

# PRINCIPLES OF STATISTICAL MECHANICS

Paul A. Pearce<sup>1</sup>

*Mathematics Department, University of Melbourne,  
Parkville, Victoria 3052, Australia*

## Abstract

These lectures comprise an introductory course in statistical mechanics. The Gibbs formulation of the canonical ensemble is introduced and illustrated by application to simple models of magnets and fluids, specifically the ideal gas and the magnetic Ising spin chain. In addition, the classical mean field theories of fluids and ferromagnets, namely the van der Waals theory of fluids and the Curie-Weiss theory of ferromagnets, are described and their critical behaviour elucidated. The lectures conclude with a general discussion of the principles of universality and scaling which form the cornerstones of the modern theory of phase transitions and critical phenomena.

## 1 Formulation of Statistical Mechanics

Statistical mechanics was the topic of the first A.N.U. Physics Summer School held in 1988. On that occasion, Colin Thompson and I shared the pleasure of presenting lectures on the general principles of statistical mechanics [1, 2]. Those lectures, although unpublished, are available in the proceedings of that first A.N.U. Summer School. The principles of statistical mechanics were in fact laid down at the turn of the century and so, not surprisingly, they have not changed since 1988. I will therefore be covering much the same ground in this series of lectures. Although this introduction is brief, a more comprehensive account of the topics covered here can be found in Colin Thompson's excellent book [3] and a review article I wrote in 1983 [4]. Other very useful general references are the books by Callen [5], Stanley [6], Huang [7], Baxter [8] and Yeomans [9]. The definitive reference for many topics in this area is of course "Phase Transitions and Critical Phenomena" edited by Domb and Green and now Domb and Lebowitz [10].

### 1.1 *Classical Mechanics and Phase Space*

Thermodynamics describes the physical properties of bulk matter (solids, liquids and gases) in terms of a few variables such as absolute temperature  $T$  and pressure  $P$ . 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.

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<sup>1</sup>Email: pap@mundoe.maths.mu.oz.au

The term statistical mechanics is a combination of *mechanics* and *statistics*. From a *mechanical* viewpoint bulk matter, such as 22.4 litres of gas or 60 gram of iron at room temperature and pressure, typically consists of a system of

$$N \approx N_A = 6.0225 \times 10^{23} \quad (\text{Avogadro's number}) \quad (1.1)$$

particles. In classical mechanics (we will not consider quantum mechanics in these lectures) the behaviour of a system of  $N$  particles with mass  $m$  is determined by writing down a Hamiltonian describing the interactions between the particles and solving, usually numerically, the resulting equations of motion in the  $6N$ -dimensional phase space

$$\Gamma = \langle \{\sigma\} \rangle = \langle \{(\mathbf{p}_1, \mathbf{q}_1, \mathbf{p}_2, \mathbf{q}_2, \dots, \mathbf{p}_N, \mathbf{q}_N)\} \rangle \quad (1.2)$$

spanned by the coordinates  $\mathbf{q}_i$  and their conjugate momenta  $\mathbf{p}_i$  in 3-dimensional space. The  $6N$ -dimensional vector  $\sigma$  describes the microscopic state of the system. Explicitly, the Hamiltonian takes the form

$$\begin{aligned} H(\sigma) &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) \\ &= \text{Kinetic} + \text{Potential Energy} \end{aligned} \quad (1.3)$$

and the equations of motion are

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i} \quad \left( = -\frac{\partial V}{\partial \mathbf{q}_i} = \text{Force} \right) \quad (1.4)$$

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i} \quad \left( = \frac{\mathbf{p}_i}{m} = \text{velocity} \right) \quad (1.5)$$

Here derivatives with respect to vectors denote the appropriate gradients and the expressions in brackets give the Newtonian interpretation equivalent to  $\mathbf{F}_i = m\ddot{\mathbf{q}}_i$ .

Unfortunately, to solve the problem this way for a system of  $6 \times 10^{23}$  particles would take a millenia of CPU time on a Cray! Moreover, in practice, we never want to know the microscopic details of every particle, rather, we want to know overall or average quantities such as the average pressure exerted by a gas on its container. In other words we need to understand the *statistics* of the *mechanical* motion of a large number of particles.

## 1.2 Canonical Ensemble

The foundations of statistical mechanics were laid down by J.W. Gibbs in 1902. His work provides an elegant mathematical prescription to calculate the thermodynamic quantities of a macroscopic system. The canonical ensemble describes a system of a fixed number  $N$  of particles weakly coupled to and in thermal equilibrium with an infinitely large heat reservoir at absolute temperature  $T$ . Essentially, the system is to be regarded as isolated but maintained at a temperature  $T$ . The fundamental postulate (in general there is no rigorous derivation) due to Gibbs is that the probability density  $\rho(\sigma)$  of points in phase space  $\Gamma$  describing such an equilibrium system is given by

$$\rho(\sigma) = \frac{\exp(-\beta H(\sigma))}{\int_{\Gamma} \exp(-\beta H(\sigma)) d\Gamma}, \quad \sigma \in \Gamma \quad (1.6)$$

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

$$\beta = \frac{1}{kT} = \text{inverse temperature} \quad (1.7)$$

where the absolute temperature  $T$  is measured in Kelvin ( $273K = 0^\circ C$ ) and

$$k = 1.3805 \times 10^{-23} \text{ Joules/Kelvin} = \text{Boltzmann's constant.} \quad (1.8)$$

Crudely speaking, the Boltzmann factor  $\rho(\sigma)$  gives the statistical probability of finding the system in the state  $\sigma$ . Notice that the properties

$$\rho(\sigma) \geq 0 \quad \text{and} \quad \int_{\Gamma} \rho(\sigma) d\Gamma = 1 \quad (1.9)$$

are in accord with the interpretation of  $\rho(\sigma)$  as a probability. The normalization factor

$$Z_N = \int_{\Gamma} \exp(-\beta H(\sigma)) d\Gamma \quad (1.10)$$

is a fundamental quantity called the *canonical partition function*. Notice also that at high temperatures ( $T \rightarrow \infty, \beta \rightarrow 0$ )

$$\rho(\sigma) \sim \frac{1}{\int_{\Gamma} d\Gamma} \quad (1.11)$$

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

### 1.3 Maxwell-Boltzmann Distribution

A simple heuristic argument can be given in favour of the Gibbs postulate in the case of  $N$  particles distributed among a number of discrete energy levels  $E_j$ ,  $j = 1, 2, 3, \dots$  with  $n_j$  particles in each level as shown in Figure 1. The probability of a given distribution (partition) is

$$\mathcal{P} = \frac{N!}{n_1! n_2! n_3! \dots} \quad (1.12)$$

Consider the thermodynamic limit so that  $N \rightarrow \infty$  and  $n_j \rightarrow \infty$ . Then by Stirling's formula

$$N! \sim \left(\frac{N}{e}\right)^N, \quad \text{etc.} \quad (1.13)$$

and

$$\log \mathcal{P} \sim N \log N - N - \sum_j (n_j \log n_j - n_j). \quad (1.14)$$

