Foundations of Statistical Mechanics

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Abstract: This is the first part of a three part series of lectures presenting an introductory Masters level course on Statistical Mechanics. Each part will consist of about 6 Lectures. The first part introduces the classical ensembles of Gibbs with applications to the ideal gas. Later parts will cover lattice spin models, scaling and universality in critical phenomena, mean-field theory, renormalization group, random walks and percolation.

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Overview and References

Overview:

- The goal of statistical mechanics is to describe the behaviour of bulk matter starting from a physical description of the interactions between its microscopic constituents.
- This course introduces the Gibbs probability distributions of classical statistical mechanics, the relations to thermodynamics and the modern theory of phase transitions and critical phenomena. The microcanonical, canonical and grand canonical ensembles will be introduced and illustrated with application to the ideal gas.

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Lecture Outline

Topic 1. Foundations of Statistical Mechanics

1. Thermodynamics versus statistical mechanics
2. Classical mechanics and phase space
3. Gibbs formulation of microcanonical ensemble

Topic 2. Canonical Ensemble

4. Maxwell-Boltzmann Distribution
5. Gibbs formulation of canonical ensemble
6. Ideal gas in canonical ensemble

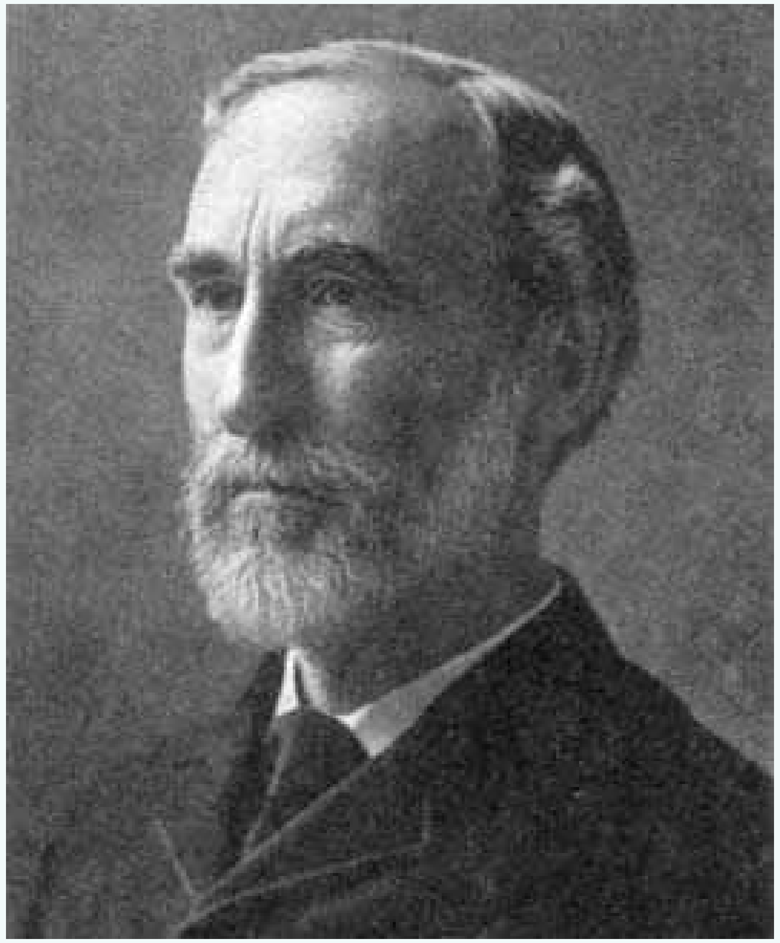
Topic 3. Grand Canonical Ensemble

7. Gibbs formulation of grand canonical ensemble
8. Ideal gas in grand canonical ensemble
9. Equivalence of ensembles

1: Statistical Mechanics Foundations

1. Thermodynamics versus statistical mechanics
2. Classical mechanics and phase space
3. Gibbs formulation of microcanonical ensemble

Josiah Willard Gibbs (1839–1903)



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Thermodynamics versus Statistical Mechanics

- *Thermodynamics* is an empirically based science. It describes many of the physical properties of bulk matter (solids, liquids, gases) in terms of a few state variables such as absolute temperature T (measured in Kelvin), internal energy U, pressure P, volume V and magnetic field h and the relationships between them.

- Ultimately, of course, all of the macroscopic properties of matter (in equilibrium with its surroundings) should be derivable from a knowledge of the fundamental interactions between the constituent particles. This is the goal of statistical mechanics.

- The foundations of statistical mechanics were laid down by J.W. Gibbs in 1902. *Statistical Mechanics* describes all of the macroscopic properties of matter (in equilibrium) starting from a knowledge of the fundamental interactions between the constituent microscopic particles. In particular, statistical mechanics provides a derivation of the relations of thermodynamics.

- The term *statistical mechanics* is a combination of *mechanics* and *statistics*. From a mechanical viewpoint bulk matter, such as 22.4 liters of gas or 60 gram of iron at room temperature ($273K = 0°C, 1K = 1°C$) and pressure, typically consists of a system of $N \approx N_A$ particles where

$$\boxed{N_A = 6.0225 \times 10^{23} \quad \text{(Avogadro's number)}}$$

1 mole $= N_A$ atoms $=$ # of atoms in 12 grams of the isotope carbon-12 (mass number $= 12$).

Large Numbers

$$\text{Computer :} \quad \begin{cases} \text{operations} = 10^{10} \text{ per second} \\ 1 \text{ TB} = 10^{13} \text{ bits} \end{cases}$$

$$\text{Human :} \quad \begin{cases} \text{brain} = 10^{14} \text{ neuron connections} \\ \text{body} = 10^{15} \text{ cells} \end{cases}$$

$$\text{Galaxy :} \quad \begin{cases} \text{age} = 10^{17} \text{ seconds} \\ \text{stars} = 10^{22} \end{cases}$$

$$\text{Avogadro :} \quad \text{mole} = 10^{23} \text{ particles}$$

$$\text{Universe :} \quad \begin{cases} \text{size} = 10^{26} \text{ meters} \\ \text{particles} = 10^{80} \end{cases}$$

$$\text{Googol :} \quad \text{number} = 10^{100}$$

$$\text{Googolplex :} \quad \text{number} = 10^{\text{Googol}}$$

Thermodynamics

In thermodynamics the following *primitive* concepts are introduced:

- *System*: Any macroscopic ensemble of a large number of constituent components, eg. a gas of particles or a magnet composed of atoms with spin or elementary magnetic moments.
- *State*: The equilibrium state (which does not change in time) of a system is determined by a set of *state variables* (measured experimentally), eg. $\{V,T\}$ for a gas and $\{h,T\}$ for a magnet.
- *State Functions*: Quantities such as pressure of a gas $P=P(V,T)$ and magnetization of a magnet $m=m(h,T)$ which depend only on the state of the system are called *state functions*. The differentials of state variables are *exact* (their integrals are independent of the path). The differentials of non-state functions such as δW (work) and δQ (heat) are not exact.
- *Equation of State*: A functional relation between the thermodynamic parameters of a system, such as $f(P,V,T)=0$ or $f(m,h,T)=0$ is called an *equation of state*, eg. for the ideal gas $PV=nRT$.
- *Thermodynamic Potential*: A function of state from which other relevant state functions can be obtained directly or by differentiation is called a *thermodynamic potential*. For example, the Helmholz free energy Ψ is defined by

$$\Psi(T,V)=U(T,V)-TS(T,V)$$

where the internal energy $U=U(T,V)$, entropy $S=S(T,V)$ and pressure $P=P(T,V)$ are

$$\boxed{U=-T^2\frac{\partial}{\partial T}\left(\frac{\Psi}{T}\right),\quad S=-\frac{\partial\Psi}{\partial T},\quad P=-\frac{\partial\Psi}{\partial V}}$$

Laws of Thermodynamics

First Law: Energy is conserved in infinitesimal thermodynamic processes, along a path in the T-V plane, converting internal energy and mechanical work into heat

$$\boxed{\delta Q \;=\; dU + \delta W \;=\; dU + P dV}$$

where the changes in heat (δQ) and work (δW) are not exact differentials (they depend on path) but dU is an exact differential (it is independent of path). Although δQ and δW are not exact differentials, the related differentials dV and dS are exact differentials

$$dV \;=\; \frac{\delta W}{P}, \qquad dS \;=\; \frac{\delta Q}{T}$$

Second Law: For irreversible changes of state in a thermally isolated system, the entropy never decreases

$$\boxed{\Delta S \;=\; S_{\text{final}} - S_{\text{initial}} \;=\; \int_\gamma dS \;=\; \int_\gamma \frac{\delta Q}{T} \;\geq\; 0}$$

The equality holds for reversible processes.

Third Law: The entropy S of a perfect crystal (one which has no residual entropy) approaches zero as $T \to 0$. Since it would require an infinite energy for cooling, absolute zero ($0\,K$) can never be reached so that physically

$$\boxed{T \;>\; 0}$$

Phase Space and Equations of Motion

- The classical mechanics of a system of N particles with mass m is determined by writing down an energy function or *Hamiltonian* describing the particle interactions and solving (usually numerically) the resulting equations of motion in the $6N$-dimensional phase space

$$\Gamma = \langle\{\sigma\}\rangle = \langle\{(\boldsymbol{p}_1, \boldsymbol{q}_1, \boldsymbol{p}_2, \boldsymbol{q}_2, \ldots, \boldsymbol{p}_N, \boldsymbol{q}_N)\}\rangle$$

spanned by the coordinates $\boldsymbol{q}_i$ and momenta $\boldsymbol{p}_i$ in 3-space. The $6N$-dimensional vector $\sigma \in \Gamma$ is the microscopic state of the system.

- The Hamiltonian takes the form

$$\boxed{H(\sigma) \;=\; \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_N) \;=\; \text{Kinetic} + \text{Potential Energy}}$$

- The equations of motion are

$$\begin{aligned} \dot{\boldsymbol{p}}_i &= -\frac{\partial H}{\partial \boldsymbol{q}_i} \qquad & \left(= -\frac{\partial V}{\partial \boldsymbol{q}_i} = \text{Force}\right) \\ \dot{\boldsymbol{q}}_i &= \frac{\partial H}{\partial \boldsymbol{p}_i} \qquad & \left(= \frac{\boldsymbol{p}_i}{m} = \text{velocity}\right) \end{aligned}$$

These are equivalent to the Newtonian equations of motion

$$\boldsymbol{F}_i = m\ddot{\boldsymbol{q}}_i, \qquad i = 1, 2, \ldots, N$$

- It is not practical to solve this system for $N = 6 \times 10^{23}$ particles. Instead we need to understand the *average statistical behaviour* of the *mechanical* motion of a large number of particles.

Statistical Averages

- Statistical mechanics is used to obtain average quantities or expected values for a large system described, within a given *ensemble*, by a suitable probability distribution function.

Discrete Random Variable: Suppose a random variable x takes the values $x_1, x_2, \ldots, x_n$ with probabilities $p_1, p_2, \ldots, p_n$ where $0 \le p_k \le 1$. The average or expected value of the observable $O(x)$ is then

$$\boxed{\langle O(x)\rangle = \mathbb{E}[O(x)] = \sum_{k=1}^{n} O(x_k)p_k = \frac{\sum_{k=1}^{n} O(x_k)p_k}{\sum_{k=1}^{n} p_k}, \qquad \sum_{k=1}^{n} p_k = 1}$$

Continuous Random Variable: Suppose that x is a continuous random variable on $[a,b]$ with the continuous *probability density function* $\rho(x)$ where $0 \le \rho(x) \le 1$. The average or expected value of the observable $O(x)$ is then

$$\boxed{\langle O(x)\rangle = \mathbb{E}[O(x)] = \int_a^b O(x)\rho(x)dx = \frac{\displaystyle\int_a^b O(x)\rho(x)dx}{\displaystyle\int_a^b \rho(x)dx}, \qquad \int_a^b \rho(x)\,dx = 1}$$

These averages are extended to higher dimensions by using multiple integrals and joint probability distribution functions $\rho(\boldsymbol{x})$.

Properties of $\langle\cdots\rangle$:

1. Normalization: $\langle 1\rangle = 1$
2. Linearity: $\langle \alpha f(x) + \beta g(x)\rangle = \alpha\langle f(x)\rangle + \beta\langle g(x)\rangle, \qquad \alpha, \beta$ constants

Indicator Functions

- Let $E \subseteq \Omega$ be a subset of Ω viewed as the universal set of all possible "events" $E \subseteq \Omega$. The *indicator (or characteristic) function* $\chi_E(x)$ is defined as

$$\boxed{\chi_E(x) = \begin{cases} 1, & x \in E \\ 0, & x \notin E \end{cases}}$$

In other words, the indicator function takes value 1 when E happens (is true) and 0 when it does not happen (is false).

Example: Write down the indicator function for throwing an odd number on a single dice.

Solution: In this example $\Omega = \{1, 2, 3, 4, 5, 6\}$ and $E = \{1, 3, 5\}$. The indicator function can be written in terms of Kronecker deltas as

$$\chi_{\{1,3,5\}}(x) = \delta_{x,1} + \delta_{x,3} + \delta_{x,5} = \begin{cases} 1, & x = 1, 3, 5 \\ 0, & x = 2, 4, 6 \end{cases}$$

Exercise: Let $x, y = 1, 2, 3, 4, 5, 6$ be the random variables for the throw of two dice.

(i) Show that Ω is given by the Cartesian product $\{1, 2, 3, 4, 5, 6\} \times \{1, 2, 3, 4, 5, 6\}$.

(ii) What is the average number rolled with two dice?

(iii) Find the average value of the observable $O(x, y) = x^2 y^2$ and show that $\langle x^2 y^2 \rangle = \langle x^2 \rangle \langle y^2 \rangle$.

(iv) Write down the indicator function $\chi_{\le 4}(x, y)$ for rolling less than or equal to 4 with two dice.

(v) Find the average of the observable $O(x, y) = \chi_{\le 4}(x, y)$ and show it equals Prob$(x+y \le 4)$.

Ensembles

- In statistical mechanics, the averages, or *ensembles* used to the describe the system depend on how the system is set up. There are three ensembles in general use. In each ensemble the details of the connection with thermodynamics is different but each ensemble yields equivalent results in the *thermodynamic limit* when N and V are taken to be infinitely large.

Ensemble	**Fixed Quantities**	
Microcanonical	N	E
Canonical	N	T
Grand Canonical	z	T

Here N is the total number of particles, E is the total energy and z is the fugacity.

- In the *microcanonical ensemble* the system is completely isolated so that the number of particles N is fixed and the total energy E is conserved.

- In the *canonical ensemble*, the system is not isolated so the energy E is not conserved — the system is in thermal equilibrium with its environment (a heat reservoir) at temperature T. The number of particles N is fixed but the average energy is determined statistically by the temperature T.

- In the *grand canonical ensemble* the system is in equilibrium with a heat and particle reservoir — neither the number of particles N or the energy E is fixed — the average number of particles is controlled by the fugacity z and the average energy is controlled by the temperature T.

Microcanonical Ensemble

- If the Hamiltonian (energy function) is autonomous, that is $H = H(\{\boldsymbol{p}_j(t), \boldsymbol{q}_j(t)\})$ does not depend explicitly on t, then the system is conservative and the energy is conserved. In this case, the mechanical motion takes place on the energy surface

$$H(\sigma) = T + V = E \quad \text{(total energy)} \qquad \sigma \in \Gamma$$

- The *Ergodic Postulate* states that the invariant phase space probability density of an isolated Hamiltonian system is the uniform distribution on this energy surface

$$\boxed{\rho(p,q) = \frac{\delta(H-E)}{\int_\Gamma \delta(H-E)\, d\Gamma}}$$

Here $\delta(x)$ is the Dirac delta function,

$$d\Gamma = d\boldsymbol{p}_1 d\boldsymbol{q}_1 d\boldsymbol{p}_2 d\boldsymbol{q}_2 \ldots d\boldsymbol{p}_N d\boldsymbol{q}_N$$

is a differential element of phase space and the $6N-1$ dimensional integral in the denominator represents the total area of the energy surface.

- Although the postulate is almost certainly not generally true, we use it as a working assumption as did Gibbs. As is the case for set theory and quantum mechanics, there is no *rigorous* foundation to Statistical Mechanics!

Justification of Statistical Mechanics

- Ultimately, the justification for statistical mechanics rests in agreement with experiments. It is the averages of observable quantities $O(p,q)$ that are measurable experimentally and these are to be compared with the averages calculated in the microcanonical ensemble

$$\langle O(p,q)\rangle = \frac{\int_\Gamma O(p,q)\delta(H-E)\,d\Gamma}{\int_\Gamma \delta(H-E)\,d\Gamma} = \frac{\int_{H=E} O(p,q)\,d\Gamma}{\int_{H=E} d\Gamma}$$

- The connection with thermodynamics in the microcanonical ensemble is due to Boltzmann and relates the entropy S with the integral over the energy surface

$$\boxed{S(U\!=\!E,V) = k\log\Omega(E), \qquad \Omega(E) = \frac{1}{N!}\int_{H=E} d\Gamma = \text{area of the energy surface}}$$

where k is Boltzmann's constant

$$k = 1.3805\times 10^{-23}\ \text{Joules/Kelvin}$$

For a discrete system $\Omega(E)$ is the counting of allowed microstates.

- The entropy is a thermodynamic potential. Other thermodynamic quantities are derived by differentiation

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \qquad P = T\left(\frac{\partial S}{\partial V}\right)_E}$$

- Although, the microcanonical ensemble is introduced first for theoretical reasons, it is the canonical and grand canonical ensembles that are used in practical calculations.

Ideal Gas in Microcanonical Ensemble

- The *ideal gas* consists of N non-intereacting *idealized* point particles of mass m. This provides a good approximation to a realistic gas at high temperatures and low pressures. It is not a good approximation at low temperatures and high pressures where the gas can undergo a phase transition to a liquid or solid.

- In the microcanonical ensemble, the ideal gas is defined by the Hamiltonian

$$\boxed{H(\sigma) \;=\; \frac{1}{2m}\sum_{i=1}^{N} \boldsymbol{p}_i^2}$$

There is only kinetic energy and no potential energy $V = 0$.

- Since $H(\sigma)$ is time-independent, conservation of energy implies that

$$H \;=\; \frac{1}{2m}\sum_{i=1}^{N} \boldsymbol{p}_i^2 \;=\; E \;=\; \text{total energy} \;=\; \text{constant}$$

- The motion of the state $\sigma \in \Gamma$ in phase space is confined to the hypersphere in $3N - 1$ dimensional momentum space

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \cdots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2 \;=\; 2mE$$

- In the problem sheets, it is shown that this ideal gas is described by the ideal gas equation

$$\boxed{PV = NkT, \qquad k = \text{Boltzmann's constant}}$$

2: Canonical Ensemble

4. Gibbs formulation of canonical ensemble
5. Ideal gas in canonical ensemble
6. Maxwell-Boltzmann distribution

James Clerk Maxwell (1831–1879)

Ludwig Eduard Boltzmann (1844–1906)

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Canonical Ensemble

- The canonical ensemble describes a system of N particles in a box of volume V weakly coupled to and in thermal equilibrium with an infinitely large heat reservoir at absolute temperature T. The number of particles in the system is fixed but heat is exchanged with the environment to maintain a temperature T.

- The fundamental postulate is that the probability density $\rho(\sigma)$ of points in phase space Γ is given by

$$\boxed{\rho(\sigma) \;=\; \frac{\exp(-\beta H(\sigma))}{\int_\Gamma \exp(-\beta H(\sigma))\, d\Gamma}, \qquad \sigma \in \Gamma}$$

Here $H(\sigma)$ is the Hamiltonian of the system (excluding interactions with the heat reservoir), the integral is over all of the accessible phase space and

$$\boxed{\beta = \frac{1}{kT} = \text{inverse temperature}}$$

where Boltzmann's constant is

$$k = 1.3805 \times 10^{-23} \text{ Joules/Kelvin}$$

- The weight $\exp(-\beta H(\sigma))$ is the *Boltzmann factor* associated with the configuration σ. Crudely speaking, it gives the unnormalized *a priori* probability of finding the system in the state σ.

Boltzmann Weights

- The probability density $\rho(\sigma)d\Gamma$ gives the statistical probability of finding the system in the phase space volume $d\Gamma$ about σ. In accord with the interpretation of $\rho(\sigma)$ as a probability

$$\rho(\sigma) \geq 0, \qquad \int_\Gamma \rho(\sigma)\, d\Gamma = 1, \qquad \langle O(\sigma)\rangle = \int_\Gamma O(\sigma)\rho(\sigma)\, d\Gamma = \frac{\int_\Gamma O(\sigma)\exp(-\beta H(\sigma))\, d\Gamma}{\int_\Gamma \exp(-\beta H(\sigma))\, d\Gamma}$$

- The normalization factor is a fundamental quantity called the *canonical partition function*

$$\boxed{Z_N = \int_\Gamma \exp(-\beta H(\sigma))\, d\Gamma}$$

- Notice also that at high temperatures $(T \to \infty, \beta \to 0)$

$$\rho(\sigma) \sim \frac{1}{\int_\Gamma d\Gamma}$$

and all states are equally likely (random) while at low temperatures $(T \to 0, \beta \to \infty)$ the low energy (ground) states are most probable.

- Note that energies are additive whereas Boltzmann weights are multiplicative. If E_1 and E_2 are the energies of two independent (non-interacting) subsystems then the total energy is

$$E = E_1 + E_2$$

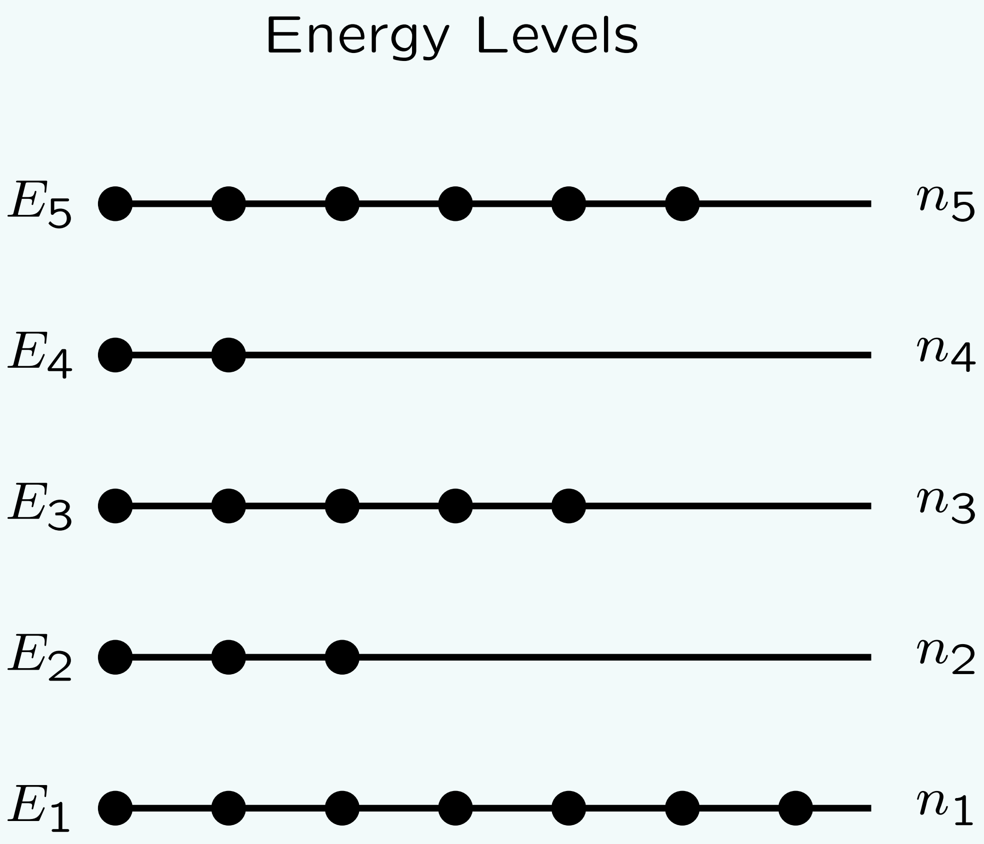
While, if $W_1 = e^{-\beta E_1}$ and $W_2 = e^{-\beta E_2}$ are the Boltzmann weights of these two independent (non-interacting) subsystems, then the Boltzmann weight of the combined system is

$$W = e^{-\beta E} = e^{-\beta(E_1+E_2)} = W_1 W_2$$

Maxwell-Boltzmann Distribution

- A heuristic argument gives the Gibbs postulate in the case of a toy model with N distinguishable particles distributed randomly, that is with equal probability, among a number of discrete energy levels E_j, with $j = 1, 2, 3, \ldots$ and n_j particles in each level. The probability of a given distribution $\{n_1, n_2, n_3, \ldots\}$ satisfies

$$\mathcal{P} \propto \frac{N!}{n_1! n_2! n_3! \ldots}$$



- In the limit $N \to \infty$, $n_j \to \infty$ Stirling's formula

$$N! \sim \left(\frac{N}{e}\right)^N, \quad \text{etc.}$$

gives

$$\boxed{\log \mathcal{P} \sim N \log N - N - \sum_j (n_j \log n_j - n_j)}$$

- To find the most probable configuration, we maximize $\log \mathcal{P}$ subject to the two constraints

$$\boxed{\sum_j n_j = N, \qquad \sum_j n_j E_j = E = \text{total energy}}$$

Lagrange Multipliers

- We treat n_j as continuous variables (properly we should use the continuous densities $\rho_j = n_j/N$), introduce Lagrange multipliers α, β and maximize

$$N \log N - N - \sum_j (n_j \log n_j - n_j) - \alpha \sum_j n_j - \beta \sum_j n_j E_j$$

Differentiating with respect to n_j gives

$$\log n_j + \alpha + \beta E_j = 0 \quad \text{or} \quad n_j = e^{-\alpha} e^{-\beta E_j}$$

- Therefore

$$N = \sum_j n_j = e^{-\alpha} \sum_j e^{-\beta E_j} = e^{-\alpha} Z_N$$

and

$$\boxed{\rho_j = \frac{n_j}{N} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \text{density of states}}$$

gives the probability of finding the particle j in the energy state E_j. This distribution is the Maxwell-Boltzmann distribution. The constant β is identified as the inverse temperature.

- The total energy E is controlled statistically by the inverse temperature $\beta = 1/kT$

$$\frac{E}{N} = \frac{\sum_j n_j E_j}{\sum_j n_j} = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \langle E_j \rangle = \frac{1}{N} \sum_j \langle E_j \rangle$$

This implies $E = E(\beta)$ and $\beta = \beta(E)$ since $E'(\beta) = -\big\langle (E_j - \langle E_j \rangle)^2 \big\rangle < 0$ for more than one energy level E_j. So $E(\beta)$ is strictly monotone decreasing and $E(T)$ is strictly monotone increasing as is sensible physically. So $\beta^{-1} = kT$ is a measure of the average energy.

Connection with Thermodynamics

- The canonical partition function Z_N is a generating function for the thermodynamic functions. The (Helmholtz) free energy $\Psi = \Psi(T,V) = U - TS$ is given by the Gibbs postulate

$$\boxed{\Psi = -kT \log Z_N}$$

where $U = U(T,V)$ is the internal energy, $S = S(T,V)$ is the entropy and V is the volume.

- The internal energy is

$$\boxed{U = -T^2 \frac{\partial}{\partial T}\left(\frac{\Psi}{T}\right) = \Psi - T\frac{\partial \Psi}{\partial T} = \Psi + TS}$$

Hence the entropy is

$$\boxed{S = -\frac{\partial \Psi}{\partial T}}$$

- Similarly, the specific heat (at constant volume) is

$$\boxed{C_V = \frac{\partial U}{\partial T} = -T\frac{\partial^2 \Psi}{\partial T^2}}$$

Maxwell Relations

- Consider an irreversible infinitesimal transformation along a curve in the V-T plane. The free energy is

$$\Psi \;=\; \Psi(V,T) \;=\; U - TS$$

Using the first law $dU = \delta Q - \delta W$, the exact differential along this curve is

$$\begin{aligned} d\Psi &= dU - TdS - SdT \;=\; \delta Q - \delta W - TdS - SdT \;=\; TdS - PdV - TdS - SdT \\ &= -PdV - SdT \;=\; \frac{\partial\Psi}{\partial V}dV + \frac{\partial\Psi}{\partial T}dT \;=\; \nabla\Psi\cdot(dV,dT) \end{aligned}$$

- It follows that the pressure $P = P(V,T)$ and entropy $S = S(V,T)$ are given by

$$\boxed{P = -\frac{\partial\Psi}{\partial V}, \qquad S = -\frac{\partial\Psi}{\partial T}}$$

where we have the Maxwell relation

$$\frac{\partial P}{\partial T} = \frac{\partial S}{\partial V} = -\frac{\partial^2\Psi}{\partial V\partial T}$$

and

$$\nabla\Psi = -\big(P(V,T), S(V,T)\big), \qquad \nabla = \left(\frac{\partial}{\partial V}, \frac{\partial}{\partial T}\right)$$

is a two-dimensional irrotational (conservative) vector field so that the integrals in the (V,T)-plane are path independent.

- Equating the functions multiplying the differentials is only valid because $d\Psi$ is an exact differential. Note that changes in heat and work, δQ and δW, are not exact differentials.

Ensemble Averages

- The average or expected value of an observable $A = A(\sigma)$ is given by the ensemble or thermal average

$$\boxed{\langle A \rangle = \frac{\displaystyle\int_\Gamma A(\sigma)\,\mathrm{exp}(-\beta H(\sigma))\,d\Gamma}{\displaystyle\int_\Gamma \mathrm{exp}(-\beta H(\sigma))\,d\Gamma}}$$

- For example, the internal energy is

$$\begin{aligned} U = \langle H \rangle &= \frac{\displaystyle\int_\Gamma H(\sigma)\,\mathrm{exp}(-\beta H(\sigma))\,d\Gamma}{\displaystyle\int_\Gamma \mathrm{exp}(-\beta H(\sigma))\,d\Gamma} \\ &= -\frac{\partial}{\partial\beta}\log\int_\Gamma \mathrm{exp}(-\beta H(\sigma))\,d\Gamma = -\frac{\partial}{\partial\beta}\log Z_N \\ &= -\left(\frac{d\beta}{dT}\right)^{-1}\frac{\partial}{\partial T}\left(-\frac{\Psi}{kT}\right) = -T^2\frac{\partial}{\partial T}\left(\frac{\Psi}{T}\right) \end{aligned}$$

as given on a previous slide.

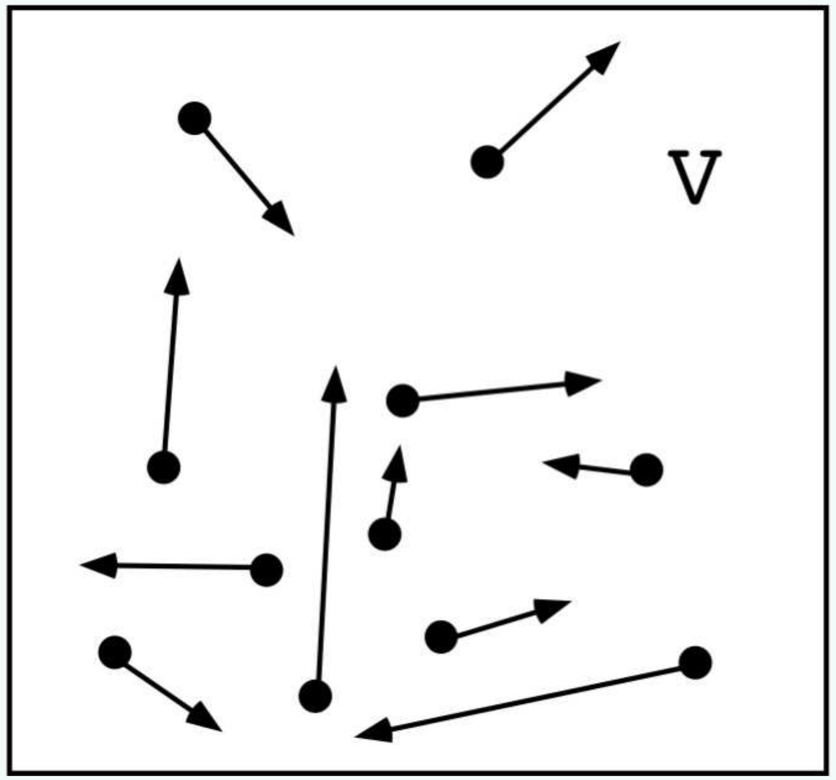
Philosophy

- Although there is in general no rigorous derivation of the Gibbs ensembles and their connection with thermodynamics, the fundamental postulates are well confirmed in applications.

