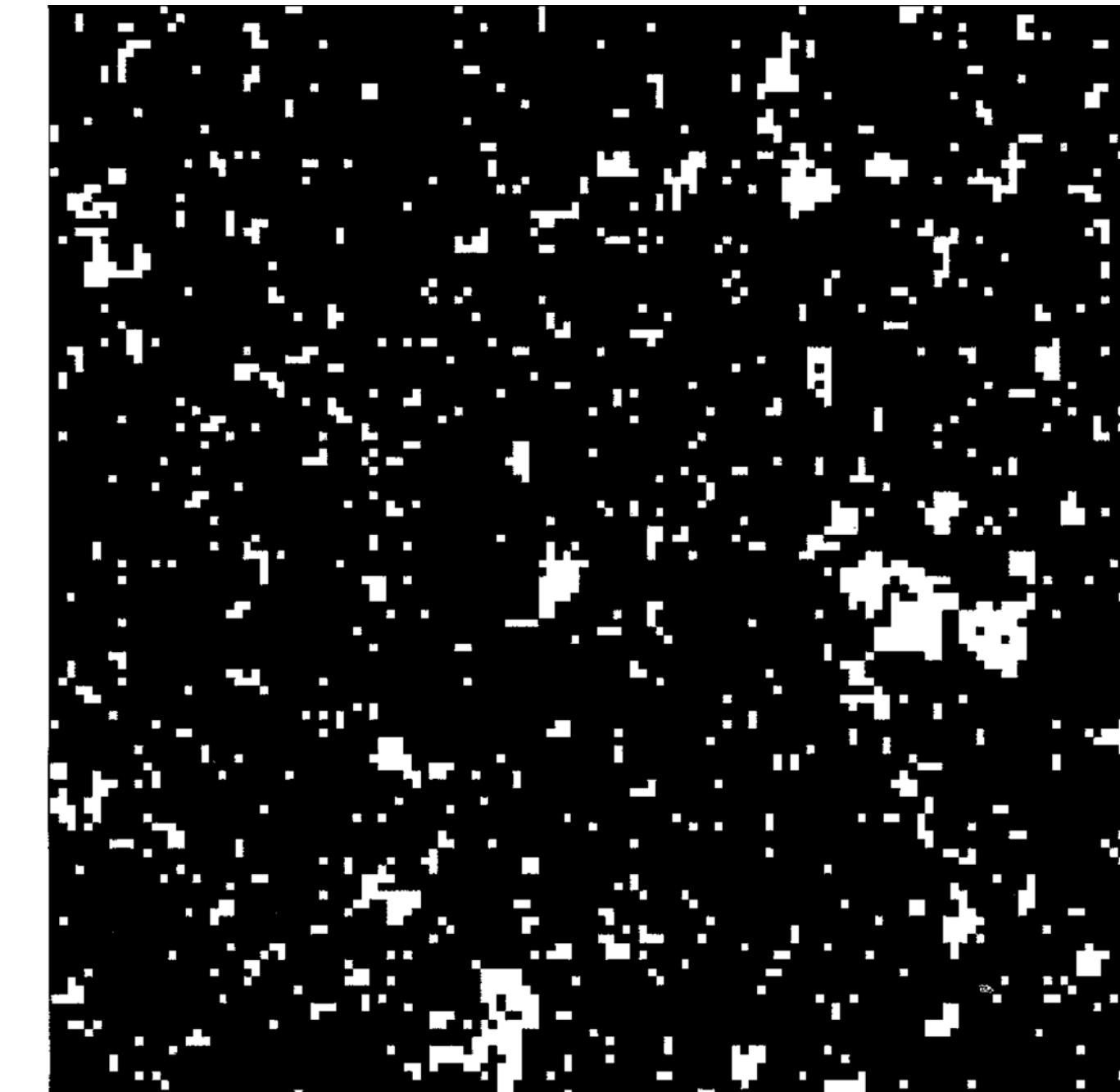
- At low temperatures for which there is little thermal disorder, there is a preponderance of aligned spins and hence a net spontaneous magnetic moment $|m| \approx 1$
- As T is raised, thermal disorder increases until at T_c , entropy drives the system through a continuous phase transition to a disordered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



$T = 1.2T_c$



$T = T_c$



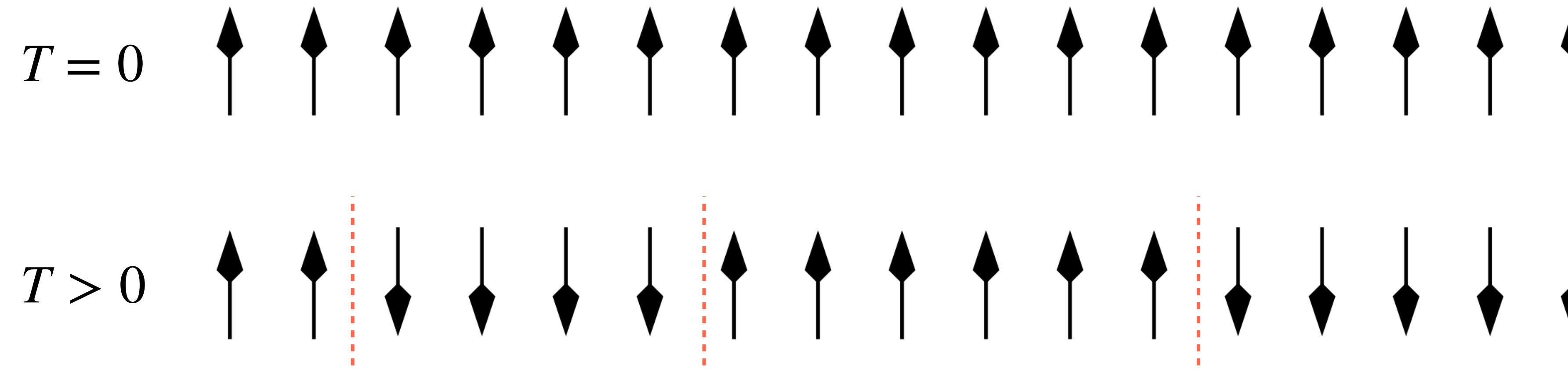
$T = 0.95T_c$

- 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 $\Delta = 2J$ independent of position (ie domain walls don't interact).
- 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

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

- The second term arises from the free energy 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

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

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

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

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.

- 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

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

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

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

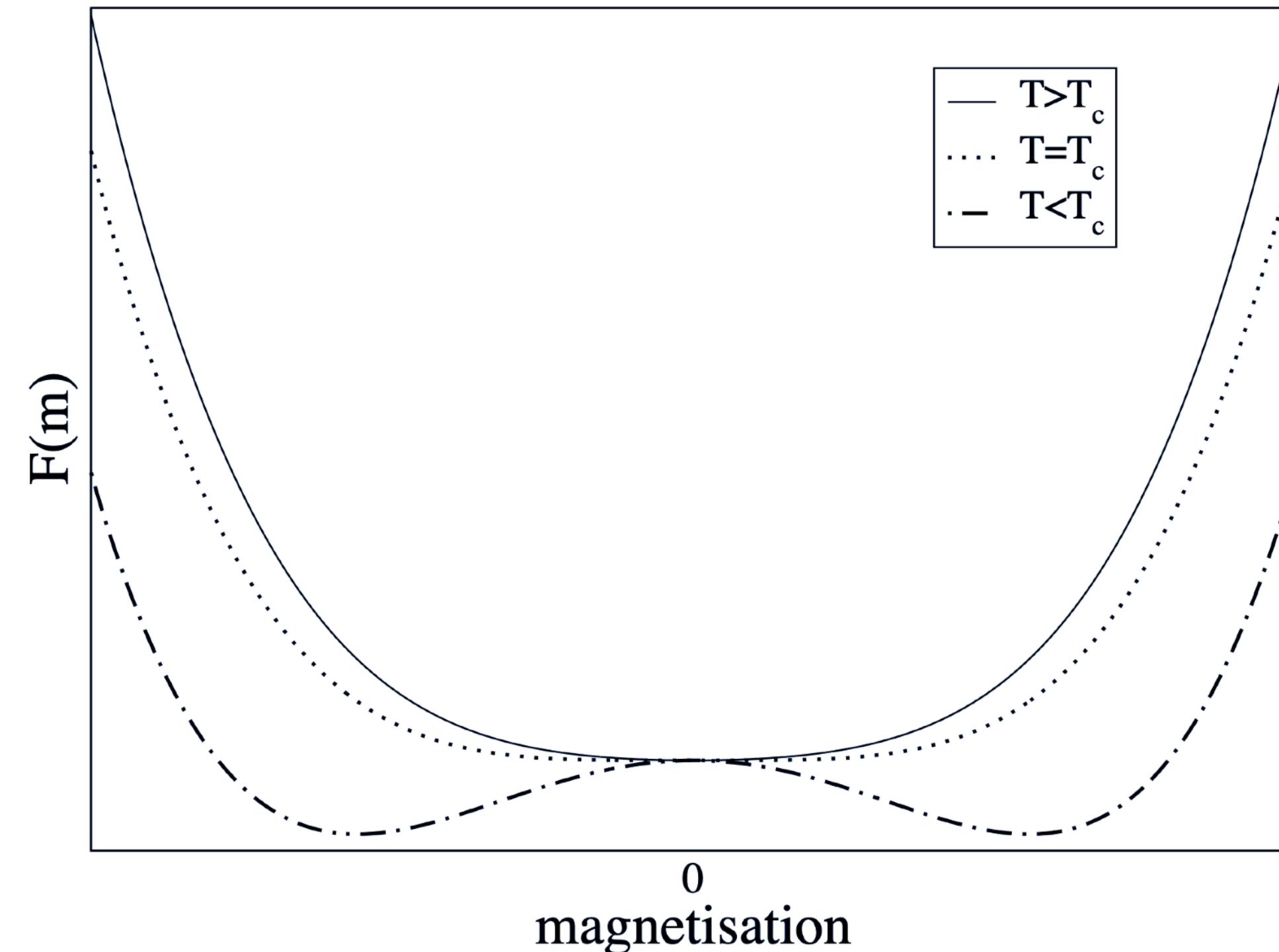
- To find $m(H, T)$, we must numerically solve this last equation self consistently.

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 → 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.

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

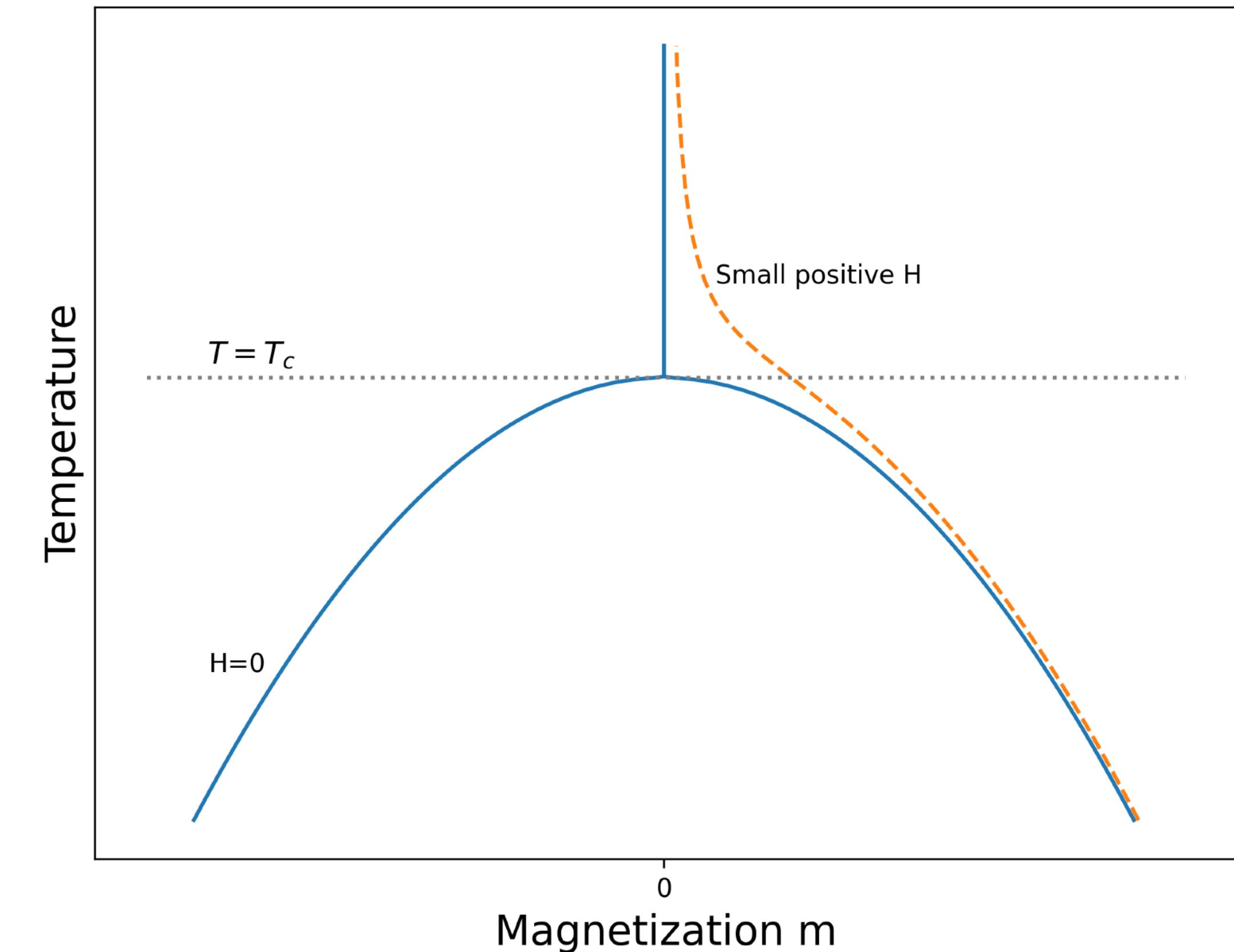
- At lower temperature: two minima at nonzero $m = \pm m^*$, where the equilibrium magnetisation m^* is the positive root (calculate explicitly below) of

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

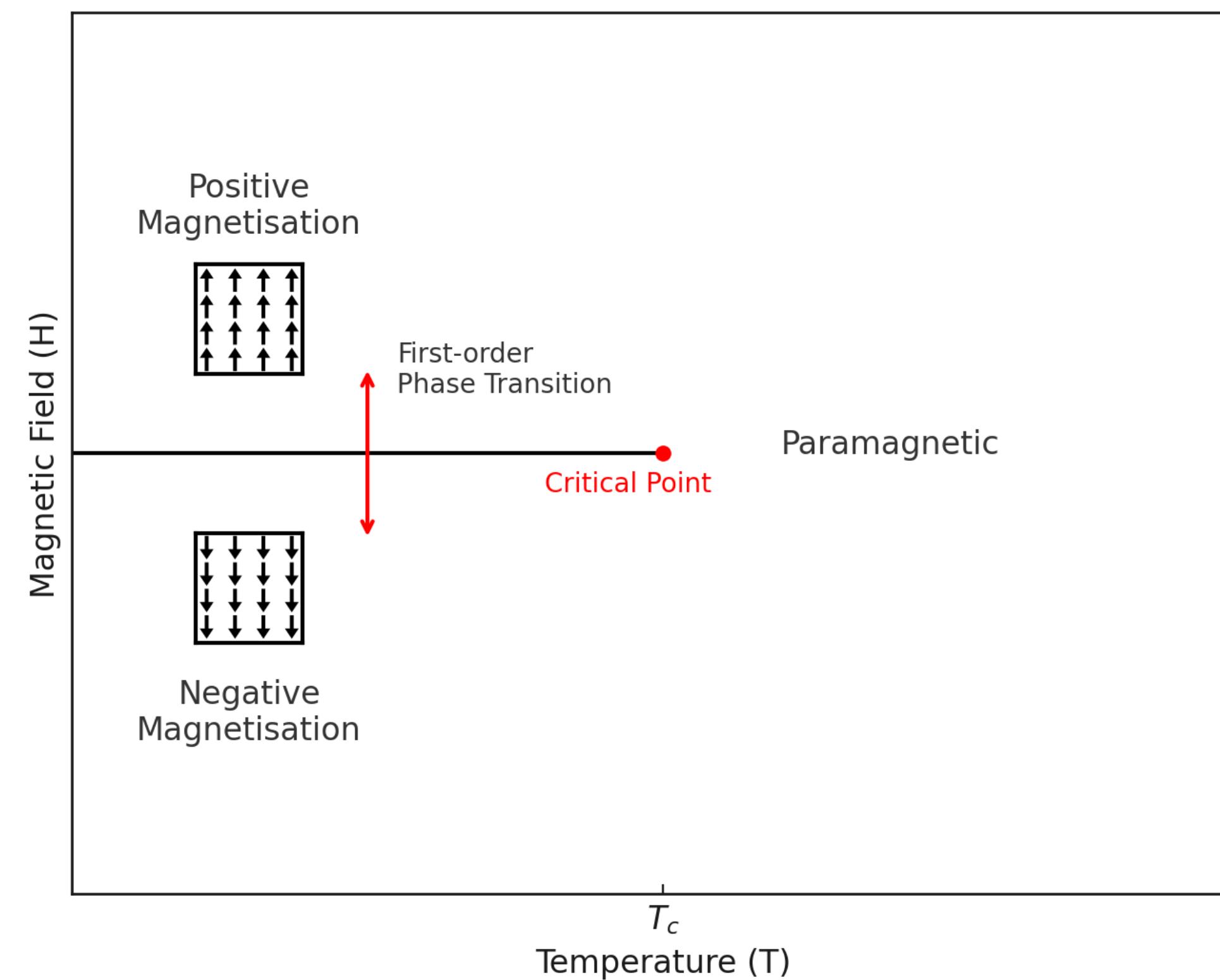
- $m^* = 0$ which remains a root of this equation, is clearly an unstable point for $T < T_c$ (since F has a maximum there).
- This is an example of spontaneous symmetry breaking: Pair of ferromagnetic states (spins mostly up, or spins mostly down) which - by symmetry - have the same free energy, lower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