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

$$\sum_j n_j = N, \quad \sum_j n_j E_j = E = \text{total energy.} \quad (1.15)$$

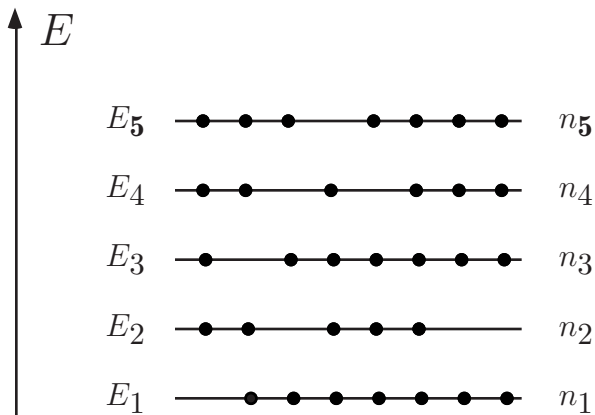


Figure 1. Distribution of  $N$  particles among a number of discrete energy levels.

We therefore cavalierly treat  $n_j$  as continuous variables (properly we should use  $\rho_j = n_j/N$ ), introduce Lagrange multipliers  $\alpha$  and  $\beta$  and maximize

$$N \log N - N - \sum_j (n_j \log n_j - n_j) - \alpha \sum_j n_j - \beta \sum_j n_j E_j. \quad (1.16)$$

Differentiating with respect to  $n_j$  gives

$$\log n_j + \alpha + \beta E_j = 0 \quad \text{or} \quad n_j = \exp(-\alpha - \beta E_j). \quad (1.17)$$

Therefore

$$N = \sum_j n_j = e^{-\alpha} \sum_j e^{-\beta E_j} = e^{-\alpha} Z_N \quad (1.18)$$

and

$$\rho_j = \frac{n_j}{N} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \text{density of states} \quad (1.19)$$

gives the probability of finding the system in the energy state  $E_j$ . This distribution is the Maxwell-Boltzmann distribution. The constant  $\beta$  is in fact identified as the inverse temperature.

#### 1.4 Connection with Thermodynamics

Mathematically, the canonical partition function  $Z_N$  can be regarded as a generating function for the usual thermodynamic functions. Explicitly, the (Helmholtz) free energy  $\Psi = \Psi(T, V)$  is related to the canonical partition function by

$$\Psi = -kT \log Z_N = U - TS \quad (1.20)$$

where  $U = U(T, V)$  is the internal energy,  $S = S(T, V)$  is the entropy and  $V$  is the volume. Other quantities are obtained by differentiation using the usual relations of

thermodynamics. The internal energy is

$$U = -T^2 \frac{\partial}{\partial T} \left( \frac{\Psi}{T} \right) = \Psi - T \frac{\partial \Psi}{\partial T} = \Psi + TS. \quad (1.21)$$

Hence the entropy is

$$S = -\frac{\partial \Psi}{\partial T}. \quad (1.22)$$

Similarly, the specific heat (at constant volume) is

$$C_V = \frac{\partial U}{\partial T} = -T \frac{\partial^2 \Psi}{\partial T^2} \quad (1.23)$$

and the pressure is

$$P = -\frac{\partial \Psi}{\partial V}. \quad (1.24)$$

More generally, the experimental value of an observable  $A = A(\sigma)$  is obtained from the ensemble average or thermal expectation

$$\langle A \rangle = \frac{\int_{\Gamma} A(\sigma) \exp(-\beta H(\sigma)) d\Gamma}{\int_{\Gamma} \exp(-\beta H(\sigma)) d\Gamma}. \quad (1.25)$$

So, for example, the internal energy is indeed given by

$$\begin{aligned} U &= \langle H \rangle = \frac{\int H(\sigma) \exp(-\beta H(\sigma)) d\Gamma}{\int \exp(-\beta H(\sigma)) d\Gamma} \\ &= -\frac{\partial}{\partial \beta} \log \int \exp(-\beta H(\sigma)) d\Gamma = -\frac{\partial}{\partial \beta} \log Z_N \\ &= -\left( \frac{\partial \beta}{\partial T} \right)^{-1} \frac{\partial}{\partial T} \left( -\frac{\Psi}{kT} \right) = -T^2 \frac{\partial}{\partial T} \left( \frac{\Psi}{T} \right). \end{aligned} \quad (1.26)$$

There are in fact three different ensembles in general use — the microcanonical ensemble, the canonical ensemble and the grand canonical ensemble. 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. By contrast, as we have seen, in the canonical ensemble the number of particles  $N$  is fixed but the average energy is determined by a temperature  $T$ . Finally, in the grand canonical ensemble neither the number of particles  $N$  nor the energy  $E$  is fixed, rather the average number of particles is controlled by the fugacity  $z$  and the average energy is controlled by the temperature  $T$ . The situation is summarized in Table 1.

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. 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

Table 1. Fixed quantities in the three standard ensembles.

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

are almost certainly correct and use them without question as the starting point for calculations. At the same time, on a mathematical level, the whole edifice of statistical mechanics is on shaky foundations! Needless to say, I will not dwell further on the foundations of statistical mechanics. Instead, I will take the Gibbs prescription as given and pragmatically concentrate on practical applications.

### 1.5 Ideal Gas

The ideal gas is a system of noninteracting point particles of mass  $m$  as shown in Figure 2. The Hamiltonian is

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \quad (1.27)$$

and the canonical partition function is

$$Z_N = \frac{1}{N!} \int_V \cdots \int_V d\mathbf{q}_1 \cdots d\mathbf{q}_N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} d\mathbf{p}_1 \cdots d\mathbf{p}_N \exp\left(-\frac{\beta}{2m} \sum_{i=1}^N \mathbf{p}_i^2\right). \quad (1.28)$$

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.