- Physicists adopt the attitude that the postulates are almost certainly correct and use them without question as the starting point for their calculations.

- Paradoxically, at the same time, mathematicians regard the whole edifice of statistical mechanics (not to mention set theory, quantum mechanics, etc.) as being based on shaky foundations! In any case let's not dwell further on the foundations of statistical mechanics. Instead, let's take the Gibbs prescription as given and pragmatically concentrate on practical applications.

Ideal Gas



- The ideal gas is a system of noninteracting point particles of mass m. In the canonical ensemble, we consider a system of N particles in a container of volume V and maintained at a temperature T by a surrounding heat reservoir.

- The Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m}$$

and the canonical partition function is

$$\boxed{Z_N = \frac{1}{N!} \int_V \cdots \int_V d\boldsymbol{q}_1 \ldots d\boldsymbol{q}_N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} d\boldsymbol{p}_1 \ldots d\boldsymbol{p}_N \exp\left(-\frac{\beta}{2m} \sum_{i=1}^{N} \boldsymbol{p}_i^2 \right)}$$

- The $N!$ appears here because the N particles are regarded as indistinguishable, that is, configurations obtained by permuting the particles are considered to be identical (*Boltzmann counting*). This is not strictly correct. A proper treatment uses quantum mechanics applied to a system of *Bosons* or *Fermions*.

- Notice that we also ignore relativity which dictates that $|\boldsymbol{v}| < c$, that is, $|\boldsymbol{p}_j| < mc$ where c is the speed of light.

Ideal Gas Law

- Using the formula for the Gaussian integral

$$\int_{-\infty}^{\infty} \exp(-\lambda x^2)\, dx = \sqrt{\frac{\pi}{\lambda}}$$

the partition function of the ideal gas is evaluated as

$$Z_N = \frac{V^N}{N!}\left[\int_{-\infty}^{\infty} \exp\left(-\frac{\beta}{2m}p^2\right) dp\right]^{3N} = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

so the pressure is given by

$$P = -\frac{\partial \Psi}{\partial V} = \frac{\partial}{\partial V}(kT \log Z_N) = \frac{NkT}{V}$$

- The ideal gas law is thus

$$\boxed{PV = NkT = nRT}$$

where n is the number of moles of gas ($N = nN_A$) and

$$R = N_A k = 8.315 \text{ Joules/Kelvin}$$

is the ideal gas constant.

Equipartition of Energy

- The internal (average kinetic) energy of the ideal gas ($V = 0$) is

$$\boxed{U = \langle H \rangle = \langle \text{kinetic energy} \rangle = -\frac{\partial}{\partial \beta} \log Z_N = \frac{3N}{2\beta} = 3N(\tfrac{1}{2}kT)}$$

This illustrates the equipartition of energy between the $3N$ (participating) degrees of freedom. Each (participating) degree of freedom contributes an energy of $\frac{1}{2}kT$. It also shows that the temperature T is indeed a measure of the average internal energy.

- Since the above arguments rely on Gaussian integrals, the participating degrees of freedom are always harmonic oscillators. Usually these are momenta components but they can include rotational degrees of freedom (for molecules for example) or spatial degrees of freedom for (trapped) particles confined by a harmonic (quadratic) potential

$$V = \sum_{j=1}^{N} \lambda \boldsymbol{q}^2$$

- Notice that, in the canonical ensemble, the internal energy is *extensive* (grows linearly with the system size N as $N \to \infty$). Similarly, P, Ψ and S are extensive while T and V are intensive quantities (independent of the system size).

Kinetic Theory of Gases

- Derive the Maxwell-Boltzmann velocity distribution of kinetic theory for an ideal gas

$$\boxed{\frac{dn}{dv} = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}, \qquad v = |\boldsymbol{v}|}$$

where the differential dn is the number of molecules with speed between v and $v + dv$.

- Since the particles do not interact, the Boltzmann factors factorize

$$\exp(-\beta H) = \exp\left(-\sum_{j=1}^{N} \frac{\beta \boldsymbol{p}_j^2}{2m}\right) = \prod_{j=1}^{N} \exp\left(-\frac{\beta \boldsymbol{p}_j^2}{2m}\right)$$

Particles are independent and identically distributed with joint probability distribution function

$$\rho(\{\boldsymbol{p}_j\}) = \prod_{j=1}^{n} \rho(\boldsymbol{p}_j), \qquad \rho(\boldsymbol{p}) = \frac{e^{-\beta \boldsymbol{p}^2/2m}}{\int_{\mathbb{R}^3} e^{-\beta \boldsymbol{p}^2/2m} d\boldsymbol{p}}$$

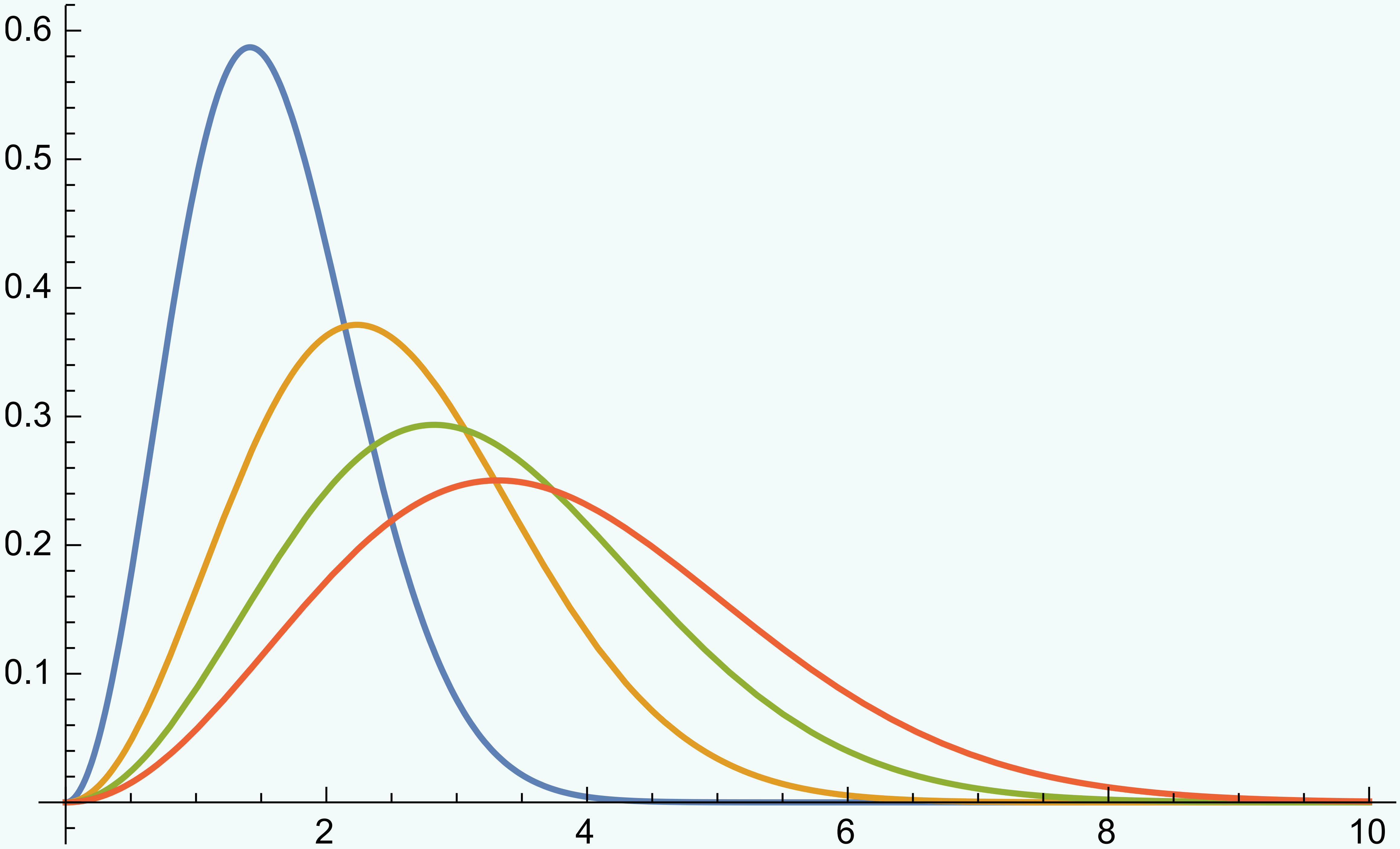
where $d\boldsymbol{p} = dp_x\, dp_y\, dp_z$ is a differential element of momentum phase space volume.

- The velocity distribution of each particle is the same. Using the one-particle distribution function $\rho(\boldsymbol{p})$ gives the number of particles in the differential phase space volume $d\boldsymbol{p}$ as

$$\begin{aligned}\frac{dn}{N} &= \rho(\boldsymbol{p})\, d\boldsymbol{p} = \frac{e^{-\beta \boldsymbol{p}^2/2m} d\boldsymbol{p}}{\int_{\mathbb{R}^3} e^{-\beta \boldsymbol{p}^2/2m} d\boldsymbol{p}} = \frac{e^{-m\boldsymbol{v}^2/2kT} d\boldsymbol{v}}{\int_{\mathbb{R}^3} e^{-m\boldsymbol{v}^2/2kT} d\boldsymbol{v}} = \frac{v^2 e^{-mv^2/2kT} dv}{\int_0^\infty v^2 e^{-mv^2/2kT} dv} \\ &= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\, dv\end{aligned}$$

where we use $\boldsymbol{p} = m\boldsymbol{v}$ and $d\boldsymbol{v} = 4\pi v^2 dv$ to integrate over spherical shells.

Maxwell-Boltzmann Distribution



Microcanonical Ideal Gas

- In the microcanonical ensemble the connection with thermodynamics is given by

$$\boxed{S(E,V) = \text{const} + k \log \frac{\Omega(E)}{N!}}$$

where N is the fixed number of particles in a container of volume V and

$$\Omega(E) = \int_{H=E} d\Gamma = \{\text{Area of energy surface } H = E\}$$

(a) Identifying the internal energy with the total energy $U = E$ and regarding the entropy $S = S(E,V)$ as a function of E and V, use the first and second laws of thermodynamics in the form

$$\delta Q = dU + \delta W = dE + P dV, \qquad dS = \frac{\delta Q}{T}$$

where Q is heat, W is work, δQ is an inexact differential and dS is an exact differential to show that

$$P = T\left(\frac{\partial S}{\partial V}\right)_E, \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$$

- From the chain rule we have

$$dS \;=\; \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \;=\; \frac{1}{T} dE + \frac{P}{T} dV$$

Since dS is an exact differential, we can equate the coefficients

$$\boxed{\frac{\partial S}{\partial E} = \frac{1}{T}, \qquad \frac{\partial S}{\partial V} = \frac{P}{T}}$$

This is the definition of the temperature T in the microcanonical ensemble!

Gamma Function

(b) The Gamma function is defined by

$$\boxed{\Gamma(z) = \int_0^\infty t^{z-1} e^{-t}\, dt}$$

Use integration by parts to show that $\Gamma(z+1) = z\,\Gamma(z)$ and hence find $\Gamma(n)$ and $\Gamma(n+1/2)$ for $n = 0, 1, 2, \ldots$

- Integration by parts gives

$$\Gamma(z+1) = \int_0^\infty t^z e^{-t}\, dt = -\Big[t^z e^{-t}\Big]_0^\infty + z\int_0^\infty t^{z-1} e^{-t}\, dt = z\,\Gamma(z)$$

So, setting $x = y^2$, gives

$$\Gamma(1) = \int_0^\infty e^{-x}\, dx = -\Big[e^{-x}\Big]_0^\infty = 1, \quad \Gamma(1/2) = \int_0^\infty x^{-1/2} e^{-x}\, dx = 2\int_0^\infty e^{-y^2}\, dy = \sqrt{\pi}$$

Hence, by recursion,

$$\Gamma(n) = (n-1)(n-2)(n-3)\cdots(3)(2)\Gamma(1) = (n-1)!$$

and

$$\Gamma\Big(n+\tfrac{1}{2}\Big) = \Big(n-\tfrac{1}{2}\Big)\Big(n-\tfrac{3}{2}\Big)\cdots\Big(\tfrac{3}{2}\Big)\Gamma(\tfrac{1}{2}) = \frac{(2n-1)!!}{2^n}\sqrt{\pi}$$

Surface Area of Hypersphere

(c) Show that the "surface area" and volume of a hypersphere of radius r in n dimensions are given respectively by

$$\boxed{A_n(r) = \frac{2\pi^{n/2}\, r^{n-1}}{\Gamma(\frac{n}{2})}, \qquad V_n(r) = \frac{\pi^{n/2} r^n}{\Gamma(\frac{n}{2}+1)}, \qquad \Gamma(z+1) = \int_0^\infty t^z e^{-t}\, dt}$$

Hence show that the volume and surface area of a unit hypersphere go to zero as $n \to \infty$. Hint: consider the integral

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\cdots+x_n^2)}\, dx_1 dx_2 \ldots dx_n$$

and evaluate it by integrating over spherical shells using spherical coordinates.

- From dimensional analysis

$$A_n(r) = \alpha_n\, r^{n-1}$$

Now consider evaluating the following multiple integral using spherical shells of volume $A_n(r)\, dr$ and then setting $r^2 = t$

$$\begin{aligned} \pi^{n/2} &= \left(\int_{-\infty}^{\infty} e^{-x^2}\, dx\right)^n = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\cdots+x_n^2)}\, dx_1 dx_2 \ldots dx_n \\ &= \int_0^\infty A_n(r) e^{-r^2} dr = \alpha_n \int_0^\infty r^{n-1} e^{-r^2} dr = \tfrac{1}{2}\alpha_n \int_0^\infty t^{\frac{n}{2}-1} e^{-t} dt = \tfrac{1}{2}\alpha_n\, \Gamma(n/2) \end{aligned}$$

Hence

$$\boxed{\alpha_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}, \qquad A_n(r) = \frac{2\pi^{n/2}\, r^{n-1}}{\Gamma(n/2)}}$$

Volume of Hypersphere

- Similarly, integrating by spherical shells, we see that

$$V_n(r) \;=\; \int_0^r A_n(r)\,dr \;=\; \alpha_n \int_0^r r^{n-1}\,dr \;=\; \frac{\alpha_n\, r^n}{n} \;=\; \frac{2\pi^{n/2}}{\Gamma(n/2)}\,\frac{r^n}{n} \;=\; \frac{\pi^{n/2}\, r^n}{\Gamma(\frac{n}{2}+1)}$$

From the convergence of the exponential

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} < \infty \qquad \Rightarrow \qquad \lim_{n\to\infty} \frac{x^n}{n!} = 0$$

we see that $\Gamma(n+1) = n!$ grows much faster than x^n for any fixed x. It therefore follows that

$$\boxed{\lim_{n\to\infty} A_n(r) = \lim_{n\to\infty} V_n(r) = 0}$$

which is not at all an intuitively obvious result.

- A ball of unit radius has the maximum surface area in 7 dimensions!
- A ball of unit radius has the maximum volume in 5 dimensions!

Ideal Gas Law and Equipartition of Energy

(d) Use parts (a) and (c) to show that for large N

$$\boxed{PV = NkT, \qquad E = \frac{3}{2}NkT}$$

- For an ideal gas, the energy surface is given by an $n = 3N$ dimensional hypersphere

$$H = \sum_{j=1}^{N} \frac{\boldsymbol{p}_j^2}{2m} = E, \qquad \sum_{j=1}^{N} \sum_{\alpha=x,y,z} p_{j\alpha}^2 = r^2, \quad r = (2mE)^{1/2}$$

with surface area $\Omega(E)$ and entropy $S(E, V)$

$$\Omega(E) = \int_{H=E} d\Gamma = \int_V d\boldsymbol{q}_1 \cdots \int_V d\boldsymbol{q}_N \int_{H=E} d^N\boldsymbol{p} \;=\; V^N \frac{2\pi^{3N/2}(2mE)^{(3N-1)/2}}{\Gamma(3N/2)}$$

$$S(E, V) = \text{const} + k \log \frac{\Omega(E)}{N!}$$

where $d^N\boldsymbol{p} = d\boldsymbol{p}_1 \ldots d\boldsymbol{p}_N$. The pressure is therefore

$$P = T\left(\frac{\partial S}{\partial V}\right)_E = NkT \frac{\partial}{\partial V} \log V = \frac{NkT}{V}$$

Similarly,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \tfrac{1}{2}(3N-1)k \frac{\partial}{\partial E} \log E = \frac{(3N-1)k}{2E}$$

Neglecting 1 compared to N, for large N, gives the equipartition of energy

$$E = \frac{3}{2}NkT$$

3: Grand Canonical Ensemble

7. Gibbs formulation of grand canonical ensemble
8. Ideal gas in grand canonical ensemble
9. Equivalence of ensembles

Satyendra Nath Bose (1894–1974)

Enrico Fermi (1901–1954)

Photographs © MacTutor Mathematics Archive (http://www-history.mcs.st-andrews.ac.uk)

Grand Canonical Ensemble

- In some circumstances, it is not sensible to work with a system of a fixed number of particles. Rather, the system should be in equilibrium with a particle reservoir and the number of particles should be controlled by a chemical potential μ, or equivalently, an activity (fugacity)

$$z = e^{\beta\mu}$$

- For such cases the *grand partition function* Ξ is defined by

$$\boxed{\Xi(V,T,z) = \sum_{N=0}^{\infty} z^N Z_N(V,T)}$$

Mathematically, this is the generating function for the canonical partition functions Z_N.

- In the grand canonical ensemble the pressure is defined by

$$\boxed{P = \frac{kT}{V} \log \Xi(V,T,z)}$$

The number of particles fluctuates and is not fixed. The average number of particles is

$$\boxed{\langle N \rangle = \frac{\sum_{N=0}^{\infty} N\, z^N\, Z_N}{\sum_{N=0}^{\infty} z^N\, Z_N} = \frac{\partial}{\partial(\beta\mu)} \log \Xi = z\frac{\partial}{\partial z} \log \Xi}$$

- Similarly, the internal energy U and the free energy Ψ are given by

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\log\Xi = \langle H\rangle = \frac{\sum\limits_{N=0}^{\infty} z^N \int_\Gamma H e^{-\beta H} d\Gamma}{\sum\limits_{N=0}^{\infty} z^N \int_\Gamma e^{-\beta H} d\Gamma} \\ \Psi &= \langle N\rangle\, kT\log z - kT\log\Xi \end{aligned}$$

It is not easy to derive this last formula for the free energy and we will not need it in this course.

- In the grand canonical ensemble Ψ, S and V are extensive while P, T and z are intensive.

- In the grand canonical ensemble, the expectation value of an observable $A = A(\sigma; N)$ is

$$\langle A\rangle = \frac{\sum\limits_{N=0}^{\infty} z^N \int_\Gamma A(\sigma;N)\, e^{-\beta H} d\Gamma}{\sum\limits_{N=0}^{\infty} z^N \int_\Gamma e^{-\beta H} d\Gamma}$$

Grand Canonical Ideal Gas

- For the ideal gas

$$Z_N = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

Hence

$$\Xi = \sum_{N=0}^{\infty} z^N Z_N = \exp\left[zV\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]$$

- It follows that

$$\begin{aligned} PV &= kT\log\Xi = kTzV\left(\frac{2\pi m}{\beta}\right)^{3/2} \\ \langle N\rangle &= z\frac{\partial}{\partial z}\log\Xi = zV\left(\frac{2\pi m}{\beta}\right)^{3/2} \end{aligned}$$

Eliminating z between these equations gives the ideal gas law in the form

$$\boxed{PV = \langle N\rangle kT}$$

- The internal energy U of the ideal gas in the grand canonical ensemble is

$$U = \langle H\rangle = \frac{\sum_{N=0}^{\infty} z^N \int_\Gamma H\, e^{-\beta H} d\Gamma}{\sum_{N=0}^{\infty} z^N \int_\Gamma e^{-\beta H} d\Gamma} = \frac{\sum_{N=0}^{\infty} z^N \langle H\rangle_{can} Z_N}{\sum_{N=0}^{\infty} z^N Z_N} = \frac{3}{2}kT\frac{\sum_{N=0}^{\infty} N z^N Z_N}{\sum_{N=0}^{\infty} z^N Z_N} = 3\langle N\rangle\,\frac{1}{2}kT$$

Equivalence of Canonical and Grand Canonical Ensembles

- The canonical and grand canonical ensembles are clearly not equivalent for finite systems since N and $\langle N\rangle$ do not coincide. However, for very large V, the fluctuations of N about its average $\langle N\rangle$ in the grand canonical ensemble are usually very small as is shown in the Problem Sheets:

$$\frac{\langle(N-\langle N\rangle)^2\rangle}{\langle N\rangle^2} = o(\langle N\rangle) = o(V)$$

$$\langle N\rangle, V \to \infty, \qquad \frac{\langle N\rangle}{V} \to \rho = \text{density}$$

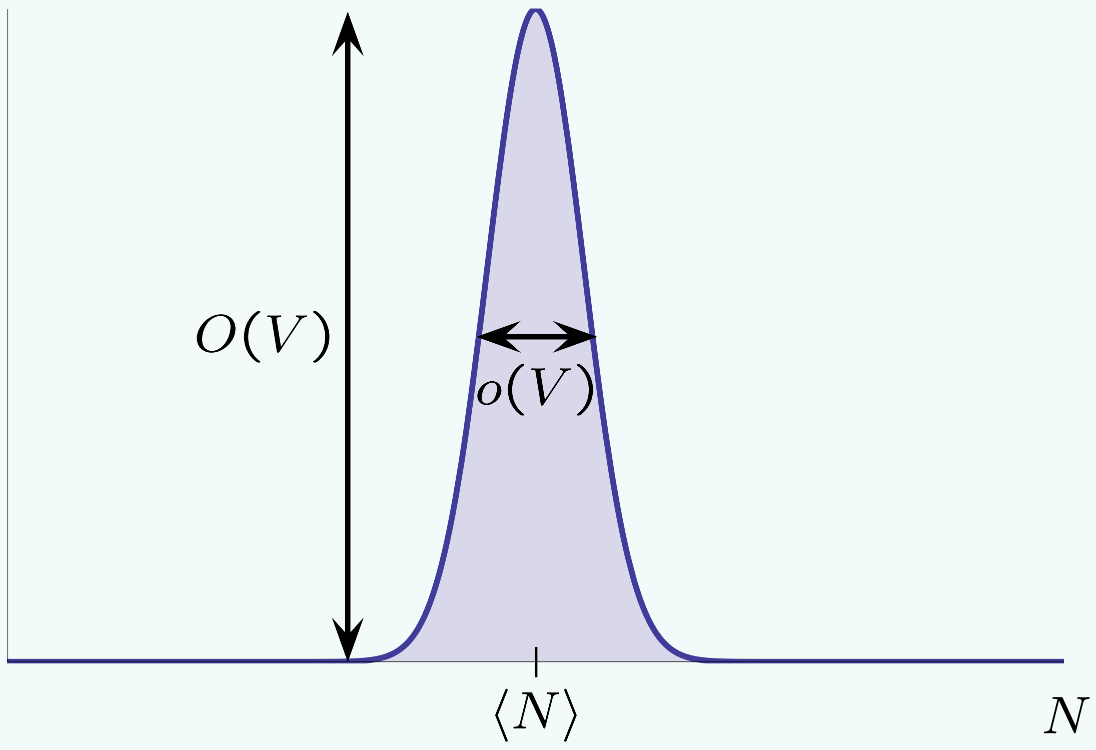
- More specifically, N exhibits a sharply peaked Gaussian distribution which approaches a Dirac delta function at $\langle N\rangle$ as $V \to \infty$.

- It follows that the canonical and grand canonical ensembles yield identical results in the limit $V \to \infty$

$$P = k\rho T$$

As we will see later, to describe the thermodynamic behaviour of bulk systems it is necessary to take the thermodynamic limit

$$\boxed{V \to \infty, \qquad \langle N\rangle \to \infty, \qquad \frac{\langle N\rangle}{V} \to \rho}$$



Derivation of Canonical from Microcanonical Ensemble

- The microcanonical formalism applies to an isolated system with a fixed total energy E_T. In the canonical ensemble, the system H is in thermal equilibrium with an infinitely large heat reservoir H_R. Since heat energy can be transferred the system is not isolated. To create an isolated system we consider the heat reservoir as part of the total system

$$\boxed{H_T = H + H_R = E + E_R = E_T = \text{const}, \qquad T = \text{Total}, \ R = \text{Reservoir}}$$

We assume that the interactions that maintain thermal equilibrium between the system and the reservoir are infinitesimally small so that they can be neglected.

- Assume that the reservoir is an ideal gas of particles with mass m in a box of volume V

$$H_R = \sum_{j=1}^{N_R} \frac{\boldsymbol{p}_j^2}{2m}$$

where we will take $N_R \to \infty$.

- The microcanonical distribution is

$$\rho_T \, d\Gamma \, d\Gamma_R = \frac{\delta(H + H_R - E_T)}{\Omega(E_T)} \, d\Gamma \, d\Gamma_R$$

where $d\Gamma$, $d\Gamma_R$, $d\Gamma_T = d\Gamma \, d\Gamma_R$ are phase-space elements for H, H_R and H_T respectively and $\Omega(E_T)$ is the area of the energy surface $H_T = H + H_R = E_T$.

Canonical Probability Distribution

- The canonical probability distribution ρ for H is

$$\rho\, d\Gamma = \Big(\int \rho_T \, d\Gamma_R \Big) d\Gamma$$

Now $d\Gamma_R = \Omega_R(E_R) dE_R$ where $\Omega_R(E_R)$ is the area of the energy surface $H_R = E_R$ for the reservoir. So, since $E_T = \text{const}$,

$$\boxed{\begin{aligned} \rho &= \frac{1}{\Omega(E_T)} \int \delta(H + H_R - E_T) \Omega_R(E_R) dE_R \\ &= \frac{\Omega_R(E_T - H)}{\Omega(E_T)} = \frac{\Omega_R(E_T - H)}{\Omega_R(E_T)} \frac{\Omega_R(E_T)}{\Omega(E_T)} = \text{const}\, \frac{\Omega_R(E_T - H)}{\Omega_R(E_T)} \end{aligned}}$$

- If R is an ideal gas in a box of volume V

$$\Omega_R(E_R) = \int_V d\boldsymbol{q}_1 \cdots \int_V d\boldsymbol{q}_{N_R} \int_{\sum_{j=1}^{N_R} \boldsymbol{p}_j^2 = 2mE_R} d^{N_R}\boldsymbol{p} = V^{N_R} C_{N_R} r^{3N_R - 1} = V^{N_R} C'_{N_R} E_R^{(3N_R-1)/2}$$

where the constant $C_n = 2\pi^{3n/2}/\Gamma(3n/2)$, $\Gamma(x)$ is the Gamma function and we have evaluated the volume of a hypersphere with radius $r = \sqrt{2mE_R}$ in $3N_R$ dimensions.

Limit of Infinitely Large Reservoir $N_R \to \infty$

- From above and using the Euler limit $\lim_{n\to\infty}\left(1-\frac{x}{n}\right)^n = e^{-x}$ gives

$$\rho \propto \lim_{N_R\to\infty} \frac{\Omega_R(E_T-H)}{\Omega_R(E_T)} = \lim_{N_R\to\infty}\left(1-\frac{H}{E_T}\right)^{(3N_R-1)/2} = \exp(-\beta H), \qquad \text{since} \quad E_T \propto N_R$$

where

$$\boxed{\beta \;=\; \lim_{N_R\to\infty}\frac{3N_R}{2E_T} \;=\; \lim_{N_R\to\infty}\frac{3N_R}{2E_R} \qquad \text{since } E<\infty}$$

- The total energy $E_T \sim E_R$ (as $N_R \to \infty$) is a measure of the temperature of the system. Since the reservoir is an ideal gas, the above result is just the equipartition theorem

$$U \;=\; E_T \;\sim\; E_R \;\sim\; 3N_R(\tfrac{1}{2}kT), \qquad N_R \to \infty$$

We therefore identify β as the inverse temperature

$$\beta = \frac{1}{kT}$$

- After normalization, we finally obtain the Gibbs canonical distribution

$$\boxed{\rho \;=\; \frac{\exp(-\beta H)}{\int \exp(-\beta H)\,d\Gamma}}$$

- The ideal gas is a *classical approximation*. In quantum mechanics, particles are either *bosons* or *fermions*. The differences between ideal, bose and fermi gases only matter at low temperatures and high pressures.

Summary of Ensembles

Microcanonical (N, E fixed)

$$\rho(p,q) \;=\; \frac{\delta(H-E)}{\int_\Gamma \delta(H-E)\,d\Gamma}$$

$$\langle O(p,q)\rangle \;=\; \frac{\int_\Gamma O(p,q)\,\delta(H-E)\,d\Gamma}{\int_\Gamma \delta(H-E)\,d\Gamma} \;=\; \frac{\int_{H=E} O(p,q)\,d\Gamma}{\int_{H=E} d\Gamma}$$

$$S(E,V) \;=\; k\log\left(\frac{1}{N!}\int_{H=E} d\Gamma\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial E}, \qquad P = T\frac{\partial S}{\partial V}$$

Canonical (N, T fixed)

$$\rho(\sigma) \;=\; \frac{\exp(-\beta H(\sigma))}{\int_\Gamma \exp(-\beta H(\sigma))\,d\Gamma}, \qquad Z_N \;=\; \int_\Gamma \exp(-\beta H(\sigma))\,d\Gamma$$

$$\langle O\rangle \;=\; \frac{\int_\Gamma O(\sigma)\exp(-\beta H(\sigma))\,d\Gamma}{\int_\Gamma \exp(-\beta H(\sigma))\,d\Gamma}$$

$$\Psi(N,V,T) = -kT \log Z_N = U - TS$$

$$U = \langle H \rangle = -T^2 \frac{\partial}{\partial T}\left(\frac{\Psi}{T}\right) = \Psi - T\,\frac{\partial \Psi}{\partial T} = \Psi + TS$$

$$S = -\frac{\partial \Psi}{\partial T}, \qquad C_V = \frac{\partial U}{\partial T} = -T\,\frac{\partial^2 \Psi}{\partial T^2}, \qquad P = -\frac{\partial \Psi}{\partial V}$$

Grand Canonical (z, T fixed)

$$\Xi(V,T,z) \;=\; \sum_{N=0}^{\infty} z^N Z_N$$

$$\langle O \rangle \;=\; \frac{\displaystyle\sum_{N=0}^{\infty} z^N \int_\Gamma O(N,\sigma)\, e^{-\beta H} d\Gamma}{\displaystyle\sum_{N=0}^{\infty} z^N \int_\Gamma e^{-\beta H} d\Gamma}$$

$$P = \frac{kT}{V}\, \log \Xi(V,T,z), \qquad \langle N \rangle = z\,\frac{\partial}{\partial z}\, \log \Xi, \qquad U = -\frac{\partial}{\partial \beta}\, \log \Xi$$

Simple Harmonic Oscillator

- The Hamiltonian of the simple harmonic oscillator is

$$\boxed{H = \tfrac{1}{2}(p^2 + q^2), \qquad p, q \in \mathbb{R}}$$

(a) Calculate the averages $\langle p^2 \rangle$, $\langle q^2 \rangle$ in the microcanonical ensemble.

(b) Calculate the averages $\langle p^2 \rangle$, $\langle q^2 \rangle$ in the canonical ensemble at temperature T.

(c) Calculate the internal energy $U = \langle H \rangle$ in the canonical ensemble.

Harmonic Oscillator Solution

(a) In the microcanonical ensemble, the energy surface is the circle $p^2 + q^2 = 2E$ of radius $r = \sqrt{2E}$ where the constant E is the total energy. This energy surface is parametrized in polar coordinates by

$$q = r\cos\theta, \qquad p = r\sin\theta$$

Hence in this ensemble

$$\boxed{\langle q^2\rangle = \frac{\int_{H=E} q^2\, dp\, dq}{\int_{H=E} dp\, dq} = \frac{\int_0^{2\pi} r^2\cos^2\theta\, d\theta}{\int_0^{2\pi} d\theta} = \frac{2E}{2} = E}$$

where we have used the fact that the element of arc length is $ds = r\,d\theta$ with r constant. Similarly, $\langle p^2\rangle = E$. In fact, by symmetry, we must have $\langle q^2\rangle = \langle p^2\rangle = \frac{1}{2}\langle 2E\rangle = E$ without evaluating any integrals!

