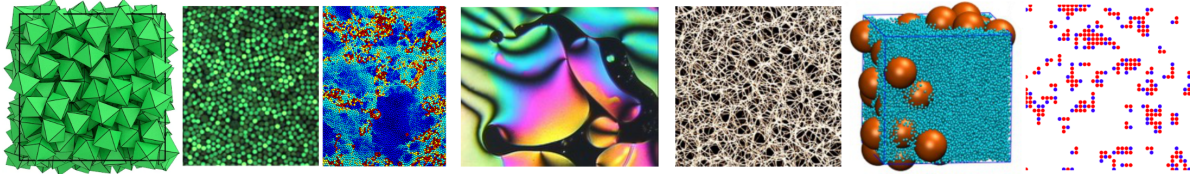# Table of contents

Welcome to the Complex Disordered Matter Course!

Overview

This course introduces your to the theoretical, computational and experimental aspects of the physics of complex disordered matter.

Complex disordered matter is the study of wide range of systems like **polymers**, **colloids**, **glasses**, **gels**, and **emulsions**, which lack long-range order but exhibit intricate behaviour. Colloids, suspensions of microscopic particles in a fluid, are useful for studying disordered structures due to their observable dynamics. Similarly, polymer systems can form amorphous solids or glasses when densely packed or cooled, showing solid-like rigidity despite their disordered structure. These materials often undergo phase transitions, such as demixing and crystallisation, and near these transitions, they can display critical phenomena with extensive fluctuations and correlations.

These various are examples of **soft matter**. systems In soft matter systems, the interplay between disorder, softness, and phase behavior leads to rich physical phenomena, particularly near critical points where even small changes in external conditions can trigger large-scale reorganizations and universal behaviour. Glasses, for instance, exhibit slow relaxation and memory effects, while colloidal systems may crystallize, phase separate, or become jammed depending on particle interactions and concentration. Understanding such behaviors involves studying how microscopic interactions and thermal fluctuations influence macroscopic properties, especially in non-equilibrium conditions. Through techniques like scattering, microscopy, rheology, and simulation, one can explore how disordered soft materials respond to stress, age, or undergo transitions—insights that are vital for applications in materials design, biotechnology, and beyond.

This course is organized into three interconnected parts, each offering a distinct perspective on the study of complex disordered matter.

- **Part 1: Unifying concepts** (Nigel Wilding) introduces the theoretical framework for rationalising complex disordered matter which is grounded in statistical mechanics and thermodynamics. We emphasize the theory of phase transitions, thermal fluctuations, critical phenomena, and stochastic dynamics—providing the essential theoretical tools needed to describe and predict the behavior of soft and disordered systems.

- **Part 2: Complex disordered matter** (Francesco Turci) explores the phenomenology of key examples of complex disordered soft matter systems, including colloids, polymers, liquid crystals, glasses, gels, and active matter. These systems will be analyzed using the theoretical concepts introduced in Part 1, highlighting how disorder, interactions, and fluctuations shape their macroscopic behavior.

- **Part 3: Experimental techniques** (Adrian Barnes) focuses on the methods of microscopy, and scattering via x-rays, neutrons and light that are used to study complex disordered matter, offering insight into how their properties are measured and understood in real-world contexts.

In addition to theory and experiment, computer simulation plays a central role in soft matter research. This course includes a substantial coursework component consisting of two computational projects. These exercises will allow you to apply state-of-the-art simulation techniques to investigate the complex behavior of disordered systems, bridging theory and observation through hands-on exploration.

Delivery and format

- Detailed e-notes (accessible via Blackboard) can be viewed on a variety of devices. Pdf is also available.

- We will give 'traditional' lectures (Tuesdays, Wednesdays, Fridays) in which we use slides to summarise and explain the lecture content. Questions are welcome (within reason...)

- Try to read ahead in the notes, then come to lectures, listen to the explanations and then reread the notes.

- Rewriting the notes or slides to express your own thoughts and understanding, or annotating a pdf copy can help wire the material into your own way of thinking.