Mean field predictions for critical exponents

- Look for a solution in zero field ($H = 0$) where m is small ($\ll 1$). Taylor expanding the \tanh function yields

$$m = \frac{mT_c}{T} - \frac{1}{3} \left(\frac{mT_c}{T} \right)^3 + O(m^5)$$

- Then $m = 0$ is one solution. The other solution is given by

$$m^2 = 3 \left(\frac{T}{T_c} \right)^3 \left(\frac{T_c}{T} - 1 \right)$$

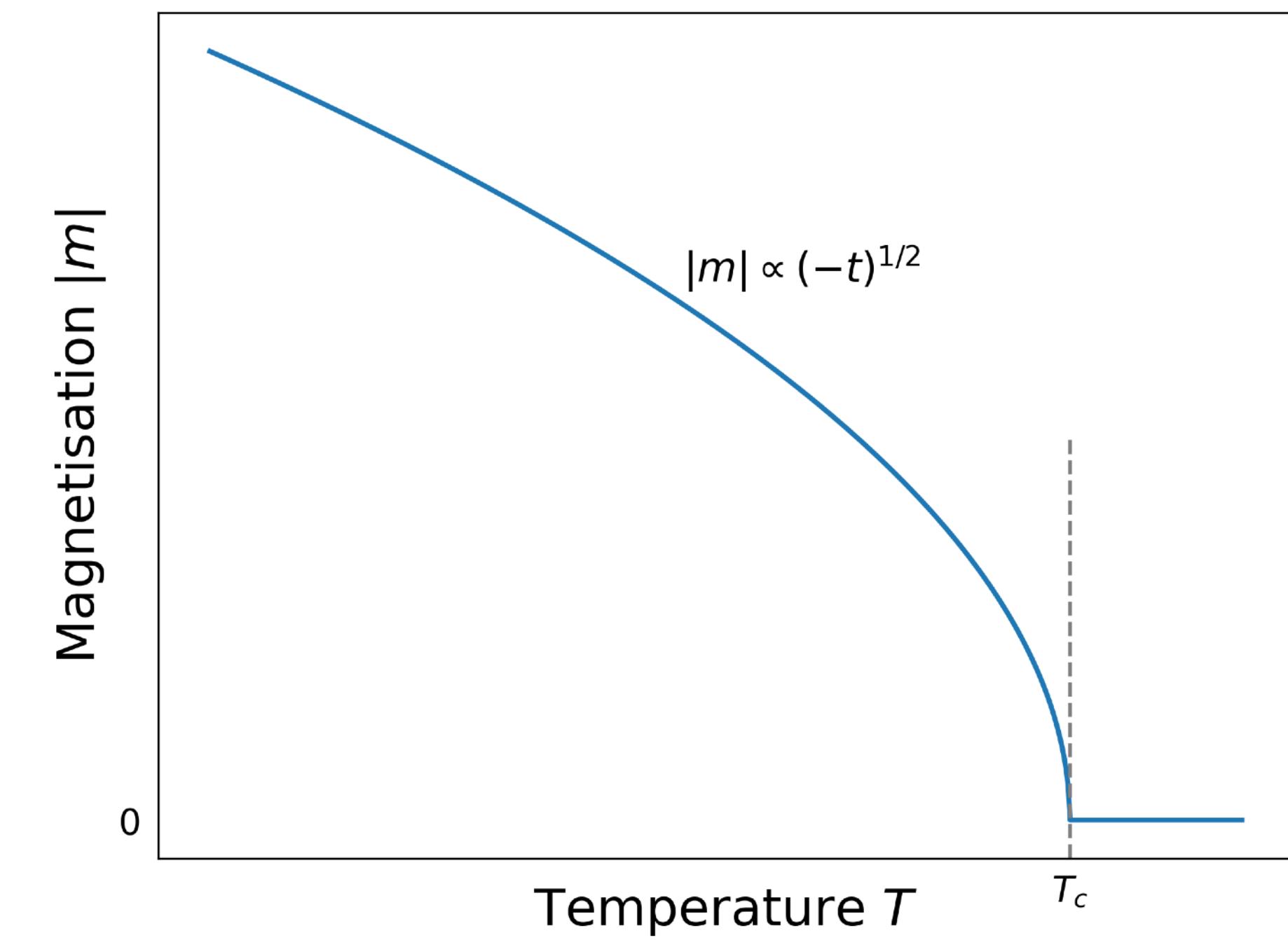
- Now, for T close to T_c (i.e. small m), and writing $t = (T - T_c)/T_c$, one finds

$$m^2 \simeq -3t$$

i.e.

$m = 0$ for $T > T_c$ since otherwise m imaginary

$m = \pm \sqrt{-3t}$ for $T < T_c$ real



- In a small finite field we can make the Taylor expansion

$$m = \frac{mT_c}{T} - \frac{1}{3} \left(\frac{mT_c}{T} \right)^3 + \frac{H}{kT}$$

- Consider now the isothermal susceptibility

$$\begin{aligned} \chi &\equiv \left(\frac{\partial m}{\partial H} \right)_T \\ &= \frac{T_c}{T} \chi - \left(\frac{T_c}{T} \right)^3 \chi m^2 + \frac{1}{k_B T} \end{aligned}$$

- Then

$$\chi \left[1 - \frac{T_c}{T} + \left(\frac{T_c}{T} \right)^3 m^2 \right] = \frac{1}{k_B T}$$

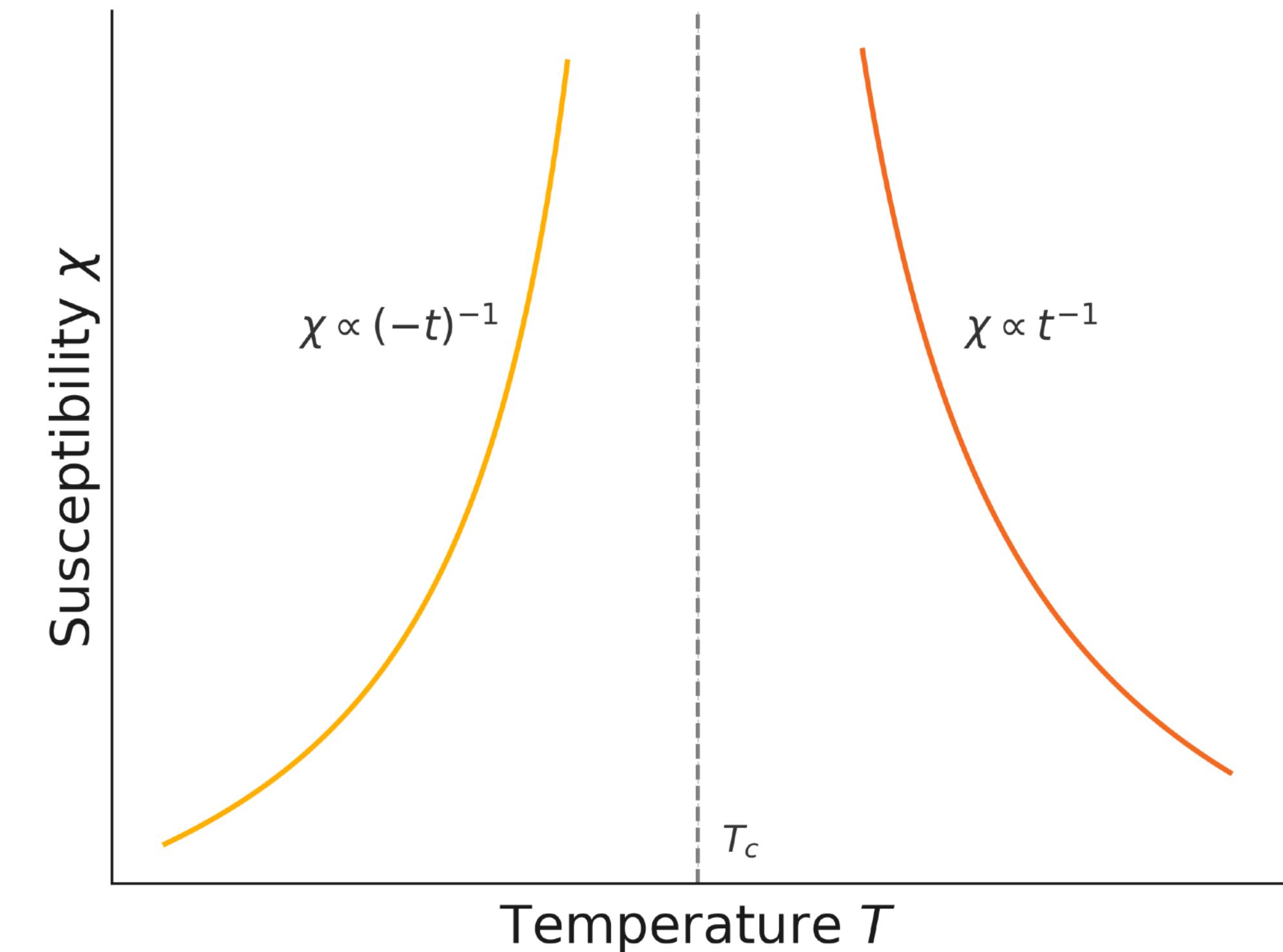
- Hence near T_c

$$\chi = \frac{1}{k_B T_c} \left(\frac{1}{t + m^2} \right)$$

And recalling that $m^2 \simeq -3t$ for $T < T_c$

$$\chi = (k_B T_c t)^{-1} \text{ for } T > T_c$$

$$\chi = (-2k_B T_c t)^{-1} \text{ for } T \leq T_c$$



where one has to take the non-zero value for m below T_c to ensure positive χ , i.e. thermodynamic stability.

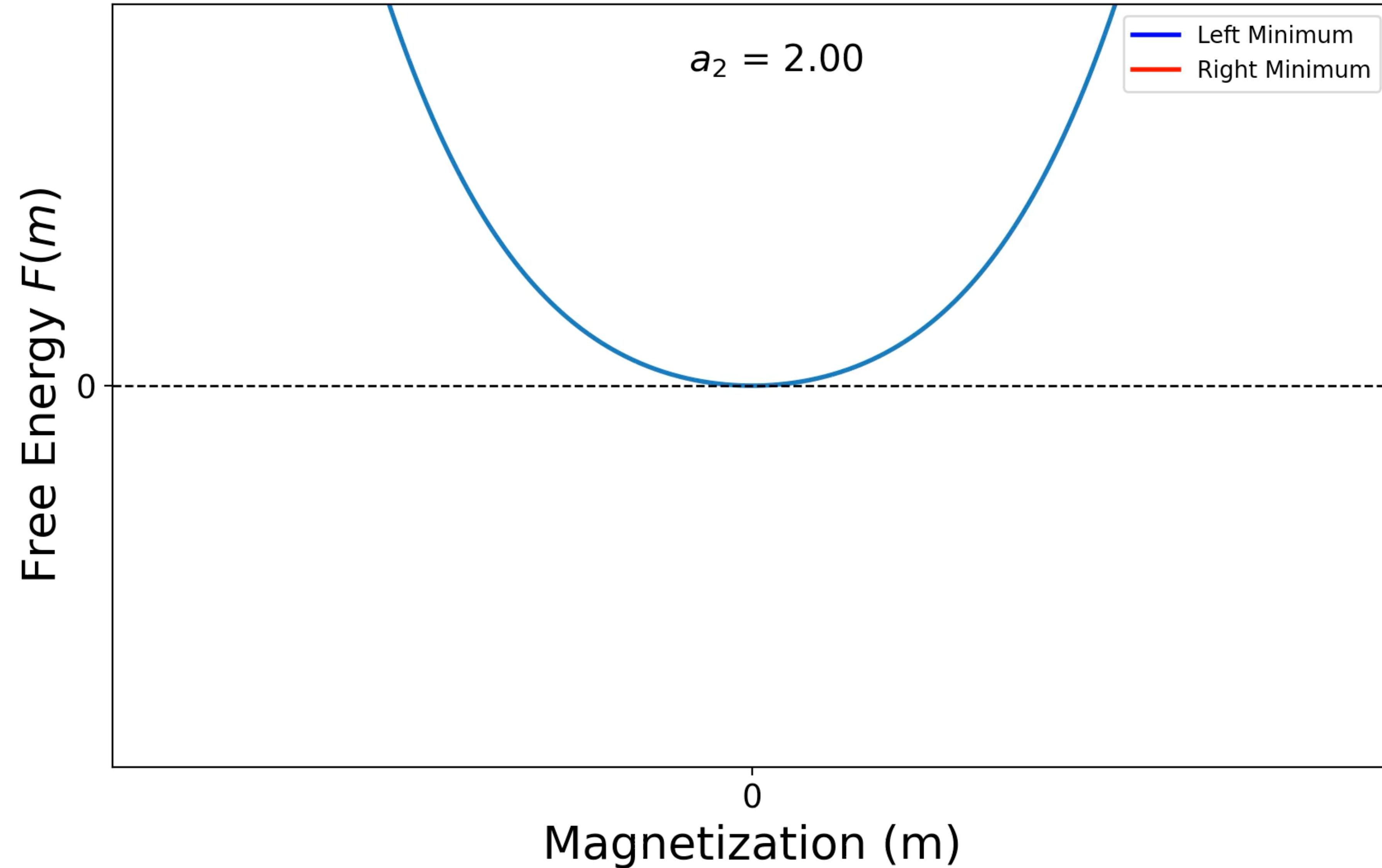
- This result implies that (within the mean field approximation) the critical exponent $\gamma = 1$.

Landau theory

- Landau theory is more general type of mean field theory. Not based on a particular microscopic model. We say that it is a **coarse-grained** theory
- Starting point is the Helmholtz free energy, which is written as a truncated power series expansion of the order parameter.
- For systems with a symmetrical order parameter (such as a ferromagnet where the energy is invariant under $m \rightarrow -m$) this takes the form

$$F(m) = F_0 + a_2 m^2 + a_4 m^4$$

- Equilibrium m is that for which $F(m)$ is minimum.
- Plots of the Landau free energy (for various a_2 , with $a_4 > 0$) show how it gives rise to a critical point



- Thermodynamics tells us that the system adopts the state of lowest free energy.
- Thus for $a_2 > 0$, the system will have $m = 0$, i.e. will be in the disordered (or paramagnetic) phase.
- For $a_2 < 0$, minimum of F occurs at two symmetric minima at $m = \pm m_0$, i.e., the ordered phase is the stable one.

- $a_2 = 0$ corresponds to the critical point which marks the border between the ordered and disordered phases.
- Thus clearly a_2 controls the deviation from the critical temperature, i.e. $a_2 = \tilde{a}_2 t$
- Can now attempt to calculate critical exponents. First find equilibrium magnetisation, corresponding to the minimum of the Landau free energy:

$$\frac{dF}{dm} = 2\tilde{a}_2 tm + 4a_4 m^3 = 0$$

$$\Rightarrow m \propto (-t)^{1/2}, \quad \text{so } \beta = 1/2, \text{ (mean field result).}$$

- We can also calculate the effect of a small field H if we sit at T_c . Since $a_2 = 0$, we have

$$F(m) = F_0 + a_4 m^4 - Hm$$

$$\frac{\partial F}{\partial m} = 0 \Rightarrow m(H, T_c) = \left(\frac{H}{4a_4} \right)^{1/3}$$

or $H \sim m^\delta$ ie. $\delta = 3$ which defines a second critical exponent.

- Thirdly, Magnetic susceptibility at zero field

$$\chi = \left(\frac{\partial m}{\partial H} \right)_{T,V} \sim |T - T_c|^{-\gamma}$$

Exercise: Show that $\gamma = 1$

- Finally heat capacity (per site or per unit volume) C_H , for $H = 0$:

$$C_H \sim |T - T_c|^{-\alpha}$$

Exercise: Show that $\alpha = 0$

Shortcomings of mean field theories

- In real ferromagnets, as well as in more sophisticated theories, the exponents β and γ are not the simple fraction and integers found here.
- This failure of mean field theory to predict the correct exponents is of course traceable to their neglect of correlations.

	Mean Field	$d = 1$	$d = 2$	$d = 3$
Critical temperature $k_B T / qJ$	1	0	0.5673	0.75
Order parameter exponent β	$\frac{1}{2}$	-	$\frac{1}{8}$	0.325 ± 0.001
Susceptibility exponent γ	1	∞	$\frac{7}{4}$	1.24 ± 0.001
Correlation length exponent ν	$\frac{1}{2}$	∞	1	0.63 ± 0.001

6. Static Scaling Hypothesis

- The static scaling hypothesis provides a basis for power law behaviour. Moreover it predicts the existence of so-called **scaling phenomena** in near-critical systems.
- The hypothesis asserts that: near criticality, the free energy is a so-called generalised homogeneous function of the thermodynamic fields.
- A function of two variables $g(u, v)$ is called a generalised homogeneous function if it has the property

$$g(\lambda^a u, \lambda^b v) = \lambda g(u, v) \quad \text{for all } \lambda$$

where the parameters a and b (known as scaling parameters) are constants

- An example of such a function is $g(u, v) = u^3 + v^2$ with $a = 1/3$, $b = 1/2$.

- For such functions one can always implement a **change of scale**, to reduce the dependence on two variables (e.g. t and h) to dependence on one new variable.
- The arbitrary scale factor λ can be chosen as $\lambda^a = u^{-1}$ giving

$$g(u, v) = u^{1/a} g\left(1, \frac{v}{u^{b/a}}\right)$$

- Thus $g(u, v)$ satisfies a simple power law in **one** variable, provided $v/u^{b/a} = C$. Note, however, that this relationship specifies neither the function g nor the parameters a and b .
- Scaling hypothesis asserts that in the critical region, the free energy F is a generalised homogeneous function of thermodynamic fields
- Thus for the ferromagnet (fields t and h):

$$F(\lambda^a t, \lambda^b h) = \lambda F(t, h)$$

- Without loss of generality, we can set $\lambda^a = t^{-1}$, implying $\lambda = t^{-1/a}$ and $\lambda^b = t^{-b/a}$.

- Then

$$F(t, h) = t^{1/a} F(1, t^{-b/a} h)$$

where our choice of λ ensures that the r.h.s is now a function of a single variable $t^{-b/a}h$

- An expression for the magnetisation can be obtained simply by taking the field derivative of F

$$m(t, h) = -t^{(1-b)/a} m(1, t^{-b/a} h)$$

- In zero applied field $h = 0$, this reduces to

$$m(t, 0) = (-t)^{(1-b)/a} m(1, 0)$$

where the r.h.s. is a power law in t

- Can now identify the exponent β in terms of the scaling parameters a and b .

$$\beta = \frac{1 - b}{a}$$

- By differentiating the free energy, other relations between scaling parameters and critical exponents may be deduced.
- Such calculations (try as an exercise!) yield the results
 $\delta = b/(1 - b)$, $\gamma = (2b - 1)/a$, $\alpha = (2a - 1)/a$
- Relationships between the critical exponents follow by eliminating the scaling parameters from these equations. The principal results (known as ``scaling laws'') are:-

$$\begin{aligned}\alpha + \beta(\delta + 1) &= 2 \\ \alpha + 2\beta + \gamma &= 2\end{aligned}$$

- Thus only two critical exponents need be specified, for all others to be deduced.