(b) In the canonical ensemble with inverse temperature $\beta = 1/kT$

$$\boxed{\langle p^2\rangle = \langle q^2\rangle = \frac{\int_\Gamma q^2\, e^{-\beta H}\, d\Gamma}{\int_\Gamma e^{-\beta H} d\Gamma} = \frac{\int_{-\infty}^{\infty} q^2\, e^{-\frac{\beta}{2}q^2}\, dq}{\int_{-\infty}^{\infty} e^{-\frac{\beta}{2}q^2}\, dq} = \frac{1}{\beta} = kT}$$

where we have used symmetry and evaluated the Gaussian moment integral.

(c) In particular, in the canonical ensemble, this gives

$$\boxed{\langle H\rangle = \left\langle \tfrac{1}{2}(p^2 + q^2)\right\rangle = kT = n(\tfrac{1}{2}kT), \quad n = 2 = \#\text{ of degrees of freedom}}$$

in accord with the equipartition theorem that asserts that each (participating) degree of freedom has $\frac{1}{2}kT$ of energy.

Statistical Mechanics of Lattice Models

APCTP, December 2016

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Abstract: This is the second part of a three part series of lectures presenting an introductory Masters level course on Statistical Mechanics. Each part consists of about 6 lectures. The first part introduced the classical ensembles of Gibbs with applications to the ideal gas. The second part introduces lattice spin models, the thermodynamic limit, one-dimensional models and mean-field theory. The third part will cover scaling and universality in critical phenomena, the renormalization group, random walks and percolation.

- These Lectures are supported under an ICTP Visiting Scholar Award in conjunction with the ICTP Affiliated Center at APCTP.

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Overview and References

Overview:

- The goal of statistical mechanics is to describe the behaviour of bulk matter starting from a physical description of the interactions between its microscopic constituents.
- The second part of this course introduces the Ising model and other lattice spin models, the thermodynamic limit, convexity and thermodynamic stability, one-dimensional models including Tonks - van der Waals gas, the transfer matrix technique and mean-field theory.

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Lecture Outline

Topic 4. Lattice Spin Models

10. Ising paramagnet
11. Ising ferromagnets
12. Ising lattice gas

Topic 5. Thermodynamic Limit

13. Extensive functions and thermodynamic limit
14. Existence of thermodynamic limit
15. Convexity and thermodynamic stability

Topic 6. One-Dimensional Models

16. Open/periodic Ising spin chains
17. Tonks gas
18. Tonks-van der Waals gas

Topic 7. Mean-Field Theory

19. Van der Waals-Maxwell fluid
20. Curie-Weiss theory of ferromagnetism
21. Equivalent neighbour model

4: Lattice Spin Models

10. Ising paramagnet
11. Ising ferromagnets
12. Ising lattice gas

Ernst Ising (1900–1998)

Lars Onsager (1903–1976)

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Lattice Spin Models

- In many applications of statistical mechanics the particles are fixed or localized in space. In such cases there is no kinetic energy contribution to the Hamiltonian. Within a magnetic crystal, for example, the atoms have an intrinsic angular momentum or spin. The interactions between these discrete spins give rise to the magnetic properties of the material.

- A spin Hamiltonian for a system of N atoms (particles) is of the form

$$\boxed{H(\sigma) = V(\sigma_1, \sigma_2, \ldots, \sigma_N)}$$

where $\sigma = \{\sigma_1, \sigma_2, \ldots, \sigma_N\}$ denotes the configuration and the spin σ_i is a discrete variable describing the state of the particle at the lattice site i.

- The canonical partition function is then given by the configurational sum

$$\boxed{Z_N = \sum_{\sigma} \exp(-\beta H(\sigma))}$$

Ising Paramagnet

- In the presence of an external magnetic field h, the magnetic moments or spins of atoms within magnetic materials tend to align themselves with the field. The first explanation of this phenomenon was due to Langevin in 1905.

- For simplicity, let us assume that the spins are given by

$$\sigma_i = \begin{cases} +1, & \text{if spin } i \text{ is \textit{parallel} to } h \\ -1, & \text{if spin } i \text{ is \textit{antiparallel} to } h \end{cases}$$

Such two-valued spins are called Ising spins after Ernst Ising who first studied such models in 1925.

- The Hamiltonian or energy function for the Ising paramagnet is

$$\boxed{H = -h \sum_{i=1}^{N} \sigma_i, \qquad h \geq 0}$$

Clearly, the lowest energy (ground) state occurs when all the spins align with the external field, that is, $\sigma_i = +1$ for all i.

Paramagnet Partition Function

- If we set $B = \beta h$, the canonical partition function is given by

$$\boxed{\begin{aligned} Z_N &= \sum_{\sigma} \exp\left(\beta h \sum_{i=1}^{N} \sigma_i\right) \\ &= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{B\sigma_1} e^{B\sigma_2} \ldots e^{B\sigma_N} = (2\cosh B)^N \end{aligned}}$$

- The (intensive) free energy per spin ψ is thus

$$-\beta\psi = -\frac{\beta\Psi}{N} = \frac{1}{N}\log Z_N = \log(2\cosh B)$$

- The magnetization is

$$\begin{aligned} m &= \left\langle \frac{1}{N}\sum_i \sigma_i \right\rangle = \frac{\sum_{\sigma}\left(\frac{1}{N}\sum_i \sigma_i\right)\exp\left(B\sum_{i=1}^{N}\sigma_i\right)}{\sum_{\sigma}\exp\left(B\sum_{i=1}^{N}\sigma_i\right)} \\ &= \frac{1}{N}\frac{\partial}{\partial B}\log Z_N = -\frac{\partial}{\partial B}(\beta\psi) = -\frac{\partial\psi}{\partial h} = \tanh B \end{aligned}$$

- In the absence of an external magnetic field ($B \to 0$) there is no permanent magnetization as in ferromagnetic materials such as iron and nickel.

Ising Magnets

- In magnets, such ferromagnets, antiferromagnets and ferrimagnets, there are additional interactions between spins that give rise to the cooperative alignment or anti-alignment of spins in the absence of an external magnetic field. The first such model of a magnet was due to Ising and Lenz.

- The Hamiltonian of an Ising magnet is

$$\boxed{H = -\sum_{\langle i,j\rangle} J_{i,j}\sigma_i\sigma_j - h\sum_i \sigma_i = -\sum_{i<j} J_{i,j}\sigma_i\sigma_j - h\sum_i \sigma_i = -\frac{1}{2}\sum_{i,j=1}^{N} J_{i,j}\sigma_i\sigma_j - h\sum_i \sigma_i}$$

where the first sum is over all distinct pairs of spins on the lattice and $J_{i,j} = J_{j,i}$ is the strength of interaction between the spins at sites i and j with $J_{j,j} = 0$ for all j.

- To energetically favour the mutual alignment of spins, as in a *ferromagnet*, we assume $J_{i,j} \geq 0$ for all i and j. Physically, the interactions between spins in a magnetic substance are short ranged. The simplest possibility is nearest neighbour interactions so that

$$J_{i,j} = \begin{cases} J, & i,j \text{ adjacent} \\ 0, & \text{otherwise} \end{cases}$$

Ising Lattice Gas

- The Ising model can also be interpreted as a model of a lattice gas. Consider a system of N particles on a regular lattice Λ of V sites corresponding to V cells.

- A typical interaction potential $\phi_{ij} = \phi_{ji} = \phi(|i-j|)$ between particles of gas is of the Lennard-Jones form with a hard-core repulsion and an attractive long-range tail. We therefore introduce occupation numbers

$$t_j = \begin{cases} 1, & \text{if site (cell) } j \text{ is occupied} \\ 0, & \text{if site (cell) } j \text{ is unoccupied} \end{cases}$$

so that the hard-core repulsion excludes multiple occupancy of a site (cell).

- The Hamiltonian of the lattice gas is then

$$\boxed{H = -\frac{1}{2} \sum_{i,j \in \Lambda} \phi_{ij} t_i t_j}$$

with $\phi_{j,j} = 0$ and

$$\sum_{j=1}^{V} t_j = N$$

Partition Function of the Ising Lattice Gas

- The canonical partition function is

$$Z_N = {\sum_t}' \exp(-\beta H)$$

where the sum on t is restricted by $\sum_{j=1}^{V} t_j = N$. Similarly, the grand partition function is

$$\boxed{\begin{aligned}\Xi(V,T,z) &= \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} \sum_{\sum_{j=1}^{V} t_j = N} z^{\sum_{j=1}^{V} t_j}\, e^{\frac{1}{2}\beta \sum_{i,j} \phi_{ij} t_i t_j} \\ &= \sum_t z^{\sum_{j=1}^{V} t_j}\, e^{\frac{1}{2}\beta \sum_{i,j} \phi_{ij} t_i t_j}\end{aligned}}$$

where $Z_N = 0$ for $N > V$ and the configurational sum over $t = \{t_1, t_2, \ldots, t_V\}$ is unrestricted.

- To see the equivalence of the Ising magnet and the lattice gas observe that we can set

$$t_j = \tfrac{1}{2}(1 - \sigma_j)$$

with $\sigma_j = \pm 1$. Substituting this into the grand partition function gives

$$\begin{aligned}\Xi &= \sum_\sigma e^{\frac{\beta}{8}\sum_{i,j} \phi_{ij}(1-\sigma_i)(1-\sigma_j) + \frac{1}{2}\log z \sum_i (1-\sigma_i)} \\ &= e^{\frac{\beta}{8}\sum_{i,j}\phi_{ij} + \frac{V}{2}\log z} \sum_\sigma e^{\frac{\beta}{8}\sum_{i,j}\phi_{ij}\sigma_i\sigma_j - (\frac{\beta}{4}\sum_j \phi_{ij} + \frac{1}{2}\log z)\sum_i \sigma_i}\end{aligned}$$

since $\sum_j \phi_{ij}$ is independent of i for regular periodic lattices. This establishes a correspondence with

$$J_{ij} = \tfrac{1}{4}\phi_{ij}, \qquad \beta h = -\frac{\beta}{8}\sum_{j=1}^{V} \phi_{ij} - \tfrac{1}{2}\log z$$

Ising Magnet/Lattice Gas Correspondence

- This correspondence extends to all the thermodynamic quantities for the gas and the magnet (even though we have not solved either). For example, we have

$$\begin{aligned}\beta P &= \frac{1}{V}\log\Xi = \tfrac{\beta}{8}\sum_j \phi_{ij} + \tfrac{1}{2}\log z + \frac{1}{V}\log Z_V^{(\text{magnet})}\\ &= -\beta h - \tfrac{\beta}{2}\sum_j J_{ij} - \frac{\beta\Psi}{V}\end{aligned}$$

where Ψ is the canonical free energy of the Ising magnet.

- Similarly, the density ρ of the lattice gas is related to the magnetization m by

$$\begin{aligned}\rho &= \left\langle \frac{1}{V}\sum_{j=1}^{V} t_j \right\rangle = \left\langle \frac{1}{V}\sum_{j=1}^{V} \tfrac{1}{2}(1-\sigma_j) \right\rangle\\ &= \tfrac{1}{2}\left(1 - \left\langle \frac{1}{V}\sum_{j=1}^{V}\sigma_j \right\rangle\right) = \tfrac{1}{2}(1-m)\end{aligned}$$

and so on where we use the fact that $\langle t_j\rangle_{grand} = \langle\frac{1}{2}(1-\sigma_j)\rangle_{canonical}$.

- The Ising model can also be interpreted as a model of a binary alloy such as brass which is an alloy of copper and zinc. In this case

$$t_j = \begin{cases} 1, & \text{if site } j \text{ is occupied by an Cu atom}\\ 0, & \text{if site } j \text{ is occupied by an Zn atom}\end{cases}$$

5: Thermodynamic Limit

13. Extensive functions and thermodynamic limit
14. Existence of thermodynamic limit
15. Convexity and thermodynamic stability

Léon Charles Prudent van Hove (1924–1990)

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Thermodynamic Limit

- In general, it is impossible to evaluate the partition function of an Ising model on a lattice of $N = 6 \times 10^{23}$ sites. Moreover, for finite N, the extensive free energy Ψ given by

$$-\beta\Psi \;=\; \log Z_N \;=\; \log \sum_{\sigma} e^{-H/kT}$$

is an analytic function of h and $T > 0$. This follows because the Boltzmann weights are analytic, so the finite sum giving Z_N is analytic and $Z_N > 0$ so the logarithm is analytic.

- Effectively N is infinite and what we need to evaluate is not the free energy Ψ, which is extensive and grows with the size of the system, but rather the free energy per site ψ in the thermodynamic limit

$$\boxed{-\beta\psi \;=\; -\lim_{N\to\infty} \frac{\beta}{N}\Psi \;=\; \lim_{N\to\infty} \frac{1}{N} \log Z_N}$$

The free energy per site ψ is an intensive quantity. The thermodynamic limit must be taken "*in the sense of van Hove*" so that, as $N \to \infty$ in d dimensions, the region Λ contains an arbitrarily large d-dimensional hypercube centred on the origin. This limit, which is often written $\Lambda \to \infty$ with $N = |\Lambda|$, ensures that the limiting region is properly d-dimensional.

- It can be shown quite generally that, for finite interactions, this limit exists and is *independent of the boundary conditions* provided the interactions decay sufficiently rapidly with distance. However, the resulting limiting free energy need not be an analytic function of the thermodynamic variables such as h and T.

Phase Transitions

- Mathematically, a phase transition should manifest itself as a singularity in the thermodynamic functions. If the free energy is an analytic function of the state variables, then all of the thermodynamic functions obtained by differentiation are also analytic. A natural definition, therefore, is that a phase transition point is a non-analytic point of the limiting free energy ψ or pressure P as a function of temperature and the other state variables. Points where the limiting free energy is singular (nonanalytic) are called *phase transition* points. This nonanalyticity leads to singular behaviour (discontinuities or divergences) in the thermodynamic functions such as order parameters, internal energies and specific heats.

- The ideal gas and the paramagnet, do not undergo phase transitions or abrupt changes of phase. The ideal gas does not admit a liquid or solid phase only a fluid phase and the paramagnet does not exhibit a ferromagentic phase which is spontaneously magnetized in the absence of an external magnetic field.

- For a gas, described by the grand canonical ensemble, the limiting pressure in the thermodynamic limit is defined by

$$\boxed{\beta P = \lim_{\substack{V\to\infty \\ \rho=\langle N\rangle/V}} \frac{1}{V} \log \Xi(V,T,z)}$$

where ρ is the particle density.

Existence of Thermodynamic Limit

- The limiting free energy will only exist for appropriate classes of interaction Hamiltonians with sufficiently rapid decay of interactions at large distances.

- Consider an Ising magnet on a square lattice with nearest-neighbour interactions and free boundary conditions (so that the spins are summed over freely on the boundary) and let $\psi(N) = \Psi/N$ be the intensive free energy so that

$$-\beta\psi = -\beta \lim_{N\to\infty} \psi(N) = \lim_{N\to\infty} \frac{1}{N} \log \sum_{\sigma} \exp(-\beta H)$$

where

$$H(N) = -J \sum_{\langle i\, j\rangle} \sigma_i \sigma_j$$

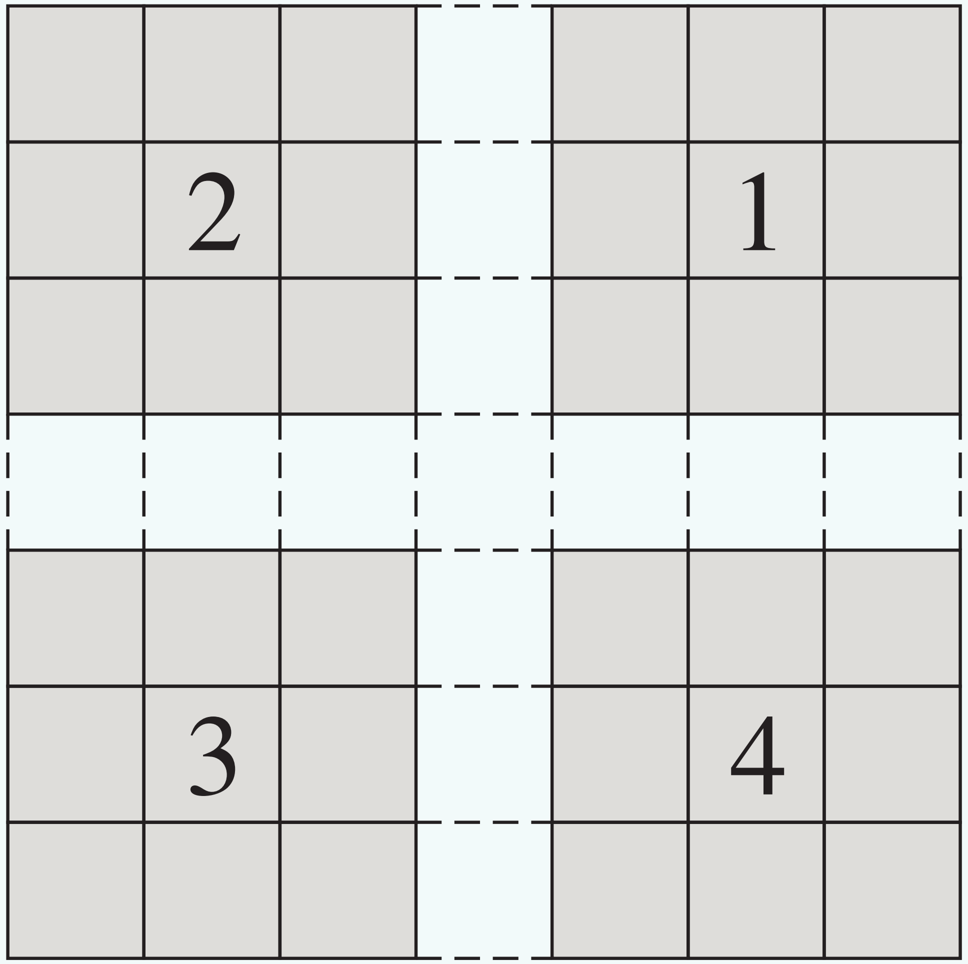
with 2^n spins along the side of the square so that $N = 2^n \times 2^n = 2^{2n}$.

- We decompose this Hamiltonian as

$$\boxed{\begin{aligned} H(2^{2n}) \;=\;& H_1(2^{2(n-1)}) + H_2(2^{2(n-1)}) \\ & + H_3(2^{2(n-1)}) + H_4(2^{2(n-1)}) + H' \end{aligned}}$$

where H' is the contribution to the energy from the (dashed) bonds in the corridors.

Division into Cells



- The two-dimensional square lattice, with 2^n spins on a side, divided into four cells (quadrants). Here $n = 3$ so $2^n = 8$ and each cell has $2^{n-1} = 4$ spins on a side. The four corridors emanating from the center (indicated with dashed interaction bonds) are one-dimensional. As $n \to \infty$, the length of both sides of the square become large so that the thermodynamic limit is approached in the sense of van Hove.

Estimates

- We now estimate

$$|H'| \leq 4|J|\, 2^{n-1} = 2^{n+1}\, |J|$$

and

$$\boxed{\begin{aligned} Z_{2^{2n}} &= \sum_\sigma e^{-\beta H} \;= \sum_\sigma^1 \sum_\sigma^2 \sum_\sigma^3 \sum_\sigma^4 e^{-\beta(H_1+H_2+H_3+H_4+H')} \\ &\leq \exp(2^{n+1}\beta|J|) \Big(\sum_\sigma^1 e^{-\beta H_1}\Big)\Big(\sum_\sigma^2 e^{-\beta H_2}\Big)\Big(\sum_\sigma^3 e^{-\beta H_3}\Big)\Big(\sum_\sigma^4 e^{-\beta H_4}\Big) \\ &= \exp(2^{n+1}\beta|J|)\, Z^4_{2^{2(n-1)}} \end{aligned}}$$

- But $\psi(N) = -\frac{1}{\beta N} \log Z_N$ so that

$$\psi(2^{2n}) \geq \psi(2^{2(n-1)}) - \frac{|J|}{2^{n-1}}$$

- Similarly,

$$Z_{2^{2n}} \geq \exp(-2^{n+1}\beta|J|)\, Z^4_{2^{2(n-1)}}$$

and

$$\psi(2^{2n}) \leq \psi(2^{2(n-1)}) + \frac{|J|}{2^{n-1}}$$

Hence

$$\left|\psi(2^{2n}) - \psi(2^{2(n-1)})\right| \leq \frac{|J|}{2^{n-1}}$$

Cauchy Sequences

- To show that $\psi(2^{2n})$ posseses a limit ψ as $n \to \infty$ we show the sequence $\psi(2^{2n})$ is Cauchy

$$\begin{aligned}
\left|\psi(2^{2(n+m)}) - \psi(2^{2n})\right| &\le \left|\psi(2^{2(n+m)}) - \psi(2^{2(n+m-1)})\right| \\
&\quad + \left|\psi(2^{2(n+m-1)}) - \psi(2^{2(n+m-2)})\right| + \cdots + \left|\psi(2^{2(n+1)}) - \psi(2^{2n})\right| \\
&\le |J|\left(\frac{1}{2^{n+m-1}} + \frac{1}{2^{n+m-2}} + \cdots + \frac{1}{2^{n}}\right) \\
&= |J| \sum_{k=n}^{n+m-1} 2^{-k} \\
&\le |J| \sum_{k=n}^{\infty} 2^{-k} = \frac{|J|}{2^{n-1}} \to 0 \quad \text{as } n \to \infty
\end{aligned}$$

- Since Cauchy sequences are convergent

$$\boxed{\psi = \lim_{n\to\infty} \psi(N)}$$

exists. Taking $m \to \infty$ in the above results gives

$$|\psi - \psi(2^{2n})| = \lim_{m\to\infty} |\psi(2^{2(n+m)}) - \psi(2^{2n})| \le \frac{|J|}{2^{n-1}}$$

so the convergence is exponentially fast.

Related Thermodynamic Limits

- The result

$$\left|\psi - \psi(L^2)\right| \le \frac{2|J|}{L}$$

follows by considering lengths $M = 2^n L$ on a side.

- Similar arguments apply for other boundary conditions (eg. periodic boundary conditions) to show that the thermodynamic limit is independent of the boundary conditions.

- The arguments also generalize to higher dimensions, to larger classes of interactions (finite-range or with suitable long-distance decay) and to continuum systems.

- Roughly speaking all that is required is that, for large system sizes, the *surface* energies obtained by dividing the volume into cells are small compared to the *bulk* energies.

- The theorem for the existence of the thermodynamic limit can break down if any of the interactions become infinitely strong $J \to \pm\infty$

Convexity

Definition: A function $f(x)$ on $[a, b]$ is *convex* on $[a, b]$ if for any $\lambda \in (0, 1)$

$$\boxed{f\Big(\lambda x_1 + (1-\lambda)x_2\Big) \leq \lambda f(x_1) + (1-\lambda)f(x_2)}$$

In words, $f(x)$ is convex if the straight line chord joining the points $(x_1, f(x_1))$ and $(x_2, f(x_2))$ lies entirely above the curve of $f(x)$. The function $f(x)$ is *concave* if $-f(x)$ is convex.

- The function $f(x) = e^x$ is convex on $\mathbb{R}$ and $f(x) = \log x$ is concave on $(0, \infty)$. A linear function is both convex and concave.

- A convex function defined on an *open* interval is continuous and piecewise differentiable, that is, differentiable at all but at most *countably many* points. It can have have corners (at the points where it is not differentiable) and straight line (polygonal) segments.

- A C^1 function $f(x)$ is *convex* if and only if, at each $x = x_0$, the tangent to the curve lies entirely below the curve
$$f(x_0) + f'(x_0)(x - x_0) \leq f(x)$$

- If $f(x)$ is C^2 on $[a, b]$, then $f(x)$ is convex on $[a, b]$ if and only if $f''(x) \geq 0$ on $[a, b]$.

Theorem 1 (Limits and Convexity)
If the pointwise limit $f(x) = \lim_{n\to\infty} f_n(x)$ *of the convex functions* $f_n(x)$ *exists, then* $f(x)$ *is convex. Furthermore, if* $f_n(x)$ *is* C^2 *and convex and* $f(x)$ *is differentiable, then*

$$\boxed{\lim_{n\to\infty} f_n(x) = f(x) \qquad \Rightarrow \qquad \lim_{n\to\infty} \frac{df_n}{dx} = \frac{d}{dx} \lim_{n\to\infty} f_n(x) = \frac{df}{dx}}$$

Convexity and Thermodynamic Stability

- Let λ be a thermodynamic field, such as J or h, that appears linearly in the Hamiltonian so that

$$\boxed{-\beta H = H_0 + \lambda H_1}$$

- Then the free energy is a concave function of λ, that is,

$$\frac{\partial^2 \Psi}{\partial \lambda^2} = \frac{\partial^2}{\partial \lambda^2}(-kT \log Z_N) \leq 0$$

- In particular, if

$$Z_N = \sum_\sigma e^{-\beta H} = \sum_\sigma e^{H_0 + \lambda H_1}$$

this follows because

$$\boxed{\begin{aligned} \frac{\partial^2}{\partial \lambda^2} \log \sum_\sigma e^{H_0+\lambda H_1} &= \frac{\partial}{\partial \lambda}\left[\frac{\sum_\sigma H_1 e^{H_0+\lambda H_1}}{\sum_\sigma e^{H_0+\lambda H_1}}\right] = \frac{\partial}{\partial \lambda}\langle H_1\rangle \\ &= \frac{\sum_\sigma H_1^2 e^{H_0+\lambda H_1}}{\sum_\sigma e^{H_0+\lambda H_1}} - \frac{(\sum_\sigma H_1 e^{H_0+\lambda H_1})^2}{(\sum_\sigma e^{H_0+\lambda H_1})^2} \\ &= \langle H_1^2\rangle - \langle H_1\rangle^2 = \Big\langle \big(H_1 - \langle H_1\rangle\big)^2 \Big\rangle \geq 0 \end{aligned}}$$

Convexity in Ising Magnet/Lattice Gas

Consider the Ising magnet

$$H = -\sum_{i,j\in\Lambda} J_{ij}\sigma_i\sigma_j - h\sum_{i\in\Lambda}\sigma_i$$

- By convexity, we can interchange the order of limits and differentiation so that

$$m = -\lim_{N\to\infty}\frac{1}{N}\frac{\partial\Psi}{\partial h} = -\frac{\partial}{\partial h}\lim_{N\to\infty}\frac{\Psi}{N} = -\frac{\partial\psi}{\partial h}$$

- The parameter $\lambda = B = \beta h$ appears linearly in $-\beta H$. It follows from convexity that

$$\boxed{\frac{1}{N}\frac{\partial^2}{\partial B^2}\log Z_N = \frac{\partial}{\partial B}\Big\langle\frac{1}{N}\sum_{i\in\Lambda}\sigma_i\Big\rangle = \frac{\partial m}{\partial B} = \frac{1}{\beta}\frac{\partial m}{\partial h} \geq 0}$$

so that, in a finite or infinite system, the magnetization or average magnetic moment m is a non-decreasing function of the external magnetic field h.

- Similarly, in the grand canonical ensemble for the Ising lattice gas we start with

$$\beta P = \frac{1}{V}\log\Xi$$

$$\Xi = \sum_{N=0}^{\infty} z^N Z_N = \sum_t e^{\sum_{i,j}\phi_{ij}t_it_j + \beta\mu\sum_{j=1}^{V}t_j}$$

$$\rho = \frac{1}{v} = z\frac{\partial}{\partial z}\Big(\frac{1}{V}\log\Xi\Big) = z\frac{\partial}{\partial z}(\beta P)$$

where

$$v = \frac{V}{\langle N\rangle} = \frac{1}{\rho} = \text{specific volume}$$

Thermodynamic Stability

- From the previous relations, we find

$$
\begin{aligned}
-\frac{z}{v^2}\frac{\partial v}{\partial z} &= z\frac{\partial}{\partial z}\Big(\frac{1}{v}\Big) = z\frac{\partial}{\partial z}z\frac{\partial}{\partial z}\Big(\frac{1}{V}\log\Xi\Big)\\
&= \frac{\partial^2}{\partial(\beta\mu)^2}\Big(\frac{1}{V}\log\Xi\Big) = \frac{1}{V}\Big\langle\big(N-\langle N\rangle\big)^2\Big\rangle \geq 0
\end{aligned}
$$

Here the result again follows by convexity since, writing $z = e^{\beta\mu}$, we see that the field $\beta\mu$ appears linearly in the exponential (Hamiltonian). It follows that $\frac{\partial v}{\partial z} \leq 0$ so that ρ increases as z increases.

- Using $v = v(T, z)$ to eliminate z gives $P = P(v, T)$. Holding T fixed means that v and P are effectively functions of one variable and

$$
\beta\frac{\partial P}{\partial v} = \beta\frac{\partial P}{\partial z}\frac{\partial z}{\partial v} = \frac{1}{vz}\frac{\partial z}{\partial v} \leq 0
$$

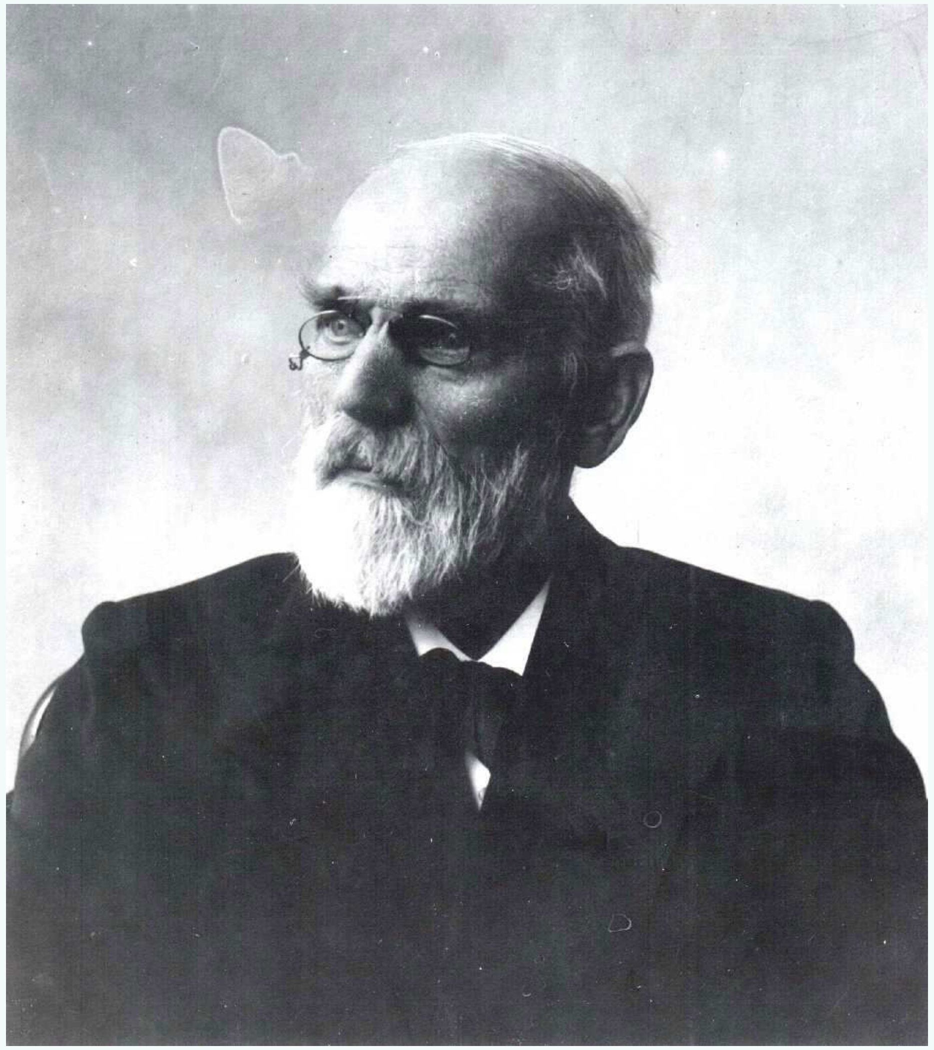
In words this states that, at constant temperature, increasing the pressure on a fluid compresses it (ie. decreases its volume). This intuitive result is called *thermodynamic stability* and it is usually stated by asserting that the isothermal compressibility K_T is positive

$$
\boxed{K_T = -\frac{1}{v}\frac{\partial v}{\partial P} \geq 0}
$$

6: One-Dimensional Models

16. Open/periodic Ising spin chains
17. Tonks gas
18. Tonks-van der Waals gas

Johannes Diderik van der Waals (1837–1923)



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Open Ising Spin Chain

- The limiting free energy of the nearest neighbour Ising model on a (one-dimensional) chain was evaluated by Ising in 1925.