- There are problem classes (Thursdays) where you can try problem sheets and seek help. Lecturers may go over some problems with the class.

- The navigation bar on the left will allow you to access the lecture notes and problem sets.

Intended learning outcomes

The course will

- Introduce you to the qualitative features of a range of complex and disordered systems and the experimental techniques used to study them.
- Introduce you to a range of model systems and theoretical techniques used to elucidate the physics of complex disordered matter.
- Provide you with elementary computational tools to model complex disordered systems numerically and predict their properties.
- Allow you to apply your physics background to understand a variety of systems of inter-disciplinary relevance.
- Connect with the most recent advances in the research on complex disordered matter.

Contact details

The course will be taught by

- Prof Nigel B. Wilding (unit director): nigel.wilding@bristol.ac.uk
- Dr Francesco Turci: F.Turci@bristol.ac.uk
- Dr Adrian Barnes: a.c.barnes@bristol.ac.uk

Questions and comments

If you have any questions about the course, please don't hesitate to contact the relevant lecturer, either by email (see above) or in a problems class.

Finally, this is a new course for 2025/26. If you find any errors or mistakes or something which isn't clear, please let us know by email, or fill in this anonymous form:

Submit an error/mistake/query

Recommended texts and literature

One motivation for supplying you with detailed notes for this course course is the absence of a single wholly ideal text book. However, it should be stressed that while these notes approach (in places) the detail of a book, the notes are not fully comprehensive and should be regarded as the 'bare bones' of the course, to be fleshed out via your own reading and supplementary note taking.

Revision on thermodynamics and statistical mechanics

See your year two Thermal Physics notes. Also

- **F. Mandl: Statistical Physics**

Phase transitions and critical phenomena

A good book at the right level for the phase transitions and critical phenomena part of the course is

- **J.M. Yeomans: Statistical Mechanics of Phase Transitions**

A good book covering all aspects of this part of the course including non-equilibrium systems is

- **D. Chandler: Introduction to Modern Statistical Mechanics**

You might also wish to dip into the introductory chapters of the following more advanced texts

- **N Goldenfeld: Lectures on Phase Transitions and the Renormalization Group**
- **J.J. Binney, N.J. Dowrick, A.J.Fisher and M.E.J. Newman: The Theory of Critical Phenomena**

Stochastic dynamics

- **N.G. van Kampen: Stochastic processess in Physics and Chemistry**

Soft matter and glasses

The best overall text for part 2 of the course is:

- **R.A.L Jones, Soft Condensed Matter**.

Additionally, the following more specialised texts (which include information on experimental techniques) might be useful.

Colloids

- **D.F.Evans, H.Wennerström: The Colloidal Domain - Where Physics, Chemistry, Biology, and Technology Meet**
- **R.J.Hunter: Introduction to Modern Colloid Science**
- **W.B.Russel, D.A.Saville, W.R.Schowalter: Colloidal Dispersions**
- **D.H.Everett: Basic Principles of Colloid Science**

Polymers and surfactants

- **R.J. Young and P.A. Lovell: Introduction to polymers**

- **M. Doi: Introduction to polymer physics**

- **J.Israelachvili, Intermolecular and Surface Forces**

Glasses

- **J. Zarzycki; Glasses and the vitreous state**

Part I

Unifying concepts

1 Introduction to phase behaviour and enhanced fluctuations

A phase transition can be defined as a macroscopic rearrangment of the internal constituents of a system in response to a change in the thermodynamic conditions to which they are subject. A wide variety of physical systems undergo such transitions. Understanding the properties of phase transitions is fundamental to the study of soft and complex matter, as these systems often exhibit rich and subtle transformations between different states of organization. Whether in colloidal suspensions, polymer blends, liquid crystals, or biological materials, phase transitions underpin a wide range of physical behaviours, from self-assembly and pattern formation to critical phenomena and dynamical arrest. By analysing how macroscopic phases emerge from microscopic interactions and external conditions, one gains crucial insight into the principles that govern structure, stability, and functionality in these intricate systems. As such, an understanding of phase transitions not only enriches theoretical understanding but also informs practical applications across materials science, biophysics, and nanotechnology. For these reasons we will devote a large proportion of this course to the study of phase transitions.