Using the integral formula

$$\int_{-\infty}^{\infty} \exp(-\lambda x^2) dx = \sqrt{\frac{\pi}{\lambda}} \quad (1.29)$$

the partition function of the ideal gas is evaluated as

$$Z_N = \frac{V^N}{N!} \left[ \int_{-\infty}^{\infty} \exp\left(-\frac{\beta}{2m} p^2\right) dp \right]^{3N} = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \quad (1.30)$$

so the pressure is given by

$$P = -\frac{\partial \Psi}{\partial V} = \frac{\partial}{\partial V} (kT \log Z_N) = \frac{NkT}{V}. \quad (1.31)$$

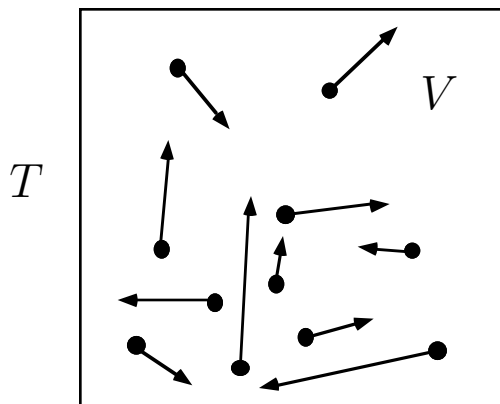


Figure 2. Ideal gas of noninteracting particles in a box of volume  $V$ . The temperature  $T$  is a measure of the average internal energy

The ideal gas law is thus

$$PV = NkT = nRT \quad (1.32)$$

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

$$R = N_A k = 8.315 \text{ Joules/Kelvin} \quad (1.33)$$

is the ideal gas constant.

The internal energy is

$$U = -\frac{\partial}{\partial \beta} \log Z_N = \frac{3N}{2\beta} = 3N\left(\frac{1}{2}kT\right). \quad (1.34)$$

This illustrates the equipartition of energy between the  $3N$  degrees of freedom. It also shows that the temperature  $T$  is indeed a measure of the average internal energy.

## 2 Lattice Spin Models

In many applications of statistical mechanics the particles are fixed or localized in space. In such cases the kinetic energy contribution to the Hamiltonian can be neglected. Within a magnetic crystal, for example, the atoms inherit an intrinsic angular momentum or spin from their valence electrons. These spins are restricted to certain discrete values and it is the interactions between these spins that are responsible for the magnetic properties of the material. A spin Hamiltonian for a system of  $N$  atoms (particles) is therefore of the form

$$H(\sigma) = V(\sigma_1, \sigma_2, \dots, \sigma_N) \quad (2.1)$$

where  $\sigma = \{\sigma_1, \sigma_2, \dots, \sigma_N\}$  denotes the microscopic configuration and the spin  $\sigma_i$  is a discrete variable describing the the state of the particle at the lattice site  $i$ . The canonical partition function of a lattice spin model is thus given by the configurational sum

$$Z_N = \sum_{\sigma} \exp(-\beta H(\sigma)). \quad (2.2)$$

## 2.1 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 [11] in 1905. For simplicity, let us assume that the spins are given by

$$\sigma_i = \begin{cases} +1, & \text{if spin } i \text{ is } \textit{parallel} \text{ to } h \\ -1, & \text{if spin } i \text{ is } \textit{antiparallel} \text{ to } h. \end{cases} \quad (2.3)$$

Such two-valued spins are called Ising spins after E. Ising [12] who first studied such models in 1925. The Hamiltonian or energy function for the Ising paramagnet is

$$H = -h \sum_{i=1}^N \sigma_i, \quad h \geq 0. \quad (2.4)$$

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

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

$$\begin{aligned} Z_N &= \sum_{\sigma} \exp\left(\beta h \sum_{i=1}^N \sigma_i\right) = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{B\sigma_1} e^{B\sigma_2} \dots e^{B\sigma_N} \\ &= (2 \cosh B)^N. \end{aligned} \quad (2.5)$$

Hence

$$-\beta\Psi = \log Z_N = N \log(2 \cosh B). \quad (2.6)$$

The average magnetic moment or magnetization is given by

$$\begin{aligned} m &= \left\langle \frac{1}{N} \sum_i \sigma_i \right\rangle = \frac{\sum_{\sigma} \left( \frac{1}{N} \sum_i \sigma_i \right) \exp\left(B \sum_{i=1}^N \sigma_i\right)}{\sum_{\sigma} \exp\left(B \sum_{i=1}^N \sigma_i\right)} \\ &= \frac{1}{N} \frac{\partial}{\partial B} \log Z_N = -\frac{1}{N} \frac{\partial}{\partial B} (\beta\Psi) = \tanh B. \end{aligned} \quad (2.7)$$

It follows that the magnetization of a paramagnet vanishes in the absence of an external magnetic field and that there is no permanent magnetization as in ferromagnetic materials such as iron and nickel.

## 2.2 Ising Ferromagnets

In ferromagnets there must be additional interactions between spins to explain the cooperative alignment of spins in the absence of an external magnetic field. The first model of a ferromagnet to entail such explicit interactions between spins was due to Ising and his Ph.D. supervisor Lenz. The Hamiltonian of an Ising ferromagnet is

$$H = - \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i \quad (2.8)$$

where the first sum is over all pairs  $\langle i, j \rangle$  of lattice sites and  $J_{ij}$  is the strength of interaction between the spins at sites  $i$  and  $j$ . Clearly, to energetically favour the mutual alignment of spins, as in a ferromagnet, we need  $J_{ij} \geq 0$  for all  $i$  and  $j$ . Physically, the interactions between spins in a magnetic substance are short ranged. The simplest possibility is that only nearest neighbour spins on a regular lattice interact so that

$$J_{ij} = \begin{cases} J, & i, j \text{ adjacent} \\ 0, & \text{otherwise.} \end{cases} \quad (2.9)$$

In general, it is impossible to evaluate the partition function even of a nearest-neighbour Ising model on a regular lattice consisting of  $N = 6 \times 10^{23}$  sites. In practice,  $N$  is effectively infinite and what we really need to evaluate is not the free energy  $\Psi$ , which is extensive and grows with the size of the system, but rather the intensive quantity  $\psi$  given by the free energy per site in the thermodynamic limit

$$-\beta\psi = -\lim_{N \rightarrow \infty} \frac{1}{N} \Psi = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N. \quad (2.10)$$

It can be shown quite generally that this limit exists, however, the resulting limiting free energy need not in general be an analytic function of the thermodynamic variables such as  $h$  and  $T$ . Points where the limiting free energy is singular are called *phase transition* points. In the special case of the nearest-neighbour Ising model on a periodic (one-dimensional) chain the limiting free energy can in fact be evaluated without much difficulty. This was first done by Ising in 1925. Here we will solve this model explicitly using transfer matrices.