- The free energy should be independent of the boundary conditions so let us begin by solving the open chain (free boundary conditions). The Hamiltonian of the open Ising spin chain in zero field is

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}$$

- Setting $K = \beta J$, the problem is to evaluate the partition function

$$\begin{aligned} Z_N &= \sum_\sigma \exp\left(K \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \right) \\ &= \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{K\sigma_1\sigma_2} \ldots e^{K\sigma_{N-1}\sigma_N} \\ &= \sum_{\sigma_1=\pm 1} (2\cosh K)^{N-1} \;=\; 2(2\cosh K)^{N-1} \end{aligned}$$

Hence

$$\boxed{-\beta\psi \;=\; \lim_{N\to\infty} \frac{1}{N} \log Z_N = \log(2\cosh K)}$$

Correlations in Open Chain

Consider an inhomogeneous open Ising chain

$$\boxed{H = -\sum_{i=1}^{N-1} J_i \sigma_i \sigma_{i+1}}$$

- The probability that σ_i and σ_{i+r} are parallel is

$$\text{Prob}(\sigma_i = \sigma_{i+r}) = \left\langle \tfrac{1}{2}(1+\sigma_i\sigma_{i+r}) \right\rangle = \tfrac{1}{2}(1+\langle \sigma_i\sigma_{i+r}\rangle)$$

where the correlation function is

$$\boxed{\langle \sigma_i\sigma_{i+r}\rangle \;=\; \frac{\sum_\sigma \sigma_i\sigma_{i+r}\,\text{exp}(-\beta H(\sigma))}{\sum_\sigma \text{exp}(-\beta H(\sigma))} \sim \text{exp}\left(-\frac{r}{\xi}\right), \qquad r\to\infty}$$

and the correlation length ξ is a measure of the distance over which the spins are corelated. Now we have the identity

$$\text{LHS} \;:=\; \sum_\sigma \text{exp}\left[\sum_{i=1}^{N-1} K_i\sigma_i\sigma_{i+1}\right] \;=\; 2\prod_{i=1}^{N-1} 2\cosh K_i \;:=\; \text{RHS}$$

- So

$$\frac{\frac{\partial}{\partial K_i}\cdots\frac{\partial}{\partial K_{i+r-1}}\text{LHS}}{\text{LHS}} = \frac{\frac{\partial}{\partial K_i}\cdots\frac{\partial}{\partial K_{i+r-1}}\text{RHS}}{\text{RHS}}$$

and

$$\begin{aligned}\langle \sigma_i\sigma_{i+r}\rangle \;&=\; (\tanh K_i)\ldots(\tanh K_{i+r-1})\\ &\to\; (\tanh K)^r, \qquad K_i\to K\end{aligned}$$

Hence

$$\xi^{-1} = -\log\tanh K \to 0 \quad \text{as} \quad T\to 0$$

Closed Ising Spin Chain

- The limiting free energy of the nearest-neighbour Ising model on a closed (periodic) chain can be evaluated, even in the presence of an external magnetic field, using transfer matrices.

- The Hamiltonian of the closed ferromagnetic Ising spin chain in a field is

$$\boxed{H = -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - h\sum_{i=1}^{N}\sigma_i, \qquad J > 0}$$

The problem is to evaluate the partition function

$$\begin{aligned} Z_N &= \sum_{\sigma}\exp\left(K\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + B\sum_{i=1}^{N}\sigma_i\right) \\ &= \sum_{\sigma}\prod_{i=1}^{N}\exp\left[K\sigma_i\sigma_{i+1} + \tfrac{1}{2}B(\sigma_i + \sigma_{i+1})\right] \end{aligned}$$

where $K = \beta J$ and $B = \beta h$ and, since the chain is periodic, $\sigma_{N+1} = \sigma_1$.

- Using periodicity, we have symmetrically shared the magnetic field B between the sites i and $i + 1$.

Matrix Trace

- Abstractly, a *trace* on an algebra of operators is a linear functional tr satisfying

$$\boxed{\operatorname{tr}(\alpha A + \beta B) = \alpha \operatorname{tr} A + \beta \operatorname{tr} B, \qquad \operatorname{tr} AB = \operatorname{tr} BA}$$

where A, B are operators and α, β are scalars. It immediately follows that tr is cyclic, that is, $\operatorname{tr} ABC \ldots G = \operatorname{tr} BC \ldots GA$.

- A matrix trace on (real or complex) $n \times n$ matrices A with entries A_{jk} is defined as the sum over diagonal entries

$$\operatorname{Tr} A = \sum_{j=1}^{n} A_{jj}$$

$$\operatorname{Tr}(\alpha A + \beta B) = \sum_{j=1}^{n} (\alpha A_{jj} + \beta B_{jj}) = \alpha \sum_{j=1}^{n} A_{jj} + \beta \sum_{j=1}^{n} B_{jj} = \alpha \operatorname{Tr} A + \beta \operatorname{Tr} B$$

$$\operatorname{Tr} AB = \sum_{i=1}^{n} (AB)_{ii} = \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} B_{ji} = \sum_{j=1}^{n} \sum_{i=1}^{n} B_{ji} A_{ij} = \sum_{j=1}^{n} (BA)_{jj} = \operatorname{Tr} BA$$

- From cyclicity, the trace Tr is invariant under similarity transformations (a change of basis)

$$\operatorname{Tr} S^{-1} A S = \operatorname{Tr} A S S^{-1} = \operatorname{Tr} A$$

Any matrix A can be brought to upper triangular (Jordan canonical form) by some similarity transformation S. Since the diagonal entries of the triangular matrix $T = S^{-1} A S$ are the eigenvalues λ_j of T and A, it follows that

$$\operatorname{Tr} A = \operatorname{Tr} T = \sum_{j=1}^{n} \lambda_j$$

Transfer Matrix

- Let us define a 2×2 *transfer matrix* $\boldsymbol{T}$ with elements

$$\boldsymbol{T}_{\sigma,\sigma'} = \langle \sigma | \boldsymbol{T} | \sigma' \rangle = \exp\left[K\sigma\sigma' + \tfrac{1}{2}B(\sigma + \sigma')\right]$$

that is

$$\boxed{\boldsymbol{T} = \begin{pmatrix} \langle 1|\boldsymbol{T}|1\rangle & \langle 1|\boldsymbol{T}|-1\rangle \\ \langle -1|\boldsymbol{T}|1\rangle & \langle -1|\boldsymbol{T}|-1\rangle \end{pmatrix} = \begin{pmatrix} e^{K+B} & e^{-K} \\ e^{-K} & e^{K-B} \end{pmatrix}}$$

where we have introduced Dirac's bra and ket notation $\langle bra|c|ket\rangle$.

- We can then write

$$Z_N = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \langle \sigma_1|\boldsymbol{T}|\sigma_2\rangle\langle \sigma_2|\boldsymbol{T}|\sigma_3\rangle \ldots \langle \sigma_{N-1}|\boldsymbol{T}|\sigma_N\rangle\langle \sigma_N|\boldsymbol{T}|\sigma_1\rangle$$

- These are matrix products so

$$Z_N = \sum_{\sigma_1} \langle \sigma_1|\boldsymbol{T}^N|\sigma_1\rangle = \mathrm{Tr}\,\boldsymbol{T}^N = \lambda_+^N + \lambda_-^N$$

where $\lambda_+ \geq \lambda_-$ are the eigenvalues of $\boldsymbol{T}$. Since $\boldsymbol{T}$ is a real symmetric matrix, it is diagonalizable with real eigenvalues $\lambda_\pm$.

- The transfer matrix technique has reduced the problem of calculating the partition function to a problem in linear algebra!

Transfer Matrix Eigenvalues

- The characteristic polynomial of $\boldsymbol{T}$ is

$$\lambda^2 - (2e^K \cosh B)\lambda + 2\sinh 2K = 0$$

so

$$\boxed{\lambda_\pm = e^K \cosh B \pm \sqrt{e^{2K}\sinh^2 B + e^{-2K}}}$$

and for $T > 0$ we have $\lambda_+ > \lambda_- > 0$.

- It follows that

$$\begin{aligned}
\frac{1}{N}\log Z_N &= \frac{1}{N}\log(\lambda_+^N + \lambda_-^N) = \frac{1}{N}\log \lambda_+^N\left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right] \\
&= \log\lambda_+ + \frac{1}{N}\log\left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right] \\
&\to \log\lambda_+ \quad \text{as } N \to \infty.
\end{aligned}$$

- Hence the free energy per spin ψ in the thermodyamic limit is given by

$$\begin{aligned}
-\beta\psi &= \lim_{N\to\infty}\frac{1}{N}\log Z_N = \log\lambda_+ \\
&\to \log(2\cosh K) \quad \text{as} \quad h \to 0
\end{aligned}$$

Since the limiting free energy per spin is independent of boundary conditions, this result agrees with the open spin chain result for $h = 0$.

No Spontaneous Magnetization in 1-d

- The magnetization is

$$\boxed{m = -\frac{\partial}{\partial B}(\beta\psi) = \frac{\partial}{\partial B}\log\lambda_+ = \frac{\sinh B}{\sqrt{\sinh^2 B + e^{-4K}}}}$$

Clearly, $0 \le m \le 1$ and $m \to 1$ if either $J \to \infty$, $h \to \infty$ or $T \to 0$.

- In zero field ($h \to 0\pm$) the magnetization vanishes, so there is no residual or spontaneous magnetization! Moreover, for $T > 0$, the limiting free energy is an analytic function of h and T so the Ising spin chain does not undergo a phase transition. This is a general feature of one-dimensional models with finite-range interactions.

Correlation Length

- The correlation length in a field can also be calculated using the transfer matrix giving

$$\begin{aligned} \xi^{-1} &= -\log\left(\frac{\lambda_-}{\lambda_+}\right) \\ &\to -\log\tanh K \quad \text{as} \quad h \to 0 \end{aligned}$$

van Hove's Theorem

Theorem 2 (van Hove)

The limiting free energy $\psi(h,T)$ *of the one-dimensional finite-range Ising model*

$$H = -\sum_{1\le i<j\le N} J(j-i)\sigma_i\sigma_j - h\sum_{i=1}^{N}\sigma_i$$

with

$$J(k) = 0 \quad \textit{for} \quad k > R, \qquad \boldsymbol{T} \textit{ primitive}$$

is an analytic function of h *and* T *for* $T > 0$ *and*

$$\boxed{\lim_{h\to 0\pm} m(h,T) = 0 \quad \textit{for} \quad T > 0}$$

Sketch of Proof: For interactions with finite-range R, we can always define a finite-dimensional transfer matrix $\boldsymbol{T}$ by grouping R consecutive spins together as a "*superspin*". Since the elements of $\boldsymbol{T}$ are Boltzmann weights, $\boldsymbol{T}$ is a nonnegative matrix (has all nonnegative entries). The van Hove theorem then follows from the Perron-Frobenius theorem.

Theorem 3 (Perron-Frobenius)

If $\boldsymbol{T}$ *is primitive, that is,* $\boldsymbol{T}^p > 0$ *(entry-by-entry) for some natural number* $p \ge 1$, *then*

(i) *There is a unique real positive (non-degenerate) eigenvector* $\boldsymbol{x}_1$ *of* $\boldsymbol{T}$

$$\boldsymbol{T}\boldsymbol{x}_1 = \lambda_1\boldsymbol{x}_1, \qquad \boldsymbol{x}_1 > 0 \textit{ (entry-by-entry)}$$

(ii) *The eigenvalues* $\lambda_j \in \mathbb{C}$ *of the* $n\times n$ *matrix* $\boldsymbol{T}$ *satisfy*

$$\lambda_1 > |\lambda_2| \ge |\lambda_3| \ge \cdots \ge |\lambda_n| \ge 0$$

Perron-Frobenius and Analyticity

- By the Perron-Frobenius theorem, the eigenvalues of $\boldsymbol{T}$ satisfy

$$\lambda_{max} = \lambda_1 > |\lambda_2| \geq |\lambda_3| \geq \cdots \geq |\lambda_n| \geq 0$$

that is, the largest eigenvalue is real, positive and nondegenerate. Hence

$$\begin{aligned} \frac{1}{N}\log Z_N &= \frac{1}{N}\log(\lambda_1^N + \cdots + \lambda_n^N) \\ &= \log\lambda_1 + \frac{1}{N}\log\left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N + \left(\frac{\lambda_3}{\lambda_1}\right)^N + \cdots + \left(\frac{\lambda_n}{\lambda_1}\right)^N\right] \\ &\to \log\lambda_{max} \quad \text{as } N \to \infty. \end{aligned}$$

- So

$$\boxed{-\beta\psi(h,T) = \lim_{N\to\infty}\frac{1}{N}\log Z_N = \log\lambda_{max}}$$

and $m(h,T)$ are analytic because $\lambda_{max} > 0$ is analytic. But the magnetization is an odd function of h, that is $m(h,T) = -m(-h,T)$, so $m(0,T) = 0 = m(0\pm,T)$ by continuity.

Theorem 4 (Analyticity) *Suppose the entries of the finite $n \times n$ matrix*

$$\boldsymbol{T} = \boldsymbol{T}(\boldsymbol{z}) = \boldsymbol{T}(z_1, z_2, \ldots, z_m)$$

are analytic in $\boldsymbol{z}$ in some common domain D. Then an individual eigenvalue $\lambda_j(\boldsymbol{z})$ is analytic in $\boldsymbol{z} \in D$ except possibly when it coalesces with another eigenvalue, $\lambda_j(\boldsymbol{z}) = \lambda_i(\boldsymbol{z})$ for some i.

Spontaneous Magnetization in Two or More Dimensions

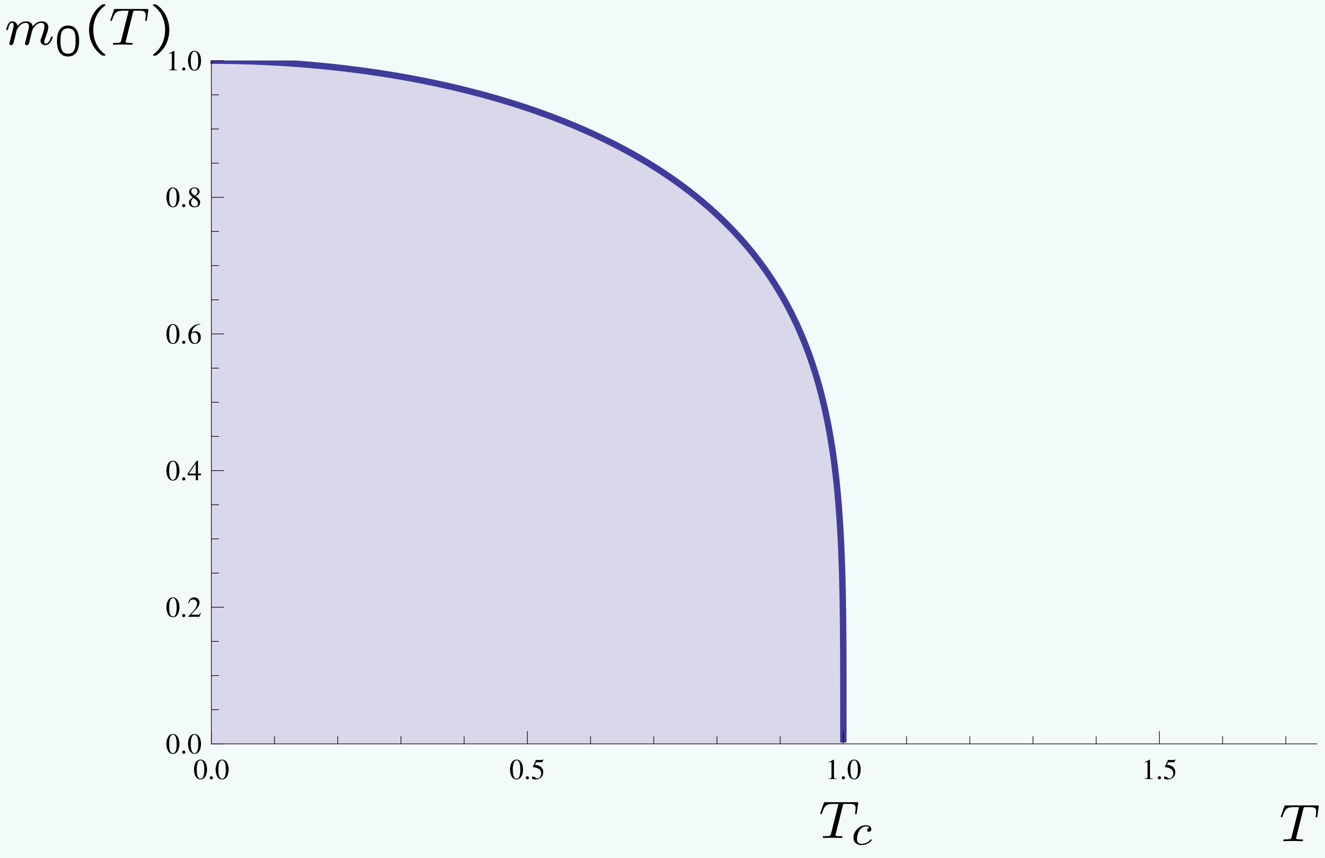
- In sharp contrast to the one dimensional Ising model, Ising models on cubic lattices in two or more dimensions

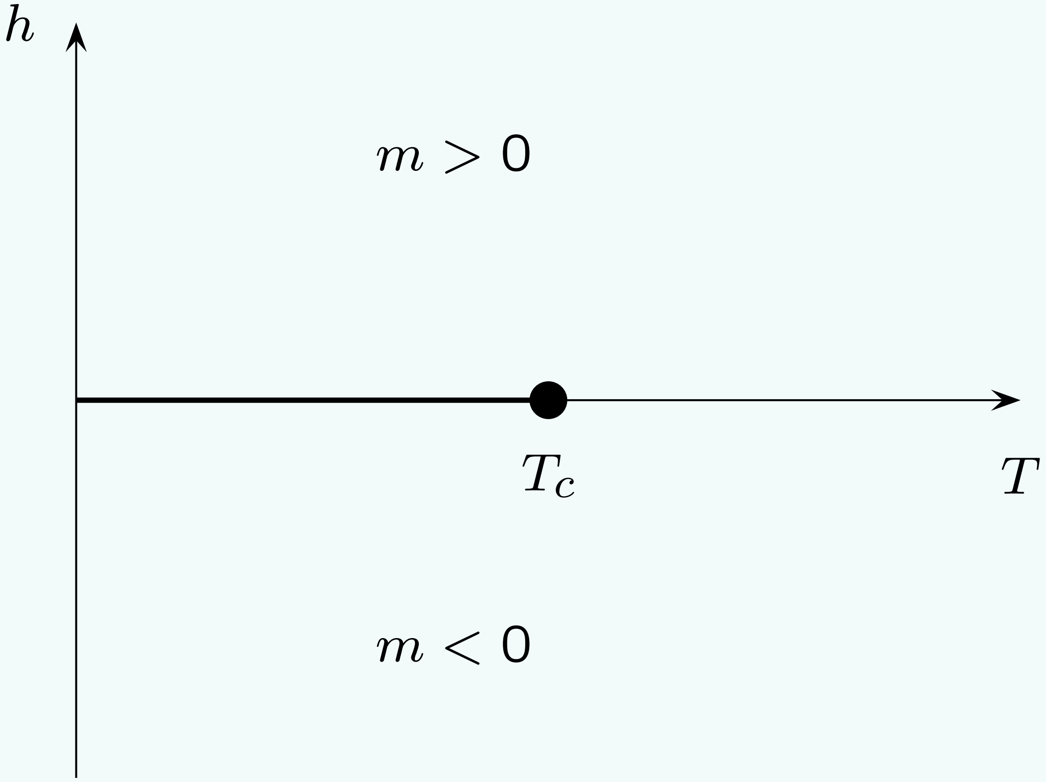
$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i$$

do exhibit spontaneous magnetization and therefore undergo phase transitions!

$$\boxed{m_0(T) \;=\; \lim_{h \to 0+} m(h,T) > 0, \qquad T < T_c}$$

- The zero-field Ising model on the square lattice was solved by L. Onsager in 1944 and the spontaneous magnetization $m_0(T)$ was calculated by C.N. Yang in 1952.





Other Lattice Models

- The spin-1 Ising model, with spins $\sigma_i = 0, \pm 1$, is

$$\boxed{H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i}$$

- The Q-state Potts model, with spins $\sigma_i = 1, 2, \ldots, Q$, is

$$\boxed{H = -J \sum_{\langle i,j \rangle} \delta(\sigma_i, \sigma_j) - h \sum_i \delta(\sigma_i, 1)}$$

where the Kronecker delta is

$$\delta(\sigma, \sigma') = \begin{cases} 1, & \sigma = \sigma' \\ 0, & \text{otherwise} \end{cases}$$

- There are many other models with different symmetries (discrete, continuous, quantum, etc.) which exhibit phase transitions and therefore are of much interest.

- The spin-$\frac{1}{2}$ Ising model is also a model of a lattice gas with occupation numbers

$$t_i = \tfrac{1}{2}(1 - \sigma_i) = \begin{cases} 1, & i \text{ is occupied } (\sigma_i = -1) \\ 0, & i \text{ is unoccupied } (\sigma_i = 1) \end{cases}$$

In this case the hard-core repulsion between atoms excludes multiple occupancy of a site. A more realistic model of a gas, however, should allow for a continuous distribution of particles with a non-zero diameter as in the one-dimensional Tonks gas.

Finding Eigenvectors from Symmetry

- Solving the characteristic polynomial to find eigenvalues of 3×3 or larger matrices is not usually practicable. However, if the matrix has symmetries, the form of the eigenvectors can often be guessed so that the corresponding eigenvalues can be obtained indirectly.

Cyclic Matrices: Let the $n \times n$ matrix C be a cyclic (circulant) matrix so that its entries are given by $C_{j,k} = c_{j-k \bmod n}$ with $j, k = 0, 1, \ldots, n-1$. The matrix has cyclic $\mathbb{Z}_n$ symmetry because it commutes with the cyclic rotation matrix Ω

$$C = \begin{pmatrix} c_0 & c_{n-1} & c_{n-2} & \cdots & c_1 \\ c_1 & c_0 & c_{n-1} & \cdots & c_2 \\ c_2 & c_1 & c_0 & \cdots & c_3 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_{n-1} & c_{n-2} & c_{n-3} & \cdots & c_0 \end{pmatrix}, \quad \Omega = \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \\ 1 & 0 & 0 & \cdots & 0 \end{pmatrix}, \quad C = \Omega^{-1} C \Omega, \quad \Omega C = C \Omega$$

The complex eigenvectors of the commuting matrices C and Ω must be common. The form of the complex eigenvectors can therefore be guessed in terms of the nth roots of unity ω_j

$$C\boldsymbol{v}_j = \lambda_j \boldsymbol{v}_j, \qquad \boldsymbol{v}_j = (1, \omega_j, \omega_j^2, \ldots, \omega_j^{n-1})^T, \qquad \omega_j = e^{2\pi i j/n}$$

This yields the complex eigenvalues

$$\lambda_j = \sum_{k=0}^{n-1} \omega_j^k \, c_{n-k}, \qquad j = 0, 1, \ldots, n-1$$

This is recognized as the discrete Fourier transform. If C is also a real symmetric matrix with $c_k = c_{n-k}$, then the eigenvalues are real.

$\mathbb{Z}_2$ Symmetric Eigenvectors

- Let A be diagonalizable with a $\mathbb{Z}_2$ symmetry so that it commutes with an involution matrix R

$$\boxed{A = R^{-1}AR, \quad RA = AR, \qquad R^2 = I, \qquad R = R^{-1}}$$

Since A and R commute, they are simultaneously diagonalizable with a common set of eigenvectors. To see this, let $\boldsymbol{x}$ be an eigenvector of A

$$A\boldsymbol{x} = \lambda\boldsymbol{x}$$

and define the symmetric/anti-symmetric orthogonal projectors

$$P_\pm = \tfrac{1}{2}(I \pm R), \quad P_\pm^2 = P_\pm, \quad P_+P_- = P_-P_+ = 0, \quad P_+ + P_- = I, \quad RP_\pm = \pm P_\pm$$

- It then follows that $P_\pm\boldsymbol{x}$ are eigenvectors of R with eigenvalues $r = \pm 1$ given by

$$R(P_\pm\boldsymbol{x}) = \pm(P_\pm\boldsymbol{x}) = r(P_\pm\boldsymbol{x})$$

and simultaneous eigenvectors of A with eigenvalue λ

$$\begin{aligned} A\boldsymbol{x} = \lambda\boldsymbol{x} \quad &\Rightarrow \quad A(P_+\boldsymbol{x} + P_-\boldsymbol{x}) = \lambda(P_+\boldsymbol{x} + P_-\boldsymbol{x}) && \times P_\pm \\ &\Rightarrow \quad A(P_\pm\boldsymbol{x}) = \lambda(P_\pm\boldsymbol{x}) && P_\pm A = AP_\pm \end{aligned}$$

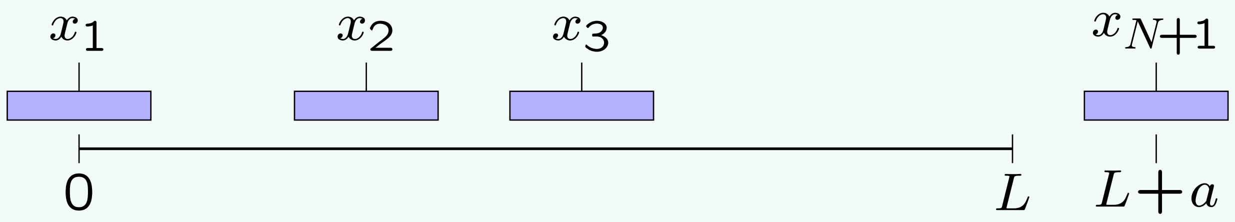
Exercise: Use symmetry to find the eigenvectors and eigenvalues of the $\mathbb{Z}_2$ symmetric matrix A and check your answer by factorizing the characteristic polynomial:

$$A = \begin{pmatrix} 1 & 3 & 2 \\ 3 & 1 & 3 \\ 2 & 3 & 1 \end{pmatrix}, \qquad R = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \qquad \text{Hint: Show eigenvectors } P_\pm\boldsymbol{x} \text{ are of the form } \begin{pmatrix} a \\ b \\ a \end{pmatrix} \text{ or } \begin{pmatrix} c \\ 0 \\ -c \end{pmatrix}$$

Tonks Gas

- Tonks gas is a model of hard-core particles (spheres or rods) in one dimension, i.e., one-dimensional billiard balls. The pair interaction (hard-core) potential is

$$\phi(r) = \phi_{hc}(r) = \begin{cases} \infty, & 0 \le r < a \\ 0, & r \ge a \end{cases}$$



- The Hamiltonian for N rods on the interval $0 \le x \le L$ is

$$\boxed{H(\boldsymbol{x}) = \sum_{1\le i<j\le N} \phi_{hc}(|x_i - x_j|)}$$

Note H is a symmetric function of x_1, $x_2, \ldots, x_N$ and the kinetic energy is omitted.

- The canonical partition function (with Boltzmann counting) is

$$Z_N = \frac{1}{N!}\int_0^L \cdots \int_0^L \exp\left[-\beta H(\boldsymbol{x})\right] dx_1 \ldots dx_N = \int \cdots \int_R \exp\left[-\beta H(\boldsymbol{x})\right] dx_1 \ldots dx_N$$

where R is the region

$$R: \quad 0 \le x_1 \le x_2 \le \ldots \le x_N \le L$$

Change of Variables

- Now $\exp(-\beta\phi_{hc}) = 0$ or 1 so

$$Z_N = \int \cdots \int_{R'} dx_1 \ldots dx_N$$

where

$$\begin{aligned} R' : \quad & 0 \leq x_1 \leq x_2 - a, \quad a \leq x_2 \leq x_3 - a, \\ & \ldots, (i-1)a \leq x_i \leq x_{i+1} - a, \ldots \\ & \ldots, (N-1)a \leq x_N \leq x_{N+1} - a \ = \ L. \end{aligned}$$

- Changing variables to $y_i = x_i - (i-1)a$ we find that

$$0 \leq y_i \leq x_{i+1} - a - (i-1)a \ = \ x_{i+1} - ia \ = \ y_{i+1}$$

- Hence

$$\boxed{Z_N \ = \ \int_0^{\ell} dy_N \int_0^{y_N} dy_{N-1} \cdots \int_0^{y_3} dy_2 \int_0^{y_2} dy_1 \ = \ \frac{\ell^N}{N!}}$$

where $\ell = L - (N-1)a$ is the effective volume.

Equation of State

- Using Stirling's formula $N! \sim (N/e)^N$, the limiting free energy is given by

$$\begin{aligned} -\beta\psi &= \lim_{\substack{N,L\to\infty \\ L/N=v}} \frac{1}{N}\log Z_N \\ &= 1 + \lim_{N,L\to\infty} \log\frac{L-(N-1)a}{N} \\ &= 1 + \log(v-a) \end{aligned}$$

where $v > a$ is the volume per particle. The limit $v \to a$ is the close packing limit.

- The pressure is

$$\boxed{P = -\frac{\partial\psi}{\partial v} = \frac{kT}{v-a}}$$

so the equation of state is

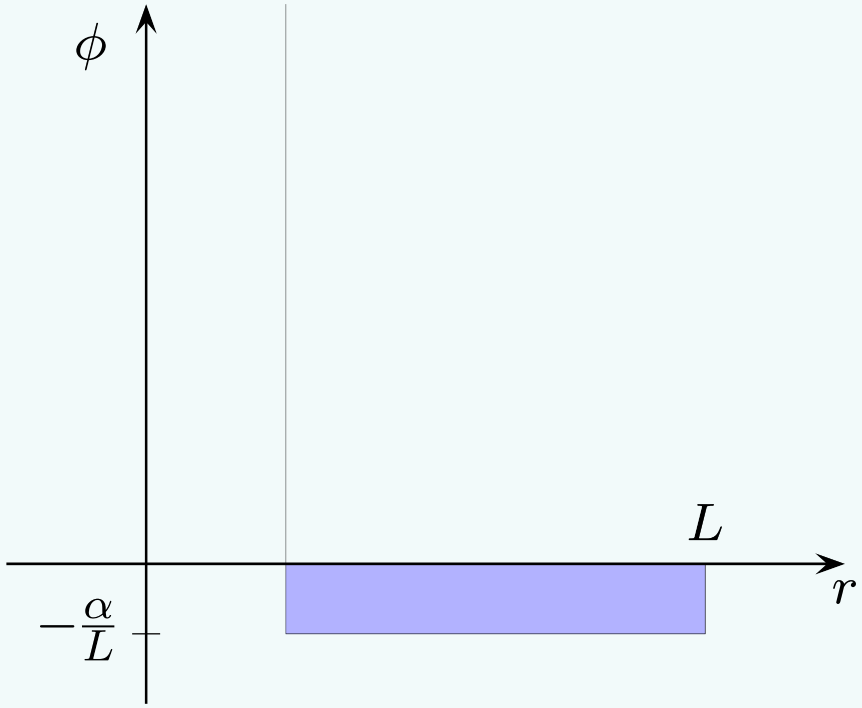
$$P(v-a) = kT$$

which is the ideal gas law with the volume per particle V/N replaced with the free volume per particle $v-a$. The free energy is analytic for $v > a$ so there is no phase transition.