Two classic examples of systems displaying phase transitions are the ferromagnet and fluid systems. For the magnet, a key observable is the magnetisation defined as the magnetic moment per spin, given by $m = M/N$, with N the number of spins. m can be positive or negative, dependent on whether the spins are aligned 'up' or 'down'. As the temperature of a ferromagnet is increased, its net magnetisation $|m|$ is observed to decrease smoothly, until at a certain temperature known as the critical temperature, T_c, it vanishes altogether (see left part of Figure **??**). We define the magnetisation to be the *order parameter* of this phase transition.

One can also envisage applying a magnetic field H to the system which, depending on its sign (i.e. whether it is aligned (positive) or anti-aligned (negative) relative to the magnetisation axis), favours up or down spin states respectively, as shown schematically in Figure **??** (right part). Changing the sign of the magnetic field H for $T < T_c$ leads to a phase transition chacterised by a discontinuous jump in m. We shall explore this behaviour in more detail in **?@sec-meanfield**.

Similarly, a change of state from liquid to gas can be induced in a fluid system (though not in an ideal gas) simply by raising the temperature. Typically the liquid-vapour transition is abrupt, reflecting the large number density difference between the states either side of the transition. However the abruptness of this transition can be reduced by applying pressure. At
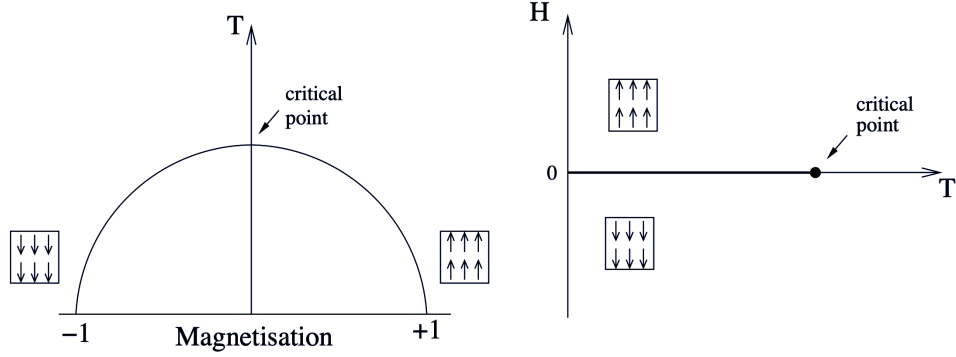
Figure 1.1: Phase diagram of a simple magnet (schematic). Left: magnetisation as a function of temperature for zero applied magnetic field, $H = 0$. Right: Applying a magnetic field that is aligned or antialigned with the direction of the magnetisation leads to a phase transition. The $H = 0$ axis at $T < T_c$ is the coexistence curve for which positive and negative magnetisations are equally likely.

one particular pressure and temperature the discontinuity in the density difference between the two states vanishes and the two phases coalesce. These conditions of pressure and temperature serve to locate the critical point for the fluid. We define the density difference $\rho_{liq} - \rho_{vap}$ to be the order parameter for the liquid-gas phase transition. We shall meet order parameters for other, more complex, systems in **?@sec-landau-theory**,
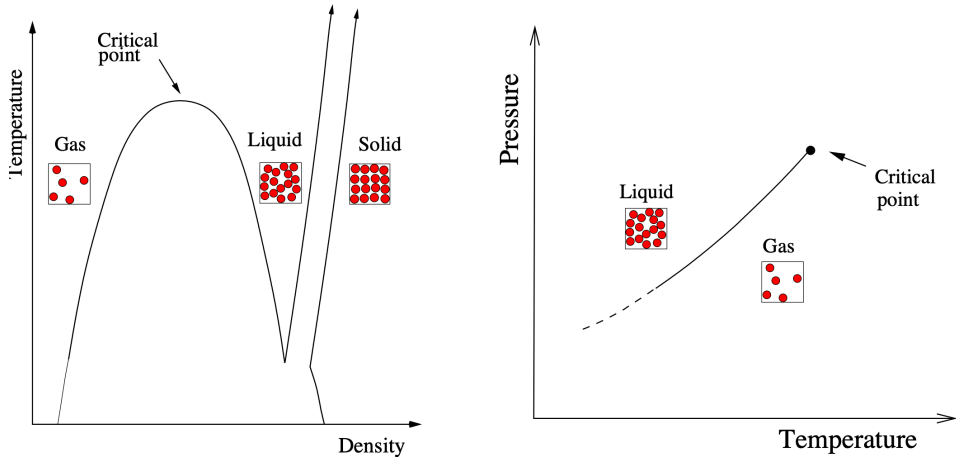