### 2.3 Ising Spin Chain

The Hamiltonian of the Ising spin chain is

$$H = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - h \sum_{i=1}^N \sigma_i, \quad J > 0. \quad (2.11)$$

The problem is to evaluate the partition function

$$Z_N = \sum_{\sigma} \exp \left( K \sum_{i=1}^N \sigma_i \sigma_{i+1} + B \sum_{i=1}^N \sigma_i \right) \quad (2.12)$$

where  $K = \beta J$  and  $B = \beta h$ . Since the chain is periodic  $\sigma_{N+1} = \sigma_1$ . Let us define a  $2 \times 2$  *transfer matrix*  $\mathbf{T}$  with elements

$$\langle \sigma | \mathbf{T} | \sigma' \rangle = \exp \left[ K \sigma \sigma' + \frac{1}{2} B (\sigma + \sigma') \right] \quad (2.13)$$

that is

$$\mathbf{T} = \begin{pmatrix} \langle 1 | \mathbf{T} | 1 \rangle & \langle 1 | \mathbf{T} | -1 \rangle \\ \langle -1 | \mathbf{T} | 1 \rangle & \langle -1 | \mathbf{T} | -1 \rangle \end{pmatrix} = \begin{pmatrix} e^{K+B} & e^{-K} \\ e^{-K} & e^{K-B} \end{pmatrix}. \quad (2.14)$$

We can then write

$$\begin{aligned} Z_N &= \sum_{\sigma} \prod_{i=1}^N \exp \left[ K \sigma_i \sigma_{i+1} + \frac{1}{2} B (\sigma_i + \sigma_{i+1}) \right] \\ &= \sum_{\sigma_1} \cdots \sum_{\sigma_N} \langle \sigma_1 | \mathbf{T} | \sigma_2 \rangle \langle \sigma_2 | \mathbf{T} | \sigma_3 \rangle \cdots \langle \sigma_{N-1} | \mathbf{T} | \sigma_N \rangle \langle \sigma_N | \mathbf{T} | \sigma_1 \rangle. \end{aligned} \quad (2.15)$$

These are matrix products so

$$Z_N = \sum_{\sigma_1} \langle \sigma_1 | \mathbf{T}^N | \sigma_1 \rangle = \text{Tr } \mathbf{T}^N = \lambda_+^N + \lambda_-^N \quad (2.16)$$

where  $\lambda_+ \geq \lambda_-$  are the eigenvalues of the real symmetric matrix  $\mathbf{T}$ . The characteristic polynomial is

$$\lambda^2 - (2e^K \cosh B)\lambda + 2 \sinh 2K = 0 \quad (2.17)$$

so

$$\lambda_{\pm} = e^K \cosh B \pm \sqrt{e^{2K} \sinh^2 B + e^{-2K}} \quad (2.18)$$

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

It follows that

$$\begin{aligned} \frac{1}{N} \log Z_N &= \frac{1}{N} \log(\lambda_+^N + \lambda_-^N) = \frac{1}{N} \log \lambda_+^N \left[ 1 + \left( \frac{\lambda_-}{\lambda_+} \right)^N \right] \\ &= \log \lambda_+ + \frac{1}{N} \log \left[ 1 + \left( \frac{\lambda_-}{\lambda_+} \right)^N \right] \rightarrow \log \lambda_+ \quad \text{as } N \rightarrow \infty. \end{aligned} \quad (2.19)$$

Hence the free energy per spin  $\psi$  in the thermodynamic limit is given by

$$-\beta\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N = \log \lambda_+. \quad (2.20)$$

The magnetization is

$$m = -\frac{\partial}{\partial B} (\beta\psi) = \frac{\partial}{\partial B} \log \lambda_+ = \frac{\sinh B}{\sqrt{\sinh^2 B + e^{-4K}}}. \quad (2.21)$$

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

In zero field ( $h \rightarrow 0\pm$ ) 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. As asserted by van Hove's theorem [13], this is a general feature of one-dimensional models with finite-range interactions. In sharp contrast, Ising models on cubic lattices in two or more dimensions do exhibit spontaneous magnetization! The zero-field Ising model on the square lattice was in fact solved by L. Onsager [14] in 1944 and the spontaneous magnetization was first calculated by C.N. Yang [15] in 1952.

**Theorem 1 (van Hove)** *The limiting free energy  $\psi(h, T)$  of the one-dimensional finite-range Ising model*

$$H = - \sum_{1 \leq i < j \leq N} J(j-i) \sigma_i \sigma_j - h \sum_{i=1}^N \sigma_i \quad (2.22)$$

with

$$J(k) = 0 \quad \text{for } k > R \quad (2.23)$$

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

$$\lim_{h \rightarrow 0\pm} m(h, T) = 0 \quad \text{for } T > 0. \quad (2.24)$$

*Sketch of Proof:* For finite-range interactions we can always define a finite-dimensional transfer matrix  $\mathbf{T}$ . Since the elements of  $\mathbf{T}$  are Boltzmann weights,  $\mathbf{T}$  is a positive matrix (has all positive entries). Hence, by the Frobenius theorem, the eigenvalues of  $\mathbf{T}$  satisfy

$$\lambda_{max} = \lambda_1 > |\lambda_2| \geq |\lambda_3| \geq \dots |\lambda_n| \quad (2.25)$$

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

$$\begin{aligned} \frac{1}{N} \log Z_N &= \frac{1}{N} \log(\lambda_1^N + \dots + \lambda_n^N) \\ &= \log \lambda_1 + \frac{1}{N} \log \left[ 1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N + \left(\frac{\lambda_3}{\lambda_1}\right)^N + \dots + \left(\frac{\lambda_n}{\lambda_1}\right)^N \right] \\ &\rightarrow \log \lambda_{max} \quad \text{as } N \rightarrow \infty. \end{aligned} \quad (2.26)$$

So the free energy

$$-\beta\psi(h, T) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N = \log \lambda_{max} \quad (2.27)$$

and the magnetization  $m(h, T)$  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 and there is no spontaneous magnetization  $\square$ .

The Ising model can also be regarded as a model of a lattice gas by transforming to occupation numbers

$$t_i = \frac{1}{2}(1 - \sigma_i) = \begin{cases} 1, & \text{if site } i \text{ is occupied } (\sigma_i = -1) \\ 0, & \text{if site } i \text{ is unoccupied } (\sigma_i = +1). \end{cases} \quad (2.28)$$

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.

### 3 Tonks and van der Waals Gases

#### 3.1 Tonks Gas

Tonks gas [16] is a model of hard-core particles (spheres or rods) in one dimension as shown in Figure 3. Effectively, this is a model of one-dimensional billiard balls. The pair interaction (hard-core) potential is

$$\phi(r) = \phi_{hc}(r) = \begin{cases} \infty, & 0 \leq r < a \\ 0, & r \geq a. \end{cases} \quad (3.1)$$

Hence the Hamiltonian for  $N$  rods on the interval  $0 \leq x \leq L$  is

$$H = \sum_{1 \leq i < j \leq N} \phi_{hc}(|x_i - x_j|). \quad (3.2)$$

Note that  $H$  is a symmetric function of  $x_1, x_2, \dots, x_N$  and we have omitted the kinetic energy term. The canonical partition function can therefore be written as

$$\begin{aligned} Z_N &= \frac{1}{N!} \int_0^L \dots \int_0^L \exp \left[ -\beta \sum_{i < j} \phi_{hc}(|x_i - x_j|) \right] dx_1 \dots dx_N \\ &= \int \dots \int_R \exp \left[ -\beta \sum_{i < j} \phi_{hc}(|x_i - x_j|) \right] dx_1 \dots dx_N \end{aligned} \quad (3.3)$$

where  $R$  is the region

$$R: \quad 0 \leq x_1 \leq x_2 \leq \dots \leq x_N \leq L. \quad (3.4)$$

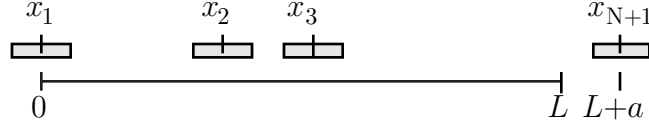


Figure 3. Tonks gas of hard-core particles distributed along a line of length  $L$ .