Tonks – van der Waals Gas

- In one dimension, Tonks gas is an improvement over the ideal gas since it takes into account the finite size of particles and the hard-core exclusion between them. However, real particles also interact through attractive Lennard-Jones dispersion forces. A simple way to model this is provided by the Tonks–van der Waals potential

$$\boxed{\phi(r) = \phi_{hc}(r) - \frac{\alpha}{L}, \qquad \alpha > 0}$$



- The parameter α is the *integrated strength* of the attractive potential.
- This model is solvable but unrealistic because the strength of the potential should not depend upon the size L of the system. The Hamiltonian is

$$\begin{aligned} H &= \sum_{1\le i<j\le N} \left[\phi_{hc}(|x_i - x_j|) - \frac{\alpha}{L}\right] \\ &= -\frac{\alpha N(N-1)}{2L} + H^{Tonks} \end{aligned}$$

- Hence

$$Z_N = \exp\left[\frac{\beta\alpha N(N-1)}{2L}\right] Z_N^{Tonks}$$

van der Waals Equation of State

- The free energy is given by

$$-\beta\psi = \lim_{\substack{N,L\to\infty \\ L/N=v}} \frac{1}{N}\log Z_N \;=\; \frac{\beta\alpha}{2v} + 1 + \log(v-a)$$

It follows that the pressure is

$$P \;=\; -\frac{\partial\psi}{\partial v} \;=\; \frac{kT}{v-a} - \frac{\alpha}{2v^2} \;=\; P_{hc} - \frac{\alpha}{2v^2}$$

- The pressure is reduced, relative to Tonks gas, due to the attractive interactions of the particles by an amount proportional to the strength α of the interactions and also proportional to the square of the density $\rho^2 = 1/v^2$ which gives the probability of two particles interacting.

- The equation of state is modified to

$$\boxed{\Big(P + \frac{\alpha}{2v^2}\Big)(v-a) = kT}$$

which is the celebrated equation of state proposed, on phenomenological grounds, by van der Waals in 1873.

7: Mean-Field Theory

19. Van der Waals-Maxwell fluid
20. Curie-Weiss theory of ferromagnetism
21. Equivalent neighbour model

Pierre Curie (1859–1906)

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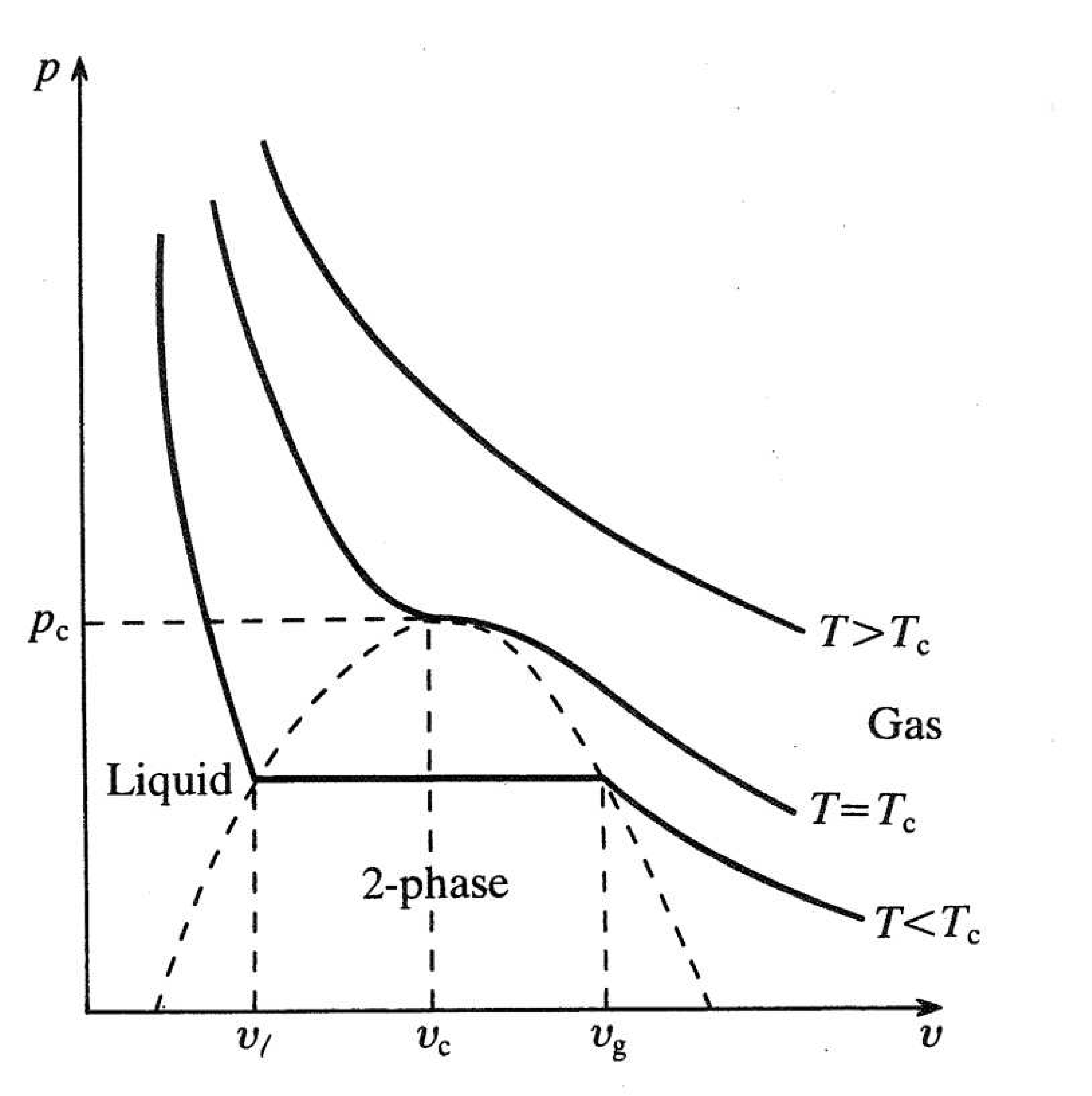
Gas-LiquidPhase Diagram



- Isotherms in the p-v plane of the van der Waals Maxwell theory of a fluid. There is a critical point at the critical pressure $p = p_c$ and critical specific volume $v = v_c$ and a 2-phase coexistence region (gas at specific volume v_g coexists with liquid at specific volume v_ℓ).

Maxwell Double Tangent Construction

- There is a well known problem with the van der Waals equation of state. If the isotherms are plotted for P as a function of v it is found that there are wiggles at low temperatures where

$$\frac{\partial v}{\partial P} > 0$$

- This asserts that the gas actually expands as you labour to compress it and violates thermodynamic stability!

- The remedy for this situation was provided by Maxwell who proposed the *double tangent formula*

$$\boxed{\psi(v) \;=\; \begin{matrix}\text{Convex}\\ \text{Envelope}\end{matrix}\left[\psi_{hc}(v) - \frac{\alpha}{2v}\right]}$$

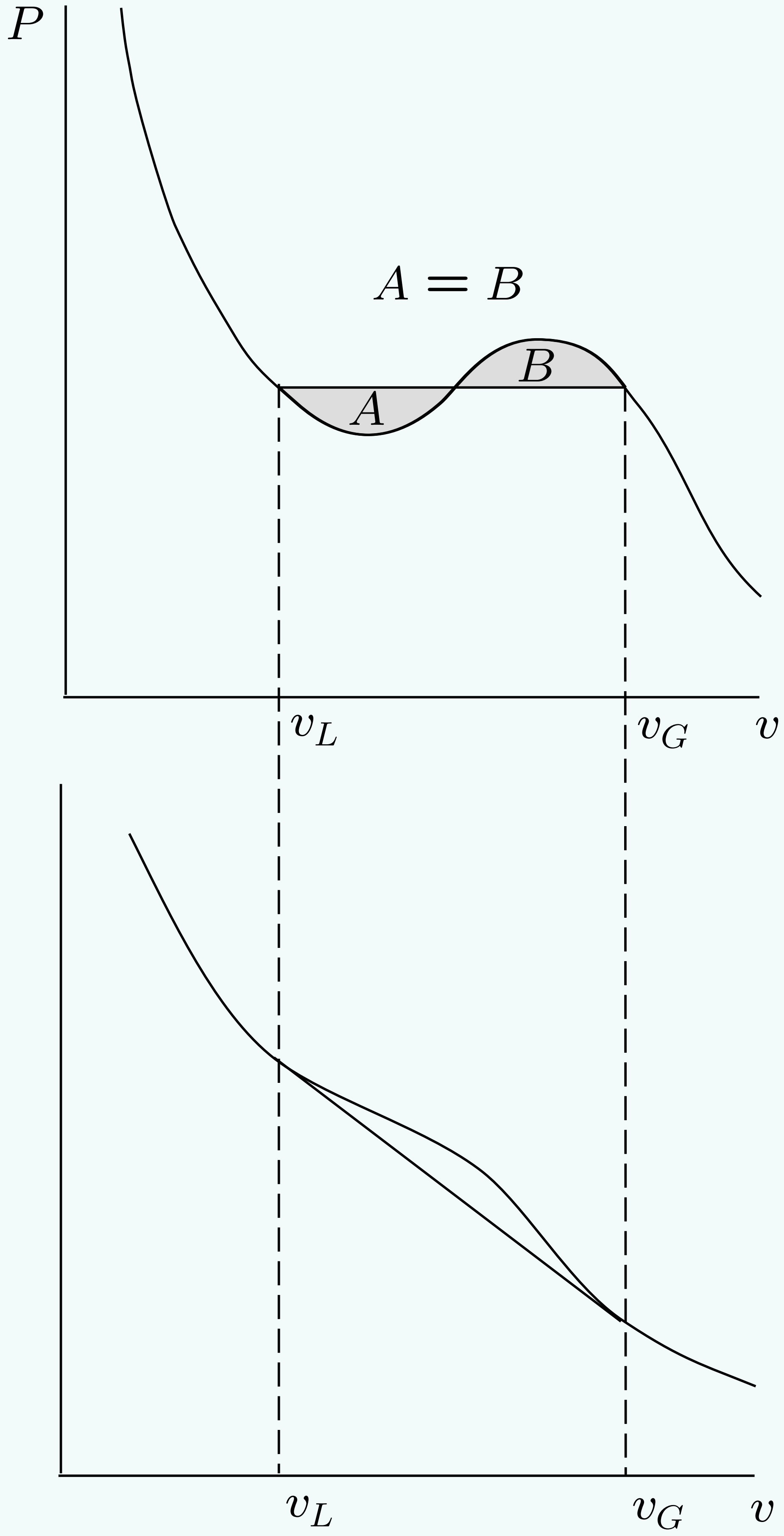
for fixed T.

- The van der Waal's gas, modified by the Maxwell construction, is called the van der Waal's – Maxwell theory.

- Schematic representation of the van der Waals wiggle in a low temperature isotherm of $P = -\frac{\partial \psi}{\partial v}$ plotted against v.

- The wiggle is removed by placing a flat segment into the isotherm according to an equal area rule as illustrated.

- Also shown is the corresponding kink in the free energy isotherm with the equivalent Maxwell double tangent (convex envelope) construction.



Maxwell Equal Area Construction

- The double tangent construction is equivalent to placing horizontal segments in the isotherms according to an equal area rule. Such flat regions are found experimentally in isotherms at low temperatures throughout the gas-liquid coexistence region.

- The Maxwell construction means that the free energy is no longer analytic and thus leads to a phase transition.

- The van der Waals-Maxwell theory can in fact be obtained rigorously by taking a limit of infinitely weak long-range potentials after the thermodynamic limit.

Validity of van der Waals–Maxwell Theory

Theorem 5 (Lebowitz and Penrose 1966)

The van der Waals–Maxwell theory can be obtained rigorously in d dimensions by considering a gas of hard-sphere particles with attractive pair potential of the form

$$\phi(\boldsymbol{r}) = -\gamma^d \exp(-\gamma|\boldsymbol{r}|)$$

by taking the limit $\gamma \to 0+$ after the thermodynamic limit. In particular, α is given by

$$\alpha = -\int \phi(\boldsymbol{r}) d\boldsymbol{r}$$

and is independent of γ.

Chronology:

- Kac, Uhlenbeck and Hemmer (1963–4) $d = 1$
- van Kampen (1964) heuristic argument in general d
- Lebowitz and Penrose (1966) rigorous result for general d

Curie-Weiss Ferromagnet

- In 1895, Pierre Curie submitted his doctoral thesis describing his experimental findings on the phase transition of ferromagnetic materials such as iron. The critical temperature at which this phase transition occurs is called the *Curie point*.

- The classical theory of ferromagnetism was proposed by Weiss in 1907. This phenomenological theory, now called the Curie-Weiss theory, is based on the paramagnet

$$H = -h_{eff} \sum_{i=1}^{N} \sigma_i$$

and assumes that, in a ferromagnet, the effective field h_{eff} consists of an internal field in addition to the external field h.

- On the average the internal field, due to the cooperative alignment of the spins, is proportional to the magnetization m so that the local effective field seen by a spin is

$$\boxed{h_{eff} = Jm + h}$$

where the constant of proportionality J is called the mean-field parameter.

- Evaluating the magnetization then leads to the transcendental equation of state

$$m = \tanh(\beta h_{eff}) = \tanh(Km + B), \qquad K = \beta J, \quad B = \beta h$$

Graphical Solution

- The self-consistency equation is used to determine $m = m(h, T)$. Since the equation cannot be solved analytically it is solved graphically in the form

$$\boxed{\frac{Jm + h}{kT} = \tanh^{-1} m}$$

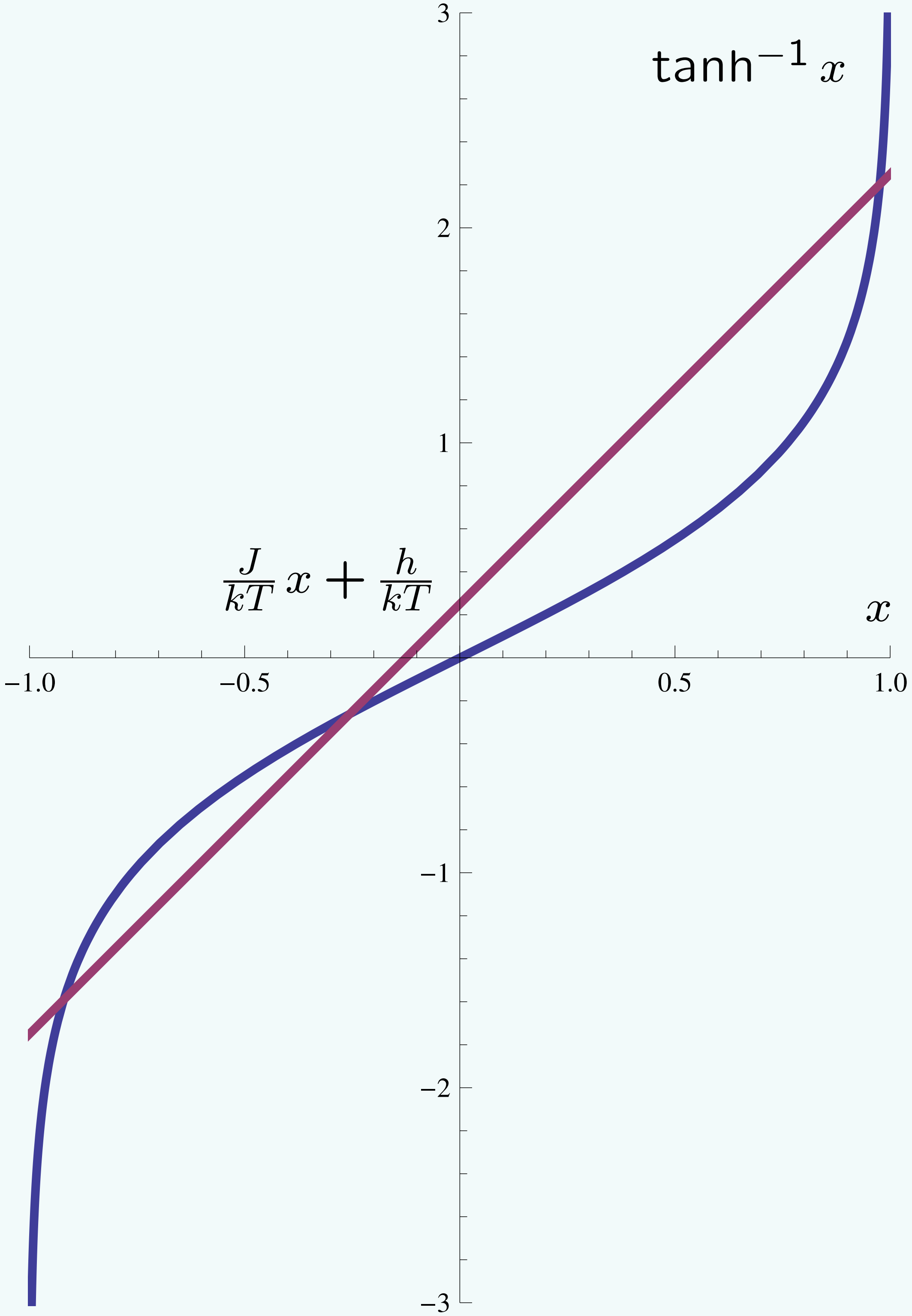
Given h and T, this equation can admit one, two or three solutions for the magnetization m.

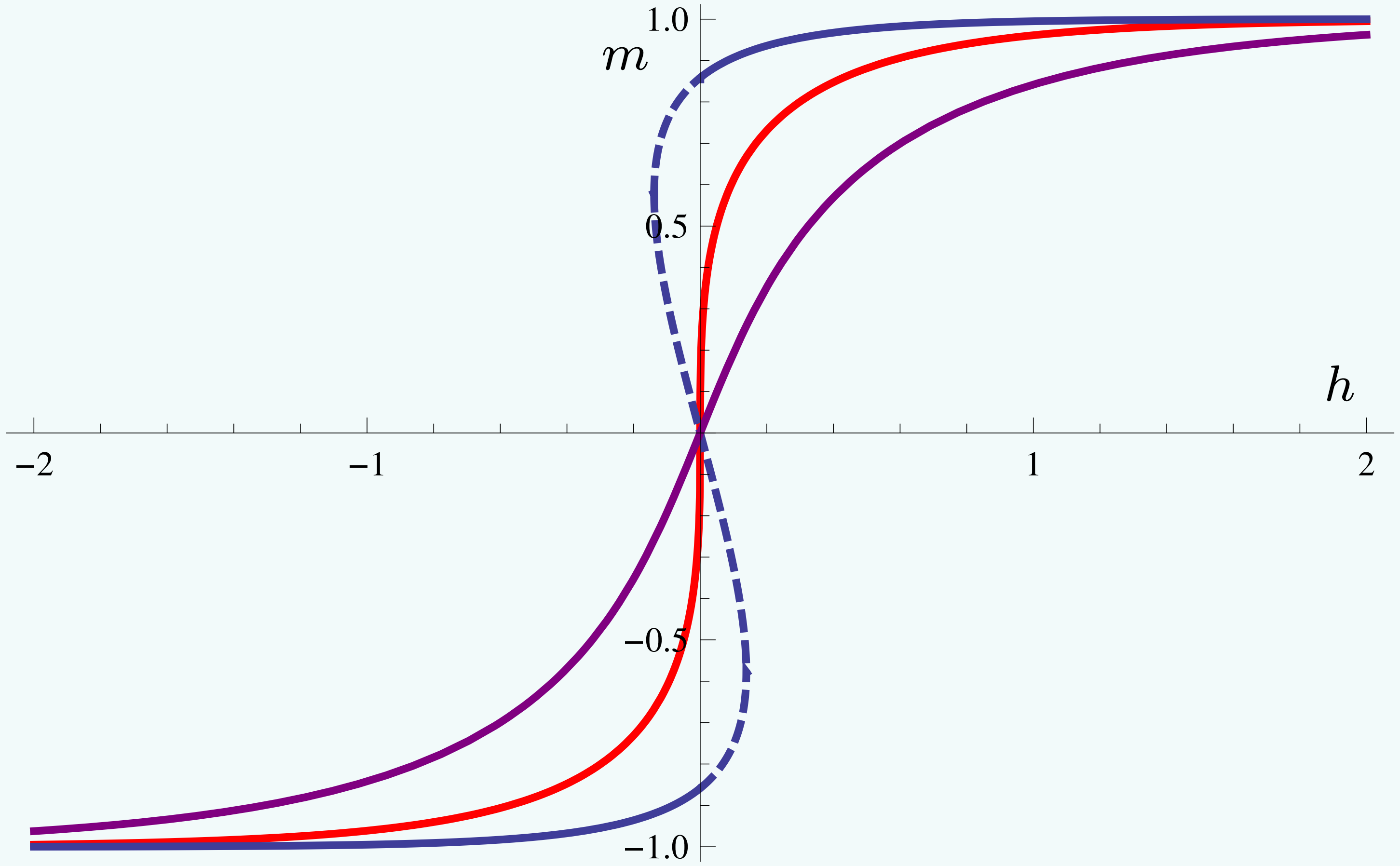
- If the slope of the straight line is less than the critical value

$$\frac{J}{kT_c} = 1$$

there is just one solution.

- In general there can be more than one solution. But, if we assume that m and h have the same sign as is physically reasonable, then for $h > 0$ the equation of state determines m uniquely. This assumption is analogous to the Maxwell construction for the van der Waals fluid.





- Graphical solution of the self-consistency equation.

- Magnetic isotherms for the Curie-Weiss theory.

Sponaneous Magnetization

- The spontaneous magnetization m_0, defined by

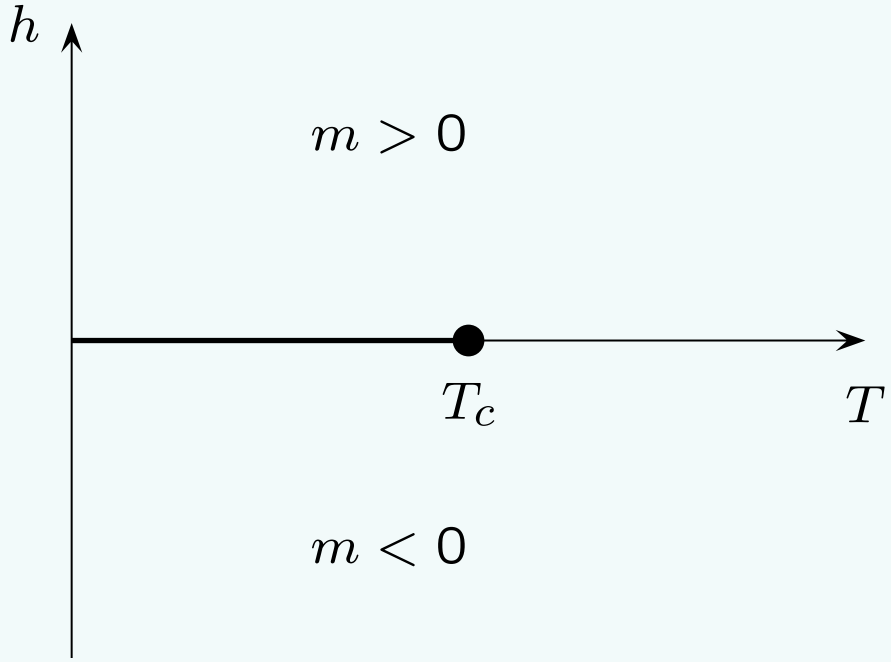
$$m_0(T) = \lim_{h \to 0+} m(h, T)$$

is given by

$$\boxed{m_0(T) = \begin{cases} 0, & T \geq T_c = J/k \\ x, & T < T_c = J/k \end{cases}}$$

where x is the positive solution of

$$x = \tanh \frac{Jx}{kT}$$



- The Curie-Weiss theory gives a topologically correct phase diagram.

- It predicts spontaneous magnetization and an order-disorder phase transition in zero field from a magnetized phase ($T < T_c$, $m > 0$) to a paramagnetic (nonmagnetized) phase ($T > T_c$, $m = 0$) as the temperature is raised through the critical value $T_c = J/k$ called the Curie point.

Equivalent Neighbour Ising Model

- The results of the Curie-Weiss theory can be obtained using the canonical ensemble by starting with the equivalent neighbour Hamiltonian

$$\boxed{H = -\frac{J}{N} \sum_{1 \le i < j \le N} \sigma_i \sigma_j - h \sum_{i=1}^{N} \sigma_i, \qquad J > 0}$$

The sites labelled $1, 2, \ldots, N$ are all equivalent. They sit on the sites of a complete graph — no lattice structure is assumed or needed.

- As for the Tonks–van der Waals gas, the interactions are unphysical because they are independent of separation and depend on the size of the system N. (The factor of N is needed to ensure the energy is extensive and that the thermodynamic limit of the free energy exists.)

Partition Function

- To calculate the partition function we begin by writing

$$H = \tfrac{1}{2}J - \frac{J}{2N}\Big(\sum_{i=1}^{N}\sigma_i\Big)^2 - h\sum_{i=1}^{N}\sigma_i$$

so that

$$\boxed{Z_N = e^{-\frac{1}{2}K}\sum_{\sigma}\exp\left[\frac{K}{2N}\Big(\sum_{i=1}^{N}\sigma_i\Big)^2 + B\sum_{i=1}^{N}\sigma_i\right]}$$

where $K = \beta J$ and $B = \beta h$.

- Next we use the identity

$$\exp(\tfrac{1}{2}\alpha S^2) = \sqrt{\frac{\alpha}{2\pi}}\int_{-\infty}^{\infty} dx\,\exp(-\tfrac{1}{2}\alpha x^2 + \alpha x S)$$

with

$$\alpha = NK \quad \text{and} \quad S = \frac{1}{N}\sum_{i=1}^{N}\sigma_i$$

Integral Formula

- The partition function is therefore

$$\begin{aligned} Z_N &\sim \sum_\sigma \int_{-\infty}^{\infty} dx\, \exp\Big[-\tfrac{1}{2}NKx^2 + (Kx+B)\sum_{i=1}^{N}\sigma_i \Big] \\ &\sim \int_{-\infty}^{\infty} dx\, e^{-\frac{1}{2}NKx^2} \left[2\cosh(Kx+B)\right]^N \\ &\sim \int_{-\infty}^{\infty} dx\, \exp\left[Nf(x)\right] \end{aligned}$$

where

$$f(x) = -\tfrac{1}{2}Kx^2 + \log 2\cosh(Kx+B)$$

and we have omitted the constant

$$A_N = \sqrt{\frac{NK}{2\pi}}\, e^{-K/2}$$

- The limiting free energy per spin is thus

$$\boxed{-\beta\psi \;=\; \lim_{N\to\infty} \frac{1}{N} \log Z_N \;=\; \lim_{N\to\infty} \frac{1}{N} \log \int_{-\infty}^{\infty} \exp[Nf(x)]\, dx}$$

This follows since

$$\lim_{N\to\infty} \frac{1}{N} \log A_N = \lim_{N\to\infty} \frac{1}{N} \log \left[\sqrt{\frac{NK}{2\pi}}\, e^{-K/2} \right] = 0$$

Laplace's Method

- For large N, the integral for Z_N is dominated by the maximum value of the integrand so ψ can be obtained by Laplace's method giving

$$\boxed{-\beta\psi = \max_x \left[-\tfrac{1}{2}Kx^2 + \log 2\cosh(Kx+B)\right] = f(x^*(B),B)}$$

where the maximum occurs at $x = x^*(B)$ and

$$f(x^*(B),B) = -\tfrac{1}{2}Kx^{*2} + \log 2\cosh(Kx^* + B)$$

- Differentiating with respect to x, we see that $x = x^*(B)$ must satisfy

$$\boxed{x = \tanh(Kx+B)}$$

This is precisely the Curie-Weiss equation of state with x identified with the magnetization

$$m = \frac{\partial}{\partial B}(-\beta\psi) = \tanh(Kx^* + B) = x^*$$

Since $\frac{\partial f}{\partial x^*} = 0$, the derivative is given by

$$\frac{\partial}{\partial B}(-\beta\psi) = \frac{d}{dB}\left[f(x^*(B),B)\right] = \frac{\partial f}{\partial x^*}\frac{dx^*}{dB} + \left(\frac{\partial f}{\partial B}\right)_{x^*} = \left(\frac{\partial f}{\partial B}\right)_{x^*} = \tanh(Kx^* + B)$$

- Furthermore, for the maximizing solution $m = x^*$ and h are always of the same sign as was previously assumed. The equivalent neighbour Ising model therefore undergoes a phase transition at the critical point $h = 0$, $T = T_c = J/k$.

Validity of Curie–Weiss Theory

Theorem 6 (Siegert and Vezzetti 1968)

The Curie-Weiss theory can be obtained rigorously in d dimensions by considering a ferromagnetic Ising model with pair interactions

$$J_{ij} = J(|i-j|) = \gamma^d \exp(-\gamma|i-j|)$$

by taking the limit $\gamma \to 0+$ after the thermodynamic limit. The mean-field parameter J is given by

$$J = \sum_j J(|i-j|)$$

and is independent of γ.

Theorem 7 (Pearce and Thompson 1978)

The Curie-Weiss theory can be obtained rigorously from a ferromagnetic Ising model with nearest-neighbour interactions of strength

$$\frac{J}{2d}$$

on a d-dimensional hypercubic lattice by taking the limit $d \to \infty$ after the thermodynamic limit.

Mean-Field Theory

- Mean-field theory is first approximation used in studying new models.

- Mean-field theory usually gives a qualitatively correct phase diagram but gives poor results near critical points.

- Other approaches to mean-field theory are the variational method (Bogoluibov inequality) and the Landau expansion (functional integral).

- Mean-field theory gives upper bounds on magnetization and critical temperatures.

- Validity of mean-field theory is reviewed by Thompson (Prog. Theor. Phys. 1993).

Critical Phenomena & Applications

APCTP, March 2018

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Abstract: This is the third part of a three part series of lectures presenting an introductory Masters level course on Statistical Mechanics. Each part consists of about 6 lectures. The first part introduced the classical ensembles of Gibbs with applications to the ideal gas. The second part introduced lattice spin models, the thermodynamic limit, one-dimensional models and mean-field theory. The third part will cover scaling and universality in critical phenomena, the renormalization group, random walks and percolation.

- Accompanying Problem Sheets and Solutions are available from Alireza Akbari.
- These Lectures are supported under an ICTP Visiting Scholar Award in conjunction with the ICTP Affiliated Center at APCTP.

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Overview and References

Overview:

- The goal of statistical mechanics is to describe the behaviour of bulk matter starting from a physical description of the interactions between its microscopic constituents.
- The third part of this course introduces critical exponents and the concepts of scaling and universality in the theory of critical phenomena. These concepts are placed into the framework of the Renomalization Group and illustrated by applying the Migdal-Kadanoff bond moving approximation to the Ising model. The course concludes with applications to random walks and percolation.