Figure 1.2: Phase diagram of a simple fluid (schematic)

In the vicinity of a critical point, a system displays a host of remarkable behaviors known as *critical phenomena*. Chief among these is the divergence of thermal response functions—such as specific heat, compressibility, or magnetic susceptibility—which signal an enhanced sensitivity to external perturbations. These singularities arise from the emergence of large-scale cooperative interactions among the system's microscopic constituents, as measured by

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a diverging *correlation length* (see Chapter **??**). One visually striking manifestation of this is *critical opalescence*, particularly observed in fluids like CO_2. As carbon dioxide nears its critical temperature and pressure, the distinction between its liquid and gas phases vanishes, giving rise to huge fluctuations in density. These fluctuations scatter visible light, rendering the fluid milky or opalescent. This scattering effect directly reflects the long-range correlations developing within the fluid. The movie below illustrates the effect as the critical temperature of CO_2 is approached from above. Note the appearence of a liquid-vapour interface (meniscus) as the system enters the two-phase region.

Movies/critical_point_1.mp4

The recalcitrant problem posed by the critical region is how best to incorporate such collective effects within the framework of a rigorous mathematical theory that affords both physical insight and quantitative explanation of the observed phenomena. This matter has been (and still is!) the subject of intense theoretical activity.

The importance of the critical point stems largely from the fact that many of the phenomena observed in its vicinity are believed to be common to a whole range of apparently quite disparate physical systems. Systems such as liquid mixtures, superconductors, liquid crystals, ferromagnets, antiferromagnets and molecular crystals may display identical behaviour near criticality. This observation 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 so-called 'universality hypothesis' which, since its inception in the 1970s, has enjoyed considerable success.

In the next few lectures, principal aspects of the contemporary theoretical viewpoint of phase transitions and critical phenomena will be reviewed. Mean field theories of phase transitions will be discussed and their inadequacies in the critical region will be exposed. The phenomenology of the critical region will we described including power laws, critical exponents and their relationship to scaling phenomena. These will be set within the context of the powerful renormalisation group technique. The notion of universality as a phenomenological hypothesis will be introduced and its implications for real and model systems will be explored. Finally, the utility of finite-size scaling methods for computer studies of critical phenomena will be discussed, culminating in the introduction of a specific technique suitable for exposing universality in model systems. Thereafter we will consider some foundational concepts in the dynamics of complex disordered matter. We shall look at the processes by which one phase transform into another and introduce differential equations that allow us to deal with the inherent stochasticity of thermal systems. The wider applicability of these unifying concepts to complex disordered systems such as colloids, polymers, liquid crystals and glasses will be covered in part 2 of the course.

2 Key concepts for phase transitions

2.1 Observables and expectation values

In seeking to describe phase transition and critical phenomena, it is useful to have a quantitative measure of the difference between the phases: this is the role of the *order parameter*, Q. In the case of the fluid, the order parameter is taken as the difference between the densities of the liquid and vapour phases. In the ferromagnet it is taken as the magnetisation. As its name suggest, the order parameter serves as a measure of the kind of orderliness that sets in when the temperature is cooled below a critical temperature.

