Part II Statistical Physics

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Preface

> *"Anyone who wants to analyze the properties of matter in a real problem might want to start by writing down the fundamental equations and then try to solve them mathematically. Although there are people who try to use such an approach, these people are the failures in this field; the real successes come to those who start from a physical point of view, people who have a rough idea where they are going and then begin by making the right kind of approximations, knowing what is big and what is small in a given complicated situation."* (Richard Feynman)

Statistical mechanics is the art of turning the microscopic laws of physics into a description of Nature on a macroscopic scale.

Suppose you've got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us? More concretely, if I give you a box containing 10^{23} particles and tell you their mass, their charge, their interactions, and so on, what can you tell me about the stuff in the box?

There's one strategy that definitely won't work: writing down the Schrödinger equation for 10^{23} particles and solving it. That's typically not possible for 23 particles, let alone 10^{23}. What's more, even if you could find the wavefunction of the system, what would you do with it? The positions of individual particles are of little interest to anyone. We want answers to much more basic, almost childish, questions about the contents of the box. Is it wet? Is it hot? What colour is it? Is the box in danger of exploding? What happens if we squeeze it, pull it, heat it up? How can we begin to answer these kind of questions starting from the fundamental laws of physics?

The purpose of this course is to introduce the dictionary that allows you translate from the microscopic world where the laws of Nature are written to the everyday macroscopic world that we're familiar with. The only relevant information is, say, how many atoms have a particular energy, then one can calculate the observable thermodynamic values. That is, one has to know the distribution function of the particles over energies that defines the macroscopic properties. This gives the name *statistical physics* and defines the scope of this subject. This will allow us to begin to address very basic questions about how matter behaves.

We'll see many examples. For centuries – from the 1600s to the 1900s – scientists were discovering "laws of physics" that govern different substances. There are many hundreds of these laws, mostly named after their discovers. Boyle's law and Charles's law relate pressure, volume and temperature of gases (they are usually combined into the ideal gas law); the Stefan-Boltzmann law tells you how much energy a hot

object emits; Wien's displacement law tells you the colour of that hot object; the Dulong-Petit law tells you how much energy it takes to heat up a lump of stuff; Curie's law tells you how a magnet loses its magic if you put it over a flame; and so on and so on. Yet we now know that these laws aren't fundamental. In some cases they follow simply from Newtonian mechanics and a dose of statistical thinking. In other cases, we need to throw quantum mechanics into the mix as well. But in all cases, we're going to see how derive them from first principles.

A large part of this course will be devoted to figuring out the interesting things that happen when you throw 10^{23} particles together. One of the recurring themes will be that $10^{23} \neq 1$. More is different: there are key concepts that are not visible in the underlying laws of physics but emerge only when we consider a large collection of particles. One very simple example is temperature. This is not a fundamental concept: it doesn't make sense to talk about the temperature of a single electron. But it would be impossible to talk about physics of the everyday world around us without mention of temperature. This illustrates the fact that the language needed to describe physics on one scale is very different from that needed on other scales. We'll see several similar emergent quantities in this course, including the phenomenon of phase transitions where the smooth continuous laws of physics conspire to give abrupt, discontinuous changes in the structure of matter.

Historically, the techniques of statistical mechanics proved to be a crucial tool for understanding the deeper laws of physics. Not only is the development of the subject intimately tied with the first evidence for the existence of atoms, but quantum mechanics itself was discovered by applying statistical methods to decipher the spectrum of light emitted from hot objects. However, physics is not a finished subject. There are many important systems in Nature – from high temperature superconductors to black holes – which are not yet understood at a fundamental level. The information that we have about these systems concerns their macroscopic properties and our goal is to use these scant clues to deconstruct the underlying mechanisms at work. The tools that we will develop in this course will be crucial in this task.

Contents

1 The Basics of Thermodynamics **1**
1.1 Introduction . . . 1
1.1.1 Ideal Gas . . . 2
1.1.1.1 Energy Storage . . . 2
1.1.1.2 Energy Flow In and Out of an Ideal Gas . . . 2
1.1.2 Van der Waals Gas and Other Systems . . . 4
1.1.2.1 Energy Storage . . . 5
1.1.3 Paramagnetic Salt in an Applied Magnetic Field . . . 5
1.1.3.1 Energy Storage . . . 6
1.1.3.2 Energy Flow In and Out of the System . . . 7
1.1.4 Assembly of One-Dimensional Simple Harmonic Oscillators . . . 8
1.1.4.1 Energy Storage . . . 8
1.1.4.2 Energy Flow In and Out of the System . . . 8
1.2 Thermodynamic Variables . . . 8
1.3 Equations of State; $p - V - T$ for a Real Substance . . . 10
1.3.1 The Equation of State of a Van der Waals Gas . . . 11
1.4 The Laws of Thermodynamics . . . 12
1.5 Entropy . . . 14
1.6 The Gibbs-Duhem Equation . . . 18

2 Thermodynamic Equilibrium **21**
2.1 Internal Equilibrium of Closed Systems . . . 21
2.1.1 Maximum Entropy Principle . . . 21
2.2 Thermodynamic Equilibrium in Open Systems . . . 24
2.2.1 The Availability . . . 24
2.2.2 Availability = Useful Work . . . 26
2.2.3 Legendre Transformations . . . 26
2.3 Overview of the Thermodynamic Potentials . . . 28
2.3.1 Energy U: Equilibrium at Constant Volume, Entropy and Particle Number . . . 30
2.3.2 Enthalpy H: Equilibrium at Constant Pressure, Entropy and Particle Number . . . 30
2.3.3 Helmholtz Free Energy F: Equilibrium at Constant Temperature, Volume and Particle Number . . . 31
2.3.3.1 Example: Bubble . . . 32
2.3.4 Gibbs Free Energy G: Equilibrium at Constant Temperature, Pressure and Particle Number . . . 33
2.3.5 Grand Potential Φ: Equilibrium at Constant Temperature, Volume and Chemical Potential . . . 34
2.4 Phase Equilibria . . . 35
2.4.0.1 Application to the Van der Waals Gas . . . 36
2.4.1 Clausius-Clapeyron Equation . . . 37
2.5 Mixtures of Ideal Gases . . . 38
2.5.1 Chemical Equilibrium . . . 40

2.5.2 The Equilibrium Constant . . . 41

3 The Basics of Statistical Mechanics 43
3.1 Microstates and Macrostates . . . 43
3.2 Principle of Equal Equilibrium Probability (PEEP) . . . 44
3.3 The Boltzmann Entropy . . . 45
3.3.1 Heat Capacity . . . 47
3.4 The Gibbs Entropy . . . 48
3.5 Statistical Ensembles . . . 50
3.5.1 Canonical Ensemble: Boltzmann Distribution and Partition Function . . . 50
3.5.2 Grand Canonical Ensemble: Gibbs Distribution and Grand Partition Function . . . 53
3.6 Solving Problems in Statistical Mechanics . . . 54
3.6.1 Canonical Ensemble . . . 54
3.6.2 Grand Canonical Ensemble . . . 55
3.6.3 Example: Defects in a Solid . . . 56
3.6.4 Example: Vacancies . . . 57
3.6.5 Example: Point Defect Occupation . . . 58
3.6.6 Example: Paramagnetic Salt . . . 59
3.6.7 Example: Zipper . . . 61
3.6.8 Example: the Planck Distribution . . . 62
3.6.9 The Microscopic Meaning of Heat and Work . . . 62

4 Classical Ideal Gas 65
4.1 Phase Space . . . 65
4.1.1 Classical Partition Function . . . 66
4.1.1.1 One-Dimensional Simple Harmonic Oscillator . . . 68
4.1.1.2 Three-Dimensional Particle in a Uniform Gravitational Field . . . 69
4.2 Ideal Gas of N Particles . . . 69
4.2.1 Thermodynamic Properties of Ideal Gas . . . 70
4.2.1.1 Example: Relativistic Gas . . . 72
4.2.1.2 Example: Spherical Trap . . . 74
4.3 Equipartition Theorem . . . 75
4.3.1 Kinetic Energy of Particles in Classical Interacting Systems . . . 75
4.4 Gas of Diatomic Molecules . . . 76
4.5 Classical to Quantum Crossover . . . 79

5 The Grand Canonical Ensemble 81
5.1 Quantum Mechanics and Indistinguishability . . . 81
5.2 Using the Grand Canonical Ensemble . . . 82
5.3 The Classical Limit . . . 84
5.4 Sign of Chemical Potential . . . 85
5.5 Grand Thermodynamic Potential . . . 87
5.6 Internal Degrees of Freedom and External Potentials . . . 89
5.7 Equilibrium Constant for Chemical Reactions . . . 91

5.7.0.1 Example: Plasma . . . 91
5.8 Langmuir Adsorption Isotherm . . . 92
5.8.1 Surface Number Density for Adsorbed Helium Atoms in a 2D Gas . . . 94

6 Ideal Fermi Gas **97**
6.1 Fermi-Dirac Statistics for the Ideal Quantum Gas . . . 97
6.2 Quantum States of an Ideal Gas . . . 97
6.2.1 Hard-Wall Boundary Conditions . . . 98
6.2.2 Periodic Boundary Conditions . . . 100
6.3 Chemical Potential of a Fermi Gas . . . 102
6.4 Ideal Fermi Gas at Low Temperatures . . . 103
6.4.1 Zero Temperature Limit . . . 104
6.4.2 Low Temperature Limit of the Grand Potential . . . 104
6.4.2.1 Example: Heat Capacity of ^{3}He in Dilute Solutions at Low Temperatures . . . 106
6.4.2.2 Sommerfeld Expansion (*non-examinable*) . . . 107
6.4.3 Application to Metals . . . 109

7 Ideal Bose Gases **111**
7.1 Bose-Einstein Statistics for the Ideal Quantum Gas . . . 111
7.2 Black-Body Radiation . . . 112
7.2.0.1 Example: Coaxial Cable Spectrum of Excitations . . . 114
7.3 Bose Condensation at Low Temperatures . . . 115
7.3.1 Energy and Heat capacity for Bose-Einstein Condensation . . . 117
7.3.2 An Exercise: Bose Condensation in 2D . . . 119
7.4 Other Elementary Excitations . . . 120
7.4.1 Phonons . . . 121
7.4.2 Spin Waves . . . 124
7.4.3 Quantum Liquids ^{4}He and ^{3}He . . . 127
7.5 Chemical potential . . . 128

8 Non-ideal Gases and Liquids **133**
8.1 Virial Theorem . . . 133
8.1.1 More on the Pair Distribution Function . . . 136
8.1.2 Internal Energy . . . 138
8.2 Virial Expansion . . . 139
8.2.1 Example: Virial Coefficient and Radial Distribution Function 141
8.3 The Van der Waals Equation of State . . . 141

9 Phase Equilibria and Transitions **143**
9.1 Examples of Phase Transitions . . . 144
9.1.1 Magnetism and the Ising Model . . . 144
9.1.1.1 Ising Model in 1D . . . 145
9.1.1.2 The Ising Model within Mean Field Theory . . . 146
9.1.2 Mixing and Phase Separation . . . 148
9.1.2.1 Spinodal and Binodal Lines . . . 151

9.2 First Order Phase Transition . . . 154
9.2.0.1 General Classification of Phase Transitions . . . 156
9.3 Landau Theory of Phase Transitions . . . 156
9.3.1 Magnetic Phase transition within Landau Theory . . . 157
9.3.2 Example: Liquid Crystal . . . 160
9.3.3 Example: Coupled Order Parameters . . . 161
9.4 Critical Exponents and Universality . . . 163

10 Fluctuations in Equilibrium **167**
10.1 Fluctuations . . . 167
10.1.1 Fluctuations and the Boltzmann-Gibbs Distribution . . . 167
10.1.1.1 Example: Fluctuations of Particle Number . . . 169
10.2 Connection with Thermodynamics . . . 170
10.2.1 Energy Fluctuations . . . 173
10.2.2 Anharmonic Oscillator . . . 175
10.3 Fluctuations near Critical Points . . . 176
10.3.1 Critical Fluctuations at Ferromagnetic Phase Transition . . . 178

11 Elements of Stochastic Physics **181**
11.1 Brownian Motion . . . 181
11.1.1 Fluctuation-Dissipation Relation . . . 182
11.2 Diffusion of Free and Confined Particles . . . 183
11.2.1 Brownian Particle in a Potential Well . . . 184
11.2.2 Brownian Particles Escaping Sink . . . 186
11.3 Damped Harmonic Oscillator . . . 187
11.3.0.1 Langevin equation . . . 187
11.4 Working with Probability Distributions . . . 188
11.4.1 1D Random Walk . . . 188
11.4.2 Diffusion Equation . . . 190
11.5 Diffusion in External Potentials . . . 191
11.5.1 The Kramers Problem: Escape over a Potential Barrier . . . 194

Bibliography **197**

A Appendix **A.1**
A.1 Microscopics of Irreversibility . . . A.1
A.1.1 Law of Increase of Entropy . . . A.2
A.1.2 The Arrow of Time . . . A.4
A.2 Liouville's Theorem . . . A.4
A.3 Fluctuation-Dissipation Theorem and Wiener-Khinchin Theorem . . . A.5
A.3.1 Wiener-Khinchin Theorem . . . A.7
A.3.2 Power Spectrum of Fluctuations Given by Imaginary Part of the Response Function . . . A.8
A.4 Stirling's Approximation . . . A.8
A.5 Lagrange Multipliers . . . A.10
A.6 The Sommerfeld Expansion . . . A.10

B Appendix: Equations **B.1**
B.1 The Basics of Thermodynamics 1 . . . . . B.1
B.2 Thermodynamic Equilibrium 2 . . . . . B.1
B.3 The Basics of Statistical Mechanics 3 . . . . . B.1
B.4 Classical Ideal Gas 4 . . . . . B.1

List of Tables

2.1 The most commonly encountered potentials for a gas. The variables which are differentiated are the "natural variables" of the corresponding thermodynamic potential. A thermodynamic potential takes its minimum value in equilibrium under the conditions that its natural variables are held fixed. 29
2.2 Potentials important for systems held at fixed temperature. 34
2.3 Potentials important for thermally isolated systems. 34

3.1 States, occupancies, and energies for a point defect in a solid. The energy for occupation by a single electron is ε, and that for 2 electrons is $2\varepsilon + U$. 58

9.1 Examples of systems with phase transitions and their order parameters. 144
9.2 Critical temperatures for the Ising model in one, two, and three dimensions. 149
9.3 Values of critical exponents within mean field theory, for the two- and three-dimensional Ising model, and experimental values for three-dimensional ferromagnets. 164

List of Figures

1.1 Microscopic model of heat and work for an ideal gas. The collisions with the moving piston are mostly inelastic, but *upon averaging over a large number of collisions* there will be a net gain or loss of energy which can be traced to the advance or retreat of the piston. In the ball and spring model of the wall there is random thermal motion. . . 3
1.2 The inter-molecular potential for a Van der Waals gas. 5
1.3 Without a magnetic field the up- and down-spin energy levels are degenerate, but the magnetic field splits the degeneracy. 6
1.4 An irreversible process in which a mass m hits a piston at velocity v and compresses the gas. 10
1.5 The $p - V - T$ surface of a generic material, and its projections into the (p, V) and (p, T) planes. The isotherm with the numbers along it is illustrated in Fig. 1.6. 11

1.6 Illustration of the states of a system along an isotherm which passes through both the liquid-vapour and the solid-liquid phase equilibria regions. The numbers correspond to those on an isotherm of Fig. 1.5. 12

1.7 Isotherms of the van der Waals equation of state. 13

1.8 Toy model of the origin of latent heat. 13

1.9 Schematic representation of a heat engine operating between a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. . 15

1.10 If we take a system around a cyclic process between reservoirs at temperatures T_1 to T_N, we can extract a total amount of work W from the process. This work can be used to drive N heat pumps that will pump heat $Q_1, \cdots, Q_N$ back into the reservoirs, extracting heat from a single reservoir at temperature T_0 in the process. The amount of work needed to drive all of these heat pumps must be at least as high as the work W we can extract from the cyclic process, otherwise we would be able to get work out of the entire arrangement, violating Kelvin's statement of the second law. 15

1.11 Considering the entropy change between two states A and B. Because the loop integral of $đQ/T$ is ≤ 0, $S_B - S_A \geq \int đQ/T$ along the irreversible path. If the system is actually isolated, then the r.h.s. is $= 0$, implying that the entropy will stay the same or increase, but cannot go down. 17

1.12 **A Carnot cycle**. $1 \to 2$: Isothermal expansion; heat absorbed from high temperature reservoir Q_{in}; work is done on surroundings. $2 \to 3$: Adiabatic expansion; $\Delta Q = 0$; work is done on surroundings, medium cools. $3 \to 4$: Isothermal compression; heat given out to cold reservoir Q_{out}; work is done by surroundings. $4 \to 1$: Adiabatic compression; $\Delta Q = 0$; work is done by surroundings, medium warms. 18