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Lecture Outline

Topic 8. Critical Exponents and Scaling

22. Critical exponents
23. Mean-field critical exponents
24. Universality and scaling

Topic 9. Renormalization Group

25. Renormalization group flows
26. Linearization around fixed points
27. Migdal-Kadanoff bond moving approximation

Topic 10. Simple and Random Walks

28. One-dimensional random walk
29. Walks on graphs and hypercubic lattices
30. Return probability and Polya’s theorem

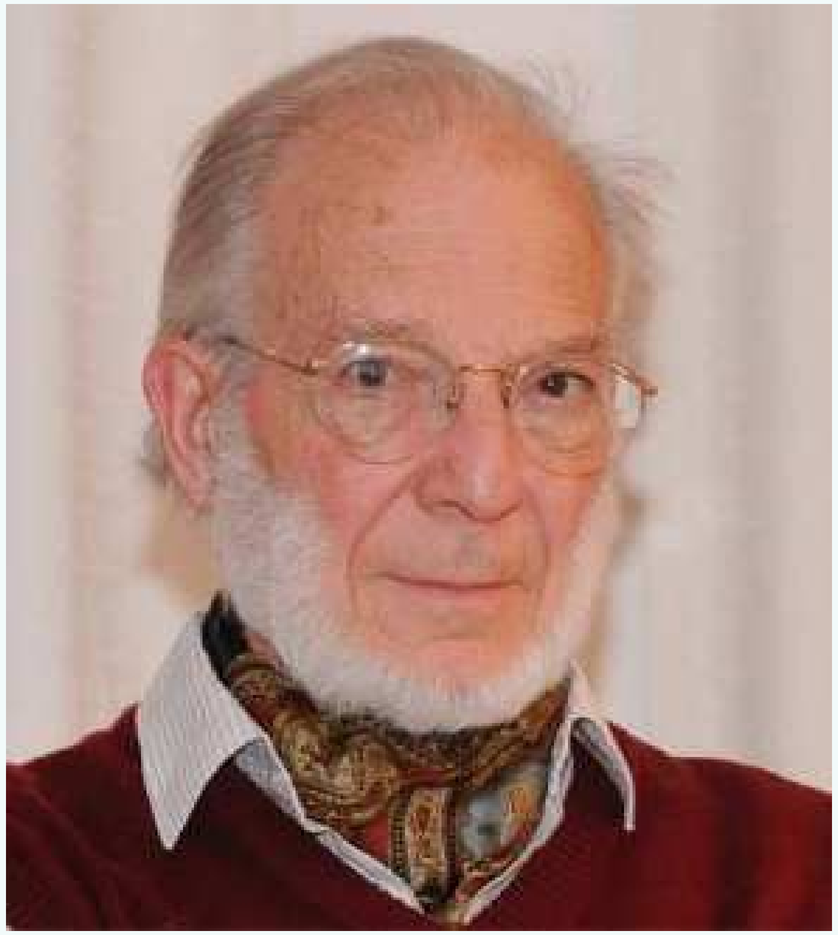
Topic 11. Percolation

31. Bond and site percolation
32. Percolation in one dimension
33. Percolation on Bethe lattice

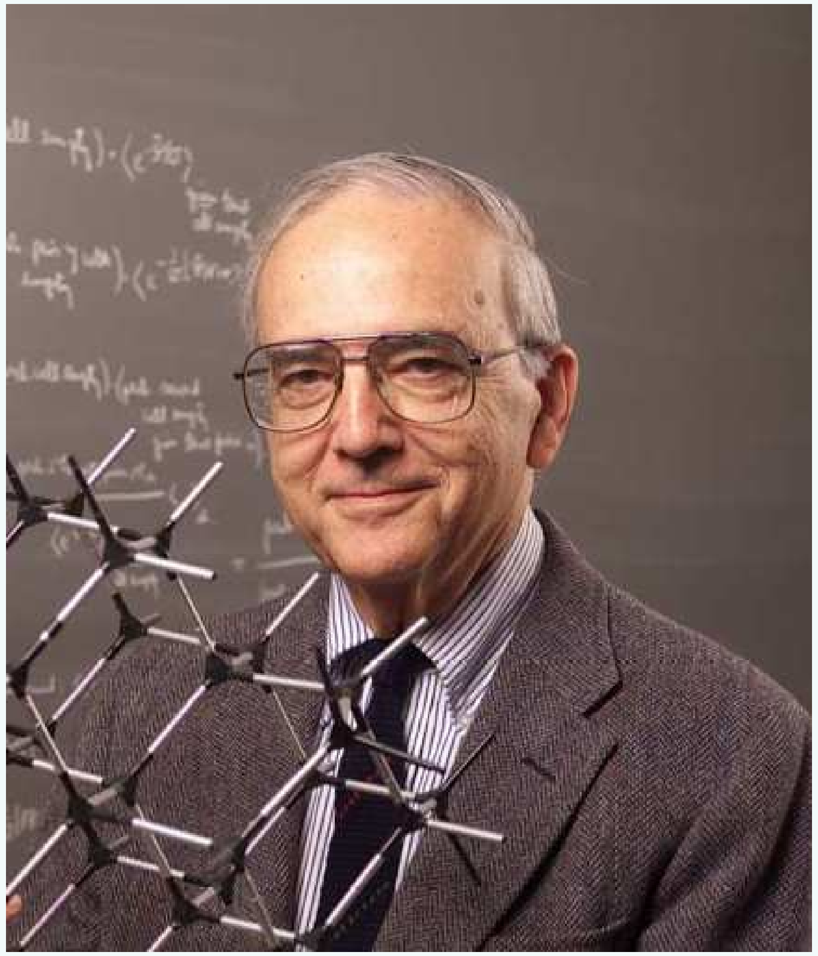
8: Critical Exponents and Scaling

22. Critical exponents
23. Mean-field critical exponents
24. Universality and scaling

Michael Ellis Fisher (1931–)



Benjamin Widom (1927–)



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Critical Exponents

- The behaviour of thermodynamic functions in the vicinity of a critical point is characterized by critical exponents. These describe the power law behaviour asymptotically close to the critical point.

- Assuming $f(x) > 0$, we write

$$\boxed{f(x) \sim x^{\epsilon} \quad \text{as} \quad x \to 0+}$$

whenever the limit

$$\epsilon = \lim_{x \to 0+} \frac{\log f(x)}{\log x}$$

exists. This limit defines the critical exponent ϵ of the function $f(x)$ at the critical point $x = 0$. Similarly, we define one-sided limits for $x \to 0-$ and two-sided limits for $x \to 0$.

- In statistical mechanics there has been a proliferation of critical exponents which now exhaust the Greek alphabet!

Definition of Critical Exponents

$$\boxed{t \;=\; \frac{T - T_c}{T_c}}$$

Magnetic Critical Exponents

Exponent	Definition
α	$C_0 \sim \lvert t\rvert^{-\alpha}, \quad t \to 0$
β	$m_0 \sim \lvert t\rvert^{\beta}, \quad t \to 0-$
γ	$\chi_0 \sim \lvert t\rvert^{-\gamma}, \quad t \to 0$
δ	$h \sim \mathrm{sgn}(m)\lvert m\rvert^{\delta}, \quad h \to 0, T = T_c$

$$m \;=\; -\frac{\partial \psi}{\partial h}, \qquad m_0 \;=\; -\frac{\partial \psi}{\partial h}\Big|_{h=0}$$

$$\begin{aligned} C_0 &= -T\frac{\partial^2 \psi}{\partial T^2}\Big|_{h=0} \\ &= \text{zero-field specific heat} \end{aligned}$$

$$\begin{aligned} \chi_0 &= -\frac{\partial^2 \psi}{\partial h^2}\Big|_{h=0} \\ &= \text{zero-field susceptibility} \end{aligned}$$

Fluid Critical Exponents

Exponent	Definition
α	$C_V \sim \lvert t\rvert^{-\alpha}, \quad t \to 0$
β	$\rho_L - \rho_G \sim \lvert t\rvert^{\beta}, \quad t \to 0-$
γ	$K_T \sim \lvert t\rvert^{-\gamma}, \quad t \to 0$
δ	$P - P_c \sim \mathrm{sgn}(\rho - \rho_c)\lvert \rho - \rho_c\rvert^{\delta},$ $\lvert \rho - \rho_c\rvert \to 0, T = T_c$

$$\rho_{L,G} \;=\; \text{liquid, gas density}$$

$$\begin{aligned} C_V &= -T\frac{\partial^2 \psi}{\partial T^2}\Big|_{V=\text{const}} \\ &= \text{constant volume specific heat} \end{aligned}$$

$$K_T \;=\; \text{isothermal compressibility}$$

$$K_T^{-1} \;=\; -V\frac{\partial P}{\partial V}\Big|_{T=\text{const}}$$

Mean-field Critical Exponents

Let us obtain the critical exponents of the Curie-Weiss ferromagnet:

$\boxed{\alpha = 0_{disc}}$

- The non-analytic zero-field free energy is

$$-\frac{\psi}{kT} = \begin{cases} \log 2, & T \geq T_c \\ -\frac{Jm_0^2}{2kT} + \log 2 \cosh\left(\frac{Jm_0}{kT}\right), & T < T_c \end{cases}$$

with

$$m_0 = \tanh K m_0$$

- Hence

$$U = -T^2 \frac{d}{dT}\left(\frac{\psi}{T}\right) = \begin{cases} 0, & T \geq T_c \\ -\frac{1}{2}Jm_0^2, & T < T_c \end{cases}$$

and

$$\boxed{C_0 = \frac{dU}{dT} = \begin{cases} 0, & T \geq T_c \\ -\frac{1}{2}J\,\frac{dm_0^2}{dT}, & T < T_c \end{cases}}$$

Since $\left.\frac{dm_0^2}{dT}\right|_{T \to T_c-} = -\frac{3k}{J}$, $\left.C_0\right|_{T \to T_c-} = \frac{3}{2}k$ and this yields a jump discontinuity in C_0 so $\alpha = 0_{disc}$.

$\boxed{\beta = 1/2}$

- If we set $h = 0$ then m_0 is small near the critical point $T = T_c = J/k$ so we can Taylor expand the equation of state

$$\frac{Jm_0}{kT} = \frac{T_c}{T} m_0 = \tanh^{-1} m_0 = m_0 + \tfrac{1}{3} m_0^3 + \ldots$$

- This gives

$$m_0^2 \sim 3\left(\frac{T_c}{T} - 1\right) = 3\,\frac{T_c}{T}\left(1 - \frac{T}{T_c}\right)$$

and hence as $T \to T_c -$

$$\boxed{m_0 \sim \left(1 - \frac{T}{T_c}\right)^{\beta} \quad \text{with} \quad \beta = 1/2}$$

- Note that

$$\left.\frac{dm_0^2}{dT}\right|_{T \to T_c -} = -\frac{3}{T_c} = -\frac{3k}{J}$$

$\boxed{\gamma = 1}$

- The zero-field susceptibility is

$$\chi_0 = \beta \left. \frac{dm}{dB} \right|_{B=0}$$

But differentiating $m = \tanh(Km + B)$ implicitly with respect to B gives

$$\frac{dm}{dB} = \frac{1 - m^2}{1 - K(1 - m^2)}$$

and so

$$\chi_0 = \frac{\beta(1 - m_0^2)}{1 - K(1 - m_0^2)}$$

- It follows that as $T \to T_c$

$$\boxed{\chi_0 \sim \left| 1 - \frac{T}{T_c} \right|^{-\gamma} \quad \text{with} \quad \gamma = 1}$$

$\boxed{\delta = 3}$

- Finally, if we set $T = T_c = J/k$ then m is small for small h so we can Taylor expand the equation of state along the critical isotherm

$$\frac{J}{kT_c} m + \frac{h}{kT_c} = m + \frac{h}{J} = \tanh^{-1} m \sim m + \tfrac{1}{3} m^3 + \dots$$

Hence we conclude that as $h \to 0$

$$\boxed{m \sim h^{1/\delta} \quad \text{with} \quad \delta = 3}$$

Summary

- In summary, the critical exponents of the Curie-Weiss ferromagnet are

$$\boxed{\alpha = 0_{disc}, \quad \beta = 1/2, \quad \gamma = 1, \quad \delta = 3}$$

- These are the *classical* values. Analysis shows that the van der Waals–Maxwell fluid has precisely the same classical values for the critical exponents.

- Typical experimental values for these exponents are

$$\boxed{\alpha \approx 0.1, \quad \beta \approx 0.33, \quad \gamma \approx 1.2, \quad \delta \approx 4.2}$$

for both fluid and magnetic systems in three dimensions. Clearly the classical critical exponents are wrong!

Some Critical Exponents

Model	α	β	γ	δ	**Symmetry**
Mean-Field	0_{disc}	1/2	1	3	$\mathbb{Z}_2$
2-d Ising	0_{log}	1/8	7/4	15	$\mathbb{Z}_2$
3-d Ising	0.10	0.33	1.24	4.8	$\mathbb{Z}_2$
$d \geq 4$ Ising	0	1/2	1	3	$\mathbb{Z}_2$
2-d 3-State Potts	1/3	1/9	13/9	14	$\mathbb{S}_3$
Hard Hexagons	1/3	1/9	13/9	14	$\mathbb{S}_3$
2-d 4-state Potts	2/3	1/12	7/6	15	$\mathbb{S}_4$
2-d Percolation	$-2/3$	5/36	43/18	91/5	$\mathbb{S}_1$

- Clearly, the mean-field critical exponents are not generally valid.

- These systems represent different symmetry classes, such as, $\mathbb{Z}_2$, $\mathbb{S}_3$ and $\mathbb{S}_4$. Clearly, the critical exponents depend on the type of symmetry. Within a symmetry class, for example 3-state Potts and hard hexagons which share an $\mathbb{S}_3$ symmetry, the critical exponents are the same.

- Observe that

$$\boxed{\alpha + 2\beta + \gamma = 2, \qquad \gamma = \beta(\delta - 1)}$$

Universality and Scaling

- The critical exponents appear to be insensitive to the microscopic details of the system. This empirical fact is embodied in the following:

Universality Hypothesis

For short-range interactions, the critical exponents depend only on the spatial dimension d *and the symmetries of the Hamiltonian* H.

- Another important hypothesis in the modern theory of critical phenomena is the scaling hypothesis. For a simple magnetic system, this takes the following form:

Scaling Hypothesis

There exist two exponents y_1 *and* y_2 *such that, asymptotically close to the critical point, the free energy can be written as*

$$\psi = \psi_{anal} + \psi_{sing}$$

where ψ_{anal} *is analytic and the singular part* ψ_{sing} *satisfies*

$$\boxed{\psi_{sing}(\lambda^{y_1} t, \lambda^{y_2} h) = \lambda \psi_{sing}(t, h)}$$

for all values of the scaling parameter λ, *that is,* ψ_{sing} *is a generalized homogeneous function of* $t = \frac{T-T_c}{T_c}$ *and* h. *The exponents* $y_1 = y_t$, $y_2 = y_h$ *are called scaling or Renormalization Group (RG) exponents.*

Scaling Relations

- The Curie-Weiss ferromagnet satisfies the scaling hypothesis. In fact, we will show later that the singular part of the mean-field free energy is

$$\boxed{\psi_{sing}(t,h) \;=\; \min_s \left\{ -\frac{h}{J}s + \tfrac{1}{2}ts^2 + \tfrac{1}{12}s^4 \right\}}$$

This is a generalized homogeneous function with exponents $y_1 = y_t = 1/2$ and $y_2 = y_h = 3/4$.

- More generally, by differentiating the homogeneous relation satisfied by ψ_{sing}, it is possible to obtain the exponents α, β, γ, δ in terms of $y_1 = y_t$ and $y_2 = y_h$. In this sense, the only relevant fields are the temperature T and the magnetic field h. Hence only two of the four critical exponents are independent. Explicitly, we will show that the exponents α, β, γ, δ satisfy the two scaling relations

$$\boxed{\alpha + 2\beta + \gamma = 2, \qquad \gamma = \beta(\delta - 1)}$$

These scaling relations are satisfied by the classical values of the critical exponents.

RG Exponents Determine Critical Exponents

- Differentiating the homogeneous relation

$$\boxed{\psi_{sing}(\lambda^{y_1} t, \lambda^{y_2} h) = \lambda \psi_{sing}(t, h)}$$

for a magnet, we find:

$$\boxed{\alpha = 2 - \frac{1}{y_1}}$$

$$\begin{aligned} C_0 &= \frac{\partial^2}{\partial t^2}\psi_{sing} \sim |t|^{-\alpha}, \qquad h = 0 \\ \lambda^{2y_1} C_0(\lambda^{y_1} t) &\sim \lambda C_0(t), \qquad \text{set } \lambda = \frac{1}{|t|^{1/y_1}} \\ C_0(t) &\sim \lambda^{2y_1-1} C_0(\pm 1) \sim |t|^{-(2-1/y_1)} \end{aligned}$$

$$\boxed{\beta = \frac{1}{y_1} - \frac{y_2}{y_1}}$$

$$\begin{aligned} m_0 &= \frac{\partial}{\partial h}\psi_{sing}\Big|_{h=0} \sim |t|^{\beta}, \qquad h = 0 \\ \lambda^{y_2} m_0(\lambda^{y_1} t) &\sim \lambda\, m_0(t), \qquad \text{set } \lambda = \frac{1}{|t|^{1/y_1}} \\ m_0(t) &\sim \lambda^{y_2-1} m_0(\pm 1) \sim |t|^{-(y_2-1)/y_1} \end{aligned}$$

$$\boxed{\gamma = \frac{2y_2}{y_1} - \frac{1}{y_1}}$$

$$\begin{aligned}
\chi_0 &= \frac{\partial^2}{\partial h^2}\psi_{sing}\Big|_{h=0} \sim |t|^{-\gamma}, \qquad h = 0 \\
\lambda^{2y_2}\chi_0(\lambda^{y_1}t) &\sim \lambda\,\chi_0(t), \qquad \text{set } \lambda = \frac{1}{|t|^{1/y_1}} \\
\chi_0(t) &\sim \lambda^{2y_2-1}\chi_0(\pm 1) \sim |t|^{-(2y_2-1)/y_1}
\end{aligned}$$

$$\boxed{\delta = \frac{y_2}{1-y_2}}$$

$$\begin{aligned}
m\Big|_{t=0} &= \frac{\partial}{\partial h}\psi_{sing}\Big|_{t=0} \sim |h|^{1/\delta}, \qquad t = 0 \\
\lambda^{y_2}\, m(\lambda y_2 h) &\sim \lambda\, m(h), \qquad \text{set } \lambda = \frac{1}{|h|^{1/y_2}} \\
m(h) &\sim \lambda^{y_2-1} m(\pm 1) \sim |h|^{-(y_2-1)/y_2}
\end{aligned}$$

- Thus we verify that

$$\alpha + 2\beta + \gamma = 2 - \frac{1}{y_1} + 2\left(\frac{1}{y_1} - \frac{y_2}{y_1}\right) + \frac{2y_2}{y_1} - \frac{1}{y_1} = 2$$

$$\beta(\delta - 1) = \left(\frac{1-y_2}{y_1}\right)\left(\frac{y_2}{1-y_2} - 1\right) = \frac{2y_2 - 1}{y_1} = \gamma$$

Curie-Weiss Singular Free Energy

- For the Curie-Weiss ferromagnet

$$\boxed{\psi_{sing}(t,h) = \min_s\{-\frac{h}{J}s + \tfrac{1}{2}ts^2 + \tfrac{1}{12}s^4\}}$$

- Expand the free energy keeping only terms linear in

$$t = \frac{T-T_c}{T_c} = \frac{T}{T_c} - 1$$

and h using $J/kT_c = 1$ and

$$K = \frac{J}{kT} = \frac{T_c}{T} = \frac{1}{1+t}, \qquad B = \frac{h}{kT} = \frac{h}{J}\frac{1}{1+t}$$

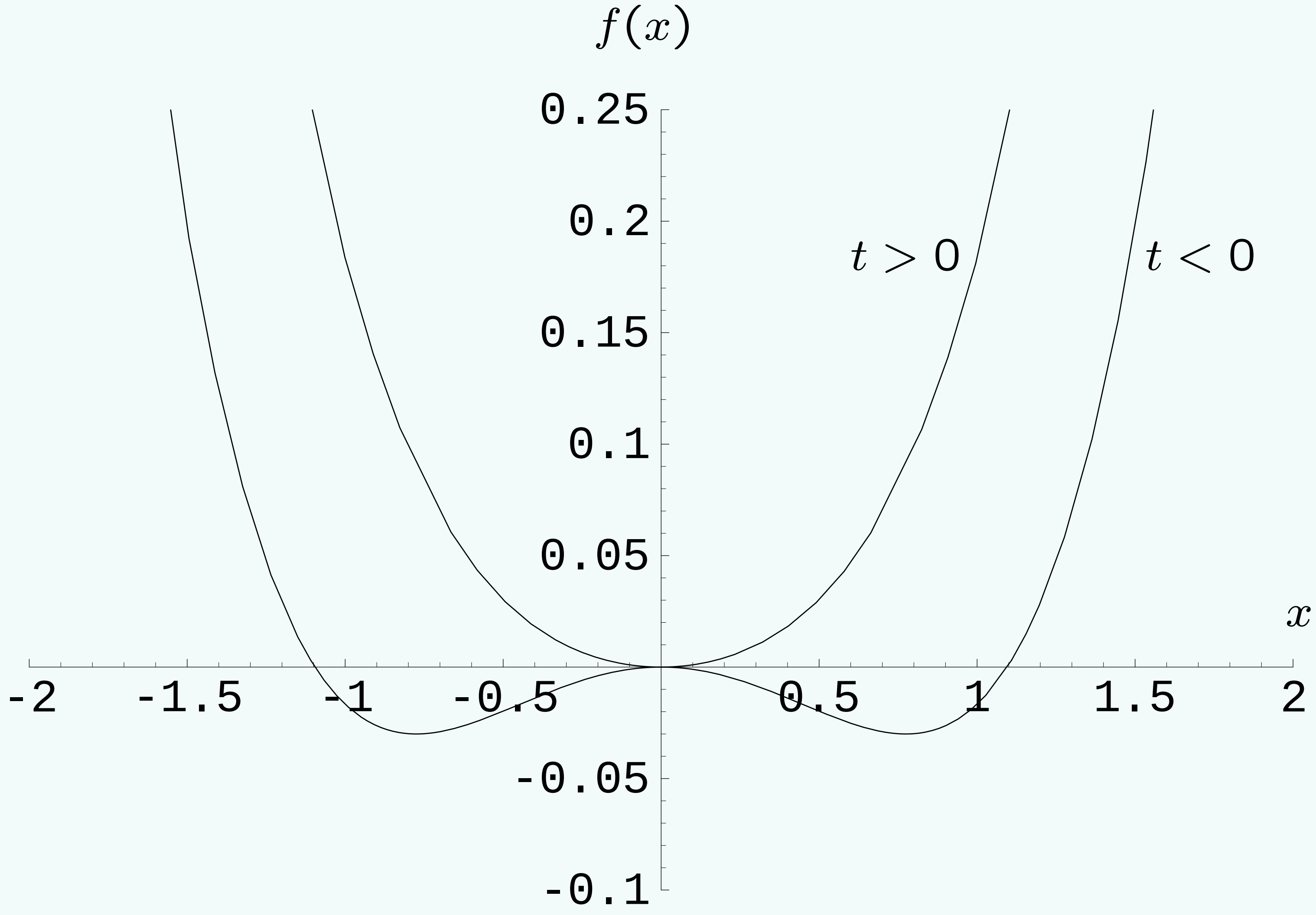
- After replacing $x \mapsto (x - B)/K$, using a Taylor expansion and keeping terms linear in h and t, we find that

$$\begin{aligned}
\beta\psi(t,h) &= \min_{-\infty<x<\infty}\left\{\tfrac{1}{2}Kx^2 - \log 2\cosh(Kx+B)\right\} \\
&= \min_{-\infty<x<\infty}\left\{\frac{1}{2K}(x-B)^2 - \log 2\cosh x\right\} \\
&= \min_{-\infty<x<\infty}\left\{\tfrac{1}{2}(1+t)\left[x - \frac{h}{J(1+t)}\right]^2 - \log 2\cosh x\right\} \\
&= \min_{-\infty<x<\infty}\left\{\tfrac{1}{2}(1+t)x^2 - \frac{xh}{J} - \left(\frac{x^2}{2} - \frac{x^4}{12} + \cdots\right)\right\} \\
&\sim \min_{-\infty<x<\infty}\left\{-\frac{xh}{J} + \tfrac{1}{2}tx^2 + \frac{1}{12}x^4\right\} \;=\; \psi_{sing}(t,h)
\end{aligned}$$

where

$$\beta^{-1} = kT = (1+t)J \sim J, \qquad t \to 0$$

Free Energy Minima



- The Curie-Weiss free energy function $f(x) = \frac{1}{2}tx^2 + x^4/12 + \cdots$ for $h = 0$ and $t > 0$ or $t < 0$. For $t > 0$ there is a single minimum at $x = 0$. For $t < 0$ there are two minima at $x = \pm x_0$ corresponding to the existence of a non-zero spontaneous magnetization.

Curie-Weiss Homogeneous Function

- The Curie-Weiss singular free energy $\psi_{sing}(t,h)$ is a generalized homogeneous function with exponents $x = 1/2$ and $y = 3/4$. After replacing $x \mapsto \lambda^{1/4}x$ we find

$$\begin{aligned} & \psi_{sing}(\lambda^{1/2}t, \lambda^{3/4}h) \\ = & \min_{-\infty<x<\infty} \Big\{ -\lambda^{3/4} x \frac{h}{J} + \tfrac{1}{2}\lambda^{1/2} t x^2 + \tfrac{1}{12} x^4 \Big\} \\ = & \lambda \min_{-\infty<x<\infty} \Big\{ - x \frac{h}{J} + \tfrac{1}{2} t x^2 + \tfrac{1}{12} x^4 \Big\} \\ = & \lambda\, \psi_{sing}(t,h) \end{aligned}$$

with

$$\boxed{\psi_{sing}(t,h) = \psi(t,h) - \psi_{anal}(t,h)}$$

Correlation Length and Hyperscaling

- The pair or two-point correlation function

$$G(i-j) = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = \Big\langle (\sigma_i - \langle \sigma_i \rangle)(\sigma_j - \langle \sigma_j \rangle) \Big\rangle$$

measures the correlation between the deviations of σ_i and σ_j from their mean values. In the completely ordered ($\sigma_j = 1$ for all j) and completely random ($\sigma_j = \pm 1$ with equal probability for all j) states, this correlation vanishes.

- As i and j become separated by large distances σ_i and σ_j become statistically independent

$$\lim_{|i-j|\to\infty} \Big[\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \Big] = 0$$

- Away from criticality, the approach to this limit is exponentially fast

$$G(i-j) = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \sim \exp\left(-\frac{|i-j|}{\xi(t)} \right), \qquad |i-j| \to \infty, \qquad t = \frac{T - T_c}{T_c} \neq 0$$

where the correlation length $\xi(t)$ measures the distance over which the spins are correlated.

- At criticality, the spins are effectively correlated at all distances and the correlation length diverges. More specifically, we can define a correlation length critical exponent ν

$$\xi \sim |t|^{-\nu}, \qquad t \to 0$$

The new critical exponent ν is not independent and satisfies the hyperscaling relation

$$\boxed{2 - \alpha = d\nu, \qquad d = \text{lattice dimensionality}}$$

For the two-dimensional Ising model, $d = 2$, $\alpha = 0_{log}$ and $\nu = 1$.

Decay of Critical Pair Correlations

- More generally, the long-distance behaviour of the pair correlations is given by

$$G(r) \sim A(d) r^{2-d-\eta} \exp\left(-\frac{r}{\xi(t)}\right), \qquad r = |i-j| \to \infty$$

where the amplitude $A(d)$ depends on the lattice dimensionality.

- At the critical point ($t = 0$, $\xi = \infty$), the pair correlations no longer decay exponentially. Instead, the correlations decay with a power-law behaviour

$$\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \sim |i-j|^{2-d-\eta}, \qquad 2 - d - \eta < 0$$

- Again, the new critical exponent η is not independent and satisfies the scaling law

$$\boxed{\frac{2-\eta}{d} = \frac{\delta - 1}{\delta + 1}, \qquad \delta = \frac{d + 2 - \eta}{d - 2 + \eta}}$$

For the two-dimensional Ising model, $d = 2$, $\delta = 15$ and $\eta = 1/4$.

- Statistical systems with relatively short correlation lengths can be well studied by perturbation or approximate methods such as mean-field theory. In constrast, systems close to critical points with a very large correlation length, are generally extremely difficult to study.

9: Renormalization Group

25. Renormalization group flows
26. Linearization around fixed points
27. Migdal-Kadanoff bond moving approximation

Kenneth Geddes Wilson (1936–)

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Renormalization Group

- The renormalization group approach to critical phenomena has its origins in the work of Wilson, Kadanoff and others in the mid 1970s. Although the RG methods have never been made rigorous, the renormalization group has proved invaluable as a language and heuristic framework to understand the implications of scaling and universality.

- The basic idea of the Renormalization Group (RG) is to reduce the correlation length $\xi \mapsto \xi/b$ by a scale factor $b > 1$, and to simultaneously reduce the number of degrees of freedom from N to $N' = N/b^d$, by applying a *transformation* that preserves the dimensionality and symmetries of the system (and hence the critical exponents)

$$\boxed{\xi' = \xi/b, \qquad L' = L/b, \qquad N' = N/b^d, \qquad b > 1}$$

- The rescaling factor b applies to all lengths $L \mapsto L/b$. In principle, by successive applications of the transformation, one moves away from the critical point to a regime where the correlation length is small and the problem becomes manageable by perturbation or approximate methods.

Renormalization Group Transformations

- To specify an RG transformation, consider a general Ising Hamiltonian

$$H = -\sum_{A \subset \Lambda} J_A \sigma_A$$

where Λ is the lattice with $N = |\Lambda|$ sites. This Hamiltonian is characterized by the set of interactions or couplings

$$\boldsymbol{K} = \{K_A = \beta J_A \ : \ A \subset \Lambda\}$$

which we consider as a vector in a suitable vector space of interactions.

- Formally, a renormalization group transformation $\mathcal{R}_b$ is a nonlinear operator given by

$$\boxed{\boldsymbol{K}' = \mathcal{R}_b(\boldsymbol{K}), \qquad b > 1}$$

or

$$K'_A = f_A(b; \boldsymbol{K}), \qquad f_A = \{\text{smooth functions}\}$$

Semi-Group Property

- An RG transformation is assumed to satisfy the semigroup property

$$\boxed{\mathcal{R}_b \circ \mathcal{R}_{b'} = \mathcal{R}_{bb'} = \mathcal{R}_{b'} \circ \mathcal{R}_b, \qquad b, b' > 1}$$

under composition and the scaling properties

$$\xi(\boldsymbol{K}') = b^{-1}\xi(\boldsymbol{K}), \qquad Z(\boldsymbol{K}') = Z(\boldsymbol{K}), \qquad \psi(\boldsymbol{K}') = b^d\,\psi(\boldsymbol{K})$$

- The RG transformations $\mathcal{R}_b$ under different rescaling factors b do not form a group since there is no inverse transformation (we restrict to $b > 1$).

- Note that the partition function remains fixed and that for a transformation relating d-dimensional hypercubic lattices of side L, L' respectively

$$\frac{1}{N'} = \frac{1}{(L')^d} = \left(\frac{b}{L}\right)^d = \frac{b^d}{L^d} = \frac{b^d}{N}$$

Renormalization Group Flows and Fixed Points

- Let us assume that there exists a renormalization group transformation $\mathcal{R}_b$. Let us start with a particular system specified by $\boldsymbol{K}_0$ and iterate the transformation to obtain a sequence of vectors

$$\boxed{\boldsymbol{K}_{\ell+1} = \mathcal{R}_b(\boldsymbol{K}_\ell), \qquad \ell = 0, 1, 2, \ldots}$$

such that

$$\xi(\boldsymbol{K}_{\ell+1}) = b^{-1}\xi(\boldsymbol{K}_\ell) = b^{-2}\xi(\boldsymbol{K}_{\ell-1}) = \cdots = b^{-(\ell+1)}\xi(\boldsymbol{K}_0)$$

- Suppose now that $\boldsymbol{K}_\ell$ approaches a finite limit $\boldsymbol{K}^*$ as $\ell \to \infty$, then $\boldsymbol{K}^*$ is a *fixed point* of $\mathcal{R}_b$, that is,

$$\boldsymbol{K}^* = \lim_{\ell\to\infty} \boldsymbol{K}_{\ell+1} = \lim_{\ell\to\infty} \mathcal{R}_b(\boldsymbol{K}_\ell) = \mathcal{R}_b\Big(\lim_{\ell\to\infty} \boldsymbol{K}_\ell\Big) = \mathcal{R}_b(\boldsymbol{K}^*)$$

- It follows that either

$$\lim_{\ell\to\infty} \xi(\boldsymbol{K}_\ell) = \xi(\boldsymbol{K}^*) = 0$$

or

$$\xi(\boldsymbol{K}_0) = \lim_{\ell\to\infty} b^\ell \xi(\boldsymbol{K}_\ell) = \infty, \qquad b > 1, \quad \xi(\boldsymbol{K}^*) > 0$$

- This says that we either converge to a *trivial* fixed point with $\xi(\boldsymbol{K}^*) = 0$ or $\xi(\boldsymbol{K}_0) = \infty$, that is, the initial system was at a critical point and we converge to a *non-trivial* (critical) fixed point.

Basins of Attraction and Universality Classes

- The critical exponents of a system can be determined by the behaviour of $\mathcal{R}_b$ in the neighbourhood of the non-trivial fixed point that the system approaches.