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

$$Z_N = \int \cdots \int_{R'} dx_1 \dots dx_N \quad (3.5)$$

where

$$R': \quad 0 \leq x_1 \leq x_2 - a, \quad a \leq x_2 \leq x_3 - a, \dots, (i-1)a \leq x_i \leq x_{i+1} - a, \dots \\ \dots, (N-1)a \leq x_N \leq x_{N+1} - a = L. \quad (3.6)$$

If we now change variables to  $y_i = x_i - (i-1)a$  we find that

$$0 \leq y_i \leq x_{i+1} - a - (i-1)a = x_{i+1} - ia = y_{i+1} \quad (3.7)$$

and hence

$$Z_N = \int_0^\ell dy_N \int_0^{y_{N-1}} dy_{N-1} \cdots \int_0^{y_3} dy_2 \int_0^{y_2} dy_1 = \frac{\ell^N}{N!} \quad (3.8)$$

where  $\ell = L - (N-1)a$  is the effective volume. Again using Stirling's formula  $N! \sim (N/e)^N$ , the limiting free energy is given by

$$-\beta\psi = \lim_{\substack{N, L \rightarrow \infty \\ L/N = v}} \frac{1}{N} \log Z_N \\ = 1 + \lim_{N, L \rightarrow \infty} \log \frac{L - (N-1)a}{N} = 1 + \log(v - a) \quad (3.9)$$

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

The pressure is

$$P = -\frac{\partial\psi}{\partial v} = \frac{kT}{v - a} \quad (3.10)$$

so the equation of state is

$$P(v - a) = kT \quad (3.11)$$

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

### 3.2 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 shown in Figure 4

$$\phi(r) = \phi_{hc}(r) - \frac{\alpha}{L}, \quad \alpha > 0. \quad (3.12)$$

This is unrealistic because the strength of the potential should not depend upon the size

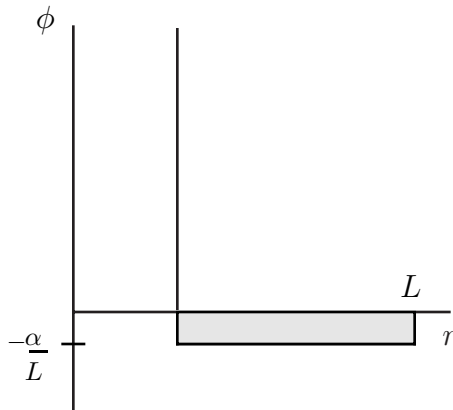


Figure 4. Tonks–van der Waals potential.

$L$  of the system. Nevertheless this assumption leads to a model that is both tractable and interesting. The Hamiltonian is

$$H = \sum_{1 \leq i < j \leq N} \left[ \phi_{hc}(|x_i - x_j|) - \frac{\alpha}{L} \right] = -\frac{\alpha N(N-1)}{2L} + H^{Tonks}. \quad (3.13)$$

Hence

$$Z_N = \exp \left[ \frac{\beta \alpha N(N-1)}{2L} \right] Z_N^{Tonks} \quad (3.14)$$

and

$$-\beta\psi = \lim_{\substack{N, L \rightarrow \infty \\ L/N=v}} \frac{1}{N} \log Z_N = \frac{\beta\alpha}{2v} + 1 + \log(v-a). \quad (3.15)$$

It follows that the pressure is

$$P = -\frac{\partial\psi}{\partial v} = \frac{kT}{v-a} - \frac{\alpha}{2v^2} = P_{hc} - \frac{\alpha}{2v^2}. \quad (3.16)$$

The outcome is that the pressure is reduced due to the attractive interactions of the particles by an amount proportional to the strength  $\alpha$  of the interactions and also proportional to the square of the density  $\frac{1}{2}\rho^2 = 1/2v^2$  which gives the probability of two particles interacting. The equation of state is thus modified to

$$\left( P + \frac{\alpha}{2v^2} \right) (v-a) = kT \quad (3.17)$$

which is the celebrated equation of state proposed, on phenomenological grounds, by van der Waals [17] in 1873.

### 3.3 Maxwell Construction

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

$$\frac{\partial v}{\partial P} > 0. \quad (3.18)$$

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 [18] who proposed the double tangent formula

$$\psi = \underset{\text{Envelope}}{\text{Convex}} \left[ \psi_{hc}(v) - \frac{\alpha}{2v} \right]. \quad (3.19)$$

This construction is equivalent to placing horizontal segments in the isotherms according to an equal area rule as illustrated in Figure 5. Such flat regions are found experimentally in isotherms at low temperatures throughout the gas-liquid coexistence region. The Maxwell construction results in a free energy which 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 [19, 20].

## 4 Curie-Weiss Ferromagnet

### 4.1 Weiss Phenomenological Theory

The classical theory of ferromagnetism was proposed by Weiss in 1907. This phenomenological theory is based on the paramagnet

$$H = h_{\text{eff}} \sum_{i=1}^N \sigma_i \quad (4.1)$$

and assumes that, in a ferromagnet, there is 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

$$h_{\text{eff}} = Jm + h \quad (4.2)$$

where the constant of proportionality  $J$  is called the mean-field parameter. Evaluating the magnetization then leads to the transcendental equation of state

$$m = \tanh(\beta h_{\text{eff}}) = \tanh(Km + B), \quad K = \beta J, \quad B = \beta h. \quad (4.3)$$