Our first task is to give some feeling for the principles which underlie the ordering process. Referring back to **?@sec-canonical**, the probability p_a that a physical system at temperature T will have a particular microscopic arrangement (alternatively referred to as a 'configuration' or 'state'), labelled a, of energy E_a is

$$p_a = \frac{1}{Z} e^{-E_a/k_B T} \tag{2.1}$$

The prefactor Z^{-1} is the *partition function*: since the system must always have *some* specific arrangement, the sum of the probabilities p_a must be unity, implying that

$$Z = \sum_a e^{-E_a/k_B T} \tag{2.2}$$

where the sum extends over all possible microscopic arrangements.

These equations assume that physical system evolves rapidly (on the timescale of typical observations) amongst all its allowed arrangements, sampling them with the probabilities Equation **??** the expectation value of any physical observable O will thus be given by averaging O over all the arrangements a, weighting each contribution by the appropriate probability:

$$\overline{O} = \frac{1}{Z} \sum_a O_a e^{-E_a/k_B T} \tag{2.3}$$

Sums like Equation **??** are not easily evaluated because the number of terms grows exponentially in the system size. Nevertheless, some important insights follow painlessly. Consider

the case where the observable of interest is the order parameter, or more specifically the magnetisation of a ferromagnet.

$$Q = \frac{1}{Z} \sum_a Q_a e^{-E_a/k_B T} \tag{2.4}$$

It is clear from Equation **??** that at very low temperature the system will be overwhelmingly likely to be found in its minimum energy arrangements (ground states). For the ferromagnet, these are the fully ordered spin arrangements having magnetisation $+1$, or -1.

Now consider the high temperature limit. The enhanced weight that the fully ordered arrangement carries in the sum of Equation **??** by virtue of its low energy, is now no longer sufficient to offset the fact that arrangements in which Q_a has some intermediate value, though each carry a smaller weight, are vastly greater in number. A little thought shows that the 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 Equation **??** and the order parameter is zero.

The competition between energy-of-arrangements weighting (or simply 'energy') and the 'number of arrangements' weighting (or 'entropy') is then the key principle at work here. The distinctive feature of a system with a critical point is that, in the course of this competition, the system is forced to choose amongst a number of macroscopically different sets of microscopic arrangements.

Finally in this section, we note that the probabilistic (statistical mechanics) approach to thermal systems outlined above is completely compatible with classical thermodynamics. Specifically, the bridge between the two disciplines is provided by the following equation

$$F = -k_B T \ln Z \tag{2.5}$$

where F is the "Helmholtz free energy". All thermodynamic observables, for example the order parameter Q, and response functions such as the specific heat or magnetic susceptibility are obtainable as appropriate derivatives of the free energy. For instance, utilizing Equation **??**, one can readily verify (try it as an exercise!) that the average internal energy is given by

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta},$$

where $\beta = (k_B T)^{-1}$.

The relationship between other thermodynamic quantities and derivatives of the free energy are given in fig. Figure **??**

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

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

$$\bar{E} = -\left(\frac{\partial(\beta F)}{\partial \beta}\right)_H \qquad \overline{M} = -\left(\frac{\partial F}{\partial H}\right)_T \qquad (M = mN)$$

$$C_H = \left(\frac{\partial \bar{E}}{\partial T}\right)_H \qquad \chi_T = \left(\frac{\partial m}{\partial H}\right)_T$$
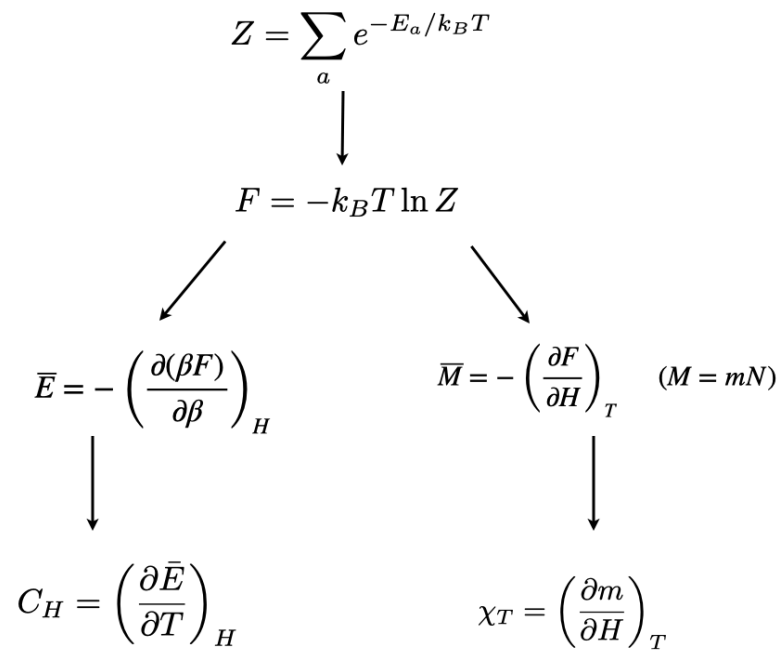
Figure 2.1: Relationships between the partition function and thermodynamic observables