2.1 A small section of the $(S - U - (T_1 - T_0))$ surface for a volume of ideal gas partitioned by an adiathermal wall. We imagine that we can transfer energy across the partition (using external heat engines for example) and then we calculate the total entropy, using the SackurTetrode expression (to be rederived later). Equilibrium of the unpartitioned system at fixed total energy occurs when the entropy is a maximum. We see that this equilibrium corresponds, at fixed total entropy, to a minimum of the energy. They both occur when $T_1 = T_0$. Because the volumes chosen are arbitrary, this tells us that in equilibrium the temperature is uniform. 22

2.2 Two systems connected by a thermal link. The heat flows from the hotter to the colder body and at equilibrium $T_1 = T_2$. 23

2.3 A container is divided into two parts by a membrane which is permeable to salt but not to water. On the left of the semi-permeable membrane the water contains some salt, and on the right is pure water. The entropy is maximised when $\mu_1 = \mu_2$, i.e., the salt concentrations are equal. 23

2.4 Reversible compression of a monatomic ideal gas connected to a reservoir at constant temperature. Fixed temperature T implies constant internal energy U (Molecules in an ideal gas are assumed to have zero interaction with each other and so have only kinetic energy directly determined by T), and so $đQ = -đW$. 28
2.5 A schematic flow process. 30
2.6 Two gases initially at pressures p_1 and p_2 are separated by a movable barrier. The temperature is fixed and equal to T. The barrier moves under the pressure forces until the Helmholtz free energy reaches its minimum value, which occurs when $p_1 = p_2$. 31
2.7 Adding particles at constant T and p. 33
2.8 The condition for a phase transition is that the Gibbs free energies of competing phases cross. The extrapolation of the Gibbs free energy of a phase to beyond the region in which that phase is stable is justified, for a short distance at least, by the metastability of supercooled and superheated phases. 35
2.9 Isotherms of the van der Waals gas (see also Section 1.3). As shown in Eq. (2.41), the vapour pressure is fixed by the requirement that the two shaded regions have equal areas if the chemical potentials of the two phases are equal. 36
2.10 Phase coexistence lines for water in the (p, T) plane. The Clausius-Clapeyron equation (2.44) gives an expression for the gradient of the phase boundaries, $\frac{\mathrm{d}p}{\mathrm{d}T} = L_m/(T\Delta v_m)$. 37
2.11 Chemical reaction at constant temperature and pressure. At a given temperature and pressure the relative amounts of the chemical components are functions of state. In our example, at high temperatures CO_2 breaks down into CO and O_2. 40
2.12 Equilibrium constant for the $2CO_2 \rightleftharpoons 2CO + O_2$ reaction (following Hayward, *Equilibrium Thermodynamics*). 42

3.1 A partition of the total energy E between two subsystems. 45
3.2 The probability, $P(E)$, that a system has energy E is proportional to the product of the statistical weight, $\Omega(E)$, and the Boltzmann factor. $P(E)$ is sharply peaked around the mean value of U, the shaded area regarded as a Gaussian. 52
3.3 Caption 60
3.4 The mean magnetisation, m, per spin, the heat capacity per spin, c, and the entropy per spin, s/k_B, for a two-level system. 61
3.5 We have $U = \sum p_i E_i \implies \mathrm{d}U = \sum E_i\,\mathrm{d}p_i + \sum p_i\,\mathrm{d}E_i$, and also that $\mathrm{d}U = đQ + đW$. Thus the internal energy can conceptually be changed in two ways: moving particles to other states- i.e. transfering energy (heat) to particles; and keeping state occupation the same, but changing state energies – i.e. doing work on the system. Hence, we see that the reversible heat flow, $đQ_{\mathrm{rev}} = \sum_i E_i\,\mathrm{d}P_i$, comes from the change in the probability distribution while the reversible work, $đW_{\mathrm{rev}} = \sum_i P_i\,\mathrm{d}E_i$, comes from the change in the energy levels. 63

4.1 Caption 74
4.2 The heat capacity of a harmonic oscillator as a function of temperature. 77
4.3 The rotational heat capacity as a function of temperature. 78
4.4 The rotational-vibrational heat capacities at constant pressure, C_p, for the diatomic gases DT, HT, and HD, as a function of temperature. 78
4.5 Particles of "size" λ^3 filling the box of volume V. 79

5.1 The pair-correlation functions for two fermions of the same spin and for two bosons of the same spin. 82
5.2 Langmuir isotherms for different ratios of the rate constants, k_d/k_a. . 95

6.1 The average occupation and entropy of an energy level as a function of energy in a Fermi gas at zero temperature (solid blue line) and at a finite temperature $T \ll T_F$ (dashed dark blue line). 98
6.2 The Fermi-Dirac Distribution function at $T = 0$ and various small T. The distribution differs from the $T = 0$ ground state only for a range of energies k_BT around ε_F as excitations are only significant within roughly k_BT of the Fermi energy. 98
6.3 The four lowest-energy eigenfunctions for a particle in a box. 99
6.4 The allowed k-values for a box with hard walls. 99
6.5 Variation of μ with T for non-interacting fermions and bosons at fixed density. [10] 103
6.6 Low-temperature heat capacity of copper as an example of a metal that gets not superconducting. The heat capacity is given by the superposition of the linear-in-T heat capacity of the electrons and of the T^3 heat capacity of the phonons. Both functions pass into the origin. [5] 110

7.1 The Fermi-Dirac, $\left\langle n^{(F)} \right\rangle$, and Bose-Einstein, $\left\langle n^{(B)} \right\rangle$, distributions as a function of $\beta(\varepsilon_{\mathbf{k}} - \mu)$. 112
7.2 Energy density for black-body radiation at 1000 and 2000K (represented here as proportional to the measurable intensity of light). The total energy densities correspond to the areas under the respective curves. 113
7.3 Black body spectral radiance curves for various temperatures after Planck, and comparison with the classical theory of Rayleigh-Jeans (in cgs units). 114
7.4 The cosmic background radiation as measured by the Cosmic Background Explorer (COBE), after Mather *et al.* (1990). [7] The continuous curve is a fit to the data using the Planck distribution, which yields a temperature of $T = 2.735 \pm 0.06$K. Since the Big Bang the background radiation has undergone expansion, with its temperature gradually decreasing. 115
7.5 Integrand of Eq. (7.17). We try to change μ as T changes, to keep the area under the curves constant. At low temperature this becomes impossible, without making μ positive, which causes infinite occupation numbers in some levels (and is thus not allowed). 116

7.6 The chemical potential as a function of temperature in an ideal Bose gas. 117
7.7 The fraction of the particles in the ground state, N_0/N, and in the excited states, $N(\varepsilon > 0)/N$, as a function of temperature. 118
7.8 The specific heat in the ideal gas theory of Bose-Einstein particles and in ^{4}He. 119
7.9 Phonon dispersion relationship of a one-dimensional monatomic chain in a simple solid, realistic model in red and the corresponding Debye approximation in blue. [4] 121
7.10 The specific heats of Al, Cu and Pb, from experiment and from the Debye model, plotted against T/Θ_D. 123
7.11 The phonon density of states of aluminium (solid line) and of the Debye model (dashed line). 123
7.12 Classical picture of a spin wave in a ferromagnet. In the ground state all the spins are parallel, but when a spin-wave excitation is present the spin vectors precess, with successive spins being advanced by a constant phase angle. The line drawn through the ends of the spins in the lower picture shows the wavelength of the excitation. 124
7.13 Dispersion relations for the ferromagnetic and lower antiferromagnetic elementary excitations. The non-interacting and interacting spin-wave calculations are shown by solid and dotted curves respectively, whereas represents the matrix product and the exact diagonalization results (up to $N = 7$). The ground state energy is supposed to be zero. [8] 125
7.14 Spin waves in many ferromagnets show a gap at low energy, due to coupling of the orbital moments to the crystalline lattice. Typically resulting in this dispersion relation curves. 125
7.15 Comparison of the low temperature specific heats of ^{4}He and ^{3}He. This difference arises because ^{3}He is a fermion, while ^{4}He is a boson. The above figure shows ^{3}He exhibits Fermi fluid behaviour at low temperature while ^{4}He shows condensation. Near 1.5 K, $C/N_k = 1$ for both films, indicating 2D ideal gas behavior. [9] The lower figure shows the measured dispersion curve for the elementary excitations in liquid ^{4}He. 129
7.16 Caption 131

8.1 A plot of the Lennard-Jones potential, (solid red line) exhibiting the repulsive and attractive contributions (dotted blue lines). [3] 134
8.2 Radial distribution functions $g(r)$ for Lennard-Jones $6-12$ potential in a simple liquid of argon in different thermodynamic states. Note that the potential always tends to 1 for large r, as expected due to the lack or correlation between the particle at $\mathcal{O}$ and at r. [6] 135
8.3 The second virial coefficient in reduced units for a Lennard-Jones gas (solid line) as a function of the reduced temperature, $T* = k_BT/\epsilon$, compared with experimental data. Note that at low $T*$ the He data does not fit the classical result because of quantum effects. 140

8.4 The form of the density-independent part of the radial distribution function versus r for $k_BT \gg \varepsilon$ and $k_BT \gg \varepsilon$. 141

9.1 Solving the self-consistent equation (9.10) graphically for $B = 0$ and various values of zJ/k_BT. The yellow plot is at $T > T_c$, the orange plot is at $T = T_c$, and the dark red bottom plot is at $T < T_c$. 149
9.2 The average value of the spin on a site, $\langle\sigma\rangle$, as a function of T/Tc within the Weiss theory. 150
9.3 Plots of the free energy of mixing (9.27) for different values of the χ-parameter. The figure illustrates that the mixture for $\chi = 3$ is energetically unfavourable compared to the fully phase separated arrangement, whereas for small χ values (higher temperatures), it is favourable for the two species to remain fully mixed 152
9.4 [Left] The sketch of $F_{\text{mix}}(c)$ illustrating stability of the mixture against separation of species. In the convex ($F'' > 0$) region, at any concentration c, any small fluctuation leading to two nearby regions $c \pm \Delta c$ leads to the overall free energy increase. A similar fluctuation in the concave ($F'' < 0$) region leads to the decrease of free energy on any small fluctuation and, therefore, instability of the mixture against macroscopic separation. The boundary of stability (labelled by χ on this sketch) gives the spinodal line on the phase diagram. [Right] Plots of the binodal and spinodal lines, as $\chi(c)$ variation. 153
9.5 The phase diagram of a mixture plotted in T, c coordinates, with the binodal, spinodal and critical point labelled. An initial mixture, prepared at concentration c_A at temperature T_A, after cooling to a temperature inside the demixing region (point A' on the diagram) will phase separate into the fractions, one rich in "1" (high c) and one rich in "2" (low c) minima of the mixing free energy. 154
9.6 : [Left] The change in the free energy, $\Delta F = F_{\text{mix}}(c) - F_{\text{mix}}(c_X)$ plotted against the fluctuation amplitude $\phi = c - c_X$ for several values of χ-parameter above the critical point. [Right] The values of $\Delta F(\phi)$ at the point of minimum $\phi = \phi^*$, as function of χ or T, showing the region of coexistence with the mixed state $\phi = 0$, $\Delta F = 0$. 155
9.7 The free energy F of a simple magnetic system as a function of magnetisation M when no magnetic field is present, for a value of $T > T_c$ in dark blue and a value of $T < T_c$ in dark red. 158
9.8 The free energy F as a function of magnetisation M with a symmetry-breaking magnetic field $B > 0$, for one value of $T > T_c$, and three values of $T < T_c$. 159
9.9 Phase diagram for a simple magnetic system. 160
9.10 Caption 162

10.1 The Helmholtz free energy is a minimum at the mean value of U, and the probability distribution for U is a sharply peaked Gaussian centred on the mean value. 172
10.2 Volume fluctuations at constant T and N. 176

10.3 The fluctuations grow as one approaches the critical point, where they diverge. 177
10.4 Specific heat of liquid ^{4}He obtained with the PIMC method around the normal-to-superfluid λ phase transition. The line corresponds to experimental results. [11] The point's name derives from the graph that results from plotting the specific heat capacity as a function of temperature, which resembles the Greek letter lambda λ. The specific heat capacity has a sharp peak as the temperature approaches the lambda point. [2] 179

11.1 An example of stochastic force acting on the Brownian particle from the surrounding medium in thermal motion. 182
11.2 Mean square displacement of labelled impurities, diffusing in pure and distorted crystalline lattices. 184
11.3 Particle moving under thermal noise in a potential well. 185
11.4 The scheme of 'detailed balance' - the change in probability $P(m)$ is due to the difference between the *rate in*, Eq. (11.32), and the *rate out*: $-(w_+ + w_-)P(m)$. 190
11.5 The time-evolution of particle concentration $c(x,t)$, proportional to the probability, during sedimentation. The left panel shows particles "sinking" from an initial delta-function distribution at $x = x_0$, and the right panel shows particles being "lifted" by the thermal excitation having started from a delta-function distribution at $x = 0$. 193
11.6 The potential energy profile of the Kramers problem. The key parameter is the height of the energy barrier, ΔE, at a position x_0. . . . 194

A.1 Four snapshots of a gas in a box approaching equilibrium. A.2

Chapter 1

The Basics of Thermodynamics

1.1 Introduction

The ideas and methods developed in this course find very broad application, not only within physics, but in biology, geology, chemistry, astronomy, engineering, computer science/artificial intelligence/information technology, finance, philosophy, etc. Indeed one of the central reasons why a physics degree is an ideal preparation for doing interdisciplinary research (not to mention investment banking, or theology) is that physicists are trained to quantitatively understand probability, entropy, equilibrium, fluctuations, irreversibility and chaos. Therefore, whether or not you end up with a career in physics, mastering the central ideas in this course will serve you well in the future.

The subject matter in this course divides into *Fundamental ideas and Methods of thermal physics*, which actually are not limited to this area and have very general relevance for the rest of physics. The topics are chosen to illustrate ideas and methods of thermal physics, but also because many important results about Nature will thus be obtained and discussed.

For the purposes of this course, the following "working definitions" might be helpful

- **Thermodynamics** is primarily concerned with *the flow of energy*: (a) from macroscopic to microscopic length scales, and vice-versa, and (b) between one kind of microscopic degree of freedom and another. Thermodynamics is a macroscopic 'phenomenological' theory which involves no assumptions about the microscopic nature of matter or radiation. Indeed much of the theory of thermodynamics was developed before accurate microscopic pictures were developed.
- **Equilibrium statistical mechanics** is primarily concerned with the "storage" and balance between energy and entropy at the microscopic level, i.e. with the question of how energy is distributed among the many internal degrees of freedom of an object. Statistical mechanics involves a detailed microscopic theory and the use of probabilities to deduce macroscopic, observable characteristics.

These definitions are illustrated in the next section, which describes basic features of model systems which will be used throughout the course.

1.1.1 Ideal Gas

1.1.1.1 Energy Storage

The energy stored in a monatomic ideal gas is the sum of the kinetic energies of all the atoms in the gas:

$$U = \sum_{i=1}^{N} \frac{1}{2} m v_i^2, \tag{1.1}$$

where m is the atomic mass and $\mathbf{v}_i$ is the velocity of the ith atom in the gas. An external field such as gravity would give an additional term of potential energy $\sum_{i=1}^{N} V(\mathbf{r}_i)$ in U. We know that the speeds of the atoms are randomly distributed according to the Maxwell distribution. You have seen it derived in previous years, and we shall also obtain it here as a classical limit of the general quantum-statistical description, as well as the steady-state limit of the probability of free Brownian motion:

$$P(v)\,\mathrm{d}v = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT} 4\pi v^2\,\mathrm{d}v\,. \tag{1.2}$$

This leads to the average total energy of mono-atomic ideal gas, in 3D: $U = N\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}Nk_BT$, in agreement with the principle of equipartition of energy.

Other properties of the ideal gas with which you should be familiar are:

$$pV = Nk_BT \qquad \text{Ideal gas law} \tag{1.3}$$

$$pV^\gamma = \text{a constant in an Adiabatic process} \tag{1.4}$$

where p is the pressure and γ is the ratio of the heat capacity at constant pressure, C_p, to that at constant volume, C_V. Note that we use Nk_B, where N is the number of molecules and k_B is the Boltzmann constant, rather than nR, where n is the number of moles and R is the molar gas constant. That is because we are developing the true microscopic theory where the 'players' are individual particles, and so we count them directly.

1.1.1.2 Energy Flow In and Out of an Ideal Gas

Macroscopic ↔ Microscopic Energy Flow As illustrated in Fig. (1.1), energy can be transferred to the gas by macroscopic motion of a piston. Atoms colliding with an advancing piston gain kinetic energy (assuming for simplicity elastic collisions), and by this mechanism the gas as a whole gains energy as it is compressed. The change in the energy of the gas, assuming that no heat can flow into or out of it, is

$$\mathrm{d}U = đW \quad (= -p\,\mathrm{d}V \quad \text{if the compression is reversible}), \tag{1.5}$$

where we have used conservation of energy to state that the work done, $đW$, must be equal to the change in the internal energy of the gas.[1] The slash through the symbol đ denotes that there is no actual function W of which we are taking the derivative; work is just one of a number of ways that energy can get into or out of the system, so it never makes sense to say that the system "contains" a given amount of work: it contains energy, in this case in the form of kinetic energy of the atoms in the gas. In other words, $đW$ is a short-hand notation which means "a change in the internal energy U which occurs as a result of work being done on the system."