Experimental Verification of Scaling

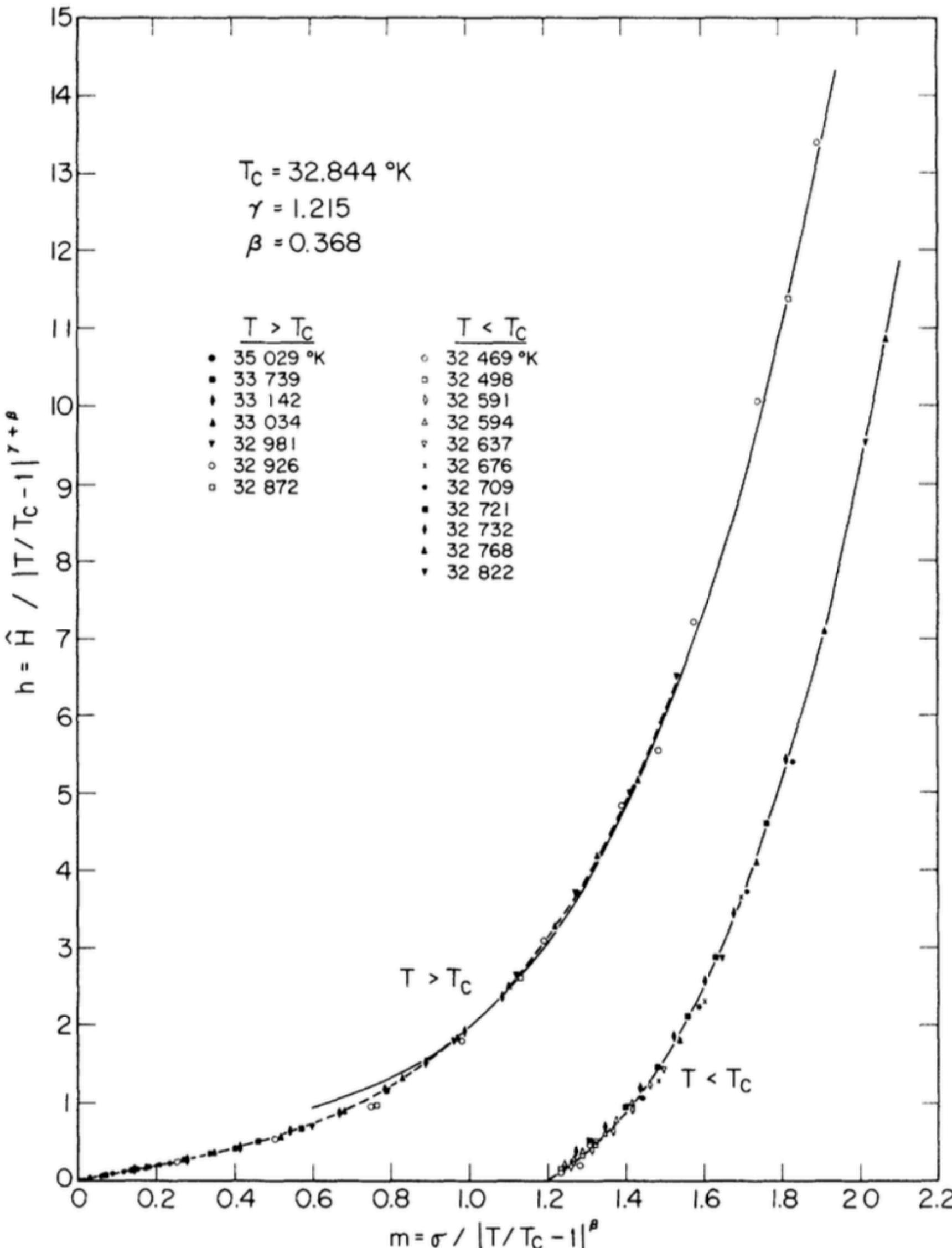
- Experiments confirm the scaling hypothesis.
- Rewriting the above expression for $m(t, h)$ in terms of the exponents β and δ , one finds

$$\frac{m(t, h)}{t^\beta} = m\left(1, \frac{h}{t^{\beta\delta}}\right)$$

where the r.h.s. is a function of the single scaled variable $\tilde{H} \equiv t^{-\beta\delta}h(t, M)$.

- For some magnet, measure m vs h for various fixed temperatures and construct $m - h$ isotherms.
- Plotting the data against the scaling variables $\tilde{M} = t^{-\beta}m(t, h)$ and $\tilde{H} = t^{-\beta\delta}h(t, M)$ one finds scaling, i.e. all isotherms collapse onto a single curve, one for $t > 0$, and another for $t < 0$.

Magnetisation of CrBr₃ in the critical region plotted in scaled form

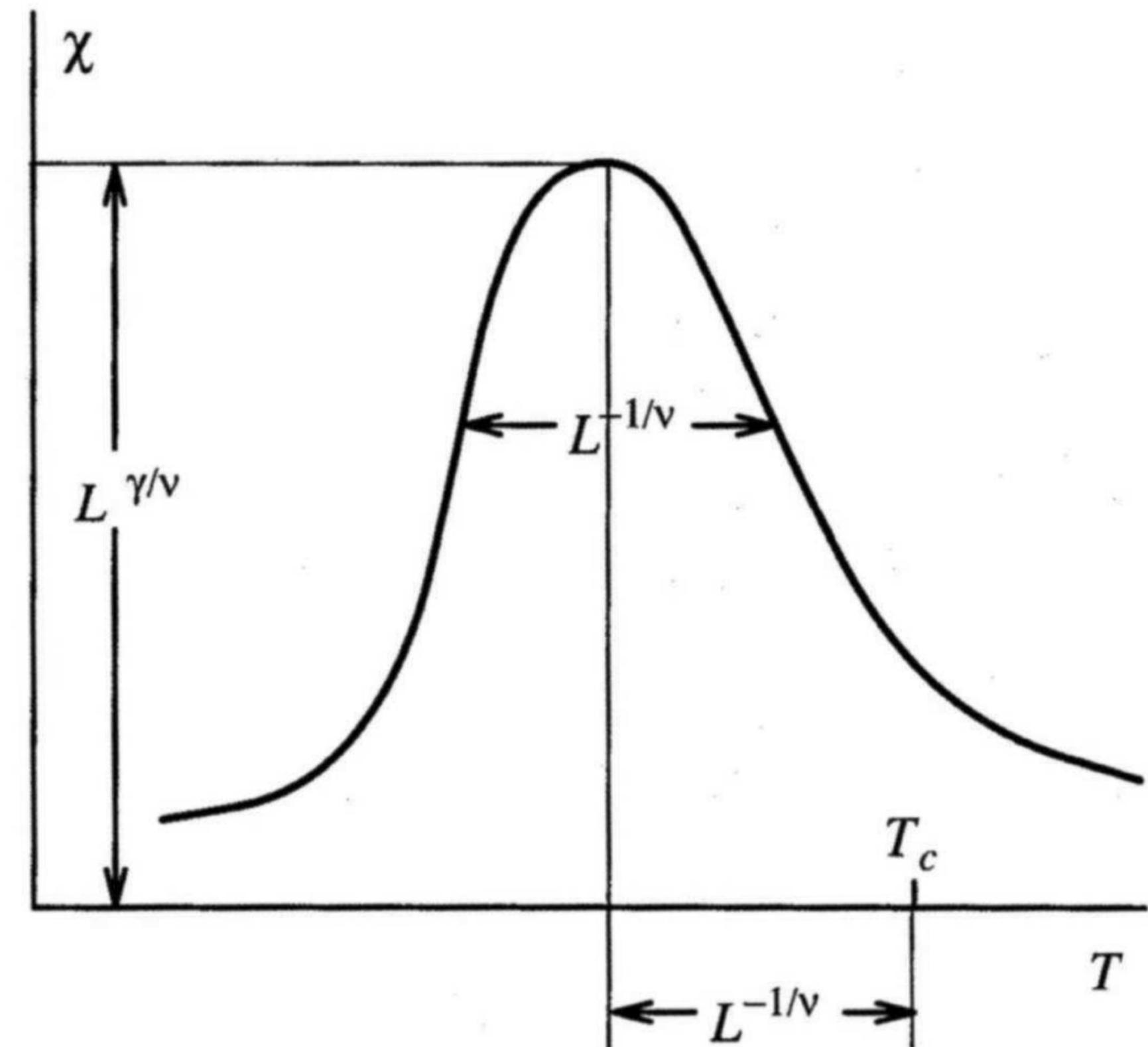


- Similar results are found using the scaled equation of state of simple fluid systems such as He³ or Xe.

Computer simulation

- Simulation widely used to study critical point phenomena,
- But computational constraints restrict one to dealing with systems of finite-size.
- Cannot access the regime of truly long ranged fluctuations that characterize the near-critical regime.

- As a consequence, the critical singularities in C_V, χ_T , order parameter, etc. appear rounded and shifted in a simulation study.
- The peak position does not provide an accurate estimate of the critical temperature.



- Although the degree of rounding and shifting reduces with system size, it still makes it hard access to the largest system sizes which would provide accurate estaimates of critical parameters.
- To deal with this, finite-size scaling methods have been developed.
- Finite-size scaling allows extraction of bulk critical properties from simulations of finite size (see later)

7. Universality and Renormalisation Group Theory

- Critical region is characterised by correlated microstructure on **all** length-scales up to and including the correlation length.
- Can only be accurately characterised by a very large number of variables.
- Mean field approaches fail because they at best incorporate interactions among only a few nearby spins.
- The scaling hypothesis fails to provide more than qualitative insight because it focuses on only one length-scale, effectively ξ .
- To obtain a fuller understanding of the critical region, must take account of existence of structure on all length-scales.

The critical point: A many length scale problem

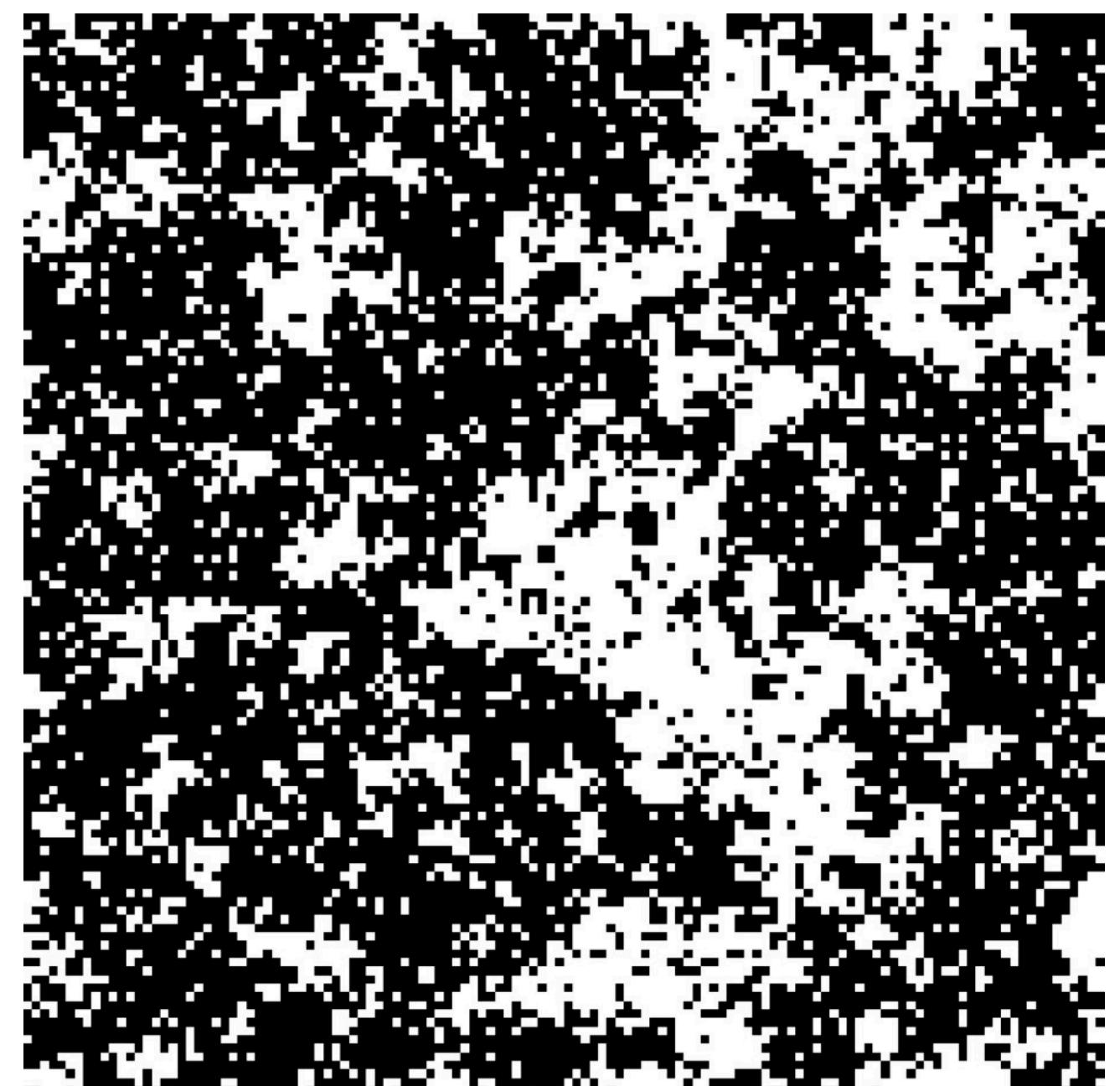
- A near critical system can be characterised by three important length scales, namely
 - (a) The correlation length, ξ , ie the size of correlated microstructure.
 - (b) Minimum length scale L_{min} , i.e. the smallest length in the microscopics of the problem, e.g. lattice spacing of a magnet or the particle size in a fluid.
 - (c) Macroscopic size L_{max} eg. size of the system.
- The authentic critical region is defined by a window condition:

$$L_{\max} \gg \xi \gg L_{\min}$$

- This regime is hard to tackle because it is characterised by configurational structure on all scales between L_{min} and ξ (it is fractal). Moreover structure on different length scales are correlated with one another.

Philosophy and Methodology of the RG

- Central idea: a stepwise elimination of the degrees of freedom of the system on successively larger length-scales.
- Introduce a fourth length scale L , which in contrast to the other three, characterises the **description** of the system.
- L typifies the size of the smallest resolvable detail in a description of the system's microstructure.
- Ising model snapshots contain **all** details of each configuration: the resolution length L in coincides with the lattice spacing i.e. $L = L_{min}$.
- But explicit form of the small scale microstructure is irrelevant to the behaviour of ξ . Microstructure is 'noise'.
- To eliminate it, select a larger value of L , the resolution (or 'coarse-graining') length

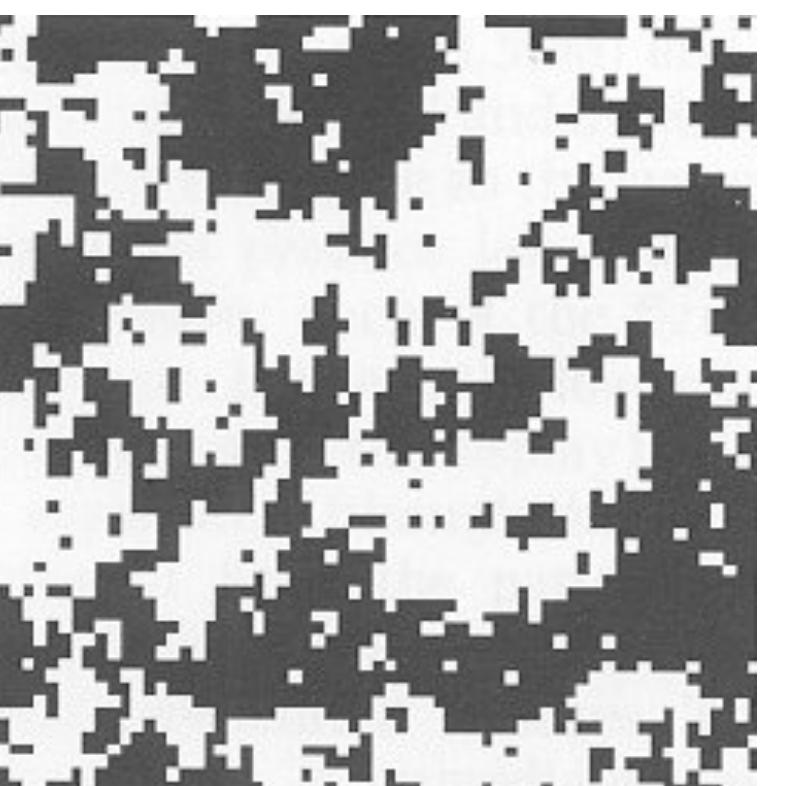
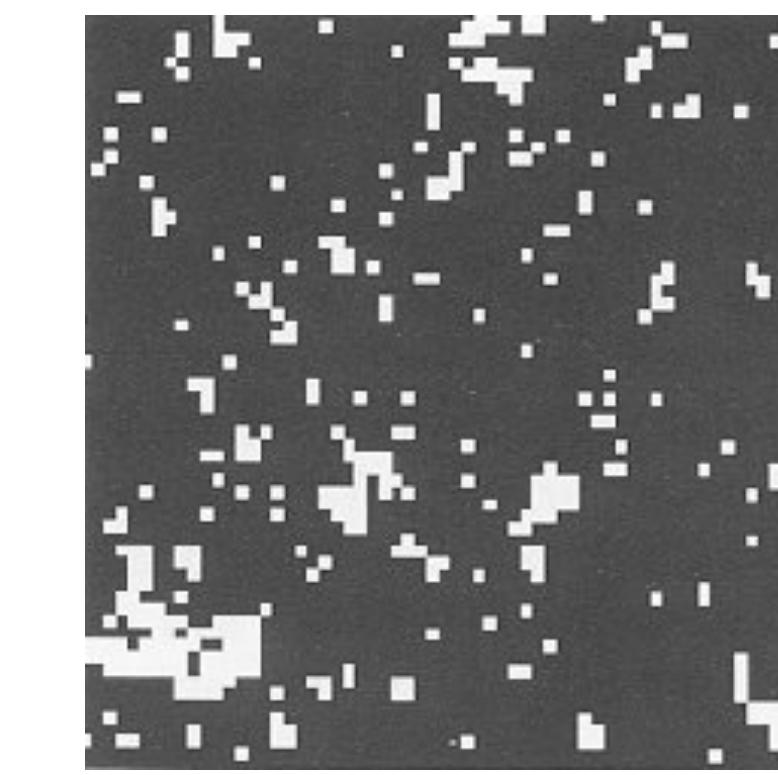
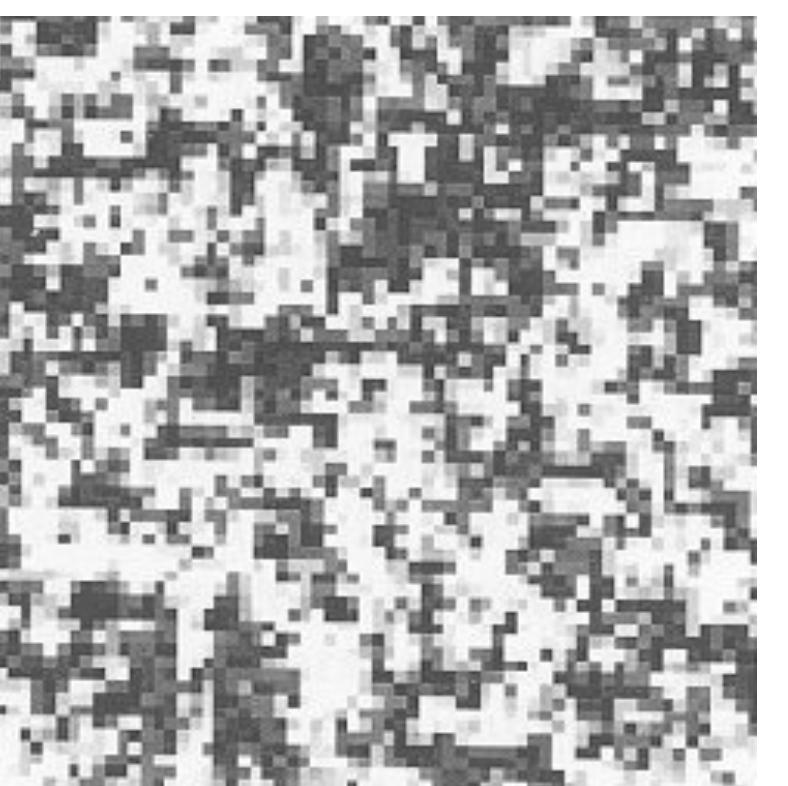
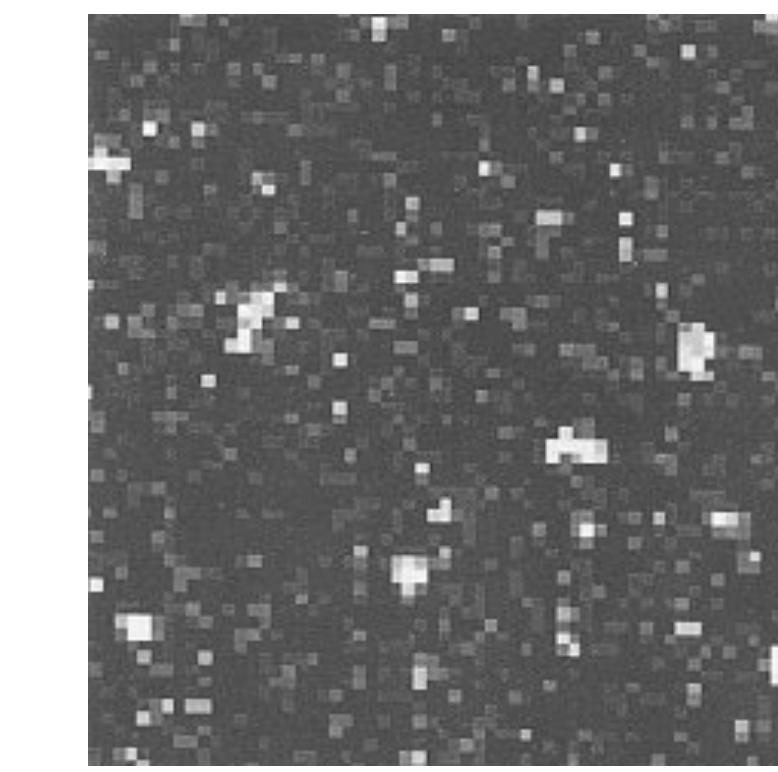
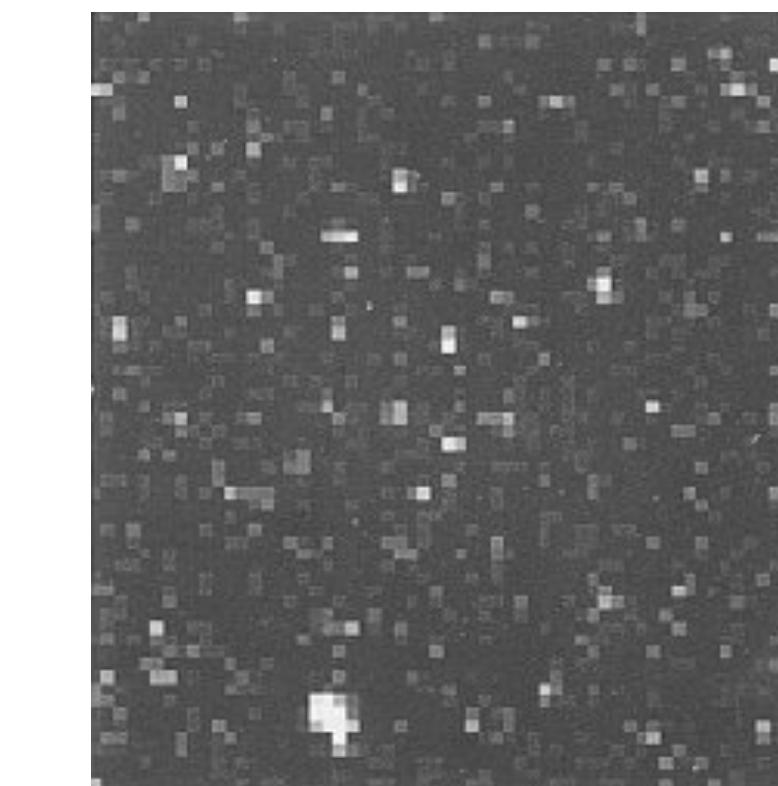