This self-consistency equation is used to determine  $m = m(h, T)$ . Since this equation cannot be solved analytically it is solved graphically, as shown in Figure 6, in the form

$$\frac{Jm + h}{kT} = \tanh^{-1} m. \quad (4.4)$$

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

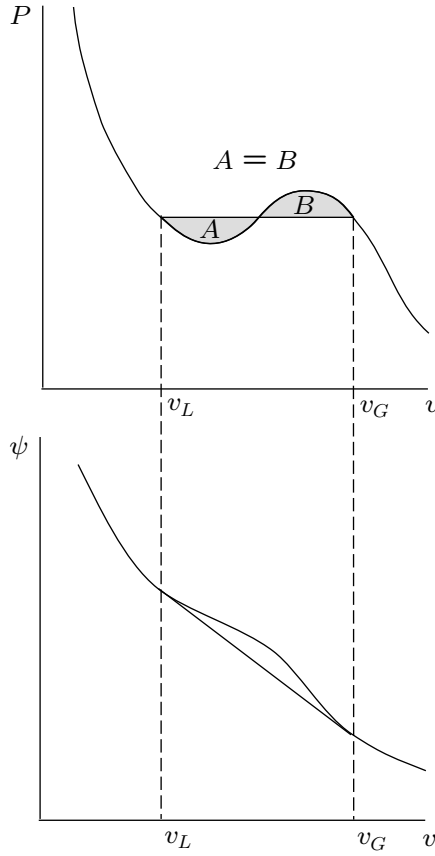


Figure 5. Schematic representation of the van der Waals wiggle in a low temperature isotherm of  $P = -\frac{\partial\psi}{\partial v}$  plotted against  $v$ . The wiggle is removed by placing a flat segment into the isotherm according to an equal area rule as illustrated. Also shown is the corresponding kink in the free energy isotherm with the equivalent Maxwell double tangent (convex envelope) construction.

$m$ . If the slope of the straight line is less than the critical value

$$\frac{J}{kT_c} = 1 \quad (4.5)$$

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 and leads to the magnetic isotherms shown in Figure 7.

The spontaneous magnetization  $m_0$  is defined by

$$m_0 = \lim_{h \rightarrow 0^+} m(h, T) \quad (4.6)$$

and

$$m_0(T) = \begin{cases} 0, & T \geq T_c = J/k \\ x, & T < T_c = J/k \end{cases} \quad (4.7)$$

where  $x$  is the positive solution of

$$x = \tanh \frac{Jx}{kT}. \quad (4.8)$$

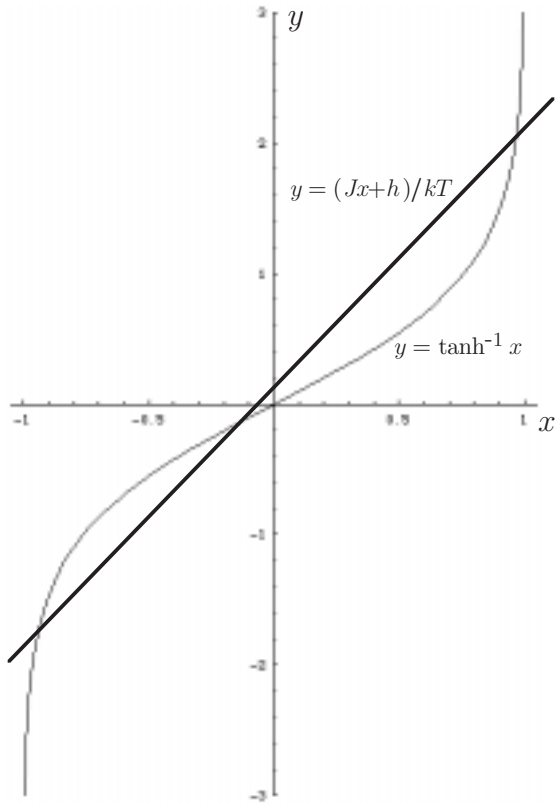


Figure 6. Graphical solution of the self-consistency equation  $\frac{Jm+h}{kT} = \tanh^{-1} m$ . At low temperatures and for small magnetic fields  $h$  there are three solutions as shown. As  $h \rightarrow 0$  the positive solution gives the spontaneous magnetization  $m_0$ .

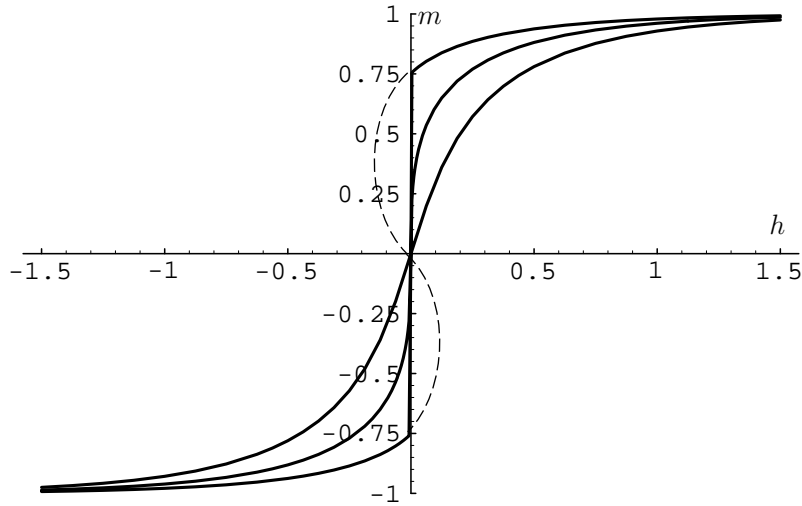


Figure 7. Magnetic isotherms for the Weiss theory. The three isotherms shown are respectively for  $T < T_c$ ,  $T = T_c$  and  $T > T_c$ . The dashed line shows the discarded solution.

Thus the Weiss theory correctly predicts spontaneous magnetization and a 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. The phase diagram is shown in Figure 8.

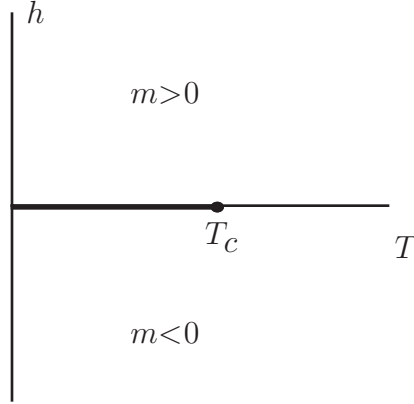


Figure 8. Phase diagram of the Ising ferromagnet. A first-order line extends along the line  $h = 0$  from zero temperature to the Curie point at  $T = T_c$ .

#### 4.2 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

$$H = -\frac{J}{N} \sum_{1 \leq i < j \leq N} \sigma_i \sigma_j - h \sum_{i=1}^N \sigma_i, \quad J > 0. \quad (4.9)$$

Here the sites labelled  $1, 2, \dots, N$  are all equivalent and 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  $N$ . (This factor of  $N$  is needed to ensure the existence of the thermodynamic limit.)