2.2 Correlations

2.2.1 Spatial correlations

The two-point connected correlation function measures how fluctuations at two spatial points are statistically related. For a scalar field $\phi(\vec{R})$, which could represent eg. the local magnetisation m in a magnet at position vector $\vec{R}$, or the local particle number density ρ in a fluid, it is defined as:

$$C(r) = \langle \phi(\vec{R})\phi(\vec{R} + \vec{r}) \rangle - \langle \phi(\vec{R}) \rangle^2,$$

where $\langle \cdot \rangle$ denotes an ensemble or spatial average over all $\vec{R}$, and $r = |\vec{r}|$ is the spatial separation between the two points.

$C(r)$ quantifies the spatial extent over which field values are correlated and in homogeneous and isotropic systems, it depends only on the separation r.

If $C(r)$ decays quickly, we say that correlations are short-ranged. Typically this occurs well away from criticality and takes the form of exponential decay

$$C(r) \sim e^{-r/\xi}$$

where the correlation length ξ is the characteristic scale over which correlations decay.

Near a critical point $C(r)$ decays more slowly - in a power-law fashion - and correlations are long-ranged.

$$C(r) \sim r^{-(d-2+\eta)}$$

where d is the spatial dimension and η is a critical exponent.

In isotropic fluids and particle systems, a closely related and more directly measurable quantity (particularly in simulations) is the **radial distribution function** $g(r)$, which describes how particle density varies as a function of distance from a reference particle. For such systems, the two-point correlation function of the number density field $\rho(\vec{r})$ is related to $g(r)$ as follows:

$$g(r) = 1 + \frac{C(r)}{\rho^2},$$

where ρ is the average number density. This relation shows that $g(r)$ encodes the same spatial correlations as $C(r)$, but in a form that is more natural for discrete particle systems. Note that by definition $g(r) \to 1$ in the absence of correlations ie. when $C(r) = 0$. This is typically the case for $r \gg \xi$.

Experimentally one doesn't typically have direct access to $C(r)$, but rather its Fourier transform known as the **structure factor**

$$S(k) = \int d^d r\, e^{-i\vec{k}\cdot\vec{r}}\, C(r),$$

where k is the scattering wavevector.

In equilibrium:

- For short-range correlations (finite ξ), $S(k)$ typically has a Lorentzian form:

$$S(k) \sim \frac{1}{k^2 + \xi^{-2}}.$$

- At criticality (where $\xi \to \infty$), $S(k)$ follows a power law:

$$S(k) \sim k^{-2+\eta}.$$

This relation enables the extraction of ξ from experimental or simulation data, especially via scattering techniques.

2.2.2 Temporal correlations

Consider a thermodynamic variable x with zero mean that fluctuates over time. Examples include the local magnetization in a magnetic system or the local density in a fluid. Here, x represents a deviation from the average value — a fluctuation.

We're interested in how such fluctuations are correlated over time when the system is in thermal equilibrium. For instance, if x is positive at some time t, it's more likely to remain positive shortly after.

These temporal correlations are characterized by the two-time correlation function (also known as an auto-correlation function):

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

In equilibrium, the correlation function must be independent of the starting time τ. Therefore, we define:

$$\langle x(\tau)x(\tau + t)\rangle = M_{xx}(t)$$

That is, $M_{xx}(t)$ depends only on the time difference t.