- There are many ways of implementing this ‘coarse-graining’ procedure.
- Adopt a simple strategy in which we divide our sample into blocks of side L , each of which contains L^d sites.
- The centres of the blocks define a lattice of points indexed by $I = 1, 2, \dots, N/L^d$. We associate with each block lattice point centre, I , a coarse-grained or block variable $S_I(L)$ defined as the spatial average of the local variables it contains:

$$S_I(L) = L^{-d} \sum_i^I s_i$$

- The set of coarse grained coordinates $\{S(L)\}$ are the basic ingredients of a picture of the system having spatial resolution of order L .

- Such a coarse graining operation is easily implemented on a computer.
- But while the underlying Ising spins can only take two possible values, the block variables $S_I(L)$ have $L^d + 1$ possible values.
- Thus, need a more elaborate colour convention to represent block spins.
Adopt a grey scale.
- Consider the results of coarse-graining configurations typical of three different temperatures: $T > T_c$, $T = T_c$, and $T < T_c$

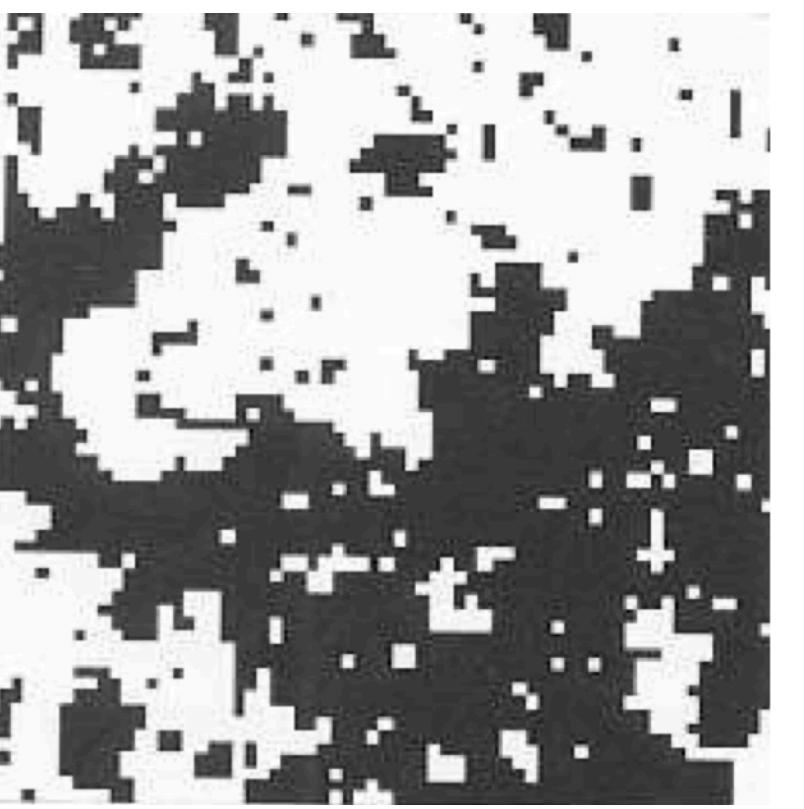
$T > T_c$ $L = 1$  $T < T_c$ $L = 1$  $L = 4$  $L = 4$  $L = 8$  $L = 8$ 

- Two auxiliary operations are implicit in these results
 - A length scaling: the lattice spacing on each blocked lattice is scaled to that of the original lattice. Can display correspondingly larger portions of the physical system.
 - A variable scaling: adjust the scale ('contrast') of the block variable so as to match block variable spectrum the full range of grey shades.
- Consider first a system marginally above T_c , having $\xi \approx 6$. Apply coarse graining with block sizes $L = 4$ and $L = 8$.
- Coarse-graining amplifies the consequences of the small deviation of T from T_c .
- As L is increased, the ratio of the size of the largest configurational features (ξ) to the size of the smallest (L) is reduced. ξ/L provides a natural measure of how 'critical' is a configuration.

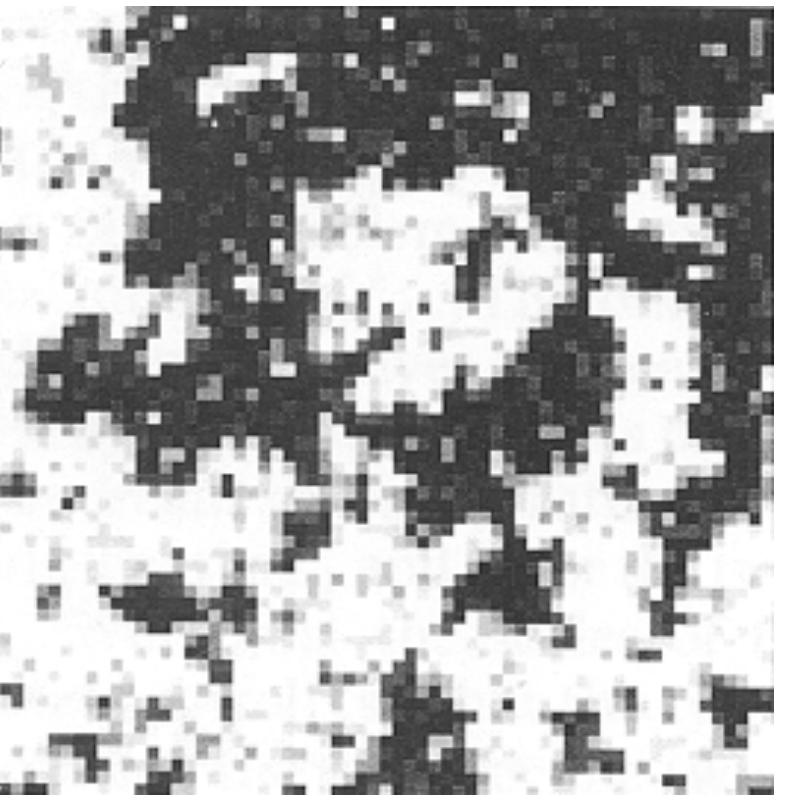
- Thus coarse-graining generates a representation of the system that is effectively less critical the larger the L value.
- Limit is an effectively fully disordered arrangement
- When viewed on lengthscales L larger than ξ , the correlated microstructure is no longer apparent; each coarse-grained variable is independent.
- A similar trend is apparent for $T < T_c$.
- Again, take $\xi \approx 6$. Coarse-graining with $L = 4$ and $L = 8$ again generates representations which are effectively less critical .
- This time the coarse-graining smoothes out the microstructure which makes the order incomplete.
- The limit point of this procedure is a homogeneously ordered arrangement.