Fig. 1.1: Microscopic model of heat and work for an ideal gas. The collisions with the moving piston are mostly inelastic, but *upon averaging over a large number of collisions* there will be a net gain or loss of energy which can be traced to the advance or retreat of the piston. In the ball and spring model of the wall there is random thermal motion.

Microscopic ↔ Microscopic Energy Flow

1. **Heat**: Energy can also leave or enter the gas as *heat*. For example, collisions between a molecule in the gas and the atoms in the wall will in general be inelastic, i.e., energy will be exchanged (see Fig. 1.1) with a net flow of energy through this route. The walls and the gas will be said to be in thermal equilibrium when, if we *average over an enormous number of such collisions*, there is no net flow of energy through this route. To get energy into the gas through this route we would first have to increase the average kinetic energy of the atoms in the wall (for example by frictional heating, a process which itself corresponds to an *irreversible* flow of energy from the macroscopic to the microscopic level).

   Energy which enters or leaves the gas through inelastic collisions, or by net absorption of energy from radiation, or by other microscopic mechanisms, is called *heat*. In a heat flow process at constant volume the change in energy of the system is written as

$$dU = đQ \quad (= T\,dS \quad \text{if the heat flow is reversible}), \tag{1.6}$$

[1] 1The sign of $đW$ can be confusing, because sometimes we talk about the system doing work on the outside world, and at other times we talk about the outside world doing work on the system. There should be no issues if you remember how $đW$ relates to dU, where U is the system energy. Positive work means that the system energy goes up, and vice-versa

The requirement of reversibility may seem mysterious if we have fixed the volume of the system, but it rules out processes such as convection, in which the temperature T is not uniform and well defined throughout the system.

2. **flow of particles**: Instead of changing the total energy of the gas by changing the energy of its molecules, we could change the *number* of molecules in the gas. If this is done in a reversible way, with the total entropy and volume of the system fixed, then the energy change is written as

$$\mathrm{d}U = \mu\,\mathrm{d}N\,, \tag{1.7}$$

where μ is called the "chemical potential", defined as the change in energy when you bring an extra particle into the system:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{1.8}$$

Particle flows have important applications in phase transitions, chemical reactions, diffusion and in much of the quantum statistical mechanics, and the discussion of chemical potential μ occupies a large part of this course. We will see later that there are a number of different but equivalent expressions for the chemical potential, but the one above is the definition.

The ideal gas will be used to illustrate methods and ideas of thermodynamics and statistical mechanics, but it has real applications: it accurately describes rarefied gases, and in quantum systems it is used to model Fermi gases (electrons in metals) and Bose gases (ultra-cold atoms) of particles, as well as statistics of quantum excitations: photons (black body radiation), or phonons in solids.

1.1.2 Van der Waals Gas and Other Systems

The van der Waals gas is a simple model system incorporating *interactions* between the particles. In this model the ideal gas law, $pV = Nk_BT$, is replaced by

$$\left(p + \frac{N^2a}{V^2}\right)(V - Nb) = Nk_BT \quad \text{or} \quad p = \frac{Nk_BT}{V - Nb} - \left(\frac{N}{V}\right)^2 a. \tag{1.9}$$

Inter-molecular interactions are represented by two new terms: Nb describes the volume from which a given molecule is excluded by the hard cores of all the other molecules, while $-N^2a/V^2$ arises from the pair inter-molecular attraction and acts to reduce the pressure at fixed V and T. The van der Waals equation of state has serious limitations as a model of matter - it doesn't give a good quantitative account of the behaviour of real gases and liquids, and it doesn't have a solid phase at all, but it does show a liquid-gas transition, which makes it an important model system.

Fig. 1.2: The inter-molecular potential for a Van der Waals gas.

1.1.2.1 Energy Storage

Energy is stored in the van der Waals gas in the form of kinetic energy, as in the ideal gas, but also in the inter-molecular *potential energy*. When the molecules are far apart, in a rarefied gas, the potential energy is small, but if they are condensed to form a liquid it becomes negative. If the system is strongly compressed so that the hard core repulsion is important, the potential energy becomes large and positive. These regimes are reflected in the *isotherms* of the van der Waals gas, which will be discussed in Section 1.3 (and which you have seen last year). Moreover, energy can be converted from kinetic to potential energy of the gas; this is the origin of the cooling seen upon Joule expansion of a van der Waals gas. The energy flow in/out of the system here is the same as in the ideal gas.

1.1.3 Paramagnetic Salt in an Applied Magnetic Field

The work required to change the magnetic moment of a substance from $\mathbf{m}$ to $\mathbf{m} + \mathrm{d}\mathbf{m}$ in an applied external field $\mathbf{H}$ depends on the precise definition of the process involved (let's not confuse the extensive total magnetic moment $\mathbf{m}$ and the intensive local field of magnetisation $\mathbf{M}$). The conventional definition regards only the work needed to change the state of the substance, returning any external sources of field back to zero. For example, a paramagnetic substance with magnetic moment $\mathbf{m}(\mathbf{H})$ at some large distance from a permanent magnet will experience an attractive force proportional to $(\mathbf{m} \cdot \boldsymbol{\nabla})\mathbf{H}$. Letting the substance approach the magnet until it experiences a field $\mathbf{H}_1$, we can extract work, so that the work done on the substance is $W' = -\mu_0 \int_0^{H_1} \mathbf{m}(\mathbf{H})\, \mathrm{d}\mathbf{H}$. However, the magnet is still near the substance, so in order to calculate the work required to change the state of the substance alone, we need to pull the magnet away to the previous separation, while the magnetic moment of the substance is clamped at its final value $\mathbf{m}_1$ (this is problematic in practice, but does not violate the laws of physics, so possible in a thought experiment).

Pulling the magnet away requires a larger work, to be done on the system, $W_1 = \mu_0 \int \mathbf{m}_1 \, \mathrm{d}\mathbf{H} = \mu_0 \mathbf{m}_1 \mathbf{H}_1$, giving a net work $W = \mu \int \mathbf{H} \, \mathrm{d}\mathbf{m}$. This argument produces the conventional expression for the work done on a magnetic substance, when its magnetisation is changed by first applying a field $\mathbf{H}$ and then removing the source of the field again:

$$đW = \mu_0 \mathbf{H} \, \mathrm{d}\mathbf{m} \tag{1.10}$$

This contrasts with the work done during the first part of the process only: $đW' = -\mu_0 \mathbf{m} \, \mathrm{d}\mathbf{H}$. The difference between the two expressions is the change in the potential energy of the dipole moment in an applied field, $-\mu_0 \, \mathrm{d}(\mathbf{mH})$, which is conventionally not counted as part of the *internal* energy. A good discussion of this argument can be found in the book by Adkins.

In statistical mechanics, we study a simple model for a paramagnetic substance, the two-level system: the system is just one ionised atom with a spin equal to 1/2, so it has only two quantum states: spin-up and spin-down. All N ions in the macroscopic body are assumed independent, so in effect we have a large statistical ensemble that probes what these spins do on average. However, in order to decide along which axis they are "up" or "down" we need an external field (see Fig. 1.3).

Fig. 1.3: Without a magnetic field the up- and down-spin energy levels are degenerate, but the magnetic field splits the degeneracy.

1.1.3.1 Energy Storage

How does the expression for the work on a macroscopic substance (Eq. (1.10)) relate to the microscopic degrees of freedom? We need to see how work can affect the potential energy of the microscopic dipoles in the paramagnetic substance. The potential energy of a dipole moment $\mathbf{m}$ in a given magnetic field is $-\mu_0 \mathbf{mH}$, so that the energy is minimal when $\mathbf{m}$ is parallel to the external $\mathbf{H}$ and maximal when it is anti-parallel. This energy can also be written as $U_{\text{pot}} = \mu_0 (N_\uparrow - N_\downarrow) \mathbf{m}_d H$, where $\mathbf{m}_d$ is the magnetic moment of an ion and $N_\uparrow$ and $N_\downarrow$ are the numbers of up and down spins.

1.1.3.2 Energy Flow In and Out of the System

Macroscopic ↔ Microscopic Energy Flow Let us again picture the situation described above, in which a paramagnetic substance approaches a permanent magnet. Now, consider the change of the internal energy, i.e. the energy stored in internal degrees of freedom. First, we apply a magnetic field, for instance as outlined above, by moving the substance infinitesimally closer to a permanent magnet. The energy levels of each microscopic moment split, and the lower energy level is more likely to be occupied than the higher one, so overall the overall energy – in this case made up from the potential energy contributions from all of the dipoles – changes as $\mathrm{d}U = -\mu_0\,\mathrm{d}(\mathbf{mH})$.. This is only correct, if the dipoles do not interact, because otherwise there would be additional contributions to the overall energy from interactions. During this process the work done on the system – as explained in the preceding section – was $đW' = -\mu_0\mathbf{m}\,\mathrm{d}\mathbf{H}$.. Setting $\mathrm{d}U = đQ + đW'$, we find that heat is extracted during this process:

$$đQ = \mathrm{d}U - đW' = -\mu_0\,\mathrm{d}(\mathbf{mH}) + \mu_0\mathbf{m}\,\mathrm{d}\mathbf{H} = -\mu_0\mathbf{H}\,\mathrm{d}\mathbf{m}\,. \tag{1.11}$$

How does this tally with the approach outlined earlier, which gave a work $đW = \mu_0\mathbf{H}\,\mathrm{d}\mathbf{m}$? If potential energy is accounted for separately, not as part of the internal energy, then the change in internal energy would have been zero during this process, because all the energy is attributed to potential energy. On the other hand, the work done would be $\mu_0\mathbf{H}\,\mathrm{d}\mathbf{m}$. This still gives $đQ = -\mu_0\mathbf{H}\,\mathrm{d}\mathbf{m}$, so heat is extracted.

Even if no heat was exchanged between the surroundings and the sample, heat must have left the spin system, because $đQ$ is negative: as the microscopic moments are aligned, their entropy is reduced, and a reduction in entropy corresponds to an equivalent loss of heat. Where does the heat go, if the sample was thermally isolated during this process?

Microscopic ↔ Microscopic Energy Flow In a solid containing paramagnetic ions the spins are normally in thermal equilibrium with the vibrations of the lattice (the phonons) and the electrons, so generally heat flow to/from the spins is from/to these other microscopic degrees of freedom of the solid, not from/to an external reservoir. So as the substance is magnetised, energy will be transferred from the spin system to the lattice, which will heat up or pass the heat further onto the environment.

The paramagnetic salt will be used to illustrate methods and ideas of thermodynamics and statistical mechanics.

1.1.4 Assembly of One-Dimensional Simple Harmonic Oscillators

The energy of a one-dimensional simple harmonic oscillator in its nth excited state is

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0. \tag{1.12}$$

1.1.4.1 Energy Storage

In an array of simple harmonic oscillators, energy is stored as the excitation energy of the individual oscillators. The total energy is $U = \sum_i (n + 1/2)\hbar\omega_0$, where the sum is over all the oscillators.

1.1.4.2 Energy Flow In and Out of the System

Macroscopic to microscopic energy flow would be accomplished by changing ω_0, which requires changing the shape of the potential wells of the oscillators (e.g., if you represent the phonons in a solid by simple harmonic oscillators, you can change the phonon frequencies by compressing the solid). Microscopic to microscopic energy flow requires for example a radiation bath (the walls of a black-body cavity might be modelled as an assembly of simple harmonic oscillators), or you could have energy exchanged via collisions with a surrounding gas.

This model system will be used to illustrate counting of states in statistical mechanics, and arises in the treatment of phonons and photons.

1.2 Thermodynamic Variables

In thermodynamics, systems are characterised by the values of *thermodynamic variables*, which can be classified in various ways. For example as intensive or extensive:

- **Extensive**: Extensive variables are proportional to the amount of stuff in the system and apply to the system as a whole. Examples are internal energy U, entropy S, volume V, particle number N, and heat capacity C. We can divide the heat capacity or energy by V, to get a quantity that is independent of the volume of the system. C/V is called the "specific" heat capacity. In physics, it is often more useful to divide by the number of molecules in the system, to obtain the energy, entropy, volume etc. *per molecule*; in these notes such variables will be written in lower case.

- **Intensive:** Intensive variables are independent of the system size and measure a local quantity. Examples are p, T and μ, or an external magnetic field B in a system with magnetic interactions.

One can also classify thermodynamic variables as *conjugate pairs* of "thermodynamic force" and "thermodynamic variable", in the sense that if one applies a constraint to the given system (an effective force), then the corresponding conjugate variable will change as a response. Many of these pairs are know to you, for instance, if the constraints are pressure p, linear force f, or magnetic field $\mu_0\mathbf{H}$, then the corresponding response variables are V (system volume), length l (in an elastic medium), or magnetisation $\mathbf{M}$.

The *thermodynamic state* of a system is defined by the values of its thermodynamic variables, which in turn depend on the contents of the system and its environment. If a macroscopic body is left undisturbed for a long time its thermodynamic variables attain constant values. This is the *equilibrium state* of the system in the given external conditions. Although in practice the state of a system can only be controlled by varying the *external* conditions, it is often useful, as a thought experiment, to place imaginary *internal* partitions in a thermodynamic system to establish *subsystems*. We then imagine we can vary the thermodynamic properties – energy, volume, or even particle number – of one subsystem, examining the overall effect on the total energy, entropy, etc. This conceptual trick is used in Chapter 2 to study the meaning of thermodynamic equilibrium and it will also be central to our development of statistical mechanics.

Thermodynamic variables and potentials are special because they are *functions of state*, i.e., properties of a system which are completely determined by the contents and environment. That is, they don't depend on what happened to the system in the past, only on the present conditions. For example, work and heat are *not* functions of state, but energy is; we can put energy into a system as work (e.g., by compressing a piston), and then remove it as heat (e.g., by putting the system in contact with a cold reservoir). Indeed, we can go around a loop in the (p, V) plane, doing net work and extracting net heat, but the system ends up with the same amount of energy at the end of each loop. Therefore the energy is a function of state, but work and heat are not.

An essential point about functions of state is that *we can find the magnitude of the change in a function of state in going between two equilibrium states, even if the path taken was irreversible, by choosing* any *convenient* reversible *path between the initial and final states and integrating along it.*

It was Clausius who identified the entropy as a "hidden" function of state, whose differential change is defined as

$$\mathrm{d}S = \frac{đQ_{\mathrm{rev}}}{T} \quad \text{or, for a finite change,} \quad \Delta S = \int_i^f \frac{đQ_{\mathrm{rev}}}{T} \tag{1.13}$$

According to this equation, to find the difference in entropy between two states, we integrate along any *reversible* path connecting those states. See 1.5 for the arguments leading to this definition.

1.3 Equations of State; $p - V - T$ for a Real Substance

The equilibrium behaviour of a real substance can be expressed by equations of the form

$$\Phi(p, T, V, N_1, N_2, \cdots) = 0. \tag{1.14}$$

(E.g., for an ideal gas, $pV - Nk_BT = 0$.) Analytic equations of state are never more than approximations, and the appropriate forms change radically depending on whether we are describing the solid, liquid or gaseous phases of a substance.

Fig. 1.4: An irreversible process in which a mass m hits a piston at velocity v and compresses the gas.

Graphical representations are commonly used to illustrate equations of state. The most obvious example is the $p - V - T$ surface, which makes it easier to grasp important features of the behaviour of materials. A typical example is shown in Fig. 1.5, along with the projections of the $p - V - T$ surface into the (p, V) and (p, T) planes.

Fig. 1.6 shows a sequence of states numbered one to eight along an isotherm which passes through both the liquid–vapour and the solid–liquid phase equilibrium regions. As the system is compressed, energy in the form of work continually enters the system, and heat passes out into the reservoir. It is important to note that the phase transitions occur at constant pressure and, while the new phase condenses and grows, heat (called *latent* heat) is continuously evolved. In the liquid-vapour coexistence region on the (p, V) diagram, the latent heat associated with the transition is smaller for isotherms near the *critical isotherm*, and along the critical isotherm the latent heat vanishes. Phase transitions which have latent heat associated with them are called *first order* phase transitions.

1.3.1 The Equation of State of a Van der Waals Gas

The van der Waals equation (Eq. (1.9)) is an example of an equation of state. Isotherms on its $p - V - T$ surface, projected into the $p - V$ plane, are shown in Fig. 1.7.

Starting at the low density side (i.e., high volume v per particle), we find behaviour approaching that of an ideal gas. As the density increases, the inter-molecular attraction term N^2a/V^2 causes the isotherm to fall below the ideal gas pressure, until we start to approach the density of closest packing, at which point the hard core repulsion term Nb causes the pressure to skyrocket. On some isotherms there is a very odd region where $\partial p/\partial V$ is positive, a situation which is mechanically unstable. This unphysical behaviour is a consequence of the tacit assumption that the density is uniform: in reality, in the region below the dashed line the system undergoes *phase separation* into a high density liquid phase and a low density vapour phase, following, in the case of the 80 K isotherm, the path $A - E$, rather than the path $A - B - C - D - E$.[2]

Fig. 1.5: The $p - V - T$ surface of a generic material, and its projections into the (p, V) and (p, T) planes. The isotherm with the numbers along it is illustrated in Fig. 1.6.