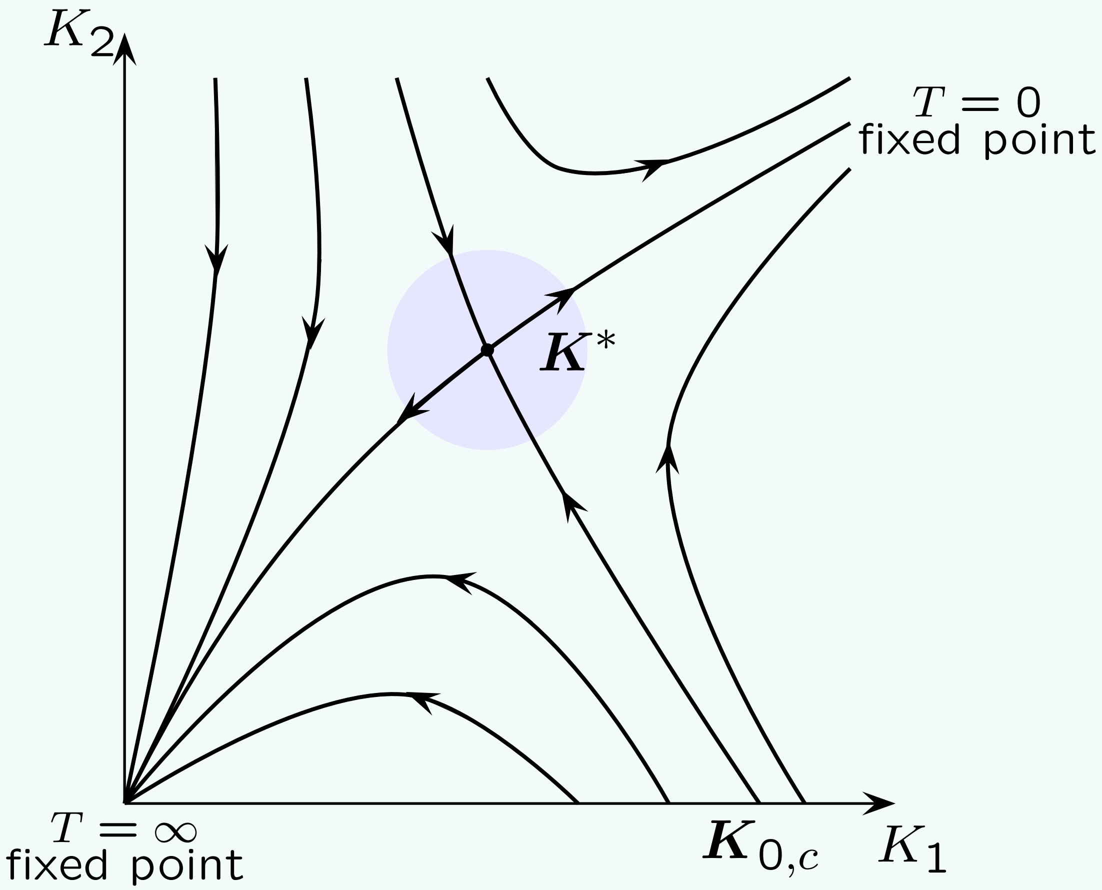
- Each such fixed point will have a domain or *basin of attraction*, or collection of physical systems, that iterate to it under the renormalization group flow. These domains of attraction constitute the various observed *universality classes* of critical behaviour.

- If $\boldsymbol{K}^*$ is non-zero and finite, it corresponds to a system at a finite temperature and thus $\xi(\boldsymbol{K}^*) > 0$ is non-zero (finite for an off-critical system or infinite for a critical system). Hence a trivial fixed point (which has $\xi(\boldsymbol{K}^*) = 0$) can only occur at $\boldsymbol{K}^* = 0$ $(T = \infty)$ or $\|\boldsymbol{K}^*\| = \infty$ $(T = 0)$.

- It follows that a non-trivial fixed point must be unstable — since points near a non-trivial fixed point with $\xi < \infty$ must ultimately iterate to a trivial fixed point on the boundary of the thermodynamic space $(T = 0$ or $T = \infty)$.

Linearization Around a Fixed Point

- Neglecting further neighbour interactions, an RG flow can be visualized by projecting onto a 2-d space spanned by the nearest and next-nearest neighbour interactions K_1, K_2:



- Suppose $\boldsymbol{K}_{0,c}$ is an initial critical system that converges to the non-trivial fixed point $\boldsymbol{K}^*$. Then if we start with $\boldsymbol{K}_0$ sufficiently close to $\boldsymbol{K}_{0,c}$, we would expect $\boldsymbol{K}_\ell$ for some large ℓ to closely approach $\boldsymbol{K}^*$ before diverging away to a trivial fixed point.

- Linearizing at the non-trivial fixed point, we write

$$\boxed{\boldsymbol{K}_\ell = \boldsymbol{K}^* + \boldsymbol{k}_\ell, \qquad \boldsymbol{k}_\ell \text{ small for } \ell \approx L}$$

Linearized RG Equations

- The linearized RG equations are given by the Jacobi matrix

$$\boldsymbol{k}_{\ell+1} \approx \mathcal{L}_b\, \boldsymbol{k}_\ell, \qquad \mathcal{L}_b = \left[\left. \frac{\partial K'_A}{\partial K_B} \right|_{\boldsymbol{K}^*} \right] = \mathcal{L}_b(A, B) = \text{matrix}, \qquad A, B \subset \Lambda$$

- Assuming that the matrix $\mathcal{L}_b$ has a complete set of orthonormal eigenvectors $\boldsymbol{\phi}_i$ with eigenvalues $\Lambda_i = \Lambda_i(b)$, $i = 1, 2, \ldots$ leads to the eigenvalue equations

$$\boxed{\mathcal{L}_b\, \boldsymbol{\phi}_i = \Lambda_i \boldsymbol{\phi}_i}$$

- The semigroup property $\mathcal{L}_b \mathcal{L}_{b'} = \mathcal{L}_{bb'} = \mathcal{L}_{b'} \mathcal{L}_b$ under matrix multiplication gives

$$\Lambda_i(b)\Lambda_i(b') = \Lambda_i(bb') \quad \Rightarrow \quad \Lambda_i(b) = b^{y_i}, \qquad y_i = \text{RG exponents}$$

- Using the complete set of basis vectors $\boldsymbol{\phi}_i$, we can decompose

$$\boldsymbol{k}_L = \sum_i u_i \boldsymbol{\phi}_i$$

where the coordinates u_i are called *scaling fields* and where, by linearization, $\boldsymbol{K}^*$ is the origin with coordinates $u_i = 0$. Thus

$$\boldsymbol{k}_{L+n} = \mathcal{L}_b^n \boldsymbol{k}_L = \mathcal{L}_b^n (\sum_i u_i \boldsymbol{\phi}_i) = \sum_i u_i \mathcal{L}_b^n \boldsymbol{\phi}_i = \sum_i u_i \Lambda_i^n \boldsymbol{\phi}_i = \sum_i u_i\, b^{n y_i} \boldsymbol{\phi}_i$$

$$\boxed{\mathcal{L}_b^n : \quad u_i \mapsto b^{n y_i} u_i}$$

Relevant and Irrelevant Scaling Fields

- If $|\Lambda_i| > 1$ $(y_i > 0)$, the effect of the scaling field u_i will grow under further iteration and so is designated *relevant*. Otherwise, if $|\Lambda_i| < 1$ $(y_i < 0)$, the scaling field will have little effect after further iteration and so is designated *irrelevant*. The case $|\Lambda_i| = 1$ $(y_i = 0)$ is *marginal*.

- In terms of the scaling fields u_i, we see that the free energy and correlation length are generalized homogeneous functions

$$\boxed{\begin{aligned} \xi(u_1, u_2, \ldots) &= b^n\, \xi(b^{ny_1}u_1, b^{ny_2}u_2, \ldots) \\ \psi(u_1, u_2, \ldots) &= b^{-dn}\, \psi(b^{ny_1}u_1, b^{ny_2}u_2, \ldots) \end{aligned}}$$

where $\Lambda_i = b^{y_i}$ and $b^n > 1$ is arbitrary.

- At criticality, $\boldsymbol{K}_\ell \to \boldsymbol{K}^*$ and hence $\boldsymbol{k}_\ell \to 0$ as $\ell \to \infty$. Accordingly, $b^{ny_i}u_i \to 0$ as $n \to \infty$ if u_i is irrelevant and $u_i = 0$ at criticality if u_i is relevant.

- For simple Ising magnetic systems there are just two relevant scaling fields

$$u_1 \sim t, \qquad u_2 \sim h, \qquad t, h \to 0$$

where we assume that $u_1 = u_1(t)$ and $u_2 = u_2(h)$ are analytic and u_n with $n > 2$ are irrelevant so that $y_1 = y_t$, $y_2 = y_h > 0$ and $y_i < 0$ for $i > 2$.

Hyperscaling

- Setting $u_1 = t$ and $u_2 = h = 0$ into the generalized homogeneous relation for the correlation length ξ gives

$$\xi(t,0) = b^n \, \xi(b^{ny_1} t, 0)$$

where here and in the sequel we omit irrelevant fields.

Choosing $b^n = |t|^{-1/y_1}$ gives

$$\xi(t,0) = |t|^{-1/y_1} \xi(\pm 1, 0) \sim |t|^{-\nu}, \qquad \nu = \frac{1}{y_1}$$

- Similarly, setting $h = 0$ and $u_2 = 0$ gives

$$\psi_0(t) = \psi(t,0) = b^{-dn} \, \psi(b^{ny_1} t, 0) = b^{-dn} \psi_0(b^{ny_1} t)$$

and

$$\psi_0''(t) = b^{n(2y_1 - d)} \, \psi_0''(b^{ny_1} t)$$

Choosing $b^n = |t|^{-1/y_1}$ gives

$$C_0 \sim \psi_0''(t) = |t|^{-(2-d/y_1)} \, \psi_0''(\pm 1) \sim |t|^{-\alpha}$$

with the *hyperscaling relation*

$$\boxed{2 - \alpha = \frac{d}{y_1} = d\nu, \qquad y_1 = y_t}$$

Gap Exponent and Universal Scaling Forms

- Similarly, setting $u_1 = t$ and $u_2 = h$ into the generalized homogeneous relation for the free energy ψ gives

$$\psi(t,h) = b^{-dn}\psi(b^{ny_1}t, b^{ny_2}h) = \frac{1}{\lambda}\psi(\lambda^{y_1/d}t, \lambda^{y_2/d}h), \qquad \lambda = b^{dn}$$

so

$$m(t,h) = \frac{\partial\psi}{\partial h}(t,h) = b^{n(y_2-d)}\frac{\partial\psi}{\partial h}(b^{ny_1}t, b^{ny_2}h)$$

- Setting $h = 0$ and choosing $b^n = (-t)^{-1/y_1}$ with $t < 0$ so that $T < T_c$ gives

$$m_0(t) \sim \frac{\partial\psi}{\partial h}(t,0) = (-t)^{(d-y_2)/y_1}\frac{\partial\psi}{\partial h}(-1,0) \sim (-t)^{\beta}, \qquad \beta = \frac{d-y_2}{y_1} = \frac{1-\frac{y_2}{d}}{\frac{y_1}{d}}$$

where $\frac{\partial\psi}{\partial h}(t,0) \equiv 0$ for $t > 0$, that is, $T > T_c$.

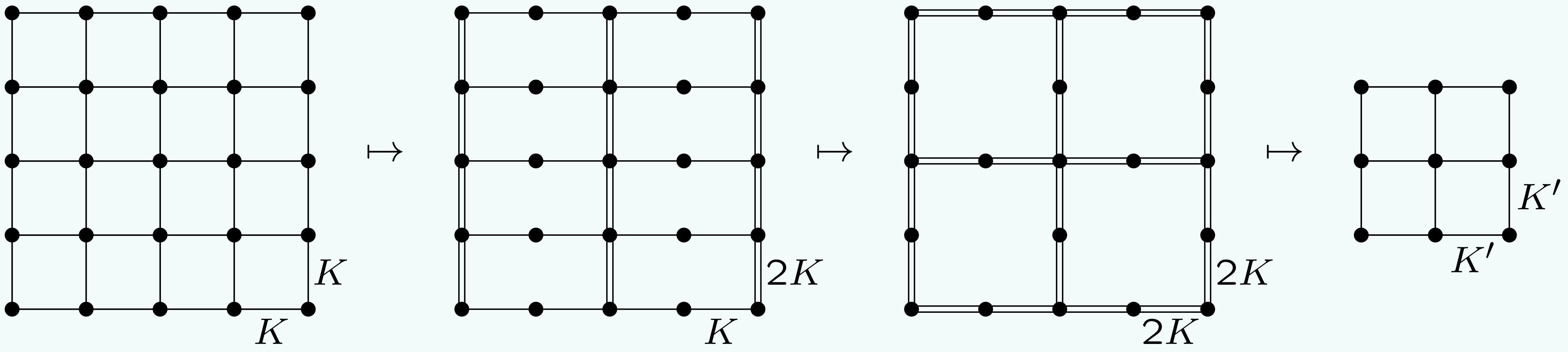
- Note also that by setting $b^n = |t|^{-1/y_1}$ we obtain *universal scaling forms* asymptotically close to the critical point

$$\boxed{\begin{aligned} \psi(t,h) &= |t|^{d/y_1}\psi\left(\pm 1, \frac{h}{|t|^{y_2/y_1}}\right) = |t|^{2-\alpha}F_{\pm}\left(\frac{h}{|t|^{\Delta}}\right) \\ m(t,h) &= (-t)^{\beta}M_{-}\left(\frac{h}{|t|^{\Delta}}\right) \end{aligned}}$$

where $\Delta = y_2/y_1 = y_h/y_t$ is called the *gap exponent* and the *scaling functions* $F_{\pm}, M_{-}$ are functions of a single variable.

Migdal-Kadanoff Bond Moving Approximation

- An approximate renormalization group transformation can be implemented by Migdal-Kadanoff bond moving. Consider the square lattice Ising model with nearest-neighbour interactions along the bonds of the lattice with periodic boundary conditions. The Migdal-Kadanoff bond moving approximation for $b = d = 2$ on the square lattice is implemented graphically:



- The algorithm is as follows:

(i) Group the faces into blocks of 2×2 faces.

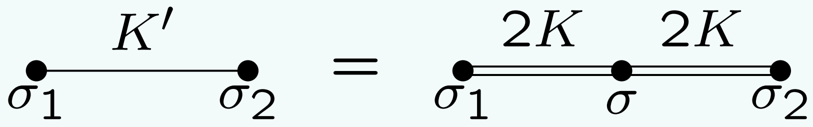
(ii) Within each 2×2 block, move the internal bonds by parallel translation to the perimeter of the block. This rescales the original lattice to a square lattice with rescaling factor $b = 2$.

(iii) In this way, the original bonds are replaced with double bonds with an extra spin in the center of each double bond.

(iv) Decimate (sum out) the extra spins so that the interaction $2K$ is replaced by K'.

Migdal-Kadanoff Decimation and RG Equation

- The extra spins at the centers of the double bonds can be decimated (summed out) using the identity



$$Ae^{K'\sigma_1\sigma_2} = \sum_{\sigma=\pm 1} e^{2K\sigma(\sigma_1+\sigma_2)} = 2\cosh[2K(\sigma_1+\sigma_2)] = 2\cosh[2K(1+\sigma_1\sigma_2)]$$

which is equivalent to the equations

$$Ae^{K'} = 2\cosh 4K, \qquad Ae^{-K'} = 2$$

- It follows that

$$e^{2K'} = \cosh 4K = \tfrac{1}{2}(e^{4K} + e^{-4K})$$

and

$$\tanh K' = \frac{e^{2K'}-1}{e^{2K'}+1} = \frac{e^{4K}+e^{-4K}-2}{e^{4K}+e^{-4K}+2} = \frac{(e^{2K}-e^{-2K})^2}{(e^{2K}+e^{-2K})^2} = \tanh^2 2K$$

- The transcendental Migdal-Kadanoff RG equation is thus

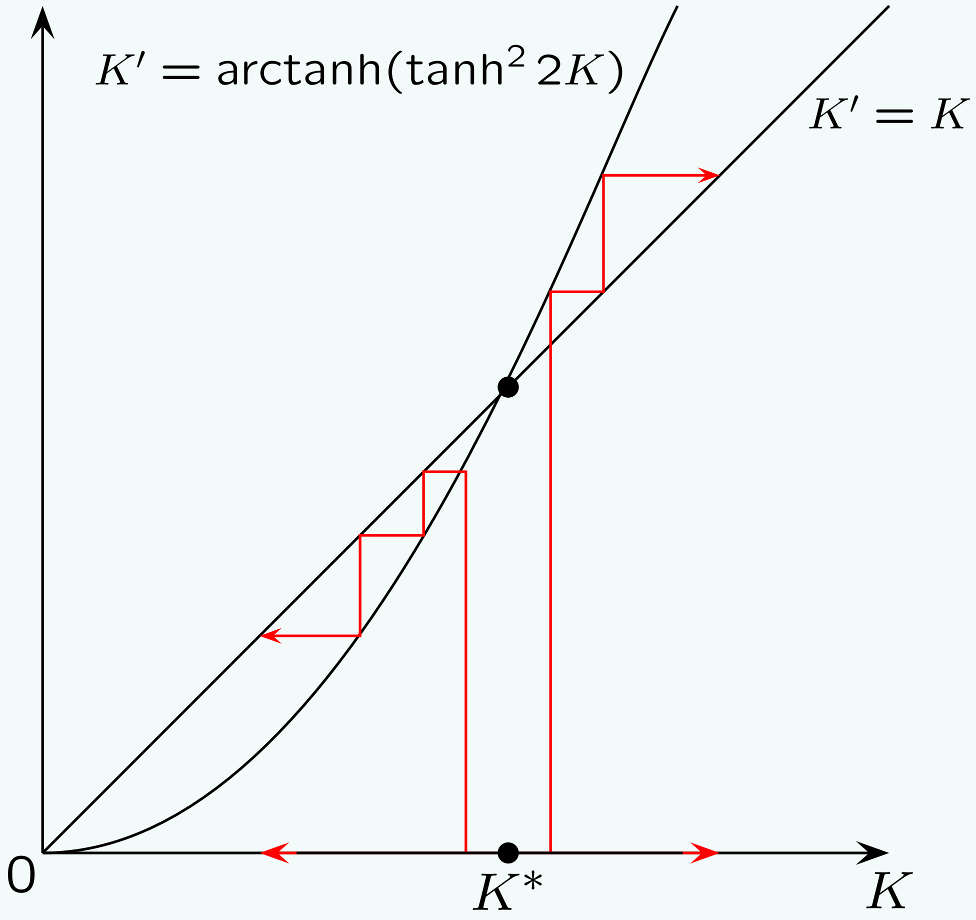
$$\boxed{K' = \text{arctanh}(\tanh^2 2K)}$$

Graphical Solution of Migdal-Kadanoff RG Equation

- The Migdal-Kadanoff RG equation $K' = \text{arctanh}(\tanh^2 2K)$ can be solved graphically and numerically. There is an unstable fixed point at $K^* = 0.3047$. This is to be compared with the exact critical point given by

$$K^* = \frac{1}{2}\log(1+\sqrt{2}) = 0.4407$$

- Starting near $K = K^*$ and iterating graphically gives:



Migdal Kadanoff Linearization with Arbitrary b and $d = 2$

- For arbitrary $b > 1$ and $d = 2$, the RG equation is

$$\boxed{\tanh K' = \tanh^b(bK), \qquad \tanh K^* = \tanh^b(bK^*)}$$

- Linearizing gives $\mathcal{L}_b = \left.\dfrac{dK'}{dK}\right|_{K^*}$ with

$$\operatorname{sech}^2 K' \frac{dK'}{dK} = b^2 \tanh^{b-1}(bK) \operatorname{sech}^2(bK)$$

so that

$$\mathcal{L}_b = \frac{b^2 \tanh K^* \operatorname{sech}^2(bK^*)}{\operatorname{sech}^2 K^* \tanh(bK^*)} = \frac{b^2 \sinh 2K^*}{\sinh 2bK^*} = \Lambda_1 = b^{y_1}$$

since

$$\frac{\tanh K^*}{\operatorname{sech}^2 K^*} = \sinh K^* \cosh K^* = \tfrac{1}{2} \sinh 2K^*$$

- For arbitrary $b > 1$ and d, the RG equation becomes

$$\boxed{\tanh K' = \tanh^b(b^{d-1}K), \qquad \tanh K^* = \tanh^b(b^{d-1}K^*)}$$

- Given b and d, the solution is obtained by solving for K^*, Λ_1 and y_1 in that order. The correlation exponent ν is then given by hyperscaling

$$\boxed{\nu = \frac{2-\alpha}{d} = \frac{1}{y_1}}$$

Migdal Kadanoff Results for $d = 2$

- For $b = 2$, we find

$$\boxed{K^* = 0.3047, \quad \Lambda_1 = 1.679, \quad y_1 = 0.7472, \quad \nu = 1.338}$$

compared with the exact results

$$\boxed{K^* = K_c = 0.4407, \qquad y_1 = 1, \qquad \nu = 1}$$

- The renormalization group flow equations make sense for $b > 1$ non-integer. If we consider the limit $b \to 1+$, we find

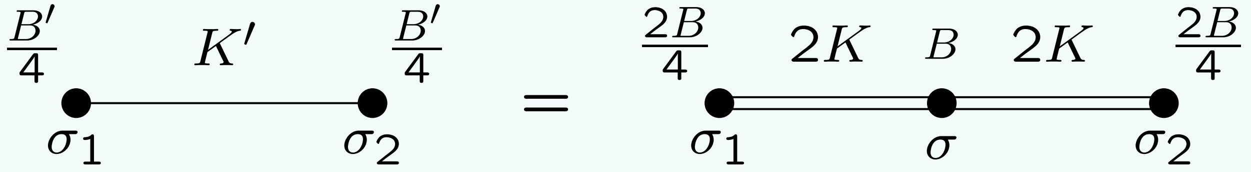
$$\boxed{K^* = K_c = 0.4407, \qquad y_1 = 0.754, \qquad \nu = 1.32}$$

These values are better than the $b = 2$ values and are reasonable estimates given the crudeness of the approximation.

Migdal-Kadanoff in a Magnetic Field

- It is also possible to include a magnetic field into the Migdal-Kadanoff RG flow equations. We just need to attach a weight $B/4$ to each site at the ends of the bonds that we move.

- On the square lattice, this leads to the modified decimation



$$\begin{aligned} Ae^{K'\sigma_1\sigma_2+B'(\sigma_1+\sigma_2)/4} &= \sum_{\sigma=\pm 1} e^{2K\sigma(\sigma_1+\sigma_2)+B\sigma+B(\sigma_1+\sigma_2)/2} \\ &= e^{B(\sigma_1+\sigma_2)/2}\, 2\cosh[2K(\sigma_1+\sigma_2)+B] \end{aligned}$$

or equivalently

$$Ae^{K'+B'/2} = 2\cosh(4K+B)\,e^{B}, \quad Ae^{K'-B'/2} = 2\cosh(4K-B)\,e^{-B}, \quad Ae^{-K'} = 2\cosh B$$

- Hence

$$\begin{aligned} e^{4K'} &= \frac{\cosh(4K+B)\cosh(4K-B)}{\cosh^2 B} = \cosh^2 4K + O(B^2) \\ e^{B'} &= e^{2B}\frac{\cosh(4K+B)}{\cosh(4K-B)} = 1 + (2+2\tanh 4K)B + O(B^2) \end{aligned}$$

which on linearization yields

$$\boxed{\frac{\partial K'}{\partial K} = \frac{4\sinh 2K^*}{\sinh 4K^*} = \frac{2}{\cosh 2K^*} = \Lambda_1, \qquad \frac{\partial K'}{\partial B} = 0, \qquad \left.\frac{\partial B'}{\partial B}\right|_{(K^*,0)} = 2 + 2\tanh 4K^* = \Lambda_2}$$

Linearized Migdal-Kadanoff in a Magnetic Field

- In a magnetic field, there is an unstable fixed point at $(K, B) = (K^*, 0)$ with K^* as before.
- We find

$$\mathcal{L}_b = \begin{pmatrix} \frac{\partial K'}{\partial K} & \frac{\partial B'}{\partial K} \\ \frac{\partial K'}{\partial B} & \frac{\partial B'}{\partial B} \end{pmatrix}\Bigg|_{(K^*,0)} = \begin{pmatrix} \Lambda_1 & * \\ 0 & \Lambda_2 \end{pmatrix}$$

and with $b = 2$

$$\Lambda_1 = b^{y_1} = 1.679, \qquad y_1 = 0.754$$

as before and

$$\boxed{\Lambda_2 = b^{y_2} = 3.679, \qquad y_2 = 1.879, \qquad \beta = \frac{d - y_2}{y_1} = 0.162}$$

whereas the exact values are

$$\boxed{y_2 = \frac{15}{8} = 1.875, \qquad \beta = \frac{1}{8} = 0.125, \qquad \Delta = \frac{y_2}{y_1} = \frac{15}{8}}$$

- It has not been shown that an RG transformation with all the required properties actually exists. In fact the usual (real-space) transformations seem to exhibit unwanted peculiarities (Griffiths and Pearce 1978). In practice, there is no way of estimating the accuracy of an approximate transformation and no systematic way to improve the results. In fact, attempts in this direction usually end up giving worse results.

10: Simple and Random Walks

28. One-dimensional random walk
29. Walks on graphs and hypercubic lattices
30. Return probability and Polya's theorem

George Polya (1887–1985)

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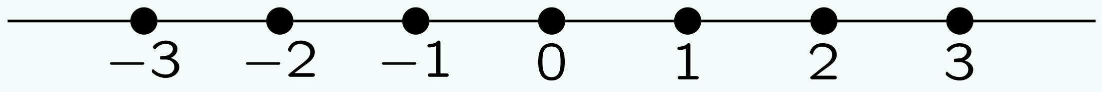
Simple One-Dimensional Walk

- Consider simple walks on an infinite one-dimensional lattice starting at the origin 0:



- These walks can be enumerated symbolically. At each step, there is either a step to the right represented by z or a step to the left represented by z^{-1} where z is a formal parameter. The set of 1-step walks can be represented by the Laurent polynomial

$$z+z^{-1}$$

Similarly, the set of four 2-step walks is enumerated as

$$zz+zz^{-1}+z^{-1}z+z^{-1}z^{-1}=(z+z^{-1})^2=z^2+2+z^{-2}$$

- More generally, the set of 2^n n-step walks can be expanded as the *generating function*

$$\boxed{(z+z^{-1})^n=\sum_{k=-n \text{ mod } 2}^{n} w_n(k)z^k}$$

where

$$\boxed{w_n(k)=\binom{n}{\frac{1}{2}(n-k)}=\{\text{number of distinct } n\text{-step walks from the origin 0 to } k\}}$$

- In accord with the binomial expansion, setting $z=1$ counts the total number of n step walks

$$2^n=(1+1)^n=\sum_{\substack{k=-n\\ k=n \text{ mod } 2}}^{n}\binom{n}{\frac{1}{2}(n-k)}$$

Generating Function for All Walks

- The generating function can be inverted to find $w_n(k)$, the number of distinct n-step walks from 0 to k.
- Write $z = e^{i\phi}$ and observe that

$$\frac{1}{2\pi}\int_0^{2\pi} d\phi\, e^{ik\phi} \;=\; \delta(k,0) \;=\; \begin{cases} 1, & k=0 \\ 0, & \text{otherwise} \end{cases} \qquad\qquad k \in \mathbb{Z}$$

- Acting on the left and right hand sides of the generating function for $(z+z^{-1})^n$ with $\int_0^{2\pi} d\phi\, e^{-ik\phi}$ and using $z + z^{-1} = 2\cos\phi$ and the above identity gives

$$w_n(k) = \frac{1}{2\pi}\int_0^{2\pi} d\phi\, e^{-ik\phi}(2\cos\phi)^n$$

- It follows that the generating function for all walks (of arbitrary length) from 0 to k is

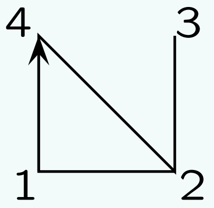
$$\boxed{\Gamma(k;z) \;=\; \sum_{n=0}^{\infty} w_n(k) z^n \;=\; \frac{1}{2\pi}\int_0^{2\pi} d\phi\, \frac{e^{-ik\phi}}{1-2z\cos\phi}}$$

where we used the geometric series which is valid provided $2|z| < 1$.

Simple Walks on Finite Graphs

- A one-dimensional chain and other lattices are particular examples of graphs. It is possible to enumerate walks on arbitrary graphs. Consider a walk on an oriented (or non-oriented) finite graph G specified by an adjacency matrix A with entriesA_{ij}

$G =$



$$A_{ij} = \{\#\ \text{1-step paths from } i \text{ to } j\}$$

$$A = \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

- From the definition of matrix product, it follows that

$$(A^n)_{ij} = \{\text{number of distinct } n\text{-step paths from } i \text{ to } j\}$$

- Assume that A is diagonalizable which is the case if A is real symmetric or A has distinct eigenvalues. The generating function of all walks (in an arbitrary number of steps) from i to j on the graph G, for $\max_k |z\lambda_k| < 1$, is then

$$\boxed{\Gamma(i \to j; z) = \sum_{n=0}^{\infty} w_n(i \to j) z^n = \sum_{n=0}^{\infty} (A^n)_{ij} z^n = [(I - zA)^{-1}]_{ij} = \frac{\text{cofactor}_{ji}(I - zA)}{\det(I - zA)}}$$

- Suppose further that the graph is *regular* in the sense that all N nodes of the graph are equivalent. Then the generating function for all returning walks (of an arbitrary number of steps) from a particular node of the graph i back to i is

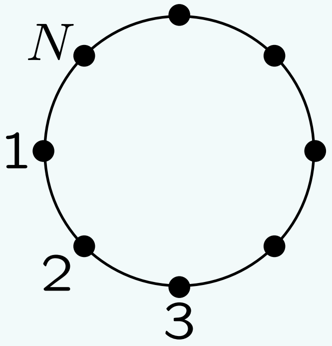
$$\boxed{\Gamma(i \to i; z) = \frac{1}{N} \sum_{i=1}^{N} [(I - zA)^{-1}]_{ii} = \frac{1}{N} \text{Tr}(I - zA)^{-1} = \frac{1}{N} \sum_{k=1}^{N} (1 - z\lambda_k)^{-1}}$$

where λ_k, $k = 1, 2, \ldots, N$ are the eigenvalues of the adjacency matrix A of G.

Simple Walks on a Periodic Chain

- For a (regular) finite periodic chain, the adjacency matrix A is cyclic and symmetric

$G =$



$$A = \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 & 1 \\ 1 & 0 & 1 & \cdots & 0 & 0 \\ 0 & 1 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 0 & 1 \\ 1 & 0 & 0 & \cdots & 1 & 0 \end{pmatrix} = N \times N \text{ matrix}$$

- The eigenvalue equations are cyclic finite difference equations

$$A\boldsymbol{x} = \lambda \boldsymbol{x}, \qquad x_{k-1} + x_{k+1} = \lambda x_k, \qquad x_{k+N} \equiv x_k, \qquad k = 1, 2, \ldots, N$$

To solve this, try $x_k = x^k$. Then

$$\lambda = x + x^{-1}, \qquad x_N = x^N = \lambda x_1 - x_2 = x(x + x^{-1}) - x^2 = 1$$

in accord with cyclicity $x_{k+N} = x^{k+N} = x^k x^N = x^k = x_k$. Choosing $x = e^{2\pi i/N}$ gives

$$x_k = e^{2\pi i k/N}, \qquad \lambda_k = 2\cos\frac{2\pi k}{N}, \qquad k = 1, 2, \ldots, N$$

- The generating function for all returning walks (of an arbitrary number of steps) from i to i on a periodic chain is thus

$$\boxed{\Gamma(i \to i; z) = \frac{1}{N}\sum_{k=1}^{N} \frac{1}{1 - 2z\cos\frac{2\pi k}{N}} \to \frac{1}{2\pi}\int_0^{2\pi} \frac{d\phi}{1 - 2z\cos\phi}, \qquad N \to \infty}$$

and we recover the previous result for an infinite one-dimensional chain.

Random Walks on Hypercubic Lattices

- Simple walks on a one-dimensional lattice are straightforwardly generalized to d-dimensional hypercubic lattices. The nodes of a hypercubic lattice are given by lattice (integer) vectors

$$\boldsymbol{k} = (k_1, k_2, \ldots, k_d) \in \mathbb{Z}^d$$

- On a hypercubic lattice, the generating function for all walks (of arbitrary length) from $\mathbf{0}$ to $\boldsymbol{k}$ is

$$\boxed{\Gamma(\boldsymbol{k}; z) = \left(\frac{1}{2\pi}\right)^d \int_0^{2\pi} d\phi_1 \cdots \int_0^{2\pi} d\phi_d \, \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{\phi}}}{1 - 2z\sum_{n=1}^{d} \cos\phi_n}}$$

where $\boldsymbol{\phi} = (\phi_1, \phi_2, \ldots, \phi_d)$.