2-state model

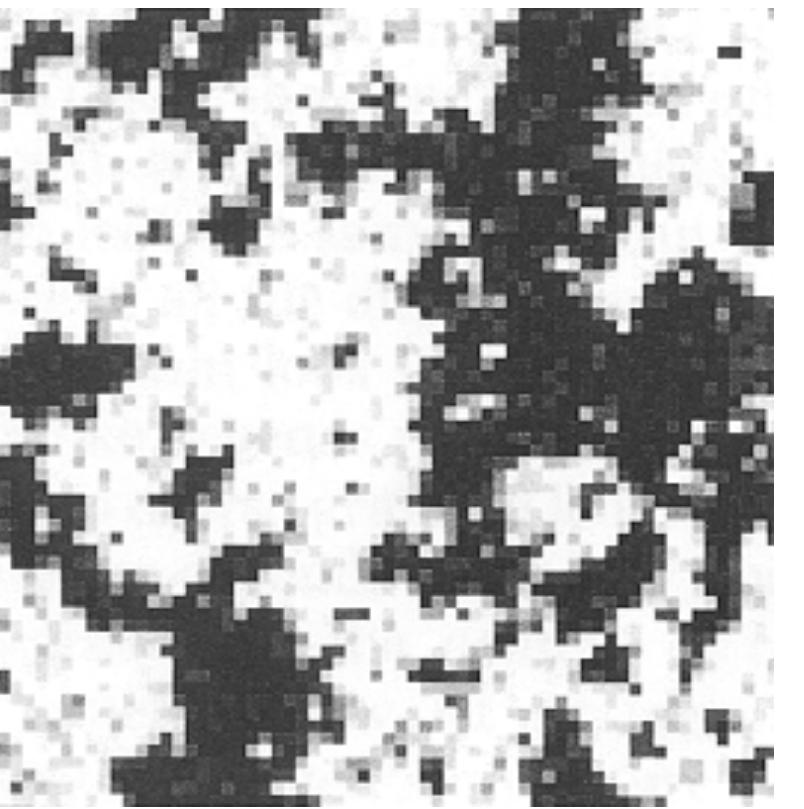
$L = 1$



$L = 4$



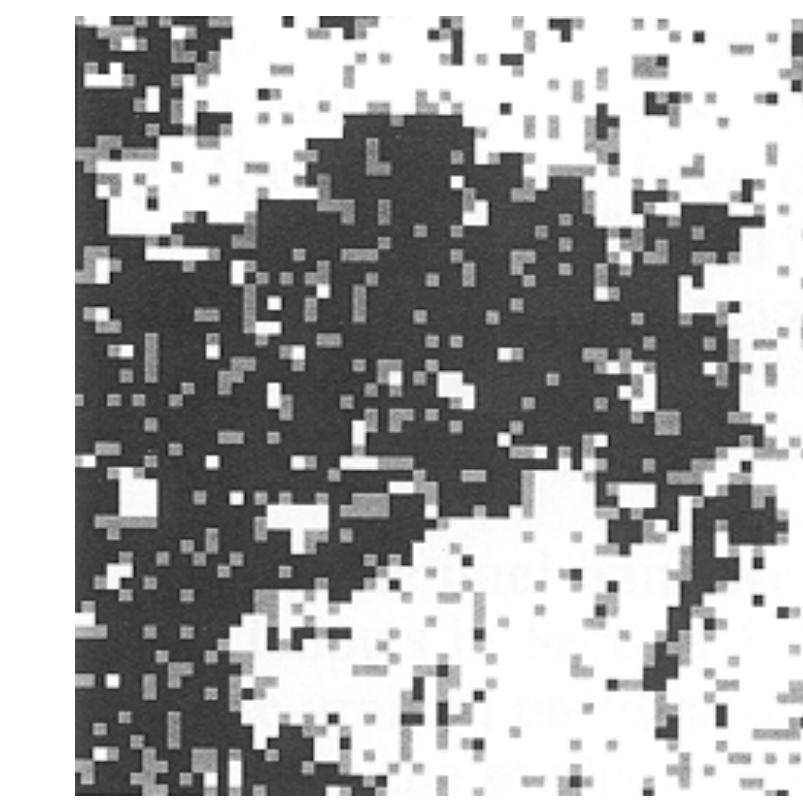
$L = 8$



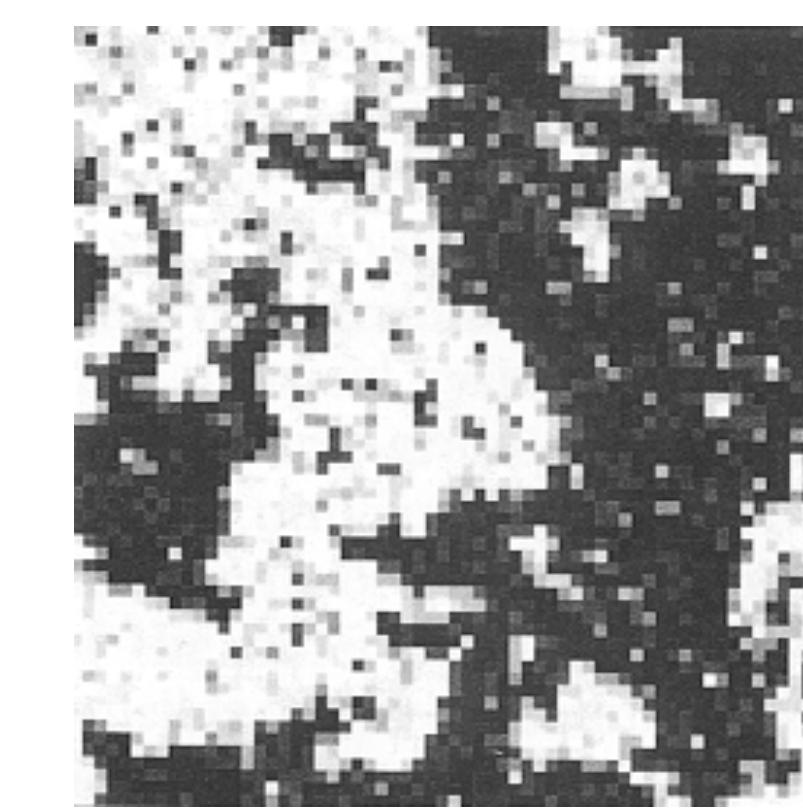
Coarse-graining at criticality

3-state model

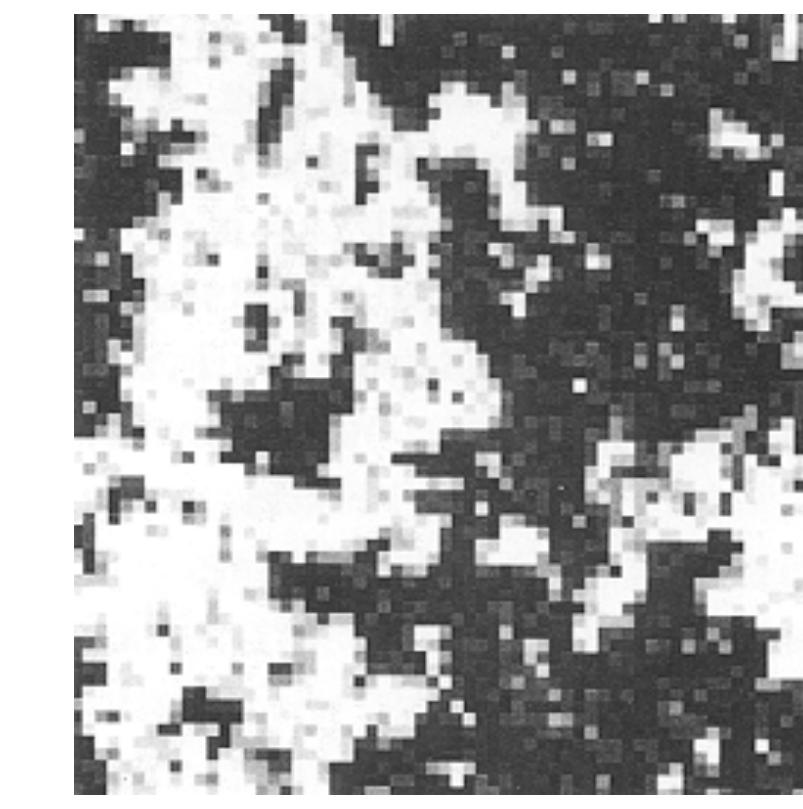
$L = 1$



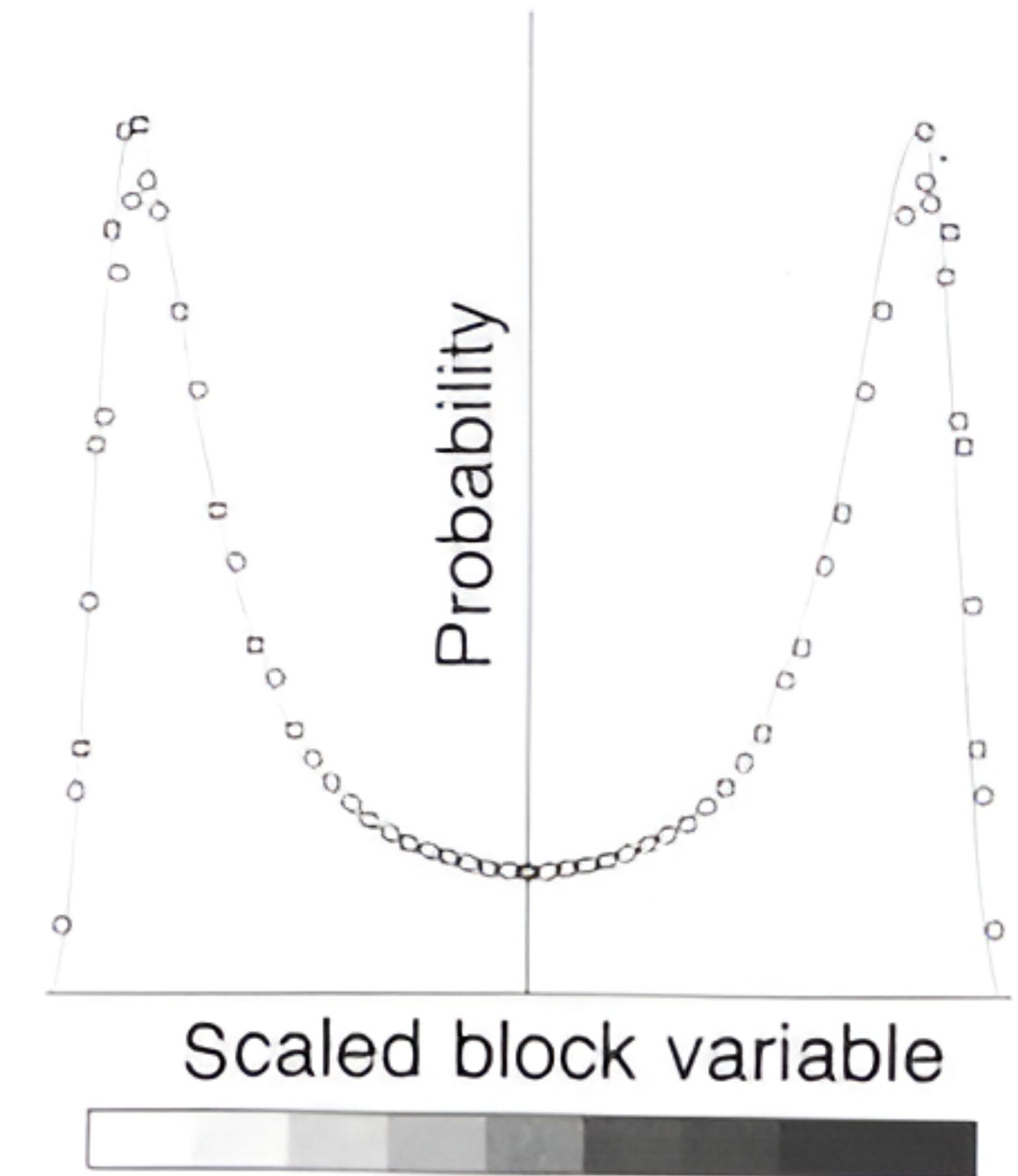
$L = 4$



$L = 8$



- Consider the situation at the critical point.
- Since ξ is as large as the system itself, coarse graining does not produce less critical representations.
- In each figure, one sees structure over all length scales between the lower limit set by L and the upper limit set by the display size.
- A limiting trend is nevertheless apparent.
- Although the $L = 4$ pattern differs qualitatively from $L = L_{min}$, the $L = 4$ and $L = 8$ patterns display qualitatively similar features.
- Thus patterns formed by the ordering variable at criticality look statistically the same when viewed on all sufficiently large length scales (fractal like).
- A statistical analysis of the spectrum of $L = 4$ configurations shows that it is almost identical to that of the $L = 8$ configurations.



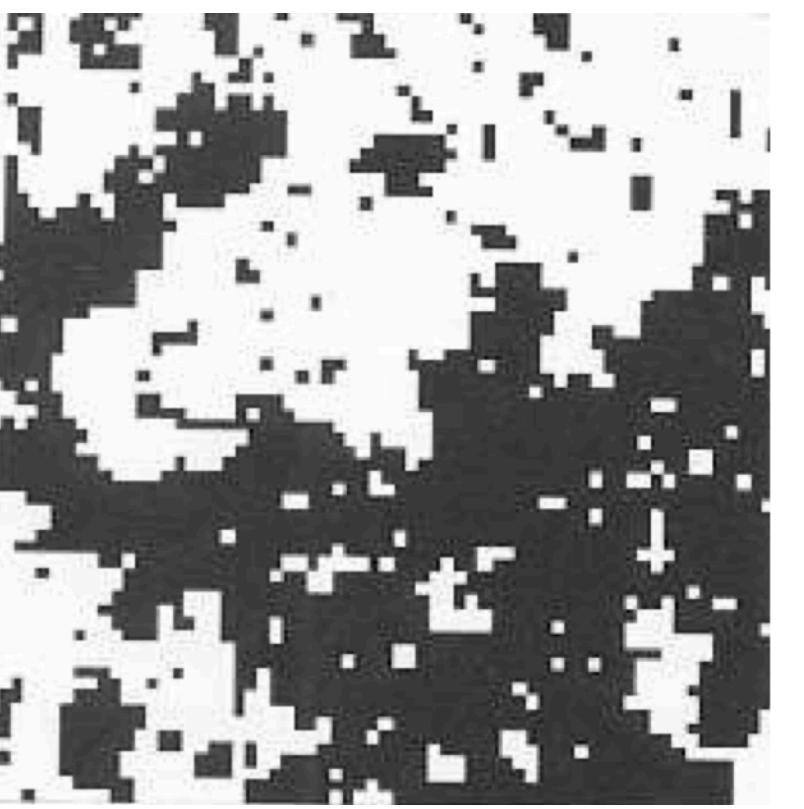
- **Summary:** Under the coarse-graining operation there is an evolution or flow of the system's configuration spectrum.
- The flow tends to a limit, or **fixed point**, such that the pattern spectrum does not change under further coarse-graining.
- These scale-invariant limits have a trivial character for $T > T_c$, (a perfectly disordered arrangement) and $T < T_c$, (a perfectly ordered arrangement).
- The hallmark of the critical point is the existence of a scale-invariant limit which is neither fully ordered nor fully disordered but which possesses structure on **all** length scales.

Universality and scaling

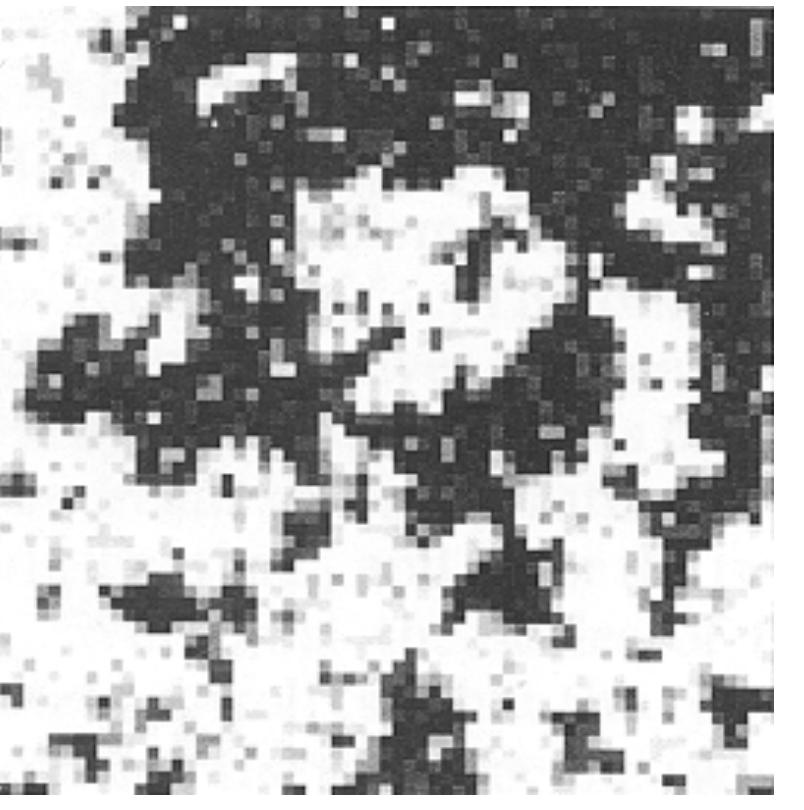
- Introduce a three state (spin-1) variant of the Ising model:
 $(s_i = 1, 0, -1)$.
- 2-state and 3-state model have properties which are clearly different: eg. T_c for the 3-state model is some 30 % lower than that of the 2-state model.
- However, the two models have the **same universal properties**. Consider the differences and similarities in the configurations.
 - Raw spin configurations are different.
 - As with 2-state model, coarse-graining operation bears the configuration spectrum to a non-trivial scale-invariant limit.
 - Remarkably, the limit is the same for both models! Coarse-graining erases the local differences apparent in configs, and exposes a profound configurational similarity.

2-state model

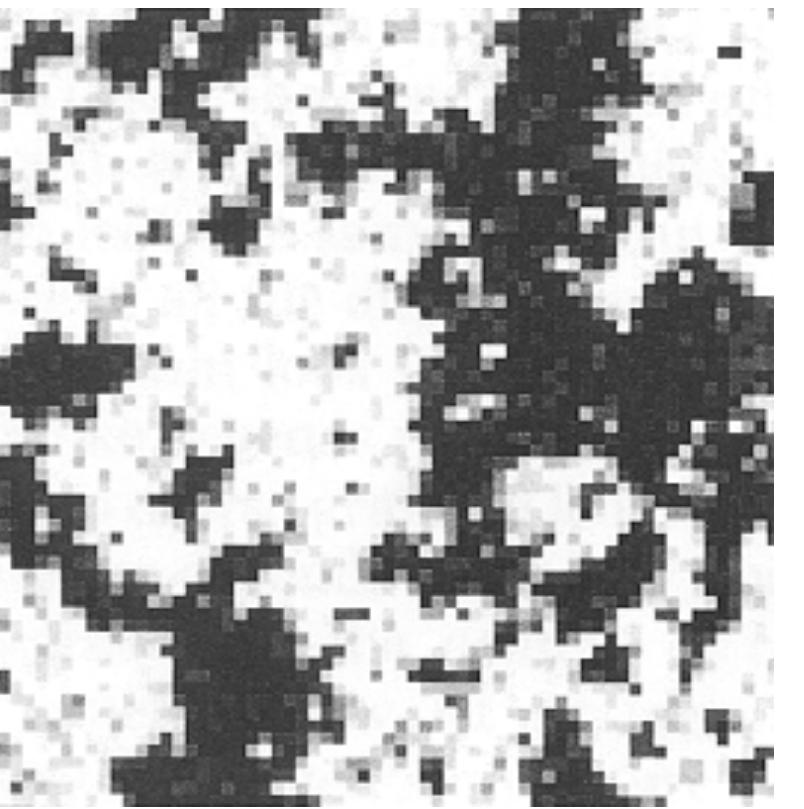
$L = 1$



$L = 4$



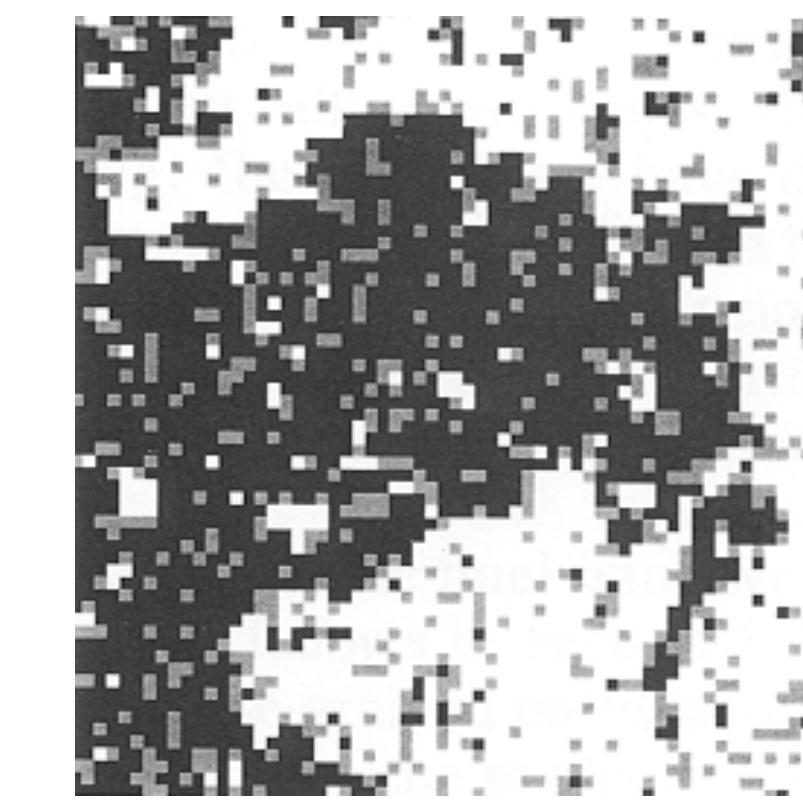
$L = 8$



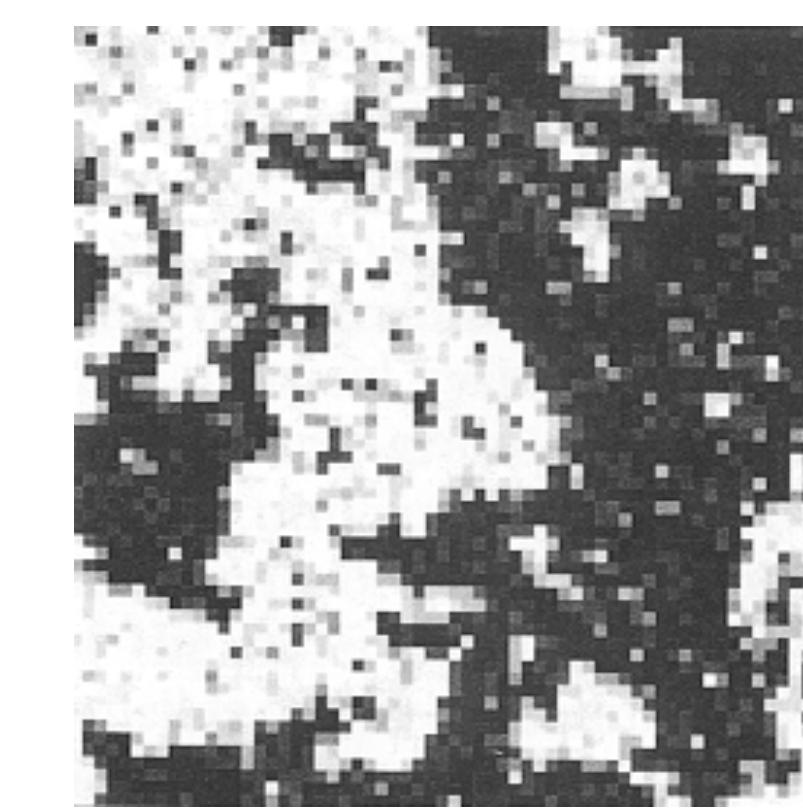
Coarse-graining at criticality

3-state model

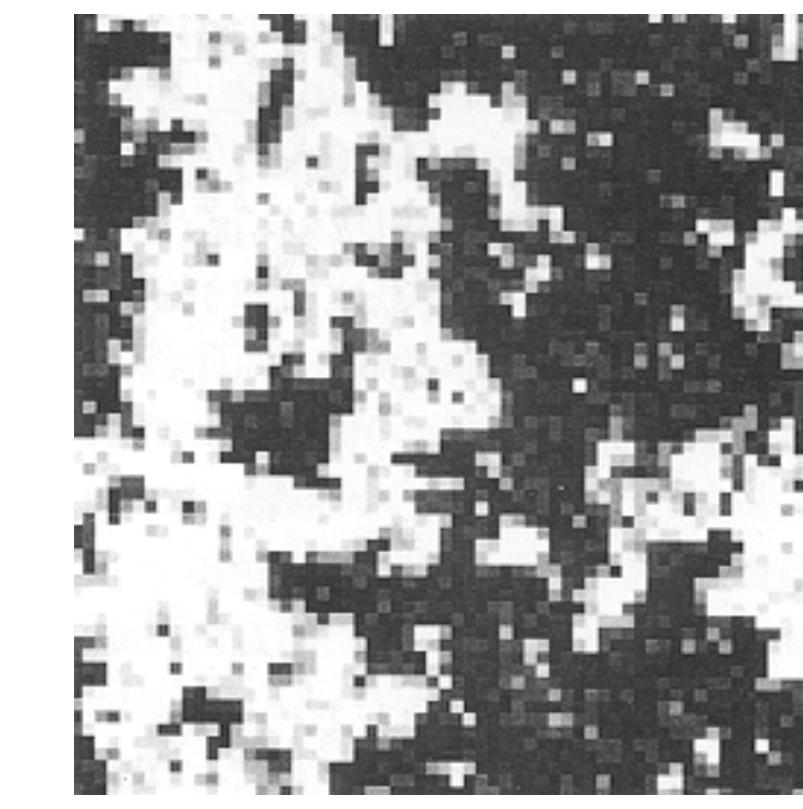
$L = 1$



$L = 4$

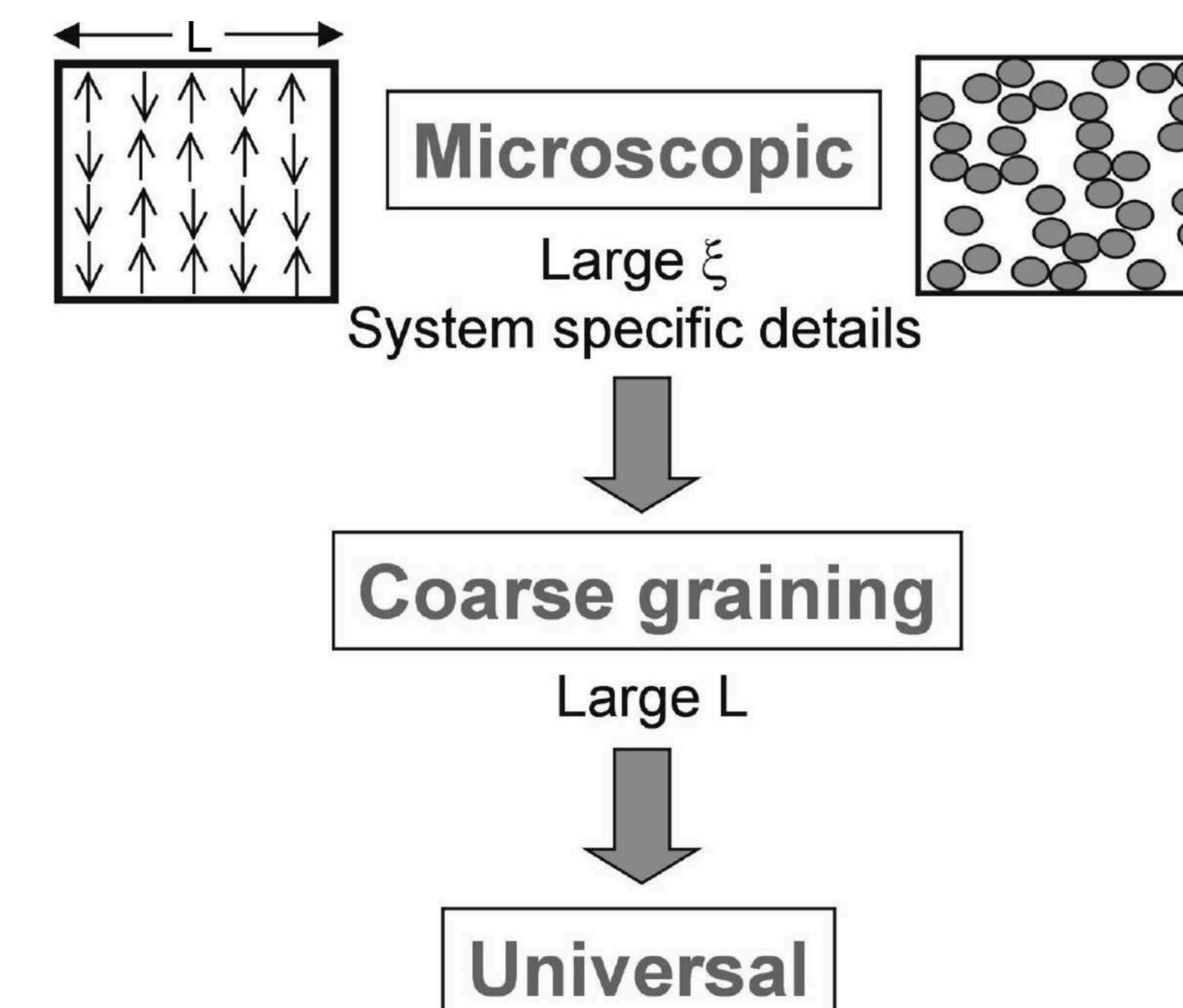


$L = 8$



- Similarity of the configurations of the different systems is not restricted to T_c itself.
- Suppose we have a 2-state model and a 3-state model each as some $t > 0$.
- Systems will have different correlation lengths, $\xi_1 = a_1 t^{-\nu}$ and $\xi_2 = a_2 t^{-\nu}$.
- Although this difference survives the coarse-graining itself, it can be suppressed by the combined coarse graining and the auxiliary length-scale operations.
- Specifically, we choose lengths L_1 and L_2 for the two models such that $\xi_1/L_1 = \xi_2/L_2$.
- We adjust the snapshot sizes so that the sizes of the minimum-length-scale structure (set by L_1 and L_2) looks the same for each system
- Then the configurations again look (statistically) identical. Precisely what they look like depends upon our choice of ξ/L .