We typically expect $M_{xx}(t)$ to decay exponentially over a characteristic correlation time t_c:
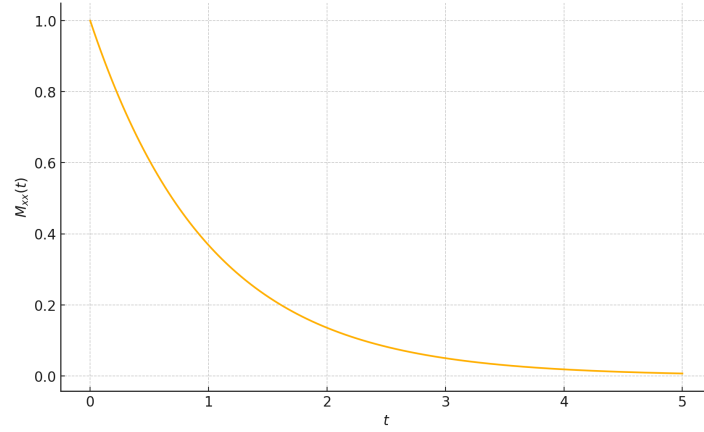
$$M_{xx}(t) \sim \exp(-t/t_c)$$

Figure 2.2: Sketch of $M_{xx}(t)$ against t

This exponential decay reflects how the memory of fluctuations fades with time.

Now consider two different fluctuating variables, x and y (e.g., local magnetizations at different positions). Their cross-correlation function is defined as:

$$\langle x(\tau)y(\tau + t)\rangle = M_{xy}(t)$$

This defines the elements of a dynamic correlation matrix, of which $M_{xx}(t)$ is the diagonal.

Tools for understanding complex disordered matter

Complex disordered systems are composed of an enormous number of interacting components—typically on the order of $\sim 10^{23}$. These interactions can lead to fascinating emergent behaviour, but they also render the systems analytically intractable; it is clearly impossible to solve Newton's equations for such vast numbers of particles. To address this difficulty, we turn to Statistical Mechanics, which you first encountered in your second year. Statistical Mechanics provides the essential framework for connecting the microscopic behaviour of individual constituents with the macroscopic thermodynamic and dynamical properties of the system as a whole.

In this section, we will revisit and expand upon key concepts relevant to our discussion, with particular emphasis on the **free energy**—a central quantity that captures the balance between energy minimisation and entropy maximisation in determining the system's equilibrium state. If any of these ideas feel unfamiliar, you may find it useful to revise the Statistical Mechanics material from your Year 2 *Thermal Physics* course notes.

Ensembles and free energies

Statistical mechanics can be formulated in a variety of ensembles reflecting the relationship between the system and its environment. In what follows we summarise the formalism, focussing on the case of a particle fluid. Analogous equations apply to lattice spin models (see lectures and the book by Yeomans). Key ensembles are:

Microcanonical ensemble

Applies to a system of N particles (or spins) in a fixed volume V having adiabatic walls so that the internal energy E is constant. Denoted as constant-NVE. Let Ω be the number of (micro)states having the prescribed energy:

$$\Omega = \sum_{\text{all states having energy E}}$$

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Thermodynamically, the states favored in the canonical ensemble are those that maximise the entropy:

$$S = k_B \ln \Omega \,.$$

where k_B is Boltzmann's constant The microcanonical ensemble is useful for defining the entropy, but is little used in practice.