- Consider a random walk on a hypercubic lattice, such that, each step of the walk has probability p. Then the probability that an n-step walk starting at the origin 0 will lead to $\boldsymbol{k}$ is given by

$$p_n(\boldsymbol{k}) = w_n(\boldsymbol{k})p^n$$

and the generating function for these probabilities is

$$P(\boldsymbol{k}; z) = \sum_{n=0}^{\infty} p_n(\boldsymbol{k})z^n = \sum_{n=0}^{\infty} w_n(\boldsymbol{k})p^n z^n = \Gamma(\boldsymbol{k}; pz)$$

- In this way, all such formulas for random walks are obtained from the corresponding formulas for simple walks by replacing z with pz.

Probability of First Return

- The probability that an n-step walk returns to the origin after *exactly* n steps is

$$p_n = p_n(\mathbf{0}) = \{\text{probability that a walk returns to the origin after } n \text{ steps}\}$$

However, this may not be the *first time* that the walk has returned to the origin. Let

$$f_n = \{\text{probability that a walk returns to the origin for the } \textit{first time} \text{ after } n \text{ steps}\}$$

Then f_n and p_n are related by the recursion

$$p_n = f_1 p_{n-1} + f_2 p_{n-2} + \cdots + f_n p_0$$

- Acting on this by $\sum_{n=1}^{\infty} z^n$ and using the Cauchy product gives the relation

$$P(z) - 1 = F(z)P(z)$$

between the generating functions

$$P(z) = P(\mathbf{0}; z) = \sum_{n=0}^{\infty} p_n z^n, \qquad F(z) = \sum_{n=1}^{\infty} f_n z^n$$

- It follows that

$$F(z) = 1 - \frac{1}{P(z)}$$

and the probability R of returning to the origin is given by

$$\boxed{R = \sum_{n=1}^{\infty} f_n = F(1) = 1 - \frac{1}{P(1)} = \begin{cases} 1, & P(1) = \infty \\ < 1, & P(1) < \infty \end{cases}}$$

Polya's Theorem

- If the steps of a random walk on a d-dimensional hypercubic lattice are equally probable

$$\boxed{p = \frac{1}{2d}, \qquad P(z) = P(\mathbf{0}; z) = \left(\frac{1}{2\pi}\right)^d \int_0^{2\pi} d\phi_1 \cdots \int_0^{2\pi} d\phi_d \left[1 - \frac{z}{d}\sum_{n=1}^{d} \cos\phi_n\right]^{-1}}$$

- The integrand of $P(z)$ with $z = 1$ only diverges in the limit

$$\boldsymbol{r} = \boldsymbol{\phi} = (\phi_1, \phi_2, \ldots, \phi_d) \to 0, \qquad z = 1$$

$$1 - \frac{1}{d}\sum_{n=1}^{d} \cos\phi_n \;\approx\; 1 - \frac{1}{d}\sum_{n=1}^{d}(1 - \tfrac{1}{2}\phi_n^2) \;\approx\; \frac{1}{2d}\sum_{n=1}^{d}\phi_n^2 \;=\; \frac{\boldsymbol{r}^2}{2d}$$

Setting $r = |\boldsymbol{r}|$ and using $dV \sim r^{d-1}dr$, the behaviour of the integral for $P(1)$ is given by

$$\int d\boldsymbol{\phi}\,[\ldots]^{-1} \sim \int_{|\boldsymbol{r}|\le\epsilon} \frac{dV}{\boldsymbol{r}^2} \sim \int_0^{\epsilon} \frac{r^{d-1}}{r^2}\,dr \;=\; \begin{cases} \displaystyle\int_0^{\epsilon} r^{d-3}dr = \left[\frac{r^{d-2}}{d-2}\right]_0^{\epsilon} = \begin{cases} \infty, & d = 1 \\ < \infty, & d \ge 3 \end{cases} \\ \displaystyle\int_0^{\epsilon} \frac{dr}{r} = \Big[\log r\Big]_0^{\epsilon} = \infty, & d = 2 \end{cases}$$

Theorem 1 (Polya's Theorem) *The probability of return to the origin for a random walk on a d-dimensional hypercubic lattice is*

$$\boxed{R = \begin{cases} 1, & d = 1, 2 \\ < 1, & d \ge 3 \end{cases}}$$

The walk is called recurrent if $d = 1, 2$ (the walk returns to the origin with probability 1). For $d \ge 3$, the walk is transient (not guaranteed to return to the origin).

Mean-Square Displacement

- Consider a random walk on an infinite one-dimensional chain. For a given walk, let

$$R_n = \{\text{displacement after } n \text{ steps}\}$$

Since $w_n(k) = w_n(-k)$, the mean displacement over all n-step walks vanishes

$$\langle R_n \rangle = \sum_{k=-n}^{n} k\, p_n(k) = \sum_{k=-n}^{n} k\, w_n(k)\, p^n = 0$$

- To measure the average extent of the walk we use the mean square displacement

$$\boxed{\langle R_n^2 \rangle = \sum_{k=-n}^{n} k^2\, p_n(k) = -\frac{\partial^2}{\partial \phi^2}\Big[\widehat{p}_n(\phi)\Big]_{\phi=0}, \qquad \widehat{p}_n(\phi) = \sum_{k=-n}^{n} e^{ik\phi} p_n(k)}$$

- Here $\widehat{p}_n(\phi)$ is the coefficient of z^n in the Fourier transform

$$\begin{aligned} \widehat{P}(\phi) &= \sum_{n=0}^{\infty} z^n\, \widehat{p}_n(\phi) = \sum_{n=0}^{\infty} z^n \sum_{k=-n}^{n} e^{ik\phi} p_n(k) = \sum_{n=0}^{\infty} (pz)^n \sum_{k=-n}^{n} w_n(k) e^{ik\phi} \\ &= \sum_{n=0}^{\infty} (pz)^n (e^{i\phi} + e^{-i\phi})^n = \frac{1}{1 - 2pz\cos\phi}, \qquad |z| < \frac{1}{2p} \end{aligned}$$

since, with z replaced by $e^{i\phi}$,

$$(e^{i\phi} + e^{-i\phi})^n = \sum_{k=-n}^{n} w_n(k) e^{ik\phi}$$

Lattice Structure Factor

- It follows that

$$\begin{aligned}\langle R_n^2\rangle &= \operatorname*{coeff}_{z^n}\left\{-\frac{\partial^2}{\partial\phi^2}\left[\frac{1}{1-2pz\cos\phi}\right]_{\phi=0}\right\} = \operatorname*{coeff}_{z^n}\left\{-\frac{\partial^2}{\partial\phi^2}\Big[(2pz)^n\cos^n\phi\Big]_{\phi=0}\right\}\\ &= (2p)^n\left\{-\frac{\partial^2}{\partial\phi^2}\Big[1-\tfrac{1}{2}n\phi^2+\cdots\Big]_{\phi=0}\right\} = n(2p)^n\end{aligned}$$

- In particular, for equally probable steps, $p=\frac{1}{2}$ and the root mean square displacement is

$$\sqrt{\langle R_n^2\rangle} = \sqrt{n}$$

in accord with the central limit theorem.

- More generally, the mean square displacement is given by

$$\langle R_n^2\rangle = -n\,\frac{\partial^2}{\partial\boldsymbol{\phi}^2}\Big[\lambda(\boldsymbol{\phi})\Big]_{\boldsymbol{\phi}=\mathbf{0}} = \sum_{\boldsymbol{k}}\boldsymbol{k}^2 p_1(\boldsymbol{k})$$

where

$$\boxed{\lambda(\boldsymbol{\phi}) = \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{\phi}}p_1(\boldsymbol{k}) = \{\text{lattice structure factor}\}}$$

For a simple one-dimensional walk with $p_1(k)=\frac{1}{2}$,

$$\lambda(\phi) = \tfrac{1}{2}(e^{i\phi}+e^{-i\phi}) = \cos\phi$$

For a walk on a square lattice

$$\lambda(\boldsymbol{\phi}) = \tfrac{1}{2}(\cos\phi_1+\cos\phi_2)$$

11: Percolation

31. Bond and site percolation
32. Percolation in one dimension
33. Percolation on Bethe lattice

John Michael Hammersley (1920–2004)

Renfrey Burnard Potts (1925–2005)

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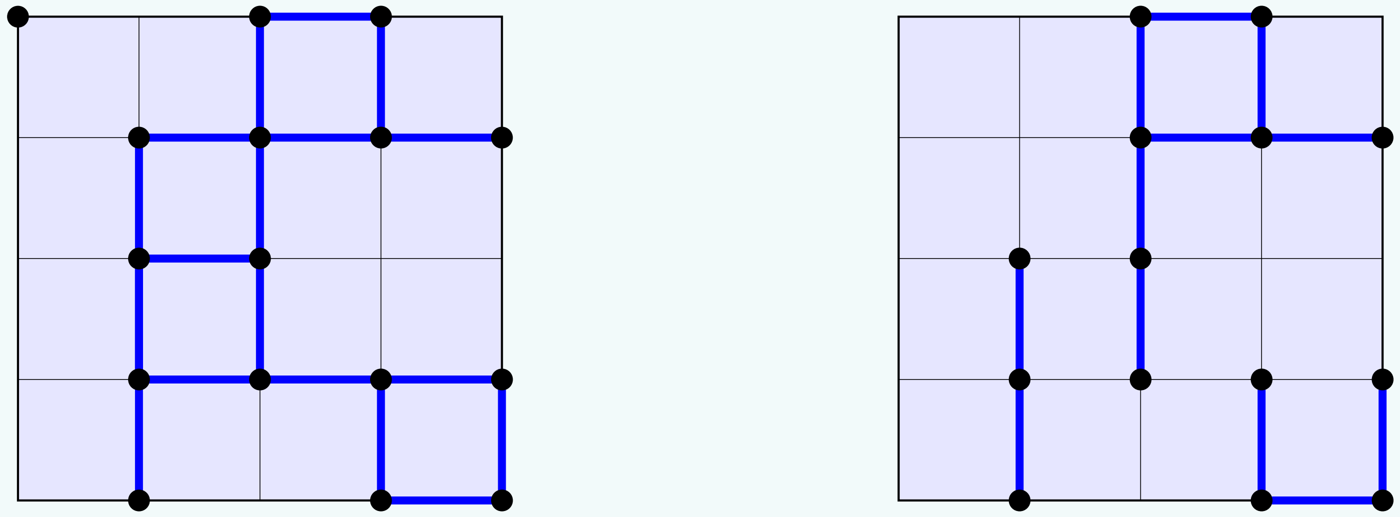
Bond and Site Percolation

- Percolation theory deals with the statistical behaviour of connected clusters in a random graph. Consider an infinite square lattice and suppose $0 \le p \le 1$.



- In site percolation (left), the sites (vertices of the lattice) are occupied randomly (and independently) with probability p. In this case, two occupied sites at opposite ends of the same bond of the lattice are considered to be in the same (connected) cluster, that is, the clusters consist of all sites mutually connected through bonds of the square lattice.
- In bond percolation (right), the bonds (edges of the lattices) are occupied randomly (and independently) with probability p. Two occupied bonds incident to the same site of the lattice are considered to be in the same (connected) cluster, that is, the clusters consist of the connected occupied bonds and the sites at their endpoints.
- Bond and site percolation on the same lattice are generally distinct statistical systems.

Percolation Threshold

- In both site and bond percolation, for small values of p, only small clusters are formed. As p increases, the size of the clusters grow. At a critical probability p_c (percolation threshold), there appears an infinite cluster. As p increases further, the clusters continue to grow until the whole lattice is filled with a single cluster.

- Mathematically, the percolation threshold is defined by

$$\boxed{\begin{aligned} p_c &= \inf\Big\{p : \mathrm{Pr}\{\text{bond/site } j \text{ belongs to an infinite cluster}\} > 0\Big\} \\ &= \sup\Big\{p : \{\text{mean size of the cluster containing } j\} < \infty\Big\} \end{aligned}}$$

- The probability of a site j belonging to an infinite cluster is zero in the low density phase ($p \leq p_c$). In this phase, the mean cluster size is finite. In the high-density phase ($p > p_c$), the probability of a site j belonging to an infinite cluster is strictly positive and the mean cluster size is infinite. Note that, at the critical percolation threshold ($p = p_c$), there is no infinite cluster for $d \geq 2$.

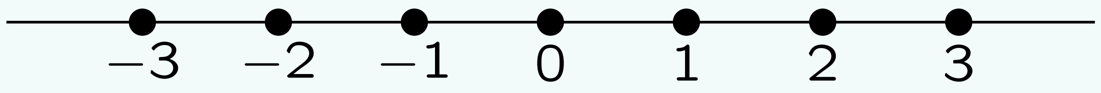
- The percolation thresholds on the square/triangular lattices are

$$p_c^{\text{sq}} = \begin{cases} \frac{1}{2}, & \text{bond} \\ 0.592746\ldots, & \text{site} \end{cases} \qquad p_c^{\text{tri}} = \begin{cases} 0.347296355\ldots = 2\sin\frac{\pi}{18}?, & \text{bond} \\ \frac{1}{2}, & \text{site} \end{cases}$$

- Critical bond percolation on the square lattice and critical site percolation on the triangular lattice can be solved exactly! This is the subject of current research.

Percolation in One-Dimension

- Consider percolation on an infinite one-dimensional lattice with the origin at 0:



On this one-dimensional lattice, bond and site percolation are equivalent so let us use the terminology of site percolation.

- Select a site, say the origin 0. The probability that this site belongs to a cluster of exactly n sites is

$$P_0(p) = 1 - p, \qquad P_n(p) = n(1-p)^2 p^n, \qquad n \geq 1$$

since a linear cluster of $n \geq 1$ occupied sites must terminate with empty sites at each end. The factor n arises since the origin can occur at any position 1 to n along the linear cluster.

- The probability that the origin 0 belongs to an infinite cluster (the percolation probability) vanishes in one dimension

$$\boxed{\begin{aligned} P_\infty(p) \;=\; 1 - \sum_{n=0}^{\infty} P_n(p) \;&=\; p - (1-p)^2 p \frac{d}{dp}\Big(\sum_{n=0}^{\infty} p^n\Big) \\ &=\; p - (1-p)^2 p \frac{d}{dp}\Big(\frac{1}{(1-p)}\Big)\Big) \;=\; p - p \;=\; 0, \quad p < 1 \end{aligned}}$$

Hence $p_c = 1$ and there is no high-density phase.

Mean Size of Finite Clusters

- Since $\sum_{n=0}^{\infty} P_n(p) = 1$, the mean size of finite size clusters containing the origin is

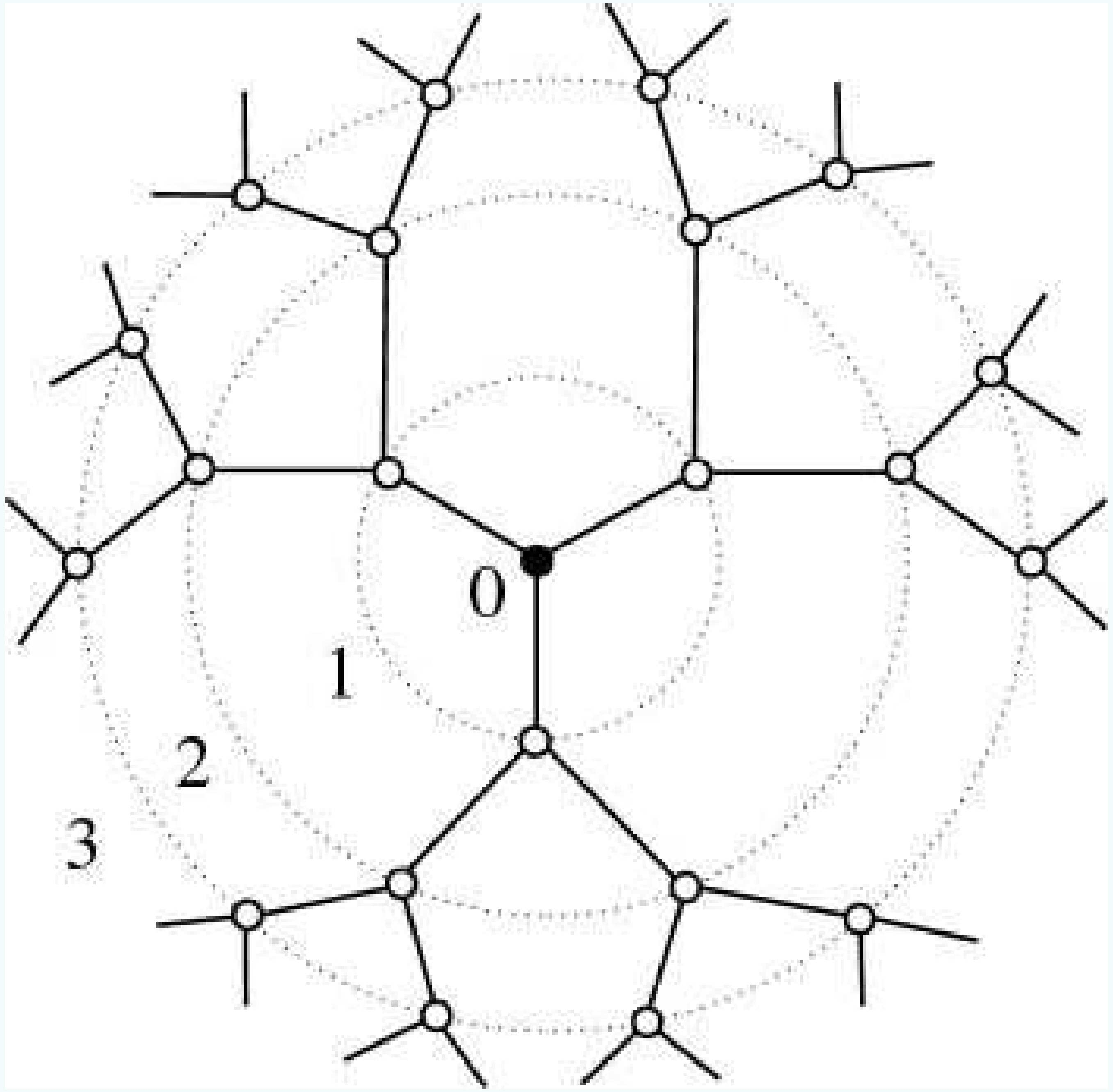
$$\boxed{\begin{aligned} \langle n \rangle &= \sum_{n=0}^{\infty} n P_n(p) \;=\; (1-p)^2 \sum_{n=0}^{\infty} n^2 p^n = (1-p)^2 p \frac{d}{dp}\Big(p \frac{d}{dp} \sum_{n=0}^{\infty} p^n\Big) \\ &= (1-p)^2 p \frac{d}{dp}\Big(p \frac{d}{dp} \frac{1}{1-p}\Big) \;=\; (1-p)^2 p \frac{d}{dp}\Big(\frac{p}{(1-p)^2}\Big) \;=\; \frac{p(1+p)}{1-p} < \infty, \qquad p < 1 \end{aligned}}$$

- Percolation in one dimension is similar to a phase transition at zero temperature. There is only one phase and consequently no phase transition at $p < 1 = p_c$. There is only a phase transition in the limit $p \to p_c = 1$.

- We can define critical exponents for this one-sided phase transition. In particular, the critical exponent γ associated with the divergence of the mean cluster size is given by

$$\langle n \rangle \sim (p_c - p)^{-\gamma}, \qquad p \to p_c-, \qquad \gamma = 1$$

Bethe Lattice



- Bethe lattice with coordination number $z = 3$. The central (root) site is labelled 0. The consecutive surrounding shells are labelled by $k = 1, 2, 3$.

- The Bethe lattice is a connected cycle-free graph (tree) where each node is connected to z neighbours where z is the coordination number. The sites are all equivalent.

- Choosing a central (root) site, all the other sites are arranged in consecutive shells with N_k sites in shell k

$$N_k = z(z-1)^{k-1}, \qquad k = 1, 2, \ldots$$

Site Percolation on Bethe Lattice

- Due to the special properties of the Bethe lattice or Cayley tree, statistical systems on this lattice are often exactly solvable and these solutions are related to the Bethe approximation. For $z = 2$, the Bethe lattice reduces to the one-dimensional chain. For this reason, we are primarily interested in $z \geq 3$.

- We will obtain a mean-field theory of percolation, which exhibits a phase transition for $p_c < 1$, by solving site percolation on the Bethe lattice. The Bethe lattice is not a sensible physical lattice since a finite fraction of the number of sites sits on the boundary (outer shell). In this sense, the lattice has similar properties to the complete graph of the equivalent neighbour model.

- On the Bethe lattice, a cluster of n occupied sites is bounded by $n(z-2)+2$ vacant sites. This is established first for linear clusters and extended to branched clusters by joining linear clusters. Hence the probability that the origin 0 belongs to a cluster of n sites is

$$P_0(p) = 1 - p, \qquad P_n(p) = c_n p^n (1-p)^{n(z-2)+2}, \qquad n \geq 1$$

where c_n is the number of possible n-site clusters that contain the origin 0.

- Hence, for $p \leq p_c$, when there are no infinite clusters

$$\boxed{1 - p + \sum_{n=1}^{\infty} P_n(p) = 1, \qquad P_\infty(p) = 0}$$

This states that, in this case, either the origin is not occupied or it belongs to a *finite* cluster.

Mean Size of Finite Clusters for $p < p_c$

- For $p < p_c$

$$\sum_{n=1}^{\infty} c_n[p(1-p)^{z-2}]^n = \frac{p}{(1-p)^2}$$

Differentiating with respect to p gives

$$\left\{\sum_{n=1}^{\infty} n\, c_n[p(1-p)^{z-2}]^n\right\}\frac{1}{p(1-p)^{z-2}}\frac{d}{dp}\Big[p(1-p)^{z-2}\Big] = \frac{d}{dp}\Big[\frac{p}{(1-p)^2}\Big]$$

- Taking the ratio of the last relations yields

$$\frac{\langle n\rangle}{(1-p)^2}\Big[\frac{1}{p} - \frac{z-2}{1-p}\Big] = \Big[\frac{1}{(1-p)^2} + \frac{2p}{(1-p)^3}\Big]$$

so that the mean size of finite clusters is

$$\boxed{\langle n\rangle \;=\; \frac{p(1+p)}{1-(z-1)p}, \qquad p < p_c = \frac{1}{z-1}}$$

- As in one dimension, the critical exponent γ associated with the divergence of the mean cluster size is given by

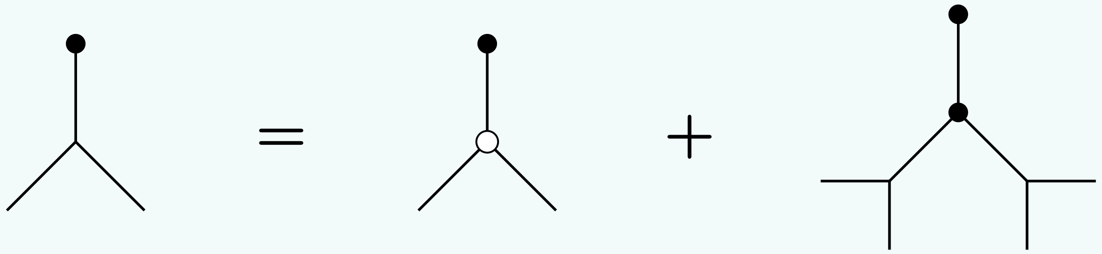
$$\langle n\rangle \sim (p_c - p)^{-\gamma}, \qquad p \to p_c-, \qquad \gamma = 1$$

- If $z = 2$, the critical probability is $p_c = 1$ and these results agree with those of the one-dimensional lattice.

Percolation Mean-Field Equation

- We want to calculate the percolation probability, that is, the probability $P_\infty(p)$ that the origin 0 belongs to an infinite cluster.

- Let $Q(p) \geq 0$ be the probability that a given branch growing from an occupied site j fails to extend to infinity. Then the mean-field equation for $Q(p)$ is



$$Q(p) = (1 - p) + p\, Q(p)^{z-1} \leq 1$$

- Since this has the trivial solution $Q(p) = 1$, it factorizes as

$$\big(Q(p) - 1\big)\big(pQ(p)^{z-2} + pQ(p)^{z-3} + \cdots + pQ(p) + p - 1\big) = 0$$

- For a solution $Q(p) \neq 1$, that is, $Q(p) < 1$ we must have

$$\boxed{p \sum_{j=0}^{z-2} Q(p)^j = 1}$$

If $Q(p) < 1$, we see that LHS $< p(z-1) \leq 1 =$ RHS for $p \leq p_c = \frac{1}{z-1}$. It follows that there are no solutions with $Q(p) < 1$, in this range, and so the unique solution is $Q(p) = 1$. If $p > p_c = \frac{1}{z-1}$, then there is a unique solution, with $0 \leq Q(p) < 1$, such that $Q(p) \to 0$ as $p \to 1$ and $Q(p) \to 1$ as $p \to p_c = \frac{1}{z-1}$. This is the physically relevant solution for $\frac{1}{z-1} = p_c < p \leq 1$.

Bethe Percolation Probability for $z = 2, 3$

- Given the solution $Q(p)$ of the mean-field equation, the required percolation probability is

$$\boxed{P_\infty(p) = 1 - (1-p) - p\,Q(p)^z = p[1 - Q(p)^z], \qquad z \text{ leaves}}$$

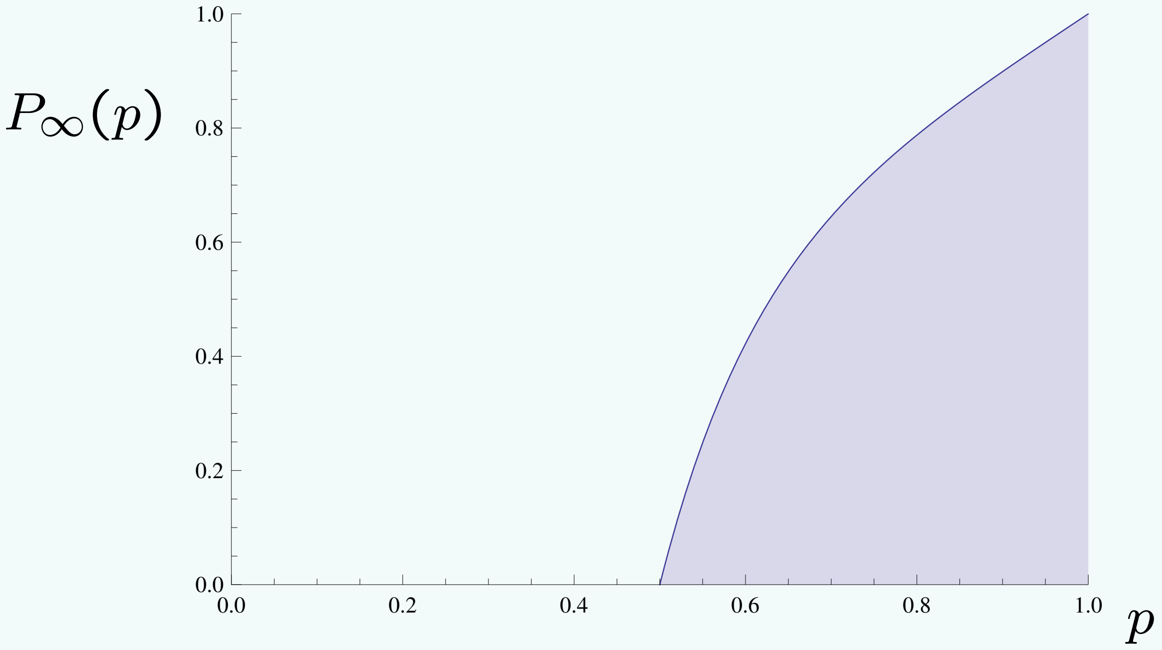
- For $z = 2$, we have $p_c = 1$ and only the trivial solution $Q(p) = 1$ giving $P_\infty(p) = 0$ in accord with the one-dimensional solution. For $z \geq 3$, the mean-field equation admits a non-trivial high-density solution for $\frac{1}{z-1} = p_c < p \leq 1$.

- For $z = 3$,

$$Q(p) = \begin{cases} \frac{1-p}{p}, & p \geq \frac{1}{2} \\ 1, & p \leq \frac{1}{2} \end{cases}$$

which implies $P_\infty(p) = 0$ for $p \leq p_c = \frac{1}{2}$ and for $p > p_c = \frac{1}{2}$

$$\boxed{P_\infty(p) = p\left[1 - \frac{(1-p)^3}{p^3}\right] = \frac{(2p-1)(p^2-p+1)}{p^2} \sim 6(p - \tfrac{1}{2})^\beta, \quad p \to \tfrac{1}{2}+, \quad \beta = 1}$$



- Percolation probability on the Bethe lattice with coordination number $z = 3$.
- The critical point is at $p_c = \frac{1}{2}$. For $p > \frac{1}{2}$ there is a positive probability of finding an infinite (percolating) cluster.

Bethe Critical Exponent β for $z \geq 3$

- More generally, for $p > p_c$, $Q(p)$ and $P_\infty(p)$ are differentiable functions of p. So differentiating the equation

$$\sum_{j=0}^{z-2} Q(p)^j = \frac{1}{p}$$

and using the fact that $Q(p) \to 1$ as $p \to p_c+$ gives

$$Q'(p) = \frac{-1}{p^2 \sum_{j=1}^{z-2} jQ(p)^{j-1}} \to -\frac{2(z-1)^2}{(z-1)(z-2)} = -\frac{2(z-1)}{(z-2)}, \qquad p \to p_c +$$

- Since $P_\infty(p_c) = 0$, it follows that

$$P'_\infty(p) = 1 - Q(p)^z - pzQ(p)^{z-1}Q'(p) \to -\frac{z}{z-1}\Big[-\frac{2(z-1)}{(z-2)}\Big] = \frac{2z}{z-2}, \qquad p \to p_c +$$

- Expanding $P_\infty(p)$ in a Taylor series out to linear order for $z \geq 3$ gives

$$\boxed{P_\infty(p) \sim (p-p_c)^\beta, \qquad \beta = 1}$$

where the associated critical exponent β is a second independent critical exponent.

Percolation and the Potts Model

- Percolation is related to the $q \to 1$ limit of the q-state Potts model with Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \delta(\sigma_i, \sigma_j), \qquad \sigma_j = 1, 2, \ldots, q$$

Formally,

$$\boxed{\text{Percolation} = \lim_{q \to 1} \{q\text{-state Potts model}\}}$$

- Mathematically, this requires a suitable analytic continuation of the q-state Potts model to arbitrary (non-integer) values of q. This can be done using the (stochastic) Fortuin-Kasteleyn interpretation of the q-state Potts model.

- This identification enables a correspondence of thermodynamic functions and associated critical exponents:

Thermodynamic Function	Potts	Percolation	Exponent
deviation from criticality	T	p	
free energy	$\psi(T)$	$\psi(p)$	$2-\alpha$
order parameter	$\left\langle \delta(\sigma_j, 1) - \frac{1}{q} \right\rangle$	$P_\infty(p)$	β
susceptibility	$\chi_0(T)$	$\langle n \rangle$	γ

$$\psi(p) = \sum_{n=1}^{\infty} \frac{1}{n} P_n(p) = \{\text{mean number of clusters per lattice site}\}$$

$$\langle n \rangle = \{\text{mean size of finite clusters}\}$$

Percolation Critical Exponents

- From scaling principles, the critical exponents should satisfy the relations

$$\boxed{\alpha + 2\beta + \gamma = 2, \qquad \gamma = \beta(\delta - 1)}$$

- The two-dimensional site percolation problem has not been solved exactly. However, bond percolation in two dimensions (which is believed to be in the same universality class as site percolation) is exactly solvable at the critical point $p = p_c = \frac{1}{2}$.

- The values for the critical exponents of percolation in various dimensions are:

d	α	β	γ
$d = 1$	1	0	1
$d = 2$	$-2/3$	$5/36$	$43/18$
$d = 3$	≈ -0.6	≈ 0.4	≈ 1.8
$d = \infty$	-1	1	1

- The $d = \infty$ values correspond to the mean-field Bethe lattice values. These values hold for $d \geq 6$. So the *upper critical dimension* for percolation is $d = 6$ for percolation compared to $d = 4$ for the Ising ferromagnet.

- Critical bond percolation on the square lattice is exactly solvable. Details can be found in A. Morin-Duchesne, A. Klümper, P.A. Pearce, *Conformal partition functions of critical percolation from D_3 Thermodynamic Bethe Ansatz equations*, arXiv2017.