To calculate the partition function we begin by writing

$$H = \frac{1}{2}J - \frac{J}{2N} \left( \sum_{i=1}^N \sigma_i \right)^2 - h \sum_{i=1}^N \sigma_i \quad (4.10)$$

so that

$$Z_N = e^{-K/2} \sum_{\sigma} \exp \left[ \frac{K}{2N} \left( \sum_{i=1}^N \sigma_i \right)^2 + B \sum_{i=1}^N \sigma_i \right] \quad (4.11)$$

where  $K = \beta J$  and  $B = \beta h$ . Next we use the identity

$$\exp\left(\frac{1}{2}\alpha S^2\right) = \sqrt{\frac{\alpha}{2\pi}} \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}\alpha x^2 + \alpha x S\right) \quad (4.12)$$

with

$$\alpha = NK \quad \text{and} \quad S = \frac{1}{N} \sum_{i=1}^N \sigma_i \quad (4.13)$$

to obtain

$$\begin{aligned} Z_N &= \sqrt{\frac{NK}{2\pi}} e^{-K/2} \sum_{\sigma} \int_{-\infty}^{\infty} dx \exp \left[ -\frac{1}{2}NKx^2 + (Kx + B) \sum_{i=1}^N \sigma_i \right] \\ &= \sqrt{\frac{NK}{2\pi}} e^{-K/2} \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}NKx^2} \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_N=\pm 1} e^{(Kx+B)\sigma_1} \dots e^{(Kx+B)\sigma_N} \\ &= \sqrt{\frac{NK}{2\pi}} e^{-K/2} \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}NKx^2} [2 \cosh(Kx + B)]^N \\ &= \sqrt{\frac{NK}{2\pi}} e^{-K/2} \int_{-\infty}^{\infty} dx \exp \left\{ N \left[ -\frac{1}{2}Kx^2 + \log 2 \cosh(Kx + B) \right] \right\} \end{aligned} \quad (4.14)$$

The limiting free energy per spin  $\psi$  is given by

$$-\beta\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N = \lim_{N \rightarrow \infty} \frac{1}{N} \log I_N \quad (4.15)$$

where

$$I_N = \int_{-\infty}^{\infty} \exp[Nf(x)] dx \quad (4.16)$$

and

$$f(x) = -\frac{1}{2}Kx^2 + \log 2 \cosh(Kx + B). \quad (4.17)$$

This follows since

$$\lim_{N \rightarrow \infty} \frac{1}{N} \log \left[ \sqrt{\frac{NK}{2\pi}} e^{-K/2} \right] = 0. \quad (4.18)$$

For large  $N$ ,  $I_N$  is dominated by the maximum value of the integrand and  $\psi$  can be obtained by Laplace's method giving

$$-\beta\psi = \max_x f(x) = \max_x \left[ -\frac{1}{2}Kx^2 + \log 2 \cosh(Kx + B) \right]. \quad (4.19)$$

Differentiating with respect to  $x$ , we see that the equation determining the maximum is

$$x = \tanh(Kx + B) \quad (4.20)$$

which is precisely the Curie-Weiss equation of state where  $x$  is identified with the magnetization

$$m = \frac{\partial}{\partial B} (-\beta\psi) = \tanh(Kx + B) = x. \quad (4.21)$$

Furthermore, for the maximizing solution we see that  $m = x$  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  $h = 0$ ,  $T = T_c = J/k$ . Again the Curie-Weiss theory can be obtained rigorously by taking a limit of infinitely weak long-range potentials [21, 20] or alternatively by taking the lattice dimensionality  $d \rightarrow \infty$  after the thermodynamic limit [22].

## 5 Critical Exponents, Universality and Scaling

### 5.1 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. We write

$$f(x) \sim x^\epsilon \quad \text{as } x \rightarrow 0+ \quad (5.1)$$

whenever the limit

$$\epsilon = \lim_{x \rightarrow 0+} \frac{\log f(x)}{\log x} \quad (5.2)$$

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

In statistical mechanics there has been a proliferation of critical exponents which now exhaust the Greek alphabet! The standard critical exponents for magnetic and fluid systems are defined in Table 2.

Table 2. The definition of some critical exponents for magnetic and fluid systems. Here  $t = (T - T_c)/T_c$ ,  $C_0 =$  zero-field specific heat,  $\chi_0 =$  zero-field susceptibility,  $K_T =$  isothermal compressibility and  $\rho_{L,G} =$  liquid, gas density.

Exponent	Magnet	Fluid
$\alpha$	$C_0 \sim  t ^{-\alpha}, \quad t \rightarrow 0$	$C_V \sim  t ^{-\alpha}, \quad t \rightarrow 0$
$\beta$	$m_0 \sim  t ^\beta, \quad t \rightarrow 0-$	$\rho_L - \rho_G \sim  t ^\beta, \quad t \rightarrow 0-$
$\gamma$	$\chi_0 \sim  t ^{-\gamma}, \quad t \rightarrow 0$	$K_T \sim  t ^{-\gamma}, \quad t \rightarrow 0$
$\delta$	$h \sim \text{sgn}(m) m ^\delta, \quad h \rightarrow 0, T = T_c$	$P - P_c \sim \text{sgn}(\rho - \rho_c) \rho - \rho_c ^\delta,$ $ \rho - \rho_c  \rightarrow 0, T = T_c$

### 5.2 Mean-field Critical Exponents

In this section we obtain the critical exponents of the Curie-Weiss ferromagnet.

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

The non-analytic zero-field free energy is

$$-\frac{\psi}{kT} = \begin{cases} \log 2, & T \geq T_c \\ -\frac{Jm_0^2}{2kT} + \log 2 \cosh\left(\frac{Jm_0}{kT}\right), & T < T_c \end{cases} \quad (5.3)$$

with

$$m_0 = \tanh Km_0. \quad (5.4)$$

Hence

$$U = -T^2 \frac{d}{dT} \left( \frac{\psi}{T} \right) = \begin{cases} 0, & T \geq T_c \\ -\frac{1}{2} J m_0^2, & T < T_c \end{cases} \quad (5.5)$$

and

$$C_0 = \frac{dU}{dT} = \begin{cases} 0, & T \geq T_c \\ -\frac{1}{2} J \frac{d m_0^2}{dT}, & T < T_c \end{cases} \quad (5.6)$$

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

$$\frac{J m_0}{kT} = \frac{T_c}{T} m_0 = \tanh^{-1} m_0 = m_0 + \frac{1}{3} m_0^3 + \dots \quad (5.7)$$

This gives

$$m_0^2 \sim 3 \left( \frac{T_c}{T} - 1 \right) = 3 \frac{T_c}{T} \left( 1 - \frac{T}{T_c} \right) \quad (5.8)$$

and hence as  $T \rightarrow T_c^-$

$$m_0 \sim \left( 1 - \frac{T}{T_c} \right)^\beta \quad \text{with} \quad \beta = 1/2. \quad (5.9)$$

$$\boxed{\gamma = 1}$$

The zero-field susceptibility is

$$\chi_0 = \beta \left. \frac{dm}{dB} \right|_{B=0}. \quad (5.10)$$

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

$$\frac{dm}{dB} = \frac{1 - m^2}{1 - K(1 - m^2)} \quad \text{and so} \quad \chi_0 = \frac{\beta(1 - m_0^2)}{1 - K(1 - m_0^2)}. \quad (5.11)$$