As another example of using microscopic reasoning to understand macroscopic thermodynamics, a simple model of inter-molecular interaction explains what latent

[2] Actually, the system can in some cases go along $A - B$ and $E - D$, if the coexistence region is approached from outside. These correspond to "super-heating" and "super-cooling" respectively, and result from failure of the new phase to nucleate. The mechanically unstable region $B - D$ is never observed.

Fig. 1.6: Illustration of the states of a system along an isotherm which passes through both the liquid-vapour and the solid-liquid phase equilibria regions. The numbers correspond to those on an isotherm of Fig. 1.5.

heat is, and why it is reduced for higher temperature isotherms in the coexistence region. Atoms are bound in the liquid by their attractive interaction with nearby atoms. Atoms at the surface are in a lopsided potential well, as shown in Fig. 1.8. The latent heat per particle is related to the amount of energy required for particles to escape into the gas from this potential well. As the temperature increases the atoms in the liquid move to higher energy states in the potential well, so less energy is required to liberate them, hence the latent heat decreases. A marginally deeper explanation comes from considering the distribution of energies of molecules in the potential well; it is the highest energy atoms which escape from the liquid, so the mean of the distribution is shifted to lower energies by the escape of atoms into the gas. Skewing the energy distribution towards lower energies is equivalent to cooling the system. To keep the liquid at constant temperature as atoms evaporate, heat must be supplied to compensate this cooling effect.

1.4 The Laws of Thermodynamics

- **0th Law** The 0th Law says that if two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other. This can be used to show the existence of a quantity called *temperature*.

- **1st Law** The First Law states that energy is conserved when heat is taken into

Fig. 1.7: Isotherms of the van der Waals equation of state.

Fig. 1.8: Toy model of the origin of latent heat.

account. This applies to the flow of energy from macroscopic to microscopic length scales and between microscopic length scales.

- **2nd Law** There are many statements of the Second Law of thermodynamics, and here are three of the best known, which can be paraphrased as follows:
  - **Clausius** *"Heat does not flow, of itself, from a colder to a hotter body."*
  - **Kelvin** *"You can't cool an object to below the temperature of its surroundings, and extract work in the process."*
  - **Carathéodory** *"In the neighbourhood of any state there are states that cannot be reached from it by an adiabatic process."*

The crowning glory of thermodynamics is that these statements (which are essentially all equivalent) imply that we can assign a value of a measurable quantity known as entropy to every equilibrium state of every system. Although it only holds on average, significant violations of it are incredibly unlikely. The Second Law of Thermodynamics is one of the most sacrosanct of all physical laws. This contrasts

with Maxwell's equations (to which there are quantum corrections), Schrödinger's equation (relativistic corrections), and Newton's law of gravitation (general relativistic corrections).

The Clausius and Kelvin statements lend themselves to discussions involving heat engines, while the more mathematical Carathéodory statement has been the starting point for a number of modern attempts to formulate the Second Law. The Carathéodory statement uses the word "adiabatic", a process in which no exchange of heat occurs. There is no implication that the process has to be slow or reversible. Examples of adiabatic processes are: expansion or compression of a gas, stirring a liquid, rubbing two objects together, smashing a plate with a hammer. Expansion or compression may be reversible, by which I mean that one can return to the original state by an adiabatic process, but rubbing, stirring and smashing are irreversible.

- **3rd Law** The contribution to the entropy of a system from each aspect which is in internal thermodynamic equilibrium tends to zero as the temperature tends to zero.

Nernst introduced this law in 1906, which he inferred from the behaviour of chemical reactions at low temperatures. The third law implies the unattainability of absolute zero temperature and that all heat capacities must go to zero as the temperature approaches zero.

1.5 Entropy

In the Part 1B course, you have learned about the Carnot cycle. During a cycle, heat Q_1 is taken from a hot reservoir at temperature T_1 and less heat Q_2 is deposited in a cold reservoir at temperature T_2. You find that if the cycle is operated reversibly (i.e. so slowly that the operating substance, the ideal gas, is in thermal equilibrium with the reservoirs when it is in contact with them), $Q_1/T_1 = Q_2/T_2$. The work that can be extracted is determined by the first law of thermodynamics as $W = Q_1 - Q_2$ (see Fig. 1.9). The efficiency $\eta = W/Q_1 = (Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1$, with which work can be extracted from the heat absorbed from the hot reservoir is the same no matter how the heat engine is actually implemented. This is the Carnot efficiency. If there was another reversible process between two reservoirs that could provide a higher efficiency, i.e. it extracts work $W' > W$ for the same Q_1, then we could use some of that work to operate the Carnot cycle in reverse. This will pump the heat Q_1 back and create a combined engine that would extract $W' - W$ from a single reservoir, which violates Kelvin's statement of the second law. If there was another reversible process between two reservoirs that worked at a *lower* efficiency than we could again exploit the discrepancy in efficiencies by using the Carnot cycle as the heat engine and using the other cycle to pump the heat back. So all *reversibly* operated heat engines *between two reservoirs* must have the same efficiency.

Fig. 1.9: Schematic representation of a heat engine operating between a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2.

The finding that $Q_1/T_1 = Q_2/T_2$ already suggests that summing the quantity $\Delta Q/T$ over the cyclic process returns zero, so if we define a new variable S such that $\mathrm{d}S = \text{đ}Q/T$, we may arrive at a new function of state. Unfortunately, this argument so far only would hold for processes between two reservoirs. We can, however, generalise it to a system undergoing a cyclic process which involves any number of reservoirs (Fig. 1.10). If we hitch up such a cyclic process involving reservoirs at temperatures $T_1, \cdots, T_N$ to N heat pumps running just between a single reservoir T_0 and each of the N reservoirs, then the work that could be extracted from this entire assembly would be $W' = W - \sum W_n = \sum Q_n - \sum Q_n(T_n - T_0)/T_n = T_0 \sum Q_n/T_n$.

Fig. 1.10: If we take a system around a cyclic process between reservoirs at temperatures T_1 to T_N, we can extract a total amount of work W from the process. This work can be used to drive N heat pumps that will pump heat $Q_1, \cdots, Q_N$ back into the reservoirs, extracting heat from a single reservoir at temperature T_0 in the process. The amount of work needed to drive all of these heat pumps must be at least as high as the work W we can extract from the cyclic process, otherwise we would be able to get work out of the entire arrangement, violating Kelvin's statement of the second law.

But we cannot extract work from this assembly, otherwise it would violate Kelvin's statement of the second law. We must have $W' \leq 0$. Hence, we find

$$\sum \frac{Q_n}{T_n} \leq 0. \tag{1.15}$$

The best we can hope for is $W' = 0$, which would happen if all the processes are operated reversibly. So we learn that for *reversible* processes, the quantity obtained from summing up heat flow over temperature, which turns into an integral for continuous changes of temperature, $\sum \Delta Q/T \to \int đQ/T$, can be used to define a function of state (because when you do that integral around a closed loop in parameter space, it gives zero). This leads to Clausius' definition of the entropy as a new function of state:

$$\mathrm{d}S = đQ_{\mathrm{rev}}/T, \tag{1.16}$$

$$S_B - S_A = \int_A^B đQ_{\mathrm{rev}}/T, \tag{1.17}$$

where $đQ_{\mathrm{rev}}$ denotes heat that flowed into the system in a reversible process and A, B denote two states of the system.

Somewhat surprisingly, maybe, the loop integral $\oint đQ/T$ for irreversible processes is actually < 0. This can be understood by noting that the temperatures in the denominator are always the reservoir temperatures. These have to exceed the system temperatures when the system accepts heat irreversibly, or they are less than the system temperatures, when the system gives up heat, so compared to the contributions $đQ/T$ for reversible processes, the contributions in the integral for irreversible processes are less.

If we now construct a process that runs from A to B and back again (Fig. 1.11), with the route from A to B potentially irreversible, but the return reversible, we find for the entire loop:

$$\oint đQ/T \leq 0, \tag{1.18}$$

and hence

$$\int_a^B đQ/T \leq \int_A^B đQ_{\mathrm{rev}}/T, \tag{1.19}$$

but the latter gives the entropy change; therefore:

$$\Delta S = S(B) - S(A) \geq \int_A^B đQ/T. \tag{1.20}$$

If, however, the outward route from A to B is taken without any heat flowing into the system or out of it, i.e. *if the system is thermally isolated, then the entropy change ΔS must be zero or positive.*

This is a key result: an isolated system will evolve in such a way that its entropy increases. At some point, it will reach an equilibrium state, from which it cannot evolve further. In this equilibrium state, its entropy will have reached a maximum.

The Second Law has a very important implication for the behaviour of the entropy of the universe, which – as a whole – is an isolated system. These are encapsulated in the Law of Increase of Entropy, sometimes called the Entropy Statement of the Second Law:

$$\Delta S_{\mathrm{total}} \geq 0. \tag{1.21}$$

Fig. 1.11: Considering the entropy change between two states A and B. Because the loop integral of $đQ/T$ is ≤ 0, $S_B - S_A \geq \int đQ/T$ along the irreversible path. If the system is actually isolated, then the r.h.s. is $= 0$, implying that the entropy will stay the same or increase, but cannot go down.

That is, in any process, the entropy of the universe increases, or in the idealised limit of a reversible process, stays constant.

For example, (meant to be illustrative, not as a proof): consider a Carnot cycle, except make the thermally isolated processes irreversible (e.g., when the piston is compressed adiabatically, friction generates heat which goes into the system, see Fig. 1.12). Over one cycle the system (consisting of the piston and the gas inside it) comes back to the same point, so $\Delta S_{\text{system}} = 0$ (one more time ... S is a function of state, so if the system comes back to the same state, the entropy returns to the same value). Because of the internal friction within the system, the reservoir sends in less heat during the warm expansion phase, $Q_h < Q_h^{(\text{rev})}$, and it absorbs more heat during the cold contraction phase, $|Q_c| > \left|Q_c^{(\text{rev})}\right|$. Note that $Q_c < 0$. Therefore, the change in the total entropy of system plus reservoir is positive:

$$\Delta S_{\text{total}} = \underbrace{\Delta S_{\text{reservoir}}}_{-(Q_h/T_h + Q_c/T_c)} + \underbrace{\Delta S_{\text{system}}}_{=0} > 0. \tag{1.22}$$

As mentioned above, the first term on the right hand side represents the heat leaving the reservoir, which is smaller in magnitude than in the reversible case. The second term represents the heat entering the reservoir, which is larger than in the reversible case. In the reversible case the two terms add to zero, but in the irreversible case they do not cancel and $\Delta S_{\text{total}} > 0$.

The First Law essentially expresses the fact that energy is conserved if we take heat into account. That is, for *any* process we can write

$$\mathrm{d}U = đQ + đW, \tag{1.23}$$

where the work term $đW$ can in general account for not just the 'volume work' $-p\,\mathrm{d}V$, but also other forms of work such as the magnetic work $\mu_0 H\,\mathrm{d}m$, the electrical work $V\,\mathrm{d}Q$ and the 'particle work', or 'chemical work' $\mu\,\mathrm{d}N$, where μ is the chemical potential and N is particle number. Note that in principle we could include not just irreversible changes between equilibrium states but also changes between non-equilibrium states. All we are saying is that the energy can only change by a flow of heat in or out, or by work being done. If the change takes place between two adjacent equilibrium states, then (ignoring other forms of work than

Fig. 1.12: A Carnot cycle. $1 \to 2$: Isothermal expansion; heat absorbed from high temperature reservoir Q_{in}; work is done on surroundings. $2 \to 3$: Adiabatic expansion; $\Delta Q = 0$; work is done on surroundings, medium cools. $3 \to 4$: Isothermal compression; heat given out to cold reservoir Q_{out}; work is done by surroundings. $4 \to 1$: Adiabatic compression; $\Delta Q = 0$; work is done by surroundings, medium warms.

volume work and chemical work)

$$đW = -p\,\mathrm{d}V + \mu\,\mathrm{d}N\,, \tag{1.24}$$

$$đQ = T\,\mathrm{d}S\,, \tag{1.25}$$

$$\Longrightarrow\ \mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V = \mu\,\mathrm{d}N\,, \tag{1.26}$$

all for reversible changes only. But $\mathrm{d}S$, $\mathrm{d}V$ and $\mathrm{d}N$ are differentials of functions of state, so *provided that we are talking about a change between two equilibrium states*,

$$\boxed{\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,,} \tag{1.27}$$

always, even if the process connecting the equilibrium states is *irreversible*.

This equation shows that U is a function of the three independent variables S, V, N – these are the "natural variables of U"; while T, p, μ are "derived quantities":

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{1.28}$$

1.6 The Gibbs-Duhem Equation

Although there are a number of ways in which changes between equilibrium states can be expressed mathematically, that based on Eq. (1.27) has a very special place. It expresses changes in the energy, which is itself an extensive quantity, in terms of changes in the other extensive quantities. We know that the energy is a homogeneous first order function of the extensive variables, or in plain English, if we simultaneously double the volume, number of particles and entropy of a system,

while holding the temperature, pressure and chemical potential constant, then its energy also doubles. Therefore, generalising to an increase by a factor of λ we can write $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$, so that

$$\begin{aligned} U(S,V,N) &= \frac{\partial(\lambda U(S,V,N))}{\partial\lambda} \\ &= \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda S)}\right)_{\lambda V,\lambda N}\frac{\partial(\lambda S)}{\partial\lambda} + \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda V)}\right)_{\lambda S,\lambda N}\frac{\partial(\lambda V)}{\partial\lambda} \\ &\quad + \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda N)}\right)_{\lambda S,\lambda V}\frac{\partial(\lambda N)}{\partial\lambda} \\ &= \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda S)}S + \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda V)}V + \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda N)}N. \end{aligned} \tag{1.29}$$

This must be true for *any* λ, so we can set $\lambda = 1$ to get

$$U(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{S,V} N. \tag{1.30}$$

But we know from Eq. (1.27) that

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p, \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu, \tag{1.31}$$

hence it must be true that

$$U = TS - pV + \mu N. \tag{1.32}$$

Again, this only worked for $U(S, V, N)$, uniquely, because of the extensive nature of all entries. You can never write this as $U = TS - pV$, even if the particle number is fixed. The μN term is essential! This equation can be generalised to the case where several species of particle are present by replacing μN by $\sum_i \mu_i N_i$. Note that there was nothing special about starting from $U(S, V, N)$, we could just as well have derived Eq. (1.32) starting from, for example, $S(U, V, N)$, as it also has all entries extensive.

One can derive useful results directly from the Eq. (1.32). We know that $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$, but Eq. (1.32) gives $\mathrm{d}U = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \mu\,\mathrm{d}N + N\,\mathrm{d}\mu$. Both of these equations can only be true at the same time if

$$N\,\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p\,, \tag{1.33}$$

$$\implies \mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p\,, \tag{1.34}$$

where s and v are the entropy and volume per particle (now intensive, as is the chemical potential μ). This important result is known as the Gibbs-Duhem equation.

Chapter 2

Thermodynamic Equilibrium

Thermodynamic equilibrium is the state in which the thermodynamic variables are independent of time. The governing principle of thermodynamic equilibrium is that the entropy of the universe tends to a maximum. This is the entropy statement of the second law of thermodynamics. Thus the equilibrium condition is that the *total* entropy is maximised.

2.1 Internal Equilibrium of Closed Systems

The method we adopt for studying the internal equilibrium of closed systems, which will be used repeatedly throughout the course, is to place imaginary partitions into a large system to partition it into two or more subsystems. This is illustrated in Fig. 2.1, which shows what happens if we partition a large volume of gas into two parts, and then independently vary their temperature.

We know from the entropy statement of the Second Law, $\mathrm{d}S \geq 0$, that the equilibrium state is characterised by maximum entropy of the universe. In this figure, if we close the system so that its total energy is fixed, then it constitutes the universe, so maximum S at fixed U is the equilibrium condition. From the figure we can observe that the state of maximum entropy at fixed total energy is also the state of minimum energy at fixed total entropy, a curious but not-very-useful condition in real systems. In the next section we explore the mathematical meaning of equilibrium using the *entropy representation*.

2.1.1 Maximum Entropy Principle

As discussed above, the actual equilibrium states we observe are the ones which maximise the entropy of the universe; in the *approach* to equilibrium, the entropy of the universe increases. We will illustrate this with two examples.

1. Two systems with constant volumes and numbers of particles are allowed to exchange heat. We bring two otherwise isolated, or "closed", systems at temperatures T_1 and T_2 into thermal contact, holding their volumes and particle numbers constant, as shown in Fig. 2.2. The entropy statement of the Second

Fig. 2.1: A small section of the $(S-U-(T_1-T_0))$ surface for a volume of ideal gas partitioned by an adiathermal wall. We imagine that we can transfer energy across the partition (using external heat engines for example) and then we calculate the total entropy, using the SackurTetrode expression (to be rederived later). Equilibrium of the unpartitioned system at fixed total energy occurs when the entropy is a maximum. We see that this equilibrium corresponds, at fixed total entropy, to a minimum of the energy. They both occur when $T_1 = T_0$. Because the volumes chosen are arbitrary, this tells us that in equilibrium the temperature is uniform.