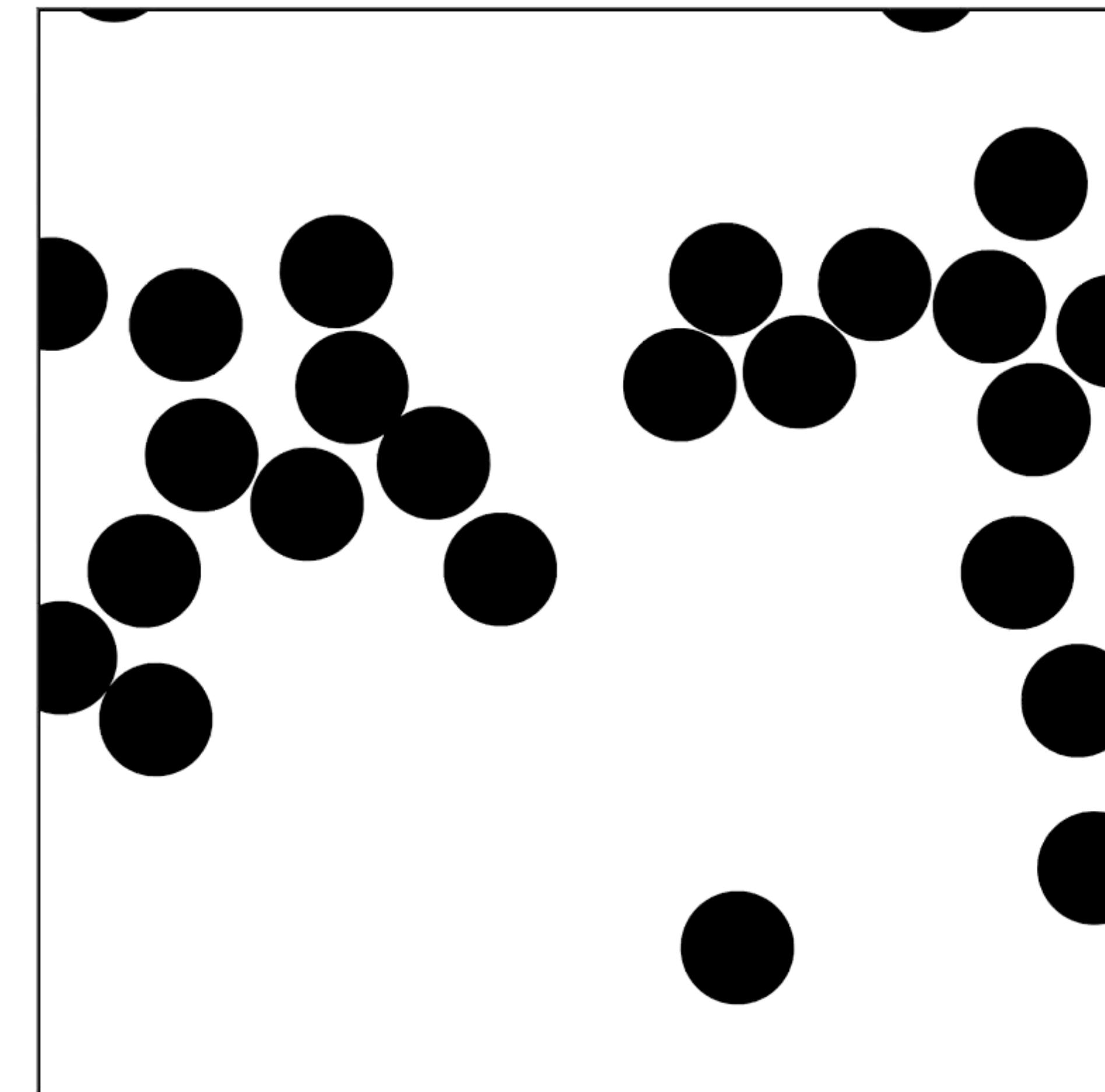
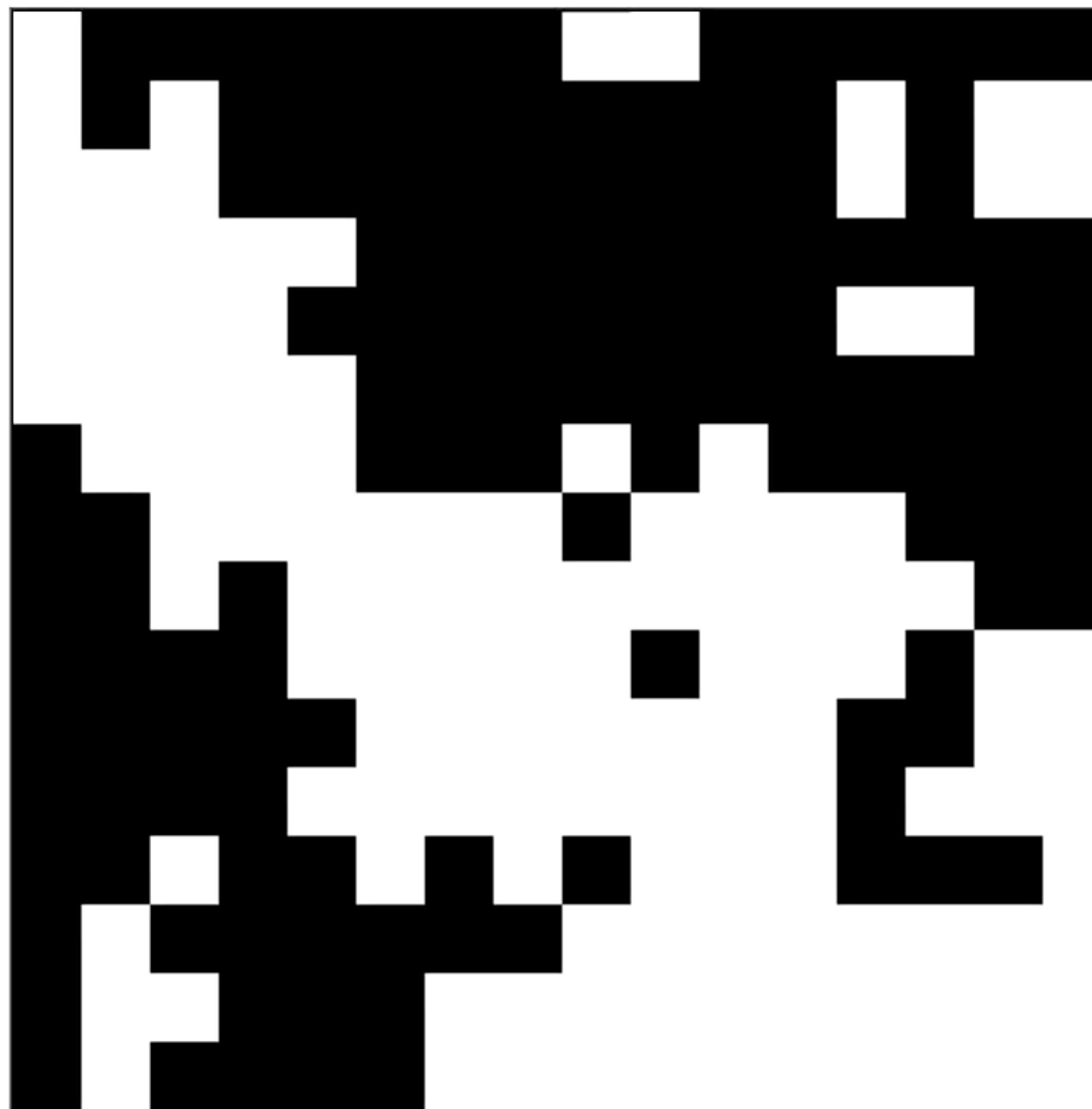
Fluid-magnet universality

- The similarities in the critical behaviour of fluids and magnets can be traced to the underlying similarity in their coarse-grained configurations
- In a magnet, the relevant configurations are those formed by the coarse-grained magnetisation (the magnetic moment averaged over a block of side L).

The diagram shows a flow from a microscopic level to a universal level, mediated by system-specific details and coarse graining.

 - Microscopic:** A grid of arrows representing magnetization. The horizontal dimension is labeled L . The arrows alternate between up (\uparrow) and down (\downarrow) directions in a regular pattern.
 - Large ξ :** A cluster of small circles representing particles or spins.
 - System specific details:** A downward-pointing arrow connects the microscopic and coarse-grained levels.
 - Coarse graining:** A downward-pointing arrow connects the microscopic and universal levels.
 - Large L :** A downward-pointing arrow connects the coarse-grained and universal levels.
 - Universal:** A single word indicating the final, universal configuration.
- In a fluid, the relevant configurations are those of the coarse-grained density (the mass averaged over a block of side L)

- Patterns of bubbles of liquid or vapour may be matched to pattern in the former (microdomains of the magnetisation), given appropriate scaling operations to camouflage the differences between the length scales and the differences between the variable scales



Universality classes

- Coarse graining does not erase all differences between the physical properties of critical systems.
- Differences in the space dimension d of two critical systems will lead to different universal properties such as critical exponents.
- Eg. critical exponents of the 2D magnet, match those of the 2d fluid, but they are different to those of 3d magnets and fluids.

	$d = 2$	$d = 3$
Critical temperature	0.5673	0.75
Order parameter exponent β	$\frac{1}{8}$	0.325 ± 0.001
Susceptibility exponent γ	$\frac{7}{4}$	1.24 ± 0.001
Correlation length exponent ν	1	0.63 ± 0.001

- d is one of a small set of qualitative features which survive coarse graining and which together serve to define the system's universal behaviour, or **universality class**.

- Set includes the number of components n of the order parameter. For the fluid and magnet the order parameter is a scalar, for which $n = 1$.
- In some ferromagnets, the order parameter may be a vector ($n = 2$ or $n = 3$) eg. X-Y or Heisenberg models
- A third important feature which can change the universality class of a critical system is the range of the interaction potential between its constituent particles
- For the Ising model, interactions are inherently nearest neighbour in range.
- Most fluids interact via short ranged dispersion forces.
- However some systems (such as electrolytes) have much longer ranged interactions and thus different critical exponents to the Ising model and fluid.

Critical exponents

- How can the critical exponents, be computed from the properties of the coarse-grained configuration spectrum?
- Consider one typical coarse-grained variable of our Ising system, denoted $S(L)$.
- Suppose that t is sufficiently small that the important observables are dominated by large-scale microstructure: $\xi \gg L_{\min}$.
- Configurational universality is expressed in the claim that, for any L and t , scale factors $a(L)$ and $b(L)$ may be found such that the probability distribution $p(s(L))$ of the coarse-grained variable can be written in the form

$$p(S(L), t) = b(L)\tilde{p}(b(L)S(L), a(L)t)$$

where \tilde{p} is a function unique to a universality class.

- The role of the scale factors a and b is to absorb the basic non-universal scales identified before.
- Values of exponents are implicit in the L dependence of these scale factors.
The key results are

$$a(L) = a_0 L^{1/\nu}$$

$$b(L) = b_0 L^{\beta/\nu}$$

- The amplitudes a_0 and b_0 are system specific (non-universal) constants.
- Thus the basic critical exponents $(\nu, \beta/\nu)$ serve to characterise the ways in which the configuration spectrum evolves under coarse-graining.

- Consider first β/ν .
- Precisely at criticality, the overall scale of the coarse-grained variable $S(L)$ is eroded with increasing L .
- Need to amplify scale of $S(L)$ to match configurations of coarse-graining length L_1 to those of a larger length L_2 .
- Required amplification is $b(L_2)/b(L_1) = (L_2/L_1)^{\beta/\nu}$.
- The index β/ν thus controls the rate at which the scale of the ordering variable decays with increasing coarse-graining length.

- Consider now $1/\nu$.
- For small but finite t (large but finite ξ) there is second way in which the configuration spectrum evolves with L .
- As noted previously, coarse graining reduces the ratio of ξ to L , and results in configurations with a less critical appearance.
- More precisely, increasing L from L_1 to L_2 at constant t has the same effect as keeping L constant while amplifying t by a factor $a(L_2)/a(L_1) = (L_2/L_1)^{1/\nu}$.
- One may think of the combination $a(L)t$ as a measure of the effective reduced temperature of the physical system viewed with resolution length L .

Finite-size scaling

- Consider the average of the block variable $S(L)$.
- This is non other than the value of the order parameter Q , measured over a block of side L .
- Now the block variable average $\bar{S}(L)$ is defined by the first moment of the probability distribution p , i.e.

$$Q(L, t) = \bar{S}(L, t) = \int S(L)p(S(L), t)dS(L)$$

substituting for $p(S(L), t)$ gives

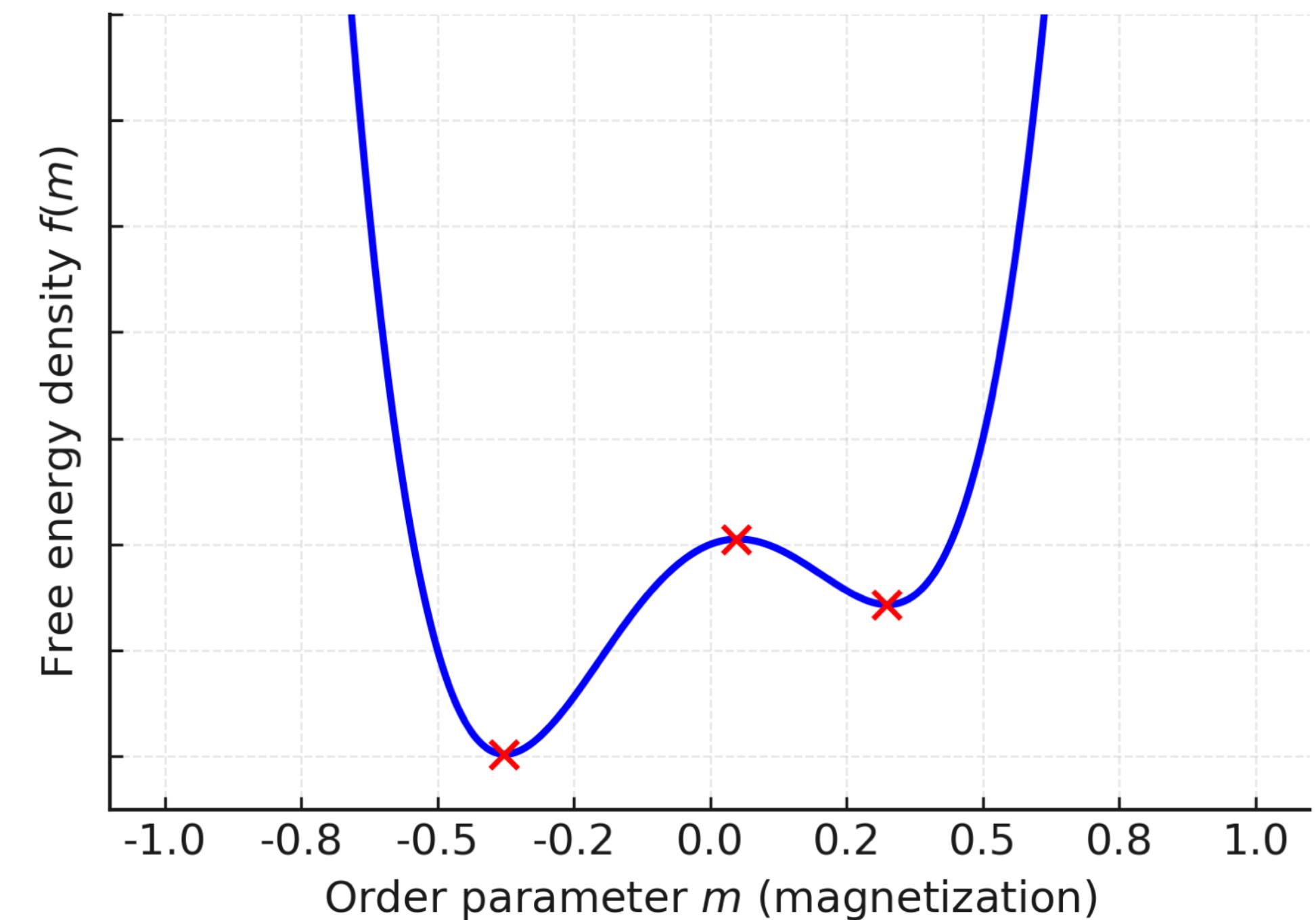
$$\begin{aligned} Q(L, t) &= \int S(L)b(L)\tilde{p}(S(L)b(L), a(L)t)dS(L) \\ &= b^{-1}(L) \int b(L)S(L)\tilde{p}(b(L)S(L), a(L)t)d(b(L)S(L)) \\ &= b^{-1}(L)f(a(L)t) \\ &= b_0 L^{-\beta/\nu} f(a_0 L^{1/\nu} t) \end{aligned}$$

where f is a universal function (defined by the first moment of \tilde{p}).

- FSS provides us with a prescription for measuring critical exponent ratios β/ν and $1/\nu$ via computer simulations of near critical systems.
- For instance, at criticality ($t = 0$) and for finite L , $Q(L,0)$ will not be zero (the T at which Q vanishes for finite L is above the true T_c).
- However, we know that its value must vanish in the limit of infinite L ; it does so like
$$Q(L,0) = b_0 L^{-\beta/\nu} f(0) \equiv Q_0 L^{-\beta/\nu}$$
- Thus by studying the critical point L dependence of Q we can estimate β/ν .
- A similar approach in which we study two block sizes L , and tune t separately in each case so that the results for $QL^{\beta/\nu}$ are identical provides information on the value of $1/\nu$

8. Dynamics of First-Order Phase Transitions

- In a first-order phase transition, the new stable phase does not appear immediately, even when it is thermodynamically favoured.
- Example: In the Ising model for $T < T_c$, the system can be prepared in the spin-up state at $H = 0$. If a small negative field $H < 0$ is applied, the spin-down phase is favoured, but the system remains trapped in the metastable spin-up state.