Canonical ensemble

Applies to a system of N particles in a fixed volume V and coupled to a heat bath at temperature T. Denoted as constant-NVT. A central quantity is the *partition function*

$$Z_{NVT} = \sum_{\text{all states i}} e^{-\beta E_i}, \qquad \beta = 1/(k_B T) \tag{2.6}$$

which is a weighted sum over the states. The partition function provides the normalisation constant in the probability of finding the system in a given state i.

$$P_i = \frac{e^{-\beta E_i}}{Z_{NVT}}. \tag{2.7}$$

The states favored in the canonical ensemble are those that minimise the free energy:

$$F_{NVT} = -\beta^{-1} \ln Z_{NVT} \,.$$

F_{NVT} is known as the Helmholtz free energy. Thermodynamics also supplies a relation for the Helmholtz free energy:

$$F_{NVT} = E - TS \,,$$

where E is the average internal energy. In minimising the free energy, the system strikes a compromise between low energy and high entropy. The temperature plays the role of arbiter, favouring high entropy at high T, and low energy at low T. The canonical ensemble is usually used to describe systems such as magnets, or a fluid held at constant volume. It is the ensemble we shall use most in this course.

Grand canonical ensemble

Applies to a system with a variable number of particle in a fixed volume V coupled to both a heat bath at temperature T and a particle reservoir with chemical potential μ (which is the field conjugate to N). Denoted as constant-μVT.

The corresponding partition function is a weighted superset of the canonical one

$$Z_{\mu VT} = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_{NVT}$$

and a state probability analogous to Equation **??** holds. One can recast this in a form similar to Equation **??**:

$$Z_{\mu VT} = \sum_{N=0}^{\infty} \sum_{\text{all states i}} e^{-\beta H_i}, \tag{2.8}$$

where $H_i = E_i - \mu N$ is the form of the Hamiltonian in the grand canonical ensemble.

Statistically, the states favored in the grand canonical ensemble are those that minimise the free energy:

$$F_{\mu VT} = -\beta^{-1} \ln Z_{\mu VT}$$

$F_{\mu VT}$ is known as the grand potential. It can also be derived from thermodynamics, from which one finds

$$F_{\mu VT} = E - TS - \mu N = -pV,$$

where p is the pressure.

The grand canonical ensemble is usually used to describe systems such as fluid connected to a particle reservoir. Sometimes for a magnet we consider the effects of an applied magnetic field, which is analogous to working in the grand canonical ensemble: the magnetic field (which is conjugate to the magnetisation) plays a similar role to the chemical potential in a fluid.

Isothermal-isobaric ensemble

Applies to a system with a fixed number of particles N that is coupled to a heat bath at temperature T and a reservoir that exerts a constant pressure p which allows the sample volume to fluctuate. Denoted as constant-NpT.

The corresponding partition function is a weighted superset of the canonical one

$$Z_{NpT} = \int_0^\infty dV e^{-\beta pV} Z_{NVT}$$

or

$$Z_{NVT} = \int_0^\infty dV \sum_i e^{-\beta H_i}, \tag{2.9}$$

where $H_i = E_i + pV$ is the form of the Hamiltonian in the constant-NpT ensemble. Again a state probability analogous to Equation **??** holds.

Statistically, the states favored in the costant-NpT ensemble are those that minimise the free energy:

$$F_{NpT} = -\beta^{-1} \ln Z_{NpT}$$

F_{NpT} is known as the *Gibb's free energy* (often denoted G). It can also be derived from thermodynamics, from which one finds

$$F_{NpT} = E - TS + pV = \mu N$$

The constant-NpT ensemble is usually used to describe systems such as a fluid subject to a variable pressure, or a magnet coupled to a magnetic field H. In the latter case the quantity HM plays the role of pV and

$$F_{NpT} = E - TS - MH \,,$$

with M the total magnetisation.

From free energies to observables

Free energies are not directly observable quantities. However, all physical observables can be expressed in terms of *derivatives* of the free energy. One can derive the appropriate relations either from Thermodynamics, or the corresponding statistical mechanics (Revise your year-2 Thermal Physics notes on this if necessary). As an example let us consider a fluid in the isothermal-isobaric ensemble for which the appropriate free energy is $F_{NpT} = E - TS + pV$, and where the volume fluctuates in response to the prescribed pressure. We shall seek an expression for the average volume in terms of the free energy. First lets us take the thermodynamic route. Differentiating the free energy and applying the chain rule we have:

$$dF = dE - TdS - sdT + pdV + VdP \,.$$

But from the first law of thermodynamics, $dE = TdS - pdV$, so