Law is

$$\begin{aligned} \mathrm{d}S_{\mathrm{tot}} &= \mathrm{d}S_1 + \mathrm{d}S_2 \\ &= \frac{\mathrm{d}U_1 + p_1\,\mathrm{d}V_1 - \mu_1\,\mathrm{d}N_1}{T_1} + \frac{\mathrm{d}U_2 + p_2\,\mathrm{d}V_2 - \mu_2\,\mathrm{d}N_2}{T_2} \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}U_1 \geq 0, \end{aligned} \tag{2.1}$$

where we have used $\mathrm{d}V_i = 0$ (constant volume), $\mathrm{d}N_i = 0$ (constant particle number), and $\mathrm{d}U_2 = -\,\mathrm{d}U_1$ (energy conservation). This equation means that if T_1 is greater than T_2, $\mathrm{d}U_1$ is negative and heat flows from 1 to 2, but if T_1 is less than T_2, $\mathrm{d}U_1$ is positive and heat flows from 2 to 1. So heat flows from hot to cold. In equilibrium, the entropy is an extremum, and small displacements of U_1 must not increase the entropy or we can't be at equilibrium. This requires $T_1 = T_2$ at equilibrium.

2. Similarly, from $\mathrm{d}S \geq 0$ we can show that particles flow from higher to lower chemical potential. Consider two systems with fixed volumes V_1 and V_2, held at the same temperature T, but arranged so that their chemical potentials differ (for example we might add a small amount of salt on one side of a semi-permeable barrier separating the two volumes shown in Fig. 2.3).

   The entropy statement of the Second Law of thermodynamics gives

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = \frac{\mathrm{d}U_1 + p_1\,\mathrm{d}V_1 - \mu_1\,\mathrm{d}N_1}{T_1} + \frac{\mathrm{d}U_2 + p_2\,\mathrm{d}V_2 - \mu_2\,\mathrm{d}N_2}{T_2} \geq 0. \tag{2.2}$$

The total energy is fixed, so $\mathrm{d}U_1 + \mathrm{d}U_2 = 0$, and the volumes are fixed so that $\mathrm{d}V_1 = \mathrm{d}V_2 = 0$. Particle number is also conserved, so $\mathrm{d}N_1 = -\mathrm{d}N_2$, and the law of increase of entropy reduces to

$$(\mu_2 - \mu_1)\,\mathrm{d}N_1 \geq 0. \tag{2.3}$$

Therefore if $\mu_2 > \mu_1$ then $\mathrm{d}N_1 > 0$, and particles flow from 2 to 1, whereas if $\mu_2 < \mu_1$, then $\mathrm{d}N_1$ and particles flow from 1 to 2. Hence

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{2.4}$$

is a good definition of the chemical potential, because it makes explicit the dependence of particle flow on the law of increase of entropy.

Fig. 2.2: Two systems connected by a thermal link. The heat flows from the hotter to the colder body and at equilibrium $T_1 = T_2$.

Fig. 2.3: A container is divided into two parts by a membrane which is permeable to salt but not to water. On the left of the semi-permeable membrane the water contains some salt, and on the right is pure water. The entropy is maximised when $\mu_1 = \mu_2$, i.e., the salt concentrations are equal.

The maximum entropy condition can be applied straightforwardly to closed systems (that is, to systems which do not exchange energy or particles with the outside world). To do this, we put internal constraints in place and then maximise the entropy with respect to those constraints. To apply this *in the most general way* to a system consisting of fluid of total energy U, total volume V, and total particle number N, we place an imaginary wall into the system which partitions it into two volumes V_1 and V_2, with energies U_1 and U_2 and particle numbers N_1 and N_2. Because the system is closed, $V_1 + V_2 = V$, $U_1 + U_2 = U$ and $N_1 + N_2 = N$. We now

maximise the total entropy $S = S_1 + S_2$, setting $\mathrm{d}S = 0$:

$$\begin{aligned}
\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 &= \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1,V_1} \mathrm{d}U_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{N_1,U_1} \mathrm{d}V_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1,V_1} \mathrm{d}N_1 + \\
&\left(\frac{\partial S_2}{\partial U_2}\right)_{N_2,V_2} \mathrm{d}U_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{N_2,U_2} \mathrm{d}V_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2,V_2} \mathrm{d}N_2 \\
0 &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \mathrm{d}U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) \mathrm{d}V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) \mathrm{d}N_1 \,, \qquad (2.5)
\end{aligned}$$

where we have used $T\,\mathrm{d}S = \mathrm{d}U + p\,\mathrm{d}V - \mu\,\mathrm{d}N$. The three separate terms mean that in equilibrium, the temperatures of the two parts are equal, the pressures are equal, and the chemical potentials are equal. Moreover, in the approach to equilibrium, heat will flow from the hot to the cold part, the high pressure part will expand and the low pressure part will contract and, finally, particles will flow from high to low chemical potential.

2.2 Thermodynamic Equilibrium in Open Systems

In order to apply the principle of maximum entropy to open systems, we consider the open system plus the reservoir as a closed system. This immediately tells us that when the system is in complete equilibrium with the reservoir, its temperature equals the reservoir temperature, its pressure equals the reservoir pressure, and its chemical potential equals that of the reservoir.

2.2.1 The Availability

For thermally isolated systems, as we have seen, thermodynamic equilibrium can be defined as the state of maximum entropy for a given total energy, or we can define it as the state of minimum energy for a given total entropy. It is generally not convenient to have to consider the entropy of the reservoir explicitly, in maximising S.

However, for a system in contact with a reservoir – and most thermodynamic systems are in thermal and/or mechanical contact with the rest of the universe – it turns out that there is a very useful alternative to maximising the total entropy of the system *and* the reservoir with respect to the state of the system: there is a property of the *system*, called the *availability*, whose is minimisation produces the same result as maximising the total entropy of the *universe* (system + reservoir) with respect to the state of the system.

To see this, consider a system (denoted by quantities without subscripts) and reservoir (labelled "R"), which can exchange energy in the form of heat and/or work,

and particles. The Entropy Statement of the Second Law is

$$\begin{aligned} \mathrm{d}S_{\text{tot}} &= \mathrm{d}S + \mathrm{d}S_R \geq 0 \\ &= \mathrm{d}S + \frac{\mathrm{d}U_R + p_R\,\mathrm{d}V_R - \mu_R\,\mathrm{d}N_R}{T_R} \qquad (2.6) \\ &= \frac{T_R\,\mathrm{d}S - \mathrm{d}U - p_R\,\mathrm{d}V + \mu_R\,\mathrm{d}N}{T_R}, \qquad (2.7) \end{aligned}$$

where we have used conservation of energy, volume and particle number, which give $\mathrm{d}U_R = -\,\mathrm{d}U$, $\mathrm{d}V_R = -\,\mathrm{d}V$ and $\mathrm{d}N_R = -\,\mathrm{d}N$.

The present situation is rather special, because it involves exchange of all possible quantities with the reservoir: there are many cases (discussed in more detail below, when thermodynamic potentials are introduced), in which the contact with the reservoir is only partial. For instance, the reservoir may receive volume from the system, but not particles. In such a case, $\mathrm{d}V_R = -\,\mathrm{d}V$, still, but $\mathrm{d}N_R = 0$. You could rederive what follows below for such special cases, and this would lead to the definitions of the various potentials, or you can take the general route (now following) and then formally – as a shortcut – set certain terms to 0. For instance, the effect of having no particle exchange, $\mathrm{d}N_R = 0$, on the reservoir entropy in Eq. (2.6) above can be achieved in Eq. (2.7) by simply setting $\mu_R = 0$.

So far we haven't used the assumption that the reservoir is large compared with the system, but if we now do so we have that for any change the system can undergo, $\mathrm{d}T_R = 0$, $\mathrm{d}p_R = 0$ and $\mathrm{d}\mu_R = 0$. We can therefore bring all of the differentials to the front, i.e., $p_R\,\mathrm{d}V = \mathrm{d}(p_R V)$. We now define the new object, called *availability* A, as $\mathrm{d}A = -T_R\,\mathrm{d}S_{\text{tot}}$ which means:

$$\boxed{\begin{aligned} \mathrm{d}A &= \mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N \\ &= (T - T_R)\,\mathrm{d}S - (p - p_R)\,\mathrm{d}V + (\mu - \mu_R)\,\mathrm{d}N \end{aligned}} \qquad (2.8)$$

The first of these differential equations tells us that availability is the function of *system variables* U, S, V and N, while the (constant) reservoir variables T_R, p_R and μ_R act as the corresponding "forces". Since they are constant, we can integrate and obtain:

$$A = U - T_R S + p_R V - \mu_R N. \qquad (2.9)$$

Since we have $\mathrm{d}S_{\text{tot}} \geq 0$ and T_R is assumed constant, we must conclude that

$$\mathrm{d}A \leq 0. \qquad (2.10)$$

We have developed a new statement for a system in contact with a reservoir which is equivalent to the Law of Increase of Entropy. In the approach to equilibrium the *entropy of the universe must increase* or, equivalently, the *availability of the system must decrease*. A stable equilibrium is stable with respect to perturbations, so $\mathrm{d}A = 0$ in equilibrium: the *availability of a system is a minimum in equilibrium.*

Because the availability is directly related to the overall entropy, Boltzmann's expression for entropy: $S_{\text{Boltz}} = k_B \ln \Omega$, where Ω is the statistical weight or degeneracy, can be used to motivated an important aspect of this analysis, namely the

relationship for the *probability* for the system (in contact with the reservoir) to have a certain set of values for its variable, e.g. X:

$$P(X) \propto e^{-\frac{A(X)}{k_B T}}. \tag{2.11}$$

2.2.2 Availability = Useful Work

The availability function in Eq. (2.9) has some subtleties: its natural variables are S, V, N (because these are the natural variables of U), as well as T_R, p_R, μ_R. So, in general, the system can be at temperature $T = (\partial A/\partial S)_{V,N} \neq T_R$, pressure $p = -(\partial A/\partial V)_{S,N} \neq p_R$ and chemical potential $\mu = (\partial A/\partial N)_{S,V} \neq \mu_R$. It would then not be in equilibrium with the reservoir. How much work could be extracted by bringing the system in contact with the reservoir? It turns out that the availability, which is also called *exergy*, directly gives the maximum useful work possible during a process that brings the system into equilibrium with a reservoir. This can be shown by revisiting the derivation of Eq. (2.9) and allowing for $\mathrm{d}U_R$ not to be $= -\mathrm{d}U$, but rather putting $\mathrm{d}U_R + \mathrm{d}U = -\mathrm{d}W_{\text{extr}}$, the amount of work extracted in the process. Alternatively, we can go directly for $-\mathrm{d}W_{\text{extr}} = \mathrm{d}U + \mathrm{d}U_R$ and replace U by $A + T_R S - p_R V + \mu_R N$:

$$\begin{aligned} -\mathrm{d}W_{\text{extr}} = \mathrm{d}U + \mathrm{d}U_R &= \mathrm{d}(A + T_R S - p_R V + \mu_R N) + T_R\,\mathrm{d}S_R - p_R \underbrace{\mathrm{d}V_R}_{=-\mathrm{d}V} + \mu_R \underbrace{\mathrm{d}N_R}_{=-\mathrm{d}N} \\ &= \mathrm{d}A + T_R \underbrace{\mathrm{d}(S + S_R)}_{\geq 0}. \end{aligned} \tag{2.12}$$

The best we can do in extracting work by bringing the system in contact with the reservoir is to do this reversibly, so that the overall entropy $S + S_R$ stays constant. In this case, the extracted work W_{extr} matches the reduction in the availability, or exergy:

$$\Delta W_{\text{extr}} = -\Delta A. \tag{2.13}$$

2.2.3 Legendre Transformations

The natural variables of A as in Eq. (2.9) are S, V, N (because these are the natural variables of U), as well as T_R, p_R, μ_R. In equilibrium, the condition $\mathrm{d}A = 0$ for all variations of S, V, N then produces $(\partial A/\partial S)_{V,N} = (\partial U/\partial S)_{V,N} - T_R = T - T_R = 0 \implies T = T_R$, and likewise $p = p_R$ and $\mu = \mu_R$. Moreover, the requirement that the gradient of U w.r.t. S is equal to the fixed reservoir temperature T_R, is only fulfilled for one value of the entropy $S = S_{\text{eq}}$, the entropy in equilibrium. Likewise for V and N. So when the system is in equilibrium with the reservoir, the system variables S, V, N assume values S_{eq}, V_{eq}, N_{eq}, which are dictated by the reservoir temperature, pressure and chemical potential. As a consequence, the availability

in equilibrium has as its natural values T_R, p_R, μ_R, which are equal to T, p, μ in equilibrium.

This is an application of *Legendre transformations*. If we have a function $f(x)$ so that $\mathrm{d}f = f'\,\mathrm{d}x$, we can use this to create a new variable y and a new function $g(x,y) = f(x) - yx$. The differential of g will now be

$$\mathrm{d}g = f'\,\mathrm{d}x - y\,\mathrm{d}x - x\,\mathrm{d}y\,. \tag{2.14}$$

If we further look for the minimum of g w.r.t. x, we find it for $f' = (\partial f/\partial x)_{x=x_0} = y$. We can now define a function g_0 as the value of g at its minimum w.r.t. x for a given value of y: $g_0(y) = \min_x g(x,y) = g(x_0,y)$, where x_0 is the value of x at the minimum. We find that this minimum value changes with y as $\mathrm{d}g_0 = (f'-y)\,\mathrm{d}x - x_0\,\mathrm{d}y = -x_0\,\mathrm{d}y$. So the natural variable of g_0 is y, when the natural value of f was x.

As an example, consider the potential energy of a spring, $U(x) = \frac{1}{2}kx^2$. Now, the spring is hanging from a ceiling, with a weight W on it. The potential energy becomes $V(x,W) = \frac{1}{2}kx^2 - Wx$. The minimum of V w.r.t. x, which gives the equilibrium position of the stretched spring for a given weight, occurs for $x = x_0$ such that $(\partial V/\partial x)_{x=x_0,W} = 0$, i.e. $kx_0 = W$. This fixes the *equilibrium potential energy* for a given W as $V_0(W) = \frac{1}{2}kx_0^2 - Wx_0 = -\frac{1}{2}W^2/l$, and $\mathrm{d}V_0 = -x_0\,\mathrm{d}W$.

Applying this further, for instance, to the entropy dependence of $U(S,V,N)$, we can define a new variable T_R and a new function $F(S,V,N,p_R) = U(S,V,N) - T_R S$. This function has the differential

$$\mathrm{d}F = \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} - T_R\right]\mathrm{d}S - S\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,, \tag{2.15}$$

which for constant T_R is zero, when $(\partial U/\partial S)_{V,N,S=S_{\mathrm{eq}}} = T = T_R$, fixing the equilibrium entropy S_{eq} at a given temperature $T = T_R$. We now find that the value of F at equilibrium, when the change w.r.t. S is zero, depends on T_R, V and N as

$$\mathrm{d}F_{\mathrm{eq}} = -S_{\mathrm{eq}}\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,. \tag{2.16}$$

Focusing solely on the equilibrium properties and replacing T_R by T and S_{eq} by S, this can be written as $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$, the well-known expression for the Helmholtz free energy, on which more is in Section 2.3. Carrying out Legendre transforms on all the variables of the system, S, V, N, leads to the availability $A = U - T_R S + p_R V - \mu_R N$, which – when equilibrium has been reached – would have the differential

$$\mathrm{d}A_{\mathrm{eq}} = -S_{\mathrm{eq}}\,\mathrm{d}T_R + V_{\mathrm{eq}}\,\mathrm{d}p_R - N_{\mathrm{eq}}\,\mathrm{d}\mu_R \tag{2.17}$$

and $T = T_R$, $p = p_R$ and $\mu = \mu_R$ as the natural variables. Actually, the availability of a system in equilibrium with a reservoir is always simply zero! This follows from the realisation, mentioned above (Subsection 2.2.2), that the availability gives the extractable work on attaining equilibrium: if the system is already in equilibrium,

then the availability must have reached zero. It also follows from Eq. (1.32), $U - TS + pV - \mu N = 0$.

Whereas the minimum in the availability when all variables T, p, μ are constrained is zero, for more specific constraints, when the link to the reservoir is only partial, the minimum availability produces the various *thermodynamic potentials*. We will now look at the important cases.

2.3 Overview of the Thermodynamic Potentials

The *thermodynamic potentials* play a central role in thermal physics. They play a role analogous to energy. Why isn't energy conservation alone sufficient to determine the equilibrium state? Consider the following:

Fig. 2.4: Reversible compression of a monatomic ideal gas connected to a reservoir at constant temperature. Fixed temperature T implies constant internal energy U (Molecules in an ideal gas are assumed to have zero interaction with each other and so have only kinetic energy directly determined by T), and so đ$Q = -$đW.