- This delay arises because the system must overcome a free energy barrier by nucleating a droplet of the stable phase.

Free energy of a droplet

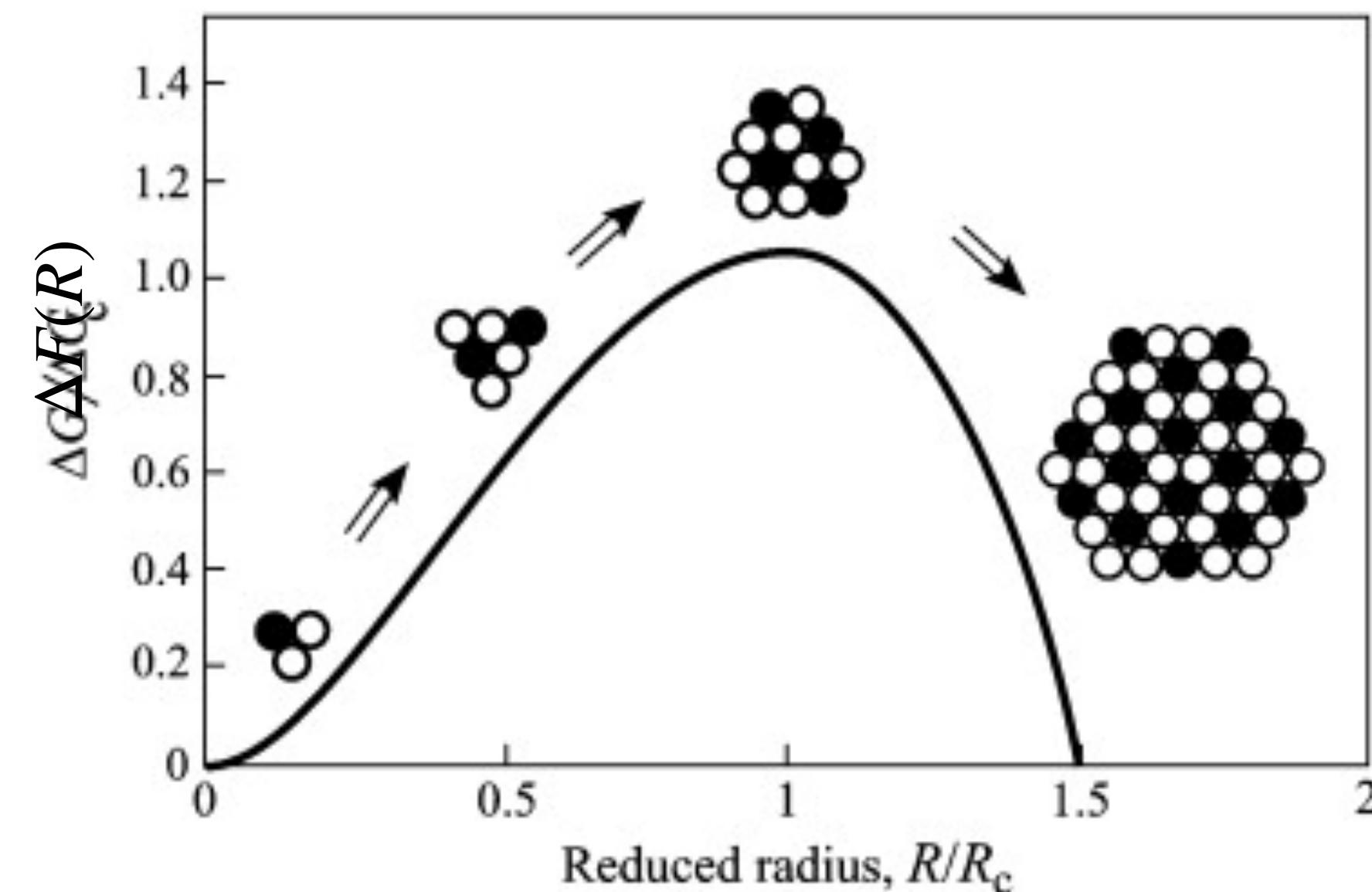
- The free energy change for a droplet of radius R inside the metastable phase is:

$$\Delta F(R) = -\Delta f V_d R^d + \sigma S_d R^{d-1}$$

Δf : free energy density difference between metastable and stable phase

σ : surface tension

- The bulk term ($\propto R^d$) lowers the free energy, while the surface term ($\propto R^{d-1}$) increases it.
- The balance defines the critical radius: $R_c = \frac{(d-1)\sigma S_d}{d |\Delta f| V_d}$
- Droplets smaller than R_c shrink, while larger droplets grow.



Nucleation barrier and rate

- The free energy barrier height associated with a critical droplet is:

$$\Delta F^* = \Delta F(R_c) = \frac{(S_d \sigma)^d}{d^d (\Delta f V_d)^{d-1}} (d - 1)^{d-1}$$

- The thermally activated nucleation rate per unit volume is:

$$I \sim I_0 \exp\left(-\frac{\Delta F^*}{k_B T}\right)$$

- Because the barrier is large, nucleation is a rare, stochastic event. This explains why metastable states can persist for long times.

Dynamics of Droplet Growth

- Once $R > R_c$, droplets grow spontaneously.
- Late time scaling of growth depends on whether the order parameter is conceived or not on a global level.

Non-Conserved Order Parameter Dynamics (Model A)

- In systems with a non-conserved order parameter (e.g., Ising with Glauber dynamics), the order parameter relaxes locally. Interfaces move by curvature, causing small, highly curved domains to shrink while flatter domains grow.
- The typical domain size grows algebraically:

$$L(t) \sim t^{1/2} \quad (z = 2)$$

- A coarse-grained description uses Allen–Cahn (Model A) dynamics: $\frac{\partial \phi}{\partial t} = - \frac{\delta F[\phi]}{\delta \phi}$ with Ginzburg–Landau free energy functional:

$$F[\phi] = \int d^d x \left[\frac{1}{2}(\nabla \phi)^2 + V(\phi) \right], \quad V(\phi) = \frac{1}{4}(\phi^2 - 1)^2$$

Conserved Order Parameter Dynamics (Model B)

- In systems with a conserved order parameter (e.g., binary alloys, liquid mixtures), the order parameter cannot relax locally; it evolves through diffusion.
- The coarse-grained dynamics are described by the Cahn–Hilliard equation:

$$\frac{\partial \phi}{\partial t} = \nabla^2 \left(\frac{\delta F[\phi]}{\delta \phi} \right)$$

with free energy functional: $F[\phi] = \int d^d x \left[\frac{1}{2}(\nabla \phi)^2 + V(\phi) \right].$

- Domain growth is controlled by diffusion of the order parameter across interfaces. The typical domain size grows as:

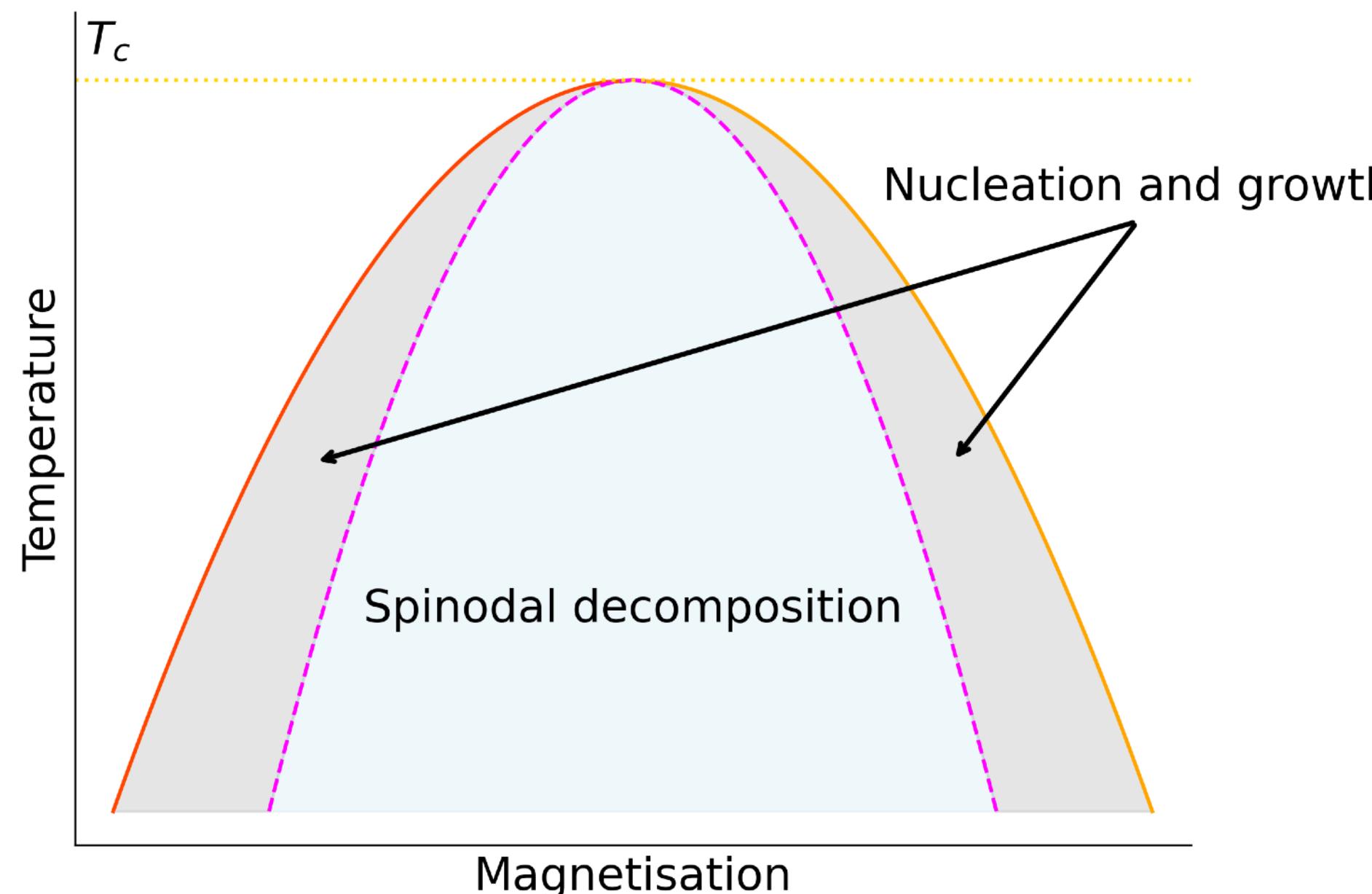
$$L(t) \sim t^{1/3} \quad (z = 3)$$

Physically, this reflects the time required to redistribute conserved quantities across the system.

Spinodal decomposition

- Deep quenches into the unstable region eliminate the barrier. The condition is:

$$\frac{\partial^2 f}{\partial m^2} < 0$$



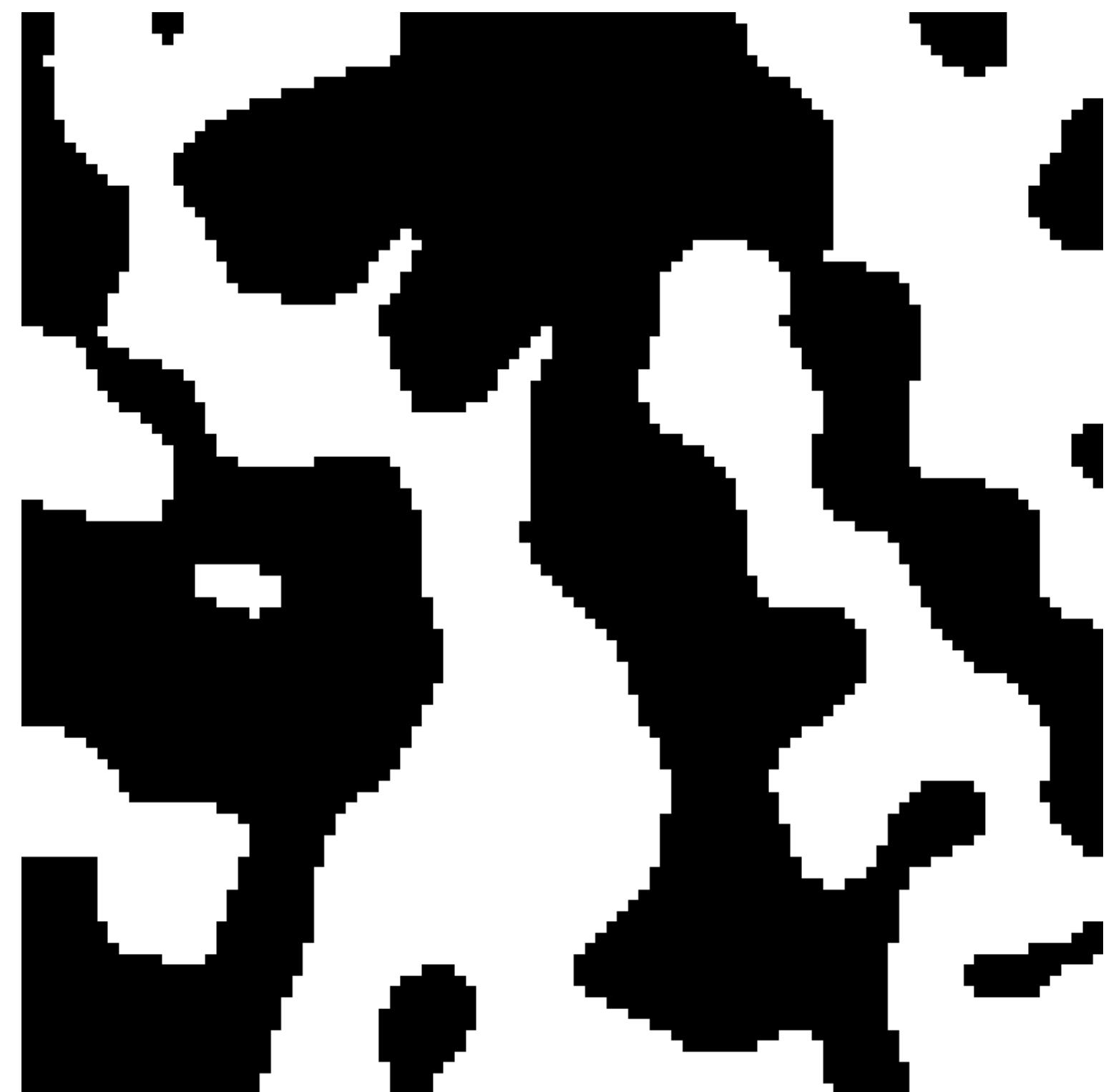
- Then there is no nucleation and growth, rather the system is unstable and immediately starts to phase separate at all points in the system.

- The dynamics are described by the Cahn–Hilliard equation
- This leads to bicontinuous domain structures, distinct from isolated droplets.

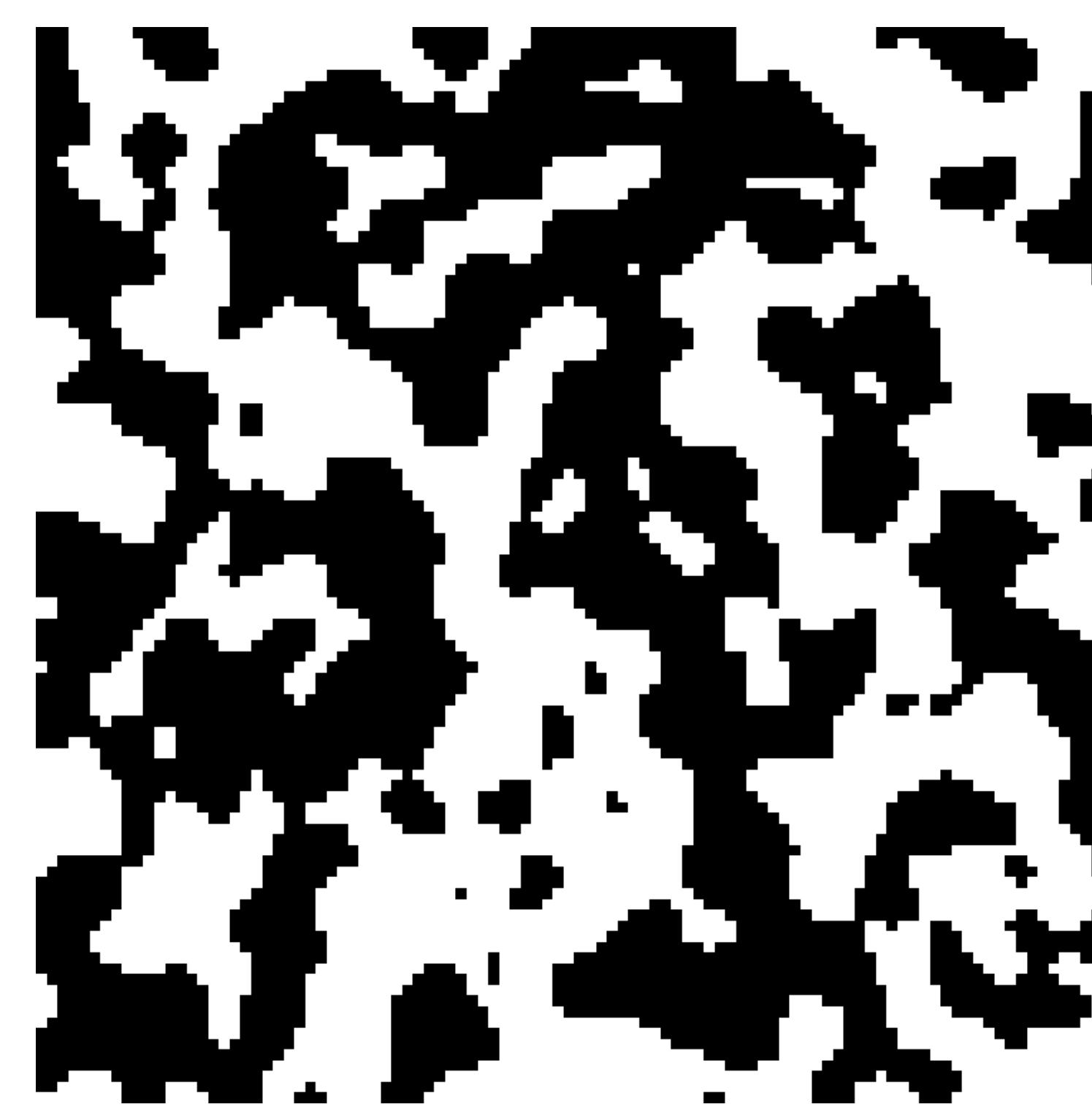
Coarsening and scaling

- With many droplets nucleating and growing, collisions and impingement lead to a patchwork of domains. At late times, the system coarsens and exhibits dynamic scaling:

$$C(r, t) = f\left(\frac{r}{L(t)}\right), \quad S(k, t) = L(t)^d g(kL(t))$$



Non-conserved order parameter



Conserved order parameter

Nucleation vs. spinodal decomposition

- Nucleation and growth:
 - A free energy barrier must be overcome.
 - Transformation occurs via rare, stochastic droplet formation.
 - Domains begin as isolated droplets and later coalesce.
- Spinodal decomposition:
 - No barrier; system is dynamically unstable.
 - Small fluctuations grow exponentially in time.
 - Morphology is bicontinuous and interconnected from the outset.