It follows that as  $T \rightarrow T_c$

$$\chi_0 \sim \left| 1 - \frac{T}{T_c} \right|^{-\gamma} \quad \text{with} \quad \gamma = 1. \quad (5.12)$$

$$\boxed{\delta = 3}$$

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

$$\frac{J}{kT_c} m + \frac{h}{kT_c} = m + \frac{h}{J} = \tanh^{-1} m \sim m + \frac{1}{3} m^3 + \dots \quad (5.13)$$

Hence we conclude that as  $h \rightarrow 0$

$$m \sim h^{1/\delta} \quad \text{with} \quad \delta = 3. \quad (5.14)$$

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

$$\alpha = 0_{disc}, \quad \beta = 1/2, \quad \gamma = 1, \quad \delta = 3. \quad (5.15)$$

These are the *classical* values for the critical exponents. A similar 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

$$\alpha \approx 0.1, \quad \beta \approx 0.33, \quad \gamma \approx 1.2, \quad \delta \approx 4.2 \quad (5.16)$$

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

### 5.3 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  $H$ .*

Critical exponents for some much studied models in statistical mechanics are given in Table 3. The hard hexagon [23] and Potts models [24] are discussed further in Rodney Baxter’s lectures at this summer school. The fact that the mean-field theories of both magnets and fluids have the same classical values values is one example of universality. Another example is that the Ising model in two dimensions exhibits precisely the same critical exponents for all the regular lattices, eg. the square, the triangular and the hexagonal lattices. Finally, the hard hexagon and 3-state Potts models in two dimensions are seen to have the same exponents. This is a consequence of universality since both models possess a  $\mathbb{Z}_3$  symmetry.

Another important hypothesis in the modern theory of critical phenomena is the scaling hypothesis. For a simple magnetic system, which has just two relevant thermodynamic fields  $h$  and  $t$ , this takes the following form:

Scaling Hypothesis

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

$$\psi = \psi_{anal} + \psi_{sing} \quad (5.17)$$

where  $\psi_{anal}$  is analytic and the singular part  $\psi_{sing}$  satisfies

$$\psi_{sing}(\lambda^x t, \lambda^y h) = \lambda \psi_{sing}(t, h) \quad (5.18)$$

Table 3. Critical exponents of some much studied lattice spin models. These values are all known exactly except for the critical exponents of the Ising model in three dimensions.

<b>Model</b>	$\alpha$	$\beta$	$\gamma$	$\delta$
Classical	$0_{disc}$	1/2	1	3
Ising ( $d = 2$ )	$0_{log}$	1/8	7/4	15
Ising ( $d = 3$ )	0.10	0.33	1.24	4.8
Ising ( $d \geq 4$ )	0	1/2	1	3
Hard Hexagons ( $d = 2$ )	1/3	1/9	13/9	14
3-state Potts ( $d = 2$ )	1/3	1/9	13/9	14
4-state Potts ( $d = 2$ )	2/3	1/12	7/6	15

for all values of the scaling parameter  $\lambda$ , that is,  $\psi_{sing}$  is a generalized homogeneous function of  $t = (T - T_c)/T_c$  and  $h$ .

By differentiating the homogeneous relation satisfied by  $\psi_{sing}$ , it is possible to obtain the exponents  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  in terms of  $x$  and  $y$ . Hence only two of these exponents are independent. In particular, the exponents  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are thus found to satisfy the scaling relations

$$\alpha + 2\beta + \gamma = 2, \quad \gamma = \beta(\delta - 1). \quad (5.19)$$

In most cases, these relations are used to calculate the values of  $\gamma$  and  $\delta$  in Table 3. However, these relations are clearly satisfied by the classical values. In fact, for the Curie-Weiss ferromagnet, it can be shown that

$$\psi_{sing}(t, h) = \min_s \left\{ -hs + \frac{1}{2}Jts^2 + \frac{1}{12}Js^4 \right\}. \quad (5.20)$$

This is a generalized homogeneous function with exponents  $x = 1/2$  and  $y = 3/4$ .

## 6 Acknowledgement

It is a pleasure to acknowledge my indebtedness to Colin Thompson from whom I first learned much of the material presented here. I thank Brian Robson, Vladimir Bazhanov and Rodney Baxter for their hospitality in Canberra.

## References

1. C. J. Thompson, "General Principles of Statistical Mechanics I", First Physics Summer School, A.N.U. unpublished 1988.
2. P. A. Pearce, "General Principles of Statistical Mechanics II", First Physics Summer School, A.N.U. unpublished 1988.

3. C. J. Thompson, “Classical Equilibrium Statistical Mechanics”, Clarendon Press, Oxford, 1988.
4. P. A. Pearce, “Thermodynamic Models with Exact Solutions”, Science Progress (Oxford) **68** (1983) 189.
5. H. B. Callen, “Thermodynamics”, Wiley, New York, 1960.
6. H. E. Stanley, “Introduction to Phase Transitions and Critical Phenomena”, Oxford University Press, Oxford, 1971.
7. K. Huang, “Statistical Mechanics”, 2nd edition, Wiley, New York, 1987.
8. R. J. Baxter, “Exactly Solved Models in Statistical Mechanics”, Academic Press, London, 1982.
9. J. M. Yeomans, “Statistical Mechanics of Phase Transitions”, Clarendon Press, Oxford, 1992.
10. C. Domb and M. S. Green/C. Domb and J. L. Lebowitz, Phase Transitions and Critical Phenomena”, Vols. 1–14, Academic Press, London, 1972–1994.
11. P. Langevin, J. de Phys. **4** (1905) 678.
12. E. Ising, Z. Phys. **31** (1925) 253.
13. L. van Hove, Physica **15** (1949) 951.
14. L. Onsager, Phys. Rev. **65** (1944) 117.
15. C. N. Yang, Phys. Rev. **85** (1952) 809.
16. L. Tonks, Phys. Rev. **50** (1936) 955.
17. J. D. van der Waals, Ph. D. Thesis, University of Leiden (1873).
18. J. C. Maxwell, Nature **11** (1874) 53.
19. J. L. Lebowitz and O. Penrose, J. Math. Phys. **6** (1966) 1282.
20. C. J. Thompson, Prog. Theor. Phys. **87** (1992) 535, and references therein.
21. C. J. Thompson and H. Silver, Commun. Math. Phys. **33** (1973) 53.
22. C. J. Thompson, Commun. Math. Phys. **36** (1974) 255; P. A. Pearce and C. J. Thompson, Commun. Math. Phys. **58** (1978) 131.
23. R. J. Baxter, J. Phys. A **13** (1980) L61.
24. R. B. Potts, Proc. Camb. Phil. Soc. **48** (1952) 106.