Reversibly compress a monatomic ideal gas that is connected to a reservoir so that its temperature is constant. Energy is being put into the system in the form of work, but because the temperature of the (ideal) gas is constant its internal energy, $U = \frac{3}{2}Nk_BT$, is constant. So where does the energy that we put in as work go? It flows directly out of the system and into the reservoir as heat:

$$\mathrm{d}U = 0 \quad \Longrightarrow \quad đQ = -đW. \tag{2.18}$$

If we re-expand the piston reversibly, we get the energy back again; it flows back across the boundary from the reservoir into the system, and appears as work done by the system on the surroundings. The energy put into an isothermal ideal gas as work is therefore "stored" in the reservoir, *not* in the system, and if we want to consider energy conservation we have to keep in mind the energy of both the system and the reservoir. In general this might be quite a problem, and it is certainly inconvenient, so it would be nice if there were *a property of the system alone, that corresponds to conservation of energy for the system plus the reservoir*, a property that in this case would act like a potential energy. In fact such a function exists; we

Internal energy	U	$=$	$TS - PV + \mu N,$	$\mathrm{d}U$	$=$	$T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$
Enthalpy	H	$=$	$U + pV,$	$\mathrm{d}H$	$=$	$T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$
Helmholtz free energy	F	$=$	$U - TS,$	$\mathrm{d}F$	$=$	$-S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$
Gibbs free energy	G	$=$	$U - TS + pV,$	$\mathrm{d}G$	$=$	$-S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$
Grand potential	Φ	$=$	$F - \mu N,$	$\mathrm{d}\Phi$	$=$	$-S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$

Table 2.1: The most commonly encountered potentials for a gas. The variables which are differentiated are the "natural variables" of the corresponding thermodynamic potential. A thermodynamic potential takes its minimum value in equilibrium under the conditions that its natural variables are held fixed.

can write for *any* system, not just ideal gases,

$$\begin{aligned} đW &= \mathrm{d}U - T\,\mathrm{d}S \\ &= \mathrm{d}(U - TS)_T \quad \text{if } T \text{ is constant} \\ &\equiv (\mathrm{d}F)_T \end{aligned} \tag{2.19}$$

where $F = (U - TS)$ is the Helmholtz free energy. We have assumed that the particle number is fixed. The free energy of an isothermal system is the quantity which corresponds to energy conservation in the system plus the reservoir.

The thermodynamic potentials are generated by adding terms like $-TS$, pV, $-\mu N$, $\mathbf{M} \cdot \mathbf{B}$, etc. to the energy (corresponding to *Legendre transformations*, see Subsection 2.2.3). For a gas the most commonly encountered potentials are included in Table 2.1. The variables which are differentiated in Table 2.1 are the "natural variables" of the corresponding thermodynamic potential, for example, the natural variables of F are (T, V, N). It follows that a thermodynamic potential takes its minimum value in equilibrium under the conditions that its natural variables are held fixed. Another important result, which is not proved here, is that, if one knows any of the thermodynamic potentials as a function of its natural variables, one has complete thermodynamic information about the equilibrium state. For example if one knows $F(T, V, N)$ one can work out any of the other thermodynamic potentials, but if one only has $F(T, V, p)$ one cannot.

As we have now seen, the thermodynamic potentials play two distinct roles in thermal systems:

1. The appropriate thermodynamic potential is the property of the *system* that reflects *global* energy conservation.
2. For given external conditions, the appropriate thermodynamic potential is a *minimum* in equilibrium: the minimisation of this thermodynamic potential of the *system* is a direct consequence of the maximisation of *global* entropy.

It is very important that you learn which thermodynamic potential to consider in a given circumstance. The tables which follow are intended to help with this. As well as the tables, there follows a brief discussion of the uses of each potential.

2.3.1 Energy U: Equilibrium at Constant Volume, Entropy and Particle Number

The minimum energy state describes the equilibrium of a completely closed system (i.e., $đQ = 0$, $đW = 0$, $\mathrm{d}N = 0$). Moreover, if you do work on a thermally isolated system then the energy of the system increases by the amount required to conserve energy (provided all irreversible processes are confined to the system, not the external mechanism). As well, because it is more fundamental, we often want to calculate the energy change in a system even when it isn't thermally isolated, so the energy arises in a number of contexts.

Fig. 2.5: A schematic flow process.

2.3.2 Enthalpy H: Equilibrium at Constant Pressure, Entropy and Particle Number

This condition is called isobaric and isentropic. Because we have constant pressure, $\mathrm{d}p = 0$, constant entropy means that $\mathrm{d}S = 0$, while constant particle number means that $\mathrm{d}N = 0$. Therefore

$$\begin{aligned}(\mathrm{d}A)_{p,S,N} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{p,S,N} \\ &= \mathrm{d}(U + pV)_{p,S,N} \quad (\text{used } \mathrm{d}S = 0, \mathrm{d}N = 0, p = p_R) \\ &\equiv \mathrm{d}(H)_{p,S,N}\,, \end{aligned} \tag{2.20}$$

where H is the *enthalpy*. Hence in the condition of constant pressure, with no heat flow and no flow of particles, the minimum availability condition is equivalent to minimum enthalpy.

The minimum enthalpy state describes the equilibrium of a system at fixed pressure and constant entropy and particle number. As an example, the enthalpy is unchanged in a Joule-Kelvin expansion. In general the change in the enthalpy at constant pressure is equal to the heat entering or leaving the system. Therefore at a first order phase transition the amount of latent heat which enters or leaves the system is equal to the change in the enthalpy.

Its "conservation of energy role" arises in flow processes and is illustrated in Fig. 2.5.

2.3.3 Helmholtz Free Energy F: Equilibrium at Constant Temperature, Volume and Particle Number

This condition is referred to as isothermal and isochoric. The effects of these constraints are: $\mathrm{d}T = 0$ because the temperature is fixed; $\mathrm{d}V = 0$ because the volume is fixed; and $\mathrm{d}N = 0$. We can then write

$$\begin{aligned}(\mathrm{d}A)_{T,V,N} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{T,V,N} \\ &= \mathrm{d}(U - TS)_{T,V,N} \quad (\text{used } T = T_R, \mathrm{d}T = 0) \\ &\equiv \mathrm{d}(F)_{T,V,N}\,, \end{aligned} \tag{2.21}$$

where F is the *Helmholtz free energy.* Hence minimisation of the availability is equivalent, for an isothermal isochoric system, to minimisation of the Helmholtz free energy.

A simple application of this principle is to find the mechanical equilibrium of an isothermal, isochoric system consisting of two gases "1" and "2", as illustrated in Fig. (2.6). The total Helmholtz free energy is

$$\begin{aligned} F &= F_1 + F_2 \\ &= (U_1 - T_1 S_1) + (U_2 - T_2 S_2). \end{aligned} \tag{2.22}$$

Using $T_1 = T_2 = T$ and $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ we have

$$\mathrm{d}F = -p_1\,\mathrm{d}V_1 - p_2\,\mathrm{d}V_2\,. \tag{2.23}$$

Since $\mathrm{d}V_2 = -\,\mathrm{d}V_1$ the equilibrium condition becomes

$$\mathrm{d}F = 0 = -(p_1 - p_2)\,\mathrm{d}V_1 \qquad \Longrightarrow \qquad p_1 = p_2. \tag{2.24}$$

Fig. 2.6: Two gases initially at pressures p_1 and p_2 are separated by a movable barrier. The temperature is fixed and equal to T. The barrier moves under the pressure forces until the Helmholtz free energy reaches its minimum value, which occurs when $p_1 = p_2$.

The change in F is the work done in a reversible process at constant temperature. As well, the Helmholtz free energy is a minimum at equilibrium for an isothermal, isochoric (constant volume) system.

2.3.3.1 Example: Bubble

Consider a bubble of air in a large container of liquid in equilibrium. We imagine that the entire system of the bubble plus the surrounding liquid is in a container of fixed volume held at constant temperature. In this case we have to minimise the total Helmholtz free energy, which is the sum of terms from the liquid, air, and surface (perhaps better to say the interface region between the liquid and air),

$$\mathrm{d}F = \mathrm{d}F_l + \mathrm{d}F_a + \mathrm{d}F_s = 0. \tag{2.25}$$

For the two bulk systems (air and liquid): $\mathrm{d}F = -S\,\mathrm{d}T + p\,\mathrm{d}V + \mu\,\mathrm{d}N$, but for the interface the corresponding work function involves the surface tension term $\Gamma\,\mathrm{d}A$ term, where Γ is the surface tension, and A is the area of the surface. Using $\mathrm{d}T = 0$, $\mathrm{d}V_l = -\,\mathrm{d}V_a$, and all components species keep their particle numbers, $\mathrm{d}N_i$, we have

$$\mathrm{d}F_l = p_l\,\mathrm{d}V_a \tag{2.26}$$
$$\mathrm{d}F_a = -p_a\,\mathrm{d}V_a \tag{2.27}$$
$$\mathrm{d}F_s = \Gamma\,\mathrm{d}A\,, \tag{2.28}$$

so that Eq. (2.25) gives

$$(p_l - p_a)\,\mathrm{d}V_a + \Gamma\,\mathrm{d}A\,. \tag{2.29}$$

The surface area and volume of the bubble are $A = 4\pi r^2$ and $V_a = 4\pi r^3/3$, so

$$\mathrm{d}V_a = 4\pi r^2\,\mathrm{d}r \tag{2.30}$$
$$\mathrm{d}A = 8\pi r\,\mathrm{d}r\,, \tag{2.31}$$

and substituting these into Eq. (2.29) gives

$$p_a = p_l + \frac{2\Gamma}{r}. \tag{2.32}$$

The pressure inside is higher than the pressure outside. The local pressure in the air inside the bubble is proportional to the local radius of curvature. If the bubble isn't spherical, there is a pressure gradient in the air inside the bubble, and this gradient will cause a flow of air inside the bubble which acts to restore the bubble to a spherical shape.

The following complication may be considered: are the numbers N_i strictly speaking constant? After all, as the surface area changes, molecules are converted from liquid to surface. The consequence would be that the work term for the surface (or interface) is $\Gamma\,\mathrm{d}A + \mu_s\,\mathrm{d}N_s$, whereas the work term for the liquid becomes $p_l\,\mathrm{d}V_a - \mu_l\,\mathrm{d}N_s$. The total free energy acquires an extra term $(\mu_s - \mu_l)\,\mathrm{d}N_s$. However, the number of molecules on the interface is proportional to its area, so this term actually can be reexpressed in terms of $\mathrm{d}A$, like the surface tension term. It can therefore simply be absorbed into the surface tension term, making $\Gamma \to \Gamma'$. In fact, this is probably exactly the origin of the surface tension in the first place.

2.3.4 Gibbs Free Energy G: Equilibrium at Constant Temperature, Pressure and Particle Number

If p, N and T are constant then

$$\begin{aligned}(\mathrm{d}A)_{T,p,N} &= \mathrm{d}(U - TS + pV)_{T,p,N} \\ &\equiv \mathrm{d}(G)_{T,p,N}\,, \end{aligned} \tag{2.33}$$

where G is the *Gibbs Free energy*. On the approach to equilibrium the Gibbs free energy decreases, and in equilibrium it must be a minimum. This has very important applications in phase equilibria and chemical equilibria, which we will return to later. The Gibbs free energy is a minimum at fixed temperature, pressure and particle number, a situation that is naturally encountered in experiments, so it plays an important role in phase and chemical equilibria. It will therefore come up a lot in this course. From $G = U - TS + pV$ we find

$$G = \mu N \tag{2.34}$$

for a pure substance; that is, the chemical potential is the Gibbs free energy per particle. This can be understood intuitively if we imagine a process whereby the system is built up by adding particles at constant T and p. Then $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N = \mu\,\mathrm{d}N$. This means in effect that the chemical potential in a pure phase is the Gibbs free energy per particle. Moreover, from $G = \mu N$ we find $\mathrm{d}G = \mu\,\mathrm{d}N + N\,\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$. Therefore we can write

$$\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p\,, \tag{2.35}$$

which is the *Gibbs-Duhem relation* again (derived in Section 1.6). This is a useful expression when analysing phase and chemical equilibria.

Fig. 2.7: Adding particles at constant T and p.

The Gibbs free energy is useful in considering phase equilibrium and chemical equilibrium. In this case, we hold the system at fixed temperature and pressure, and consider particle equilibrium between the two phases, or between the molecular species taking part in the chemical reaction. To illustrate the application to phase equilibrium, we write the total Gibbs free energy as the sum over the Gibbs free energies of (say) the liquid phase and the vapour phase: $G = G_l + G_v$. At fixed temperature and pressure $\mathrm{d}G_l = \mu_l\,\mathrm{d}N_l$, and $\mathrm{d}G_v = \mu_v\,\mathrm{d}N_v$, and using $\mathrm{d}N_v = -\,\mathrm{d}N_l$

Name	Helmholtz Free Energy	Gibbs Free Energy	Grand Potential	
	$F = U - TS$	$G = U - TS + pV = \mu N$	$\Phi = F - \mu N = -pV$	$\Phi_2 = G - \mu N = 0$
Differential	$-S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$	$-S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$	$-S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$	$-S\,\mathrm{d}T + V\,\mathrm{d}p - N\,\mathrm{d}\mu = 0$
Minimised when constraints are	T, V, N	T, p, N	T, V, μ	Cannot be varied: T, p, μ are intensive and so not independent
Probability of fluctuation proportional to	$e^{-F/kT}$	$e^{-G/kT}$	$e^{-\Phi/kT}$	
Statistical formula	$-kT \ln Z$	$-kT \ln Z_p$	$-kT \ln \Xi$	
Important in	Mechanical equilibrium	Phase equilibrium	Fermions and Bosons	

Table 2.2: Potentials important for systems held at fixed temperature.

Name	Internal Energy	Enthalpy		
	U	$H = U + pV$	$\Phi_3 = U - \mu N$	$\Phi_4 = H - \mu N = TS$
Differential	$T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$	$T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$	$T\,\mathrm{d}S - p\,\mathrm{d}V - N\,\mathrm{d}\mu$	$T\,\mathrm{d}S + V\,\mathrm{d}p - N\,\mathrm{d}\mu$
Constant for isolated system when constraints are	V, N	p, N	V, μ	p, μ
Fluctuation probability proportional to	$e^{S/k}$	$e^{S/k}$	$e^{S/k}$	$e^{S/k}$
Important in	Isolated systems on which no work is done	Constant flow processes. ΔH is the heat energy in phase and chemical changes	Unimportant, not realised in practice	

Table 2.3: Potentials important for thermally isolated systems.

we conclude that the equilibrium condition is $\mu_l = \mu_v$. The change in the Gibbs free energy along phase equilibrium lines can also be used to derive the Clausius-Clapeyron equation (2.44): $\mathrm{d}p/\mathrm{d}T = L_m/T\Delta V_m$, where L_m is the latent heat per mole, and ΔV_m is the change in the molar volume at the transition. We also used G to derive the equal area rule, which allows us to determine the vapour pressure along a van der Waals isotherm (see Subsection 2.4.0.1).

2.3.5 Grand Potential Φ: Equilibrium at Constant Temperature, Volume and Chemical Potential

Under these conditions we have

$$\begin{aligned}(\mathrm{d}A)_{T,V,\mu} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{T,V,\mu} \\ &= \mathrm{d}(U - TS - \mu N)_{T,V,\mu} \\ &\equiv \mathrm{d}(\Phi)_{T,V,\mu}\end{aligned} \tag{2.36}$$

where Φ is the *grand potential*. Minimum availability in this case corresponds to minimum grand potential.

Fig. 2.8: The condition for a phase transition is that the Gibbs free energies of competing phases cross. The extrapolation of the Gibbs free energy of a phase to beyond the region in which that phase is stable is justified, for a short distance at least, by the metastability of supercooled and superheated phases.

2.4 Phase Equilibria

We turn now to a thermodynamic analysis of a central feature of the $p - V - T$ surfaces of real materials (see Section 1.3), enquiring into the stability of different phases and the nature of phase equilibrium. Consider a one component system at constant temperature, pressure and particle number, so that the equilibrium condition is that the Gibbs free energy is minimised. If we consider, for the sake of concreteness, the liquid-vapour transition, we hypothesise that we can calculate separate Gibbs free energies $G_l(T, p)$ and $G_v(T, p)$ for the liquid and vapour phases. At a given temperature and pressure, the stable phase will be the one with the lower Gibbs free energy. As illustrated in Fig. 2.8, if we imagine very slowly increasing the temperature of the reservoir at constant pressure, the phase transition will occur when the two functions cross. During the actual phase transition both phases are present, and we can express the total Gibbs free energy as the sum of G_l and G_v:

$$\begin{aligned} G &= G_l + G_v \\ \mathrm{d}G = 0 &\Rightarrow \mathrm{d}G_l = -\,\mathrm{d}G_v \\ \Longrightarrow\ -S_l\,\mathrm{d}T + V_l\,\mathrm{d}p + \mu_l\,\mathrm{d}N_l &= S_v\,\mathrm{d}T - V_v\,\mathrm{d}p - \mu_v\,\mathrm{d}N_v \\ \Longrightarrow\ \mu_l\,\mathrm{d}N_l &= -\mu_v\,\mathrm{d}N_v \qquad (T, p \text{ are constant}). \end{aligned} \tag{2.37}$$

Matter conservation requires $\mathrm{d}N_l = -\,\mathrm{d}N_v$, so that

$$\mu_l = \mu_v. \tag{2.38}$$

The condition for phase equilibrium is that the chemical potentials of the two phases are equal.[1] It is quite clear that if you, instead, keep p and N constant, then the

[1] Anyone trying to follow this discussion in *Atkins* [1] may easily get confused by terminology and notation here. *Atkins* discusses phase equilibria using a quantity g which relates to the transport of mass from one phase to the other, whereas we are using transport of particles (because this allows consistent notation throughout the course). To convert between notations, $g\,\mathrm{d}m = \mu\,\mathrm{d}N$. To further confuse things for you, *Atkins* calls g the 'chemical potential", and he defines a quantity μ as the molar partial potential which refers to transfer of moles of material from one component or phase to the other. I.e. to convert from his μ to our μ, use $\mu_{\text{Atkins}}\,\mathrm{d}n = \mu\,\mathrm{d}N$. Where n is the number of moles, and N is the number of molecules.

argument above gives you

$$T_l = T_v, \quad \text{or, similarly,} \quad p_l = p_v, \tag{2.39}$$

when T and N are constant. The equality of T, p, μ between any two subsystems is the condition for equilibrium.