9. Stochastic processes

Master Equation and Diffusion

- The master equation provides a probabilistic framework for describing the evolution of stochastic systems.
- It governs the time dependence of the probability distribution over possible states.
- In physics, chemistry, and biology, it underpins processes such as reaction kinetics, population dynamics, and transport phenomena.
- Connection to diffusion emerges in the continuum limit.

- The time evolution of probabilities is given by a linear first order differential eq.:

$$\frac{dp_i(t)}{dt} = \sum_j [\nu_{ji}p_j(t) - \nu_{ij}p_i(t)]$$



 inflow into i . outflow from i

- $p_i(t)$: probability of being in state i .
- ν_{ij} : transition rate from $i \rightarrow j$.
- In matrix form: $\frac{d\mathbf{p}}{dt} = W\mathbf{p}$

$W_{ij} = \nu_{ji}$ for $i \neq j$,
$W_{ii} = - \sum_{j \neq i} \nu_{ij}$
- Structure ensures probability conservation $\sum_i p_i = 1$.

Two-state example

- For states A and B:

$$\frac{dp_A}{dt} = -\nu_{BA}p_A + \nu_{AB}p_B$$

$$\frac{dp_B}{dt} = -\nu_{AB}p_B + \nu_{BA}p_A$$

- At equilibrium, probabilities are stationary (not changing in time). Thus **detailed balance** holds:

$$\nu_{BA}p_A^{eq} = \nu_{AB}p_B^{eq}$$

From the Master Equation to Diffusion Equation

- Consider states corresponding to positions $x_i = ia$ on a 1D lattice:
- Transitions only between nearest neighbors.
- Symmetric rates: $\nu_{i,i+1} = \nu_{i,i-1} = \nu$.
- Master equation becomes:

$$\frac{dp_i}{dt} = \nu(p_{i+1} + p_{i-1} - 2p_i)$$

- Define continuous variable $x = ia$, and $p(x, t) \approx p_i(t)$.
- Expand using Taylor series:

$$p(x \pm a, t) = p(x, t) \pm a\partial_x p + \frac{a^2}{2}\partial_x^2 p + \dots$$

- Substitute back to obtain continuum equation.

Diffusion Equation

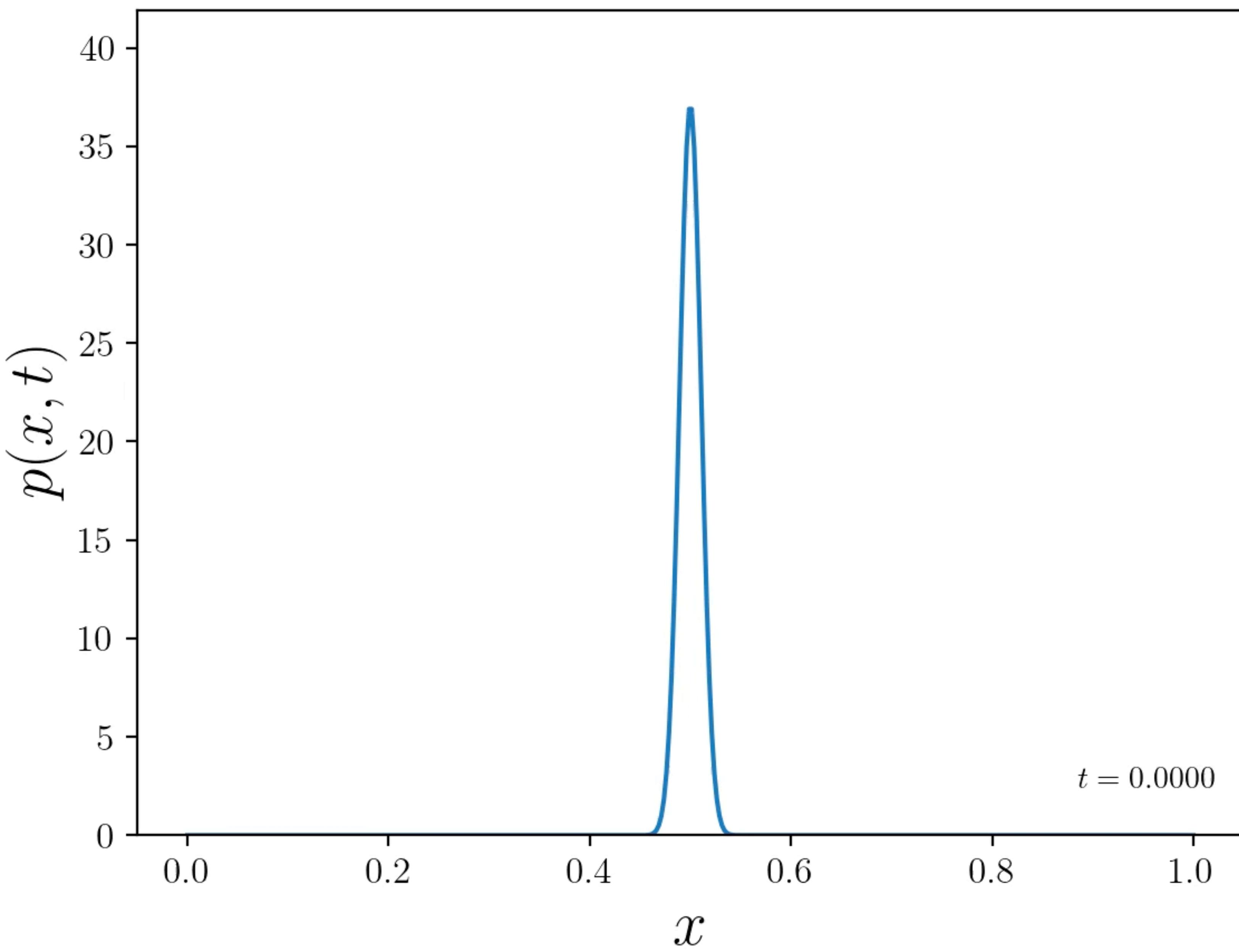
- Resulting PDE:

$$\frac{\partial p}{\partial t} = \nu a^2 \frac{\partial^2 p}{\partial x^2}$$

- Define diffusion constant $D = \nu a^2$ having dimensions of [length]²/[time]:

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}$$

- For systems of many particles, replace p with density ρ , such that $\int dx \rho = M$.
- Often set lattice spacing $a = 1$ after expansion
- Violates time-reversal symmetry \rightarrow entropy increases.



The Langevin approach

- The random walk leads to the diffusion equation for the probability density $p(x, t)$
- In contrast, the Langevin equation provides a stochastic differential equation for the **trajectory** $x(t)$.
- Over a small time step Δt : $x(t + \Delta t) = x(t) + \Delta x(t)$, where $\Delta x(t)$ is a random displacement uncorrelated in time.
- Consider initially the trajectory as discrete jumps on a 1d lattice with spacing a and jump rate per unit time. In a small Δt , the displacement is:

$$\Delta x(t) = \begin{cases} +a & \text{with probability } \nu \Delta t \\ -a & \text{with probability } \nu \Delta t \\ 0 & \text{with probability } 1 - 2\nu \Delta t \end{cases}$$

From which one finds $\langle \Delta x \rangle = 0$, $\langle (\Delta x)^2 \rangle = 2a^2\nu\Delta t = 2D\Delta t$

- Taking the continuum limit $a \rightarrow 0, \Delta t \rightarrow 0$ such that $a \propto \sqrt{\Delta t}$, one obtains the **Langevin equation**

$$\dot{x}(t) = \eta(t)$$

where $\eta(t)$ is a stochastic force (noise) satisfying:

$$\langle \eta(t) \rangle = 0$$

$$\langle \eta(t)\eta(t') \rangle = \Gamma\delta(t - t')$$

- **Autocorrelation function** $\langle \eta(t)\eta(t') \rangle$ measures how η at time t' is correlated with itself at time t
- This form of $\eta(t)$ is known as white noise — it has zero mean and is uncorrelated at different times. Γ sets the noise amplitude.
- The velocity $\dot{x}(t)$ is driven by noise. Integrating to get the displacement:

$$x(t) - x_0 = \int_0^t \eta(t') dt$$

- The mean displacement is: $\langle x(t) - x_0 \rangle = 0$

- The mean squared displacement is

$$\langle [x(t) - x_0]^2 \rangle = \int_0^t \int_0^t \langle \eta(t')\eta(t'') \rangle dt' dt'' = \Gamma \int_0^t dt' = \Gamma t$$

Comparing with the diffusion equations we see $\Gamma = 2D$

- Hence, the Langevin description yields the same physical behavior — not just the mean-square displacement but also the full probability distribution — as the diffusion (Fokker-Planck) equation.
- Equivalence arises from the fact that the integral of many small, independent random steps leads to a Gaussian distribution, in agreement with the solution of the diffusion equation.

Brownian motion

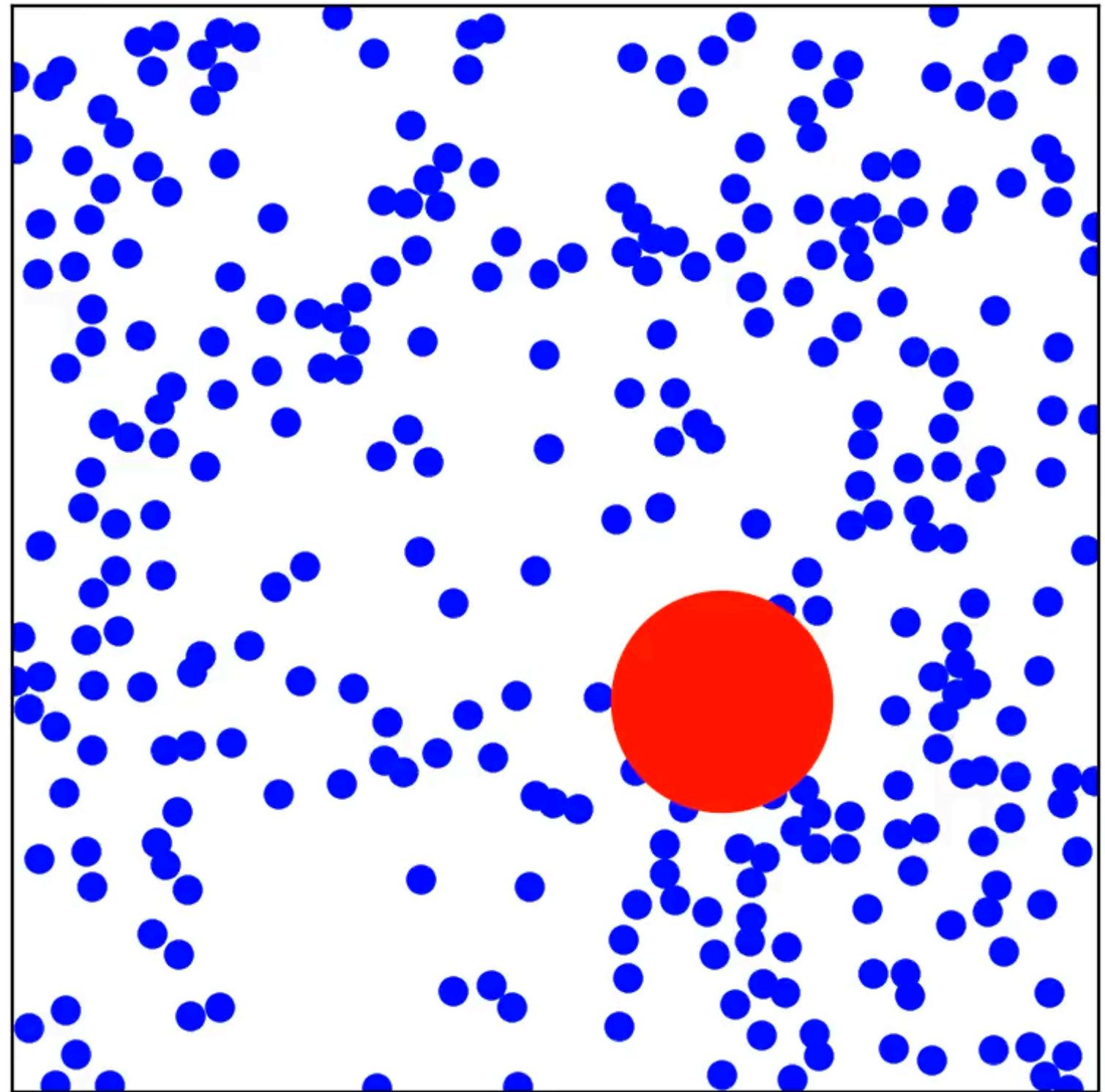
- Erratic motion of colloidal particles suspended in a fluid.
- Arises from random collisions with fluid molecules.
- The Langevin approach describes this behavior. For a particle of mass m in one dimension

$$m\ddot{x} = -\gamma\dot{x} + f(t)$$

– $-\gamma\dot{x}$ is a frictional damping force, where γ is the damping coefficient

$f(t)$ is a random force due to molecular collisions.

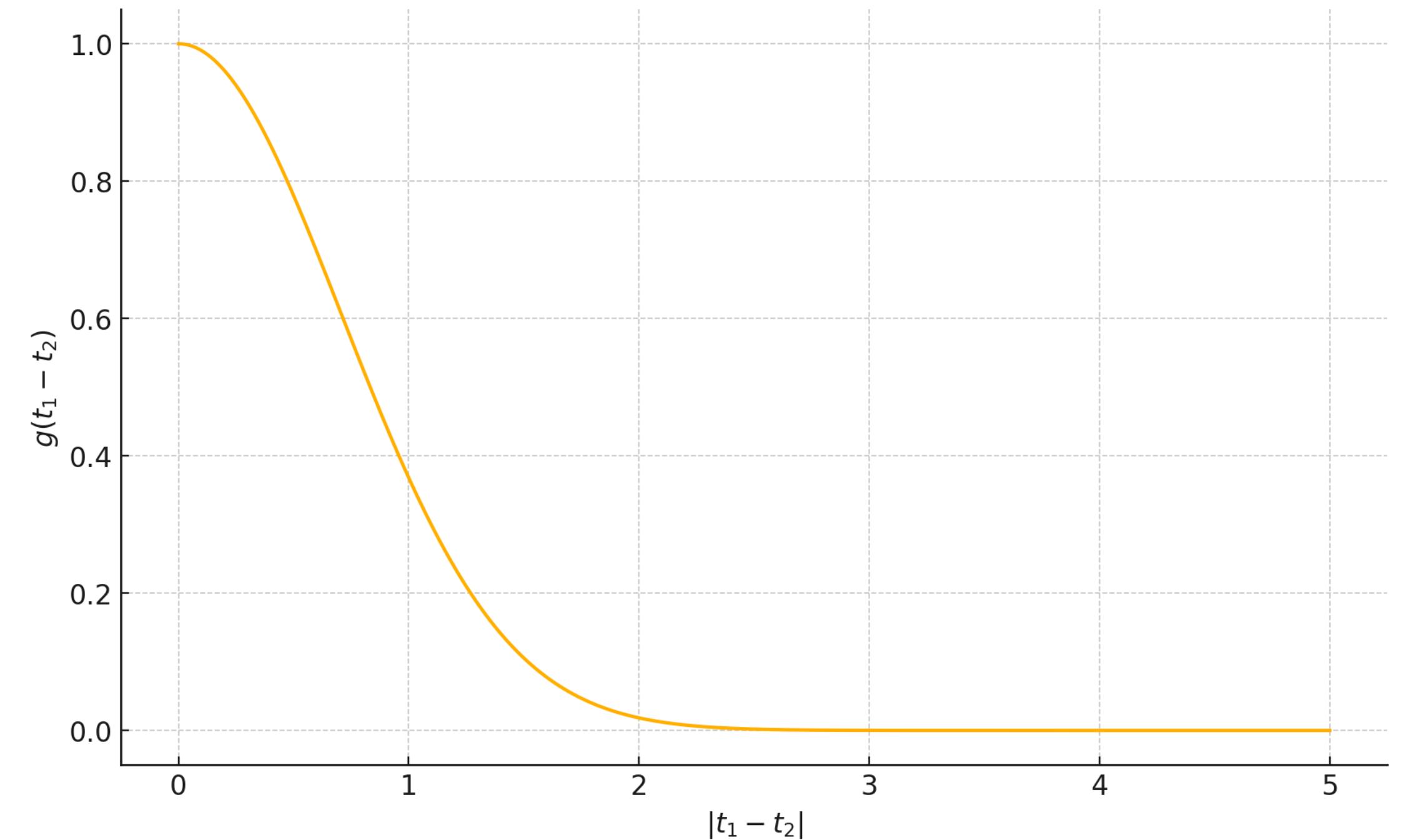
- Define mobility as $\mu = 1/\gamma$



- Assume that the collisions are auto-correlated over time t_c over which $\langle f(t_1)f(t_2) \rangle = g(t_1 - t_2)$ decays rapidly
- As long as we consider timescales $\gg t_c$ we can replace $g(t_1 - t_2)$ by a δ -function:

$$\langle f(t) \rangle = 0$$

$$\langle f(t_1)f(t_2) \rangle = \Gamma\delta(t_1 - t_2)$$



- Such uncorrelated noise is known as "white noise". The collisions are treated as independent, instantaneous 'kicks' of the colloid.

Solving the Langevin equation for Brownian motion

- Consider first the **velocity** of the colloid. Set $m = 1$ for simplicity

$$\dot{v} + \gamma v = f(t)$$

- Find (see notes)

$$v(t) = v_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-t')} f(t') dt'$$

- Using $\langle f(t) \rangle = 0$

$$\langle v(t) \rangle = v_0 e^{-\gamma t}$$

- At short times ($\gamma t \ll 1$) : $\langle v \rangle \approx v_0$ ie. friction is negligible.
- At long times ($\gamma t \gg 1$) : $\langle v \rangle \rightarrow 0$ ie. the system loses memory of the initial velocity.

- Next consider the **mean-squared velocity**

$$\langle v(t)^2 \rangle = v_0^2 e^{-2\gamma t} + \Gamma \int_0^t e^{-2\gamma(t-t')} dt' = v_0^2 e^{-2\gamma t} + \frac{\Gamma}{2\gamma} (1 - e^{-2\gamma t})$$

Implying that

Short times: $\langle v^2 \rangle \approx v_0^2$

Long times: $\langle v^2 \rangle \rightarrow \Gamma/(2\gamma)$

- At equilibrium, the equipartition theorem gives: $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$

Thus: $\Gamma = 2\gamma k_B T$

Deep result: relates the noise strength to the damping and temperature — they have the same microscopic origin (molecular collisions).

- Finally consider the **mean-squared displacement**

Integrate $v(t)$ again to get position $x(t)$ and using $\Gamma = 2\gamma k_B T$:

$$\langle [x(t) - x_0]^2 \rangle = \frac{(v_0^2 - k_B T)}{\gamma^2} (1 - e^{-\gamma t})^2 + \frac{2k_B T}{\gamma} \left[t - \frac{1 - e^{-\gamma t}}{\gamma} \right]$$

- Limiting behaviours:

- Short times: ($\gamma t \ll 1$): $\langle [x(t) - x_0]^2 \rangle \approx v_0^2 t^2$ (ballistic)

- Long time ($\gamma t \gg 1$): $\langle [x(t) - x_0]^2 \rangle \approx \frac{2k_B T}{\gamma} t$ (diffusive)

- The effective diffusion constant is given by the

Einstein relation: $D = \frac{k_B T}{\gamma}$

- Allows eg to calculate the diffusion constant of a

colloidal sphere: $D = \frac{6\pi\eta a}{k_B T}$ (Stokes-Einstein relation)