2.4.0.1 Application to the Van der Waals Gas

We can also understand the general structure of $p-V-T$ diagrams via the chemical potential (although this is even easier to understand from microscopic considerations). Recall the Gibbs-Duhem relation (1.34), $\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p$, where s and v are the entropy and volume per particle.[2] This equation tells us that at high temperatures the phase with the highest entropy per particle will have the smallest chemical potential (and will therefore be stable), while at high pressures the phase with the smallest volume per particle will be stable.

Fig. 2.9: Isotherms of the van der Waals gas (see also Section 1.3). As shown in Eq. (2.41), the vapour pressure is fixed by the requirement that the two shaded regions have equal areas if the chemical potentials of the two phases are equal.

The condition for phase equilibrium is

$$\begin{aligned} \mu_v(E) &= \mu_l(A) \\ \text{but} \quad \mu_v(E) &= \mu_l(A) + \int_A^E \left(\frac{\partial \mu}{\partial p}\right)_T \mathrm{d}p \\ &= \mu_l(A) + \int_A^E v\,\mathrm{d}p\,. \end{aligned} \tag{2.40}$$

The first and last lines are true provided that

$$\int_A^E v\,\mathrm{d}p = 0, \tag{2.41}$$

i.e., the shaded regions in Fig. 2.9 must have equal areas. This allows us to calculate the vapour pressure, $p_{vap}(T)$, which is the pressure at which the phase transition takes place along the isotherm.

[2] This equation can only be applied to a pure phase, mixtures are more complicated.

2.4.1 Clausius-Clapeyron Equation

You have seen this derived last year, but perhaps not in the same way. To calculate the latent heat is more difficult; it is equal to the difference in the enthalpies of the two phases at the transition temperature, and such calculations are well beyond the scope of this course. However applying thermodynamic arguments to the latent heat we will show that it can be related to the pressure dependence of the transition temperature.

Fig. 2.10: Phase coexistence lines for water in the (p, T) plane. The Clausius-Clapeyron equation (2.44) gives an expression for the gradient of the phase boundaries, $\frac{\mathrm{d}p}{\mathrm{d}T} = L_m/(T\Delta v_m)$.

Starting from the Gibbs-Duhem eqaution (Eq. (1.34))

$$\mathrm{d}\mu_1 = v_1\,\mathrm{d}p - s_1\,\mathrm{d}T \tag{2.42}$$

where v_1 and s_1 are the volume and entropy per particle in phase 1, and using the fact that on the coexistence line $\mu_1 = \mu_2$, so that if we move along it $\mathrm{d}\mu_1 = \mathrm{d}\mu_2$, we have

$$\begin{aligned} v_1\,\mathrm{d}p - s_1\,\mathrm{d}T &= v_2\,\mathrm{d}p - s_2\,\mathrm{d}T \\ \implies \frac{\mathrm{d}p}{\mathrm{d}T} &= \frac{s_1 - s_2}{v_1 - v_2} = \frac{Ts}{Tv} \equiv \frac{L}{T\Delta v}, \end{aligned} \tag{2.43}$$

where $L = T\Delta s$ is the latent heat per particle. This result is more commonly quoted in units of L_m and v_m, the latent heat and volume per mol, and is called the Clausius-Clapeyron equation:

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L_m}{T\Delta v_m}.} \tag{2.44}$$

This applies to first order phase transitions and, at the time it was invented, it led to predictions of unexpected effects, and played a role in demonstrating the validity of the Second Law of Thermodynamics. It predicts the pressure dependence of the transition temperature in terms of the latent heat and the change in the molar volume. The best known application is the lowering of the freezing point of water

by pressure, a consequence of the expansion of water upon freezing (i.e., Δv_m has an unusual sign for the water-ice transition).

The liquid-solid coexistence curve can have either negative or positive slope, depending on the sign of Δv (consider water, which expands on freezing), but we expect the liquid–vapour curve to always have a positive slope and to be much flatter than the liquid-solid line, because in the liquid-vapour case the change in volume per particle is positive and large.

2.5 Mixtures of Ideal Gases

The molecules of an ideal gas by definition do not interact with each other, or with the molecules of other ideal gases. Hence the molecules in a mixture of ideal gases move independently, regardless of how many different species are present, and the thermodynamic properties of the mixture are just the sum of the independent contributions of each species of "component" of gas, so these contributions can be calculated as if each component was present on its own. (*Adkins* gives a derivation of this using purely thermodynamic arguments, but we will accept the microscopic argument). Therefore, for example, the total pressure is the sum of the *partial pressures* (Dalton's Law)

$$p = \sum_i p_i \quad \text{where} \quad p_i \frac{N_i k_B T}{V}. \tag{2.45}$$

Similarly for the entropy. If you recall, in 1B Thermodynamics we have derived the phenomenological Sackur-Tetrode formula via the following simple steps (starting from the definition of $\mathrm{d}U$):

$$\begin{aligned} \text{integrate} \quad \mathrm{d}S &= \frac{\mathrm{d}U}{T} + \frac{p\,\mathrm{d}V}{T} = \frac{C_v\,\mathrm{d}T}{T} + \frac{Nk_B\,\mathrm{d}V}{V} \\ \text{obtain} \quad S &= C_v \ln T + Nk_B \ln V + S_0. \end{aligned} \tag{2.46}$$

Here we need to connect with the partial pressures (intensive variables) rather than volume (which is the same for the mixture components), so you should either repeat the above derivation in the (p, T) variables (i.e. starting from the definition of $\mathrm{d}H$ instead of $\mathrm{d}U$), or simply replace $V = Nk_BT/p$ in Eq. (2.46) and then collect $\ln T$ terms into $C_p = C_v + Nk_B$. This gives for the entropy of a pure (single component) gas at pressure p:

$$S = C_p \ln T - Nk_B \ln p + S_0 \tag{2.47}$$

where the integration constant S_0 is not the same as in Eq. (2.46).

Starting with a collection of vessels all at the same pressure p and containing numbers of particles N_i of gas component i, we could achieve the mixing process

by first, an isothermal expansion of each component i to the desired final partial pressure p_i, followed by joining together all the containers, then isothermally compressing again to the same pressure p as we had to start with. As a particular component i is diluted from initial pressure p to partial pressure p_i, its entropy changes by $\Delta S_i = -N_i k_B \ln(p_i/p)$, because both C_p and S_0 do not depend on pressure.

Therefore the entropy of the mixture differs from the entropy of a separated out assembly of pure gases each at pressure p by

$$\begin{aligned}\Delta S = S - S_{\text{pure}} &= -k_B \sum_i N_i \ln(p_i/p) \\ &= -k_B \sum_i N_i \ln c_i = -N k_B \sum_i c_i \ln c_i, \end{aligned} \tag{2.48}$$

where $c_i = N_i/N = p_i/p$ is the concentration of the ith component, directly related to the volume fraction. This is called the *entropy of mixing*.

To obtain the Gibbs free energy and thereby the chemical potential μ, we could make use of this expression for the mixing entropy and use $G = U - TS + pV$. Because U and the product pV are the same for the components, whether in pure form or mixed, the change in G on mixing is entirely due to TS_i : $G_i(p_i, T) = G_i(p, T) + N_i k_B T \ln c_i$. However, we can also get G for the mixture directly from $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$, and considering a process at constant T we have

$$\left(\frac{\partial G}{\partial p}\right)_T = V = \frac{N k_B T}{p}, \tag{2.49}$$

and noting that $\mu = G/N$ we have

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V = \frac{k_B T}{p}. \tag{2.50}$$

Integrating from some reference pressure p_0 to pressure p at constant T we obtain

$$\mu(T, p) = \mu(T, p_0) + k_B T \ln \frac{p}{p_0}. \tag{2.51}$$

We now apply this formula to each species, i. The Gibbs free energy of the mixture is

$$G = \sum_i G_i. \tag{2.52}$$

Using $(\partial G_i/\partial p_i)_{T,N_i} = V$ we can relate the Gibbs free energy at partial pressure p_i to that at the total pressure p (which would be the Gibbs free energy if the system were composed of N_i atoms of pure component i at pressure p):

$$\begin{aligned} G_i(p_i, T) &= G_i(p, T) + \int_p^{p_i} V\,\mathrm{d}p \\ &= G_i(p, T) + N_i k_B T \int_p^{p_i} \frac{\mathrm{d}p}{p} \\ &= G_i(p, T) + N_i k_B T \ln \frac{p_i}{p} \\ &= G_i(p, T) + N_i k_B T \ln c_i. \end{aligned} \tag{2.53}$$

Using $G_i = \mu_i N_i$ we obtain, similarly,

$$\boxed{\mu_i(p_i, T) = \mu_{0i}(p, T) + k_B T \ln c_i.} \tag{2.54}$$

That is, the chemical potential of the ith component, which is present with concentration c_i in a mixture of ideal gases, differs from the chemical potential for the pure gas at the same total pressure by $k_B T \ln c_i$.

The chemical potentials of the different components are related. Since

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}N_i \quad \text{we have} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{l\neq i}}. \tag{2.55}$$

So for two components i and j

$$\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,N_{l\neq j}} = \frac{\partial^2 G}{\partial N_i \partial N_j} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,p,N_{l\neq i}}. \tag{2.56}$$

2.5.1 Chemical Equilibrium

Fig. 2.11: Chemical reaction at constant temperature and pressure. At a given temperature and pressure the relative amounts of the chemical components are functions of state. In our example, at high temperatures CO_2 breaks down into CO and O_2.

We will illustrate the equations with the equilibrium of carbon dioxide with carbon monoxide and oxygen, for which at high temperatures there is significant dissociation of CO_2 (see Fig. (2.11)).

$$2\mathrm{CO}_2 \rightleftharpoons 2\mathrm{CO} + \mathrm{O}_2. \tag{2.57}$$

As was the case for phase equilibrium, in chemical equilibrium we start from the condition that the availability must be a minimum:

$$\begin{aligned}(\mathrm{d}A)_{T,p} &= \mathrm{d}U - T\,\mathrm{d}S + p\,\mathrm{d}V \\ &= \mathrm{d}(U - TS + pV) \quad \text{constant temperature and pressure} \\ &= \mathrm{d}G = 0.\end{aligned} \tag{2.58}$$

where

$$G = \sum_i G_i = \sum_i \mu_i N_i. \tag{2.59}$$

Because $\mathrm{d}\mu_i = -s_i\,\mathrm{d}T = v_i\,\mathrm{d}p$ (Gibbs-Duhem) is zero at constant T and p, a variation of G about the equilibrium ratio of chemical components satisfies

$$\mathrm{d}G = \sum_i \mu_i\,\mathrm{d}N_i = 0, \tag{2.60}$$

i.e., $\mu_{\mathrm{CO_2}}\,\mathrm{d}N_{\mathrm{CO_2}} + \mu_{\mathrm{CO}}\,\mathrm{d}N_{\mathrm{CO}} + \mu_{\mathrm{O_2}}\,\mathrm{d}N_{\mathrm{O_2}} = 0$. But the $\mathrm{d}N_i$'s are related by matter conservation, which can be expressed as $2\mathrm{CO_2} - 2\mathrm{CO} - \mathrm{O_2} = 0$, so that $\mathrm{d}N_i/\mathrm{d}\nu_i =$ const., i.e., $\mathrm{d}N_{\mathrm{CO_2}}/2 = -\,\mathrm{d}N_{\mathrm{CO}}/2 = -\,\mathrm{dO_2}$, which gives

$$\sum_i \nu_i \mu_i = 0, \tag{2.61}$$

i.e., $2\mu_{\mathrm{CO_2}} - 2\mu_{\mathrm{CO}} - \mu_{\mathrm{O_2}} = 0$.

2.5.2 The Equilibrium Constant

Combining $\sum_i \nu_i$ and Eq. (2.54) gives

$$\sum_i \nu_i \mu_{0i} + k_B T \sum_i \nu_i \ln c_i = 0 \tag{2.62}$$

$$\Longrightarrow \sum_i \nu_i \mu_{0i} + k_B T \ln\left(\prod_i c_i^{\nu_i}\right) = 0. \tag{2.63}$$

This allows us to compute the "*equilibrium constant for concentration*", $K_c(T)$, defined as

$$\boxed{K_c(T) = \prod_i c_i^{\nu_i},} \tag{2.64}$$

where

$$\ln K_c(T) = -\frac{1}{k_B T} \sum_i \nu_i \mu_{0i}(T, p). \tag{2.65}$$

For the particular case of chemical decomposition of $\mathrm{CO_2}$ the equilibrium constant is the ratio of concentrations of three ingredients, raised to the power corresponding to each reaction coefficient:

$$K_c = \frac{c_{\mathrm{CO_2}}^2}{c_{\mathrm{CO}}^2 c_{\mathrm{O_2}}}. \tag{2.66}$$

But how can we regard a particular chemical reaction as an ideal-gas situation when many of them take place in the liquid or even solid state? It is in fact correct: even though there may be many (even densely packed) molecules in the system - every individual group, such as in (2.57), reacts on its own, independently of its

neighbours. In order to calculate the equilibrium constant for an ideal gas reaction we need to calculate $\mu_{0i}(T, p)$ for each component as a function of temperature. We will do this much later, in Section 5.7.

Chemists commonly use a version of the equilibrium constant K_p that relates the partial pressures of the reactants, rather than their concentrations; moreover they give the partial pressures in atmospheres, assuming that the total pressure of the mixture is 1 atmosphere. In this case, $c_i = p_i/p = p_i$, so $\ln K_p$, shown in Fig. 2.12, has the same form as $\ln K_c$. From microscopic theory we will later derive yet another, related, equilibrium constant, $K_N(T) = \prod_i N_i^{\nu_i}$, from which K_c can be obtained by recognising that $c_i = N_i/N$, where $N = \sum_i N_i$. We will use the results of this section later.

Fig. 2.12: Equilibrium constant for the $2CO_2 \rightleftharpoons 2CO + O_2$ reaction (following Hayward, *Equilibrium Thermodynamics*).

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Chapter 3

The Basics of Statistical Mechanics

3.1 Microstates and Macrostates

From quantum mechanics follows that the states of the system do not change continuously (like in classical physics) but are quantised. In a quantum mechanical system the *microstates* (or microcanonical states) can be identified with the set of solutions of the Schrödinger equation with fixed energies E_i. There could be many such states, which gives rise to the "degeneracy of a microstate" $\omega(E_i)$, as importantly there is no way to distinguish states within a given microstate. In a system such as a gas of classical point-like non-interacting particles, each microstate corresponds to a particular set of positions and momenta of the particles. Normally a system will have other constraints, for example fixed volume, in which case we will only be interested in the microstates with that volume.

A *macrostate* is the most-probably, equilibrium, observable microstate. In a large system, where due to the Central Limit Theorem the mean of the probability distribution coincides with its median, the energy of the macrostate is $\langle E \rangle = U$, which satisfies the other imposed constraints, for example, fixed volume V and particle number N. Of course it may be a difficult task to find the macrostate among the microcanonical states available to the system, but if one can, then statistical mechanics will yield all equilibrium thermodynamic information about the system

One can think of boxes i into which particles are placed, N_i particles in the ith box. The particles can be distributed over the boxes in a number of different ways, corresponding to different microstates, in which the state i of each particle is specified. The information contained in the microstates is excessive, and the only meaningful information is provided by the numbers N_i that define the distribution of particles over their quantum states. These numbers N_i specify what in statistical physics is called macrostate. If these numbers are known, the energy and other quantities of the system can be found. It should be noted that also the statistical macrostate contains more information than the macroscopic physical quantities that follow from it, as a distribution contains more information than an average over it.

3.2 Principle of Equal Equilibrium Probability (PEEP)

Suppose we have a gas of energy E which consists of N classical particles in an isolated container of volume V. Due to the motion of the particles, and the collisions between them and with the walls, the system continually moves between different microstates. We would like to find a condition which determines the equilibrium of this system. In equilibrium, the macrostate must be completely specified by the thermodynamic set of extensive parameters (U, V, N).

We now introduce the Postulate of Equal Equilibrium Probability (PEEP), which is also sometimes called the principle of equal *a priori* probability:

> For an isolated system, all states within the microstate of a given energy E, compatible with the given constraints, are equally likely to occur.

The main justification for the PEEP is the enormous success of the resulting theory, although it can also be proved to hold in some cases. A philosophical argument may be advanced as "there is no reason to think otherwise", but this is hardly a sufficient basis for a physical theory! A proper derivation of statistical mechanics should start from the laws of quantum or classical mechanics which govern the microscopic behaviour. This problem has not been solved in a satisfactory manner, but see Appendix A.1 for more discussion of this point.

There are some subtleties involved in thinking about and applying the PEEP. In experiments we normally measure *time* averages of quantities, but we will use the PEEP to calculate averages over the *ensemble* of all accessible states, asserting that these are equivalent to time averages. An "accessible" state is one that is compatible with the given constraints, while an "inaccessible" one is not. The idea that, in the course of a sufficiently long period, an isolated system will pass through all of its accessible states is known as the "ergodic hypothesis". Measurements are sometimes made over some fairly short time-scale and the system will not go through *all* of its states in the time-scale of the measurement. However, for the theory to work one only requires the system to go through a large number of states during the times-scale of the measurement which are "representative" of all the accessible ones.

All of this has to be consistent with quantum mechanics. Are the microstates the same as the energy eigenstates, with their own degeneracy, discussed in quantum mechanics courses? We will assume this to be the case and will obtain physically correct results by doing so. However, the energy levels of a macroscopic system are extremely close in energy and such systems are never sufficiently well isolated from the surroundings for the energy to be well defined to within the energy level spacing. In the cases of interest to us (i.e. in statistical thermodynamics) this doesn't matter, but for future reference it turns out that one can formulate the problem in terms of "density matrices" which incorporate the idea that the system is not in a eigenstate of energy.

3.3 The Boltzmann Entropy

Consider two systems with energies E_1 and E_2, which are isolated from their surroundings. If we place them in thermal contact with one another we expect that eventually they will come into thermal equilibrium. The energy of the two systems must be

$$E = E_1 + E_2, \tag{3.1}$$

where E_1 and E_2 may now vary with time, but their sum is constant.

Fig. 3.1: A partition of the total energy E between two subsystems.

At a particular time, subsystem 1 is equally likely to be in any of its microstates, $\Omega_1(E_1)$, while subsystem 2 is equally likely to be in any of its microstates, $\Omega_2(E_2)$. Therefore

$$\Omega(E; E_1) = \Omega_1(E_1)\Omega_2(E_2), \tag{3.2}$$

where $\Omega(E; E_1)$ is the number of microstates of the composite system with total energy E, such that there is energy E_1 in subsystem 1 and energy $E_2 = E - E_1$ subsystem 2.

For what value of E_1 (and hence E_2 since E is conserved) will the composite system be in equilibrium? The answer is the value of E_1 which maximises $\Omega(E; E_1)$. The idea is that although the system passes through many macrostates denoted by E_1 and E_2, on coming into equilibrium the PEEP implies that it will spend almost all its time in the macrostate for which $\Omega(E; E_1)$ takes its maximum value. (The phrase "almost all its time" is true only if the equilibrium state is overwhelmingly more likely than ones which are close by in energy, but this is almost always the case.)

Let us denote the equilibrium value of E_1 by U_1. Differentiating Eq. (3.2) with respect to E_1 and evaluating at the macrostate U_1 we have

$$\left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=U_1} \Omega_2(U_2) + \Omega_1(U_1) \left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=U_2} \frac{\partial E_2}{\partial E_1} = 0. \tag{3.3}$$

Since $\partial E_2/\partial E_1 = -1$, we have

$$\left.\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right|_{E_1=U_1} = \left.\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right|_{E_2=U_2}. \tag{3.4}$$

The condition for equilibrium amounts to the equality of the parameters $\beta_1 = \beta_2 = \beta$ for the two subsystems, where

$$\beta = \left.\frac{\partial \ln \Omega(E)}{\partial E}\right|_{E=U}. \tag{3.5}$$

It is natural to expect that β is related to the temperature. Recalling the relationship

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}, \tag{3.6}$$

we can therefore make the identifications:

$$\frac{1}{k_B T} = \beta, \quad \text{and} \quad S = k_B \ln \Omega, \tag{3.7}$$

where the quantities on the left hand sides of Eq. (3.7) refer to the thermodynamic quantities and those on the right hand side refer to the statistical mechanical quantities in equilibrium (macrostate). This is the definition of the statistical *Boltzmann entropy*. For our composite system we have

$$S = k_B \ln \Omega_1 \Omega_2 = k_B[\ln \Omega_1(U_1) + \ln \Omega_2(U_2)] = S_1 + S_2, \tag{3.8}$$

so the Boltzmann entropy is just the sum of the Boltzmann entropies of the two parts. The entropy is therefore extensive (and, of course, its conjugated thermodynamic variable - the temperature T is intensive).

Consider Eq. (3.4), where the system has rearranged its energy such that $S_1(U_1) + S_2(U_2)$ is maximal, at equilibrium, where there is no energy transfer at all,

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=U_1} - \left.\frac{\partial S_1}{\partial E_2}\right|_{E_2=U_2} = 0 \quad \Longrightarrow \quad T_1 = T_2, \tag{3.9}$$

and so no energy transfer corresponds to equal $T_1 = T_2$ (before contact) as expected.

Let us assume instead a small energy transfer, $\Delta E_1 = -\delta E_2$,

$$\delta S \approx \left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=U_1} \delta E_1 + \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=U_2} \delta E_2 = \left(\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=U_1} + \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=U_2}\right)\delta E_1 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1. \tag{3.10}$$

From the second law, $\delta S > 0$ because S is maximised, so if $T_1 > T_2$ implies $\delta E_1 < 0$, and energy flows from hot to cold. We will later evaluate T for an ideal gas to check out definition corresponds to the usual idea of temperature.

The Boltzmann entropy is well defined for large systems, but not for small ones because the distinction between accessible and inaccessible states is not well defined in a small system, and also the identification of the highest-probability state with equilibrium is uncertain. We will come back to the problem of small systems later, but here I want to make a point about large systems.

$\Omega(E)$ is absurdly large! E.g. 10^{23} 2-state particles $\Omega(E) = 2^{\left(10^{23}\right)}$. In QM, energy levels are discrete. For $N \sim 10^{23}$ they are finely spaced, almost like continuum. We implicitly define $\Omega(E)$ as the number of states with energy $\in [E, E + \Delta E)$ where we must have $\Delta E \ll$ measurement accuracy, $\gg$ level spacing.

In practice systems are never isolated and their internal energy E fluctuates in some range, which may increase the number of accessible states. Suppose the number is increased by a factor of 2, is the entropy significantly altered? The new entropy is

$$S = k_B \ln 2\Omega = k_B \ln 2 + k_B \ln \Omega. \tag{3.11}$$

However, Ω is typically of order 10^N, where N is the number of atoms (note that $\ln \Omega$ is proportional to the size of the system). If $N = 10^{23}$ atoms, then increasing Ω by a factor of two only increases S by roughly one part in 10^{23}!

3.3.1 Heat Capacity

We define heat capacity, or really we should call this "energy capacity", as

$$C \equiv \frac{\partial E}{\partial T}. \tag{3.12}$$

C is nice as it can easily be directly measured (compared to other quantities). Let us consider E as a function of T,

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C}{T} \tag{3.13}$$

$$\implies \quad C = T\frac{\partial S}{\partial T}. \tag{3.14}$$

We will see this as $C = \delta Q/\delta T$ in thermodynamics, where we also specify what's kept constant: $C_V, C_p, \cdots$.

We can measure entropy differences, which beats counting $\sim \exp(10^{23})$ states,

$$\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\, \mathrm{d}T\,. \tag{3.15}$$

Also note that it follows

$$\frac{\partial S}{\partial E} = \frac{1}{T} \quad \implies \quad \frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\frac{1}{T} = \frac{T}{E}\frac{\partial}{\partial T}\frac{1}{T} = -\frac{1}{T^2 C}. \tag{3.16}$$

Almost all substances have $C > 0$, and so $\partial^2 S/\partial E^2 < 0$, thus the extremum in Eq. (3.4) is really a maximum leading to "thermodynamically stable systems." Some exceptions do exist, such as black holes and Hawking radiation.

3.4 The Gibbs Entropy

Consider a small system in contact with a reservoir with which it can exchange energy. The fluctuations in the energy of the system will be an appreciable fraction of the mean energy. The states of the system cannot simply be labelled as "accessible" or inaccessible", we have to think about the *probabilities* that the system will be in each of its possible states.

Gibbs introduced a form of the entropy which is valid for both large and small systems,

$$S = -k_B \sum_i P_i \ln P_i, \tag{3.17}$$

where P_i is the probability of finding the system in state i, satisfying the usual constraint $\sum_i P_i = 1$. This is a function of the *probabilities* rather than the microstates themselves. You will, of course, see the connection between this expression and the expression (2.48) where $c_i = N_i/N$ is essentially the probability to find a particle of species i in the mixture.

It is very important to note that for a large system in equilibrium the Gibbs and Boltzmann entropies are equal. This is easily seen because in a large system the probability distribution is very sharply peaked in energy, so that $P_i \simeq 1/\Omega$ for all accessible states, and

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i 1/\Omega \ln 1/\Omega = k_B ln\Omega = S_B, \tag{3.18}$$

where we have used $\sum_i P_i = 1 = \sum_i 1/\Omega$. For very small non-isolated systems or for systems away from equilibrium, the Gibbs and Boltzmann entropies may not be equal.

When it comes to answering problems in equilibrium statistical mechanics I want you to use the Gibbs entropy. Unlike the Boltzmann entropy, the Gibbs entropy can be used at the microscopic level, which is a very significant advantage. Also, the Gibbs entropy is precisely defined and is much the simplest entropy to use for problems in equilibrium statistical mechanics.

Gibbs used the idea of *ensembles* to think about problems in statistical physics. An ensemble is a very large number of imaginary replicas of the system of interest all prepared in the same way. The ensemble gives a concrete meaning to probabilities. For example, the probability of finding the system in a particular microstate or macrostate is equal to the fraction of members of the ensemble in that state. Consider an ensemble of N replicas of a system in thermal contact with one another. For a particular member of the ensemble, the other $N-1$ replicas act as a heat reservoir. The ensemble of replicas is isolated from the surroundings and therefore its internal energy, E, is constant. Because all of the accessible states of the microcanonical ensemble have internal energy E, according to the PEEP they are all equally likely. Thus, there cannot be more than a single microstate in a

closed system, and a system must be open to change its energy in order to explore other microstates.

Each of the replicas has identical contents, but they are distinguishable from one another by their position within the ensemble. Let the number of replicas in microstate i be N_i, and the total number of states of each system be m, so that $\sum_i^m N_i = N$. The total number of distinct configurations of the ensemble is then

$$\Omega = \frac{N!}{N_1! N_2! \cdots N_m!}. \tag{3.19}$$

The entropy of the entire ensemble is given by the Boltzmann formula

$$S = k_B \ln \Omega, \tag{3.20}$$

and using Stirling's approximation (See Appendix A.4) we obtain

$$\begin{aligned} S &= k_B \left[N \ln N - \sum_i^m N_i \ln N_i \right] = k_B \left[\sum_i^m N_i \ln N - \sum_i^m N_i \ln N_i \right] \\ &= -k_B N \sum_i^m \frac{N_i}{N} \ln \frac{N_i}{N}. \end{aligned} \tag{3.21}$$

The entropy per system is therefore given by the Gibbs formula (3.17), where $P_i = N_i/N$ is the probability of finding the system in state i. Now the connection with the phenomenological expression (2.48) is even more transparent.

The entropy should take its maximum value in equilibrium. This leads naturally to the idea of maximising S with respect to the distribution of the probabilities, P_i, with the constraint that $\sum_i P_i = 1$ and any other constraints which apply (constant energy or whatever). This is sometimes called the "method of most probable distributions", which is a very satisfying way to proceed.[1]

Let us start with the method of Lagrangian Multipliers (See Appendix A.5) to maximise S subject to the constraing $\sum_i P_i = 1$,

$$L(P, \lambda) = -k_B \sum_i P_i \ln P_i - \lambda \sum_i P_i, \tag{3.22}$$

and so we can differentiate this with respect to P_j, keeping all other variables constant

$$\begin{aligned} \frac{\partial}{\partial P_j} L(P, \lambda) &= \frac{\partial}{\partial P_j} \left(-k_B \sum_i P_i \ln P_i - \lambda \sum_i P_i \right) \\ &= -k_B \ln P_i - k_B - \lambda = 0 \qquad (\partial P_i / \partial P_j = \delta_{ij}) \end{aligned} \tag{3.23}$$

[1]The method may be discussed in the lectures. It produces probabilities of the form $\exp(-E_n\beta)/Z$ by maximising the Shannon information entropy $-k \sum p_n \ln p_n$ subject to constraints such as $\langle E \rangle = \sum p_n E_n = U$. This approach, which makes the link between entropy and lack of information explicit, is first presented in detail in a paper by Jaynes: Phys. Rev. **106**, 620 (1957).

Thus from this we now see that the probabilities P_i will be given by

$$P_i = e^{-\lambda/k_B - 1} = \text{const.}, \tag{3.24}$$

i.e. we see that this is the same for all states in the microcanonical ensemble.

One of the strange features of the Gibbs entropy is that it depends on probabilities of the system being in particular configurations. But surely at any one time the system can only be in one configuration, so how can the other configurations, in which it is not, affect a physical variable such as the entropy or pressure? One important point to make is that if the system obeys the PEEP then an average over the probabilities of the system being in a particular configuration is the same as an average over time. One can object that we can measure some quantities over rather short times, such as the pressure of a gas, and it is not clear that an average over the probabilities of all configurations is relevant on short time-scales. To answer this we appeal to one of Boltzmann's ideas - with an overwhelmingly high probability the system will be in one of the microstates corresponding to the equilibrium macrostate, and all such microstates "look the same" so the value of *all* thermodynamic quantities is much the same for *all* the accessible microstates.

3.5 Statistical Ensembles

Gibbs defined three kinds of ensembles, the microcanonical, the canonical, and the grand canonical. Microcanonical is the ensemble of all states that have the same energy E. Essentially "canonical" means "standard"; Gibbs wrote: "This distribution, on account of its unique importance in the theory of statistical equilibrium, I have ventured to call *canonical*". The canonical and grand canonical ensembles represent what actually takes place in most thermodynamic systems. When we make a measurement with a physical device such as a thermometer, the device takes an average over a large number of quasi-independent regions of the system (assuming a macroscopically sized thermometer), each of which sees the rest of the system as a reservoir. Therefore most measurement systems do ensemble averaging in some sense.

3.5.1 Canonical Ensemble: Boltzmann Distribution and Partition Function

The *canonical* ensemble is an infinite collection of subsystems each connected to a large reservoir with which they can exchange energy (alternatively the subsystems can be connected to each other). If we wish to calculate average values of thermodynamic quantities we need to calculate the probability distribution for the

microstates. Unlike the microcanonical ensemble, different microstates of a subsystem have different probabilities of occurring, because each is weighted by the number of compatible microstates of the reservoir.

We ask for the probability of finding the ith subsystem (e.g. a particle) in energy eigenstate E_i, if the total energy of a closed system is U. This is an awkward moment, as we use the letter U normally reserved for the 'average energy' (thermodynamic potential), but since the big system is isolated - its energy E is not conserved, and so no different from U. This probability is proportional to the number of accessible states corresponding to this partition of the energy, which is 1 for the subsystem and $\Omega_R(U - E_1)$ for the reservoir, by which here we simply mean the whole system minus the particle i. Since in a large system E_i is much less than U we expand in a Taylor series:

$$\begin{aligned} P_i \propto 1 \times \Omega_R(U - E_i) &= e^{ln\Omega_R(U-E_i)} \\ &= \exp\left(\ln \Omega_R(U) - E_i\left(\frac{\partial \ln \Omega_R(U)}{\partial U}\right) + \cdots\right) \\ &\simeq e^{\ln \Omega_R(U)} e^{-\beta E_i}, \end{aligned} \tag{3.25}$$

where we have used $S = k_B \ln \Omega_R(U)$ for the entropy of the reservoir, and have also used $\partial S/\partial U = 1/T$, and $\beta = 1/k_B T$ as usual. Note that we are assuming that U, S, and T are thermodynamic (average) quantities in order for these last relations to hold. This is valid for a large closed system, where the total energy is constant and so is $\Omega_R(U)$. Therefore, for an individual system: $P_i(E_i) \propto e^{-\beta E_i}$. Now we need to find the normalisation constant for P_i, which we denote by Z,

$$Z = \sum_{\text{all states } i} e^{-\beta E_i}. \tag{3.26}$$

This is called the *partition function*, and it turns out to be the single most important object in statistical mechanics! We can now write the normalised Boltzmann distribution:

$$P_i = \frac{1}{Z} e^{-\beta E_i}. \tag{3.27}$$

Now, step back and look at a system that could have different ways to achieve its total energy, and now we really need to distinguish between the value of energy E_i and the average energy U. The probability, $P(E_i)$, that the system has an energy value E_i is increased by the number of distinct configurations of the system with energy E_i, and proportional to the Boltzmann factor itself:

$$P(E_i) \propto \Omega(E_i) e^{-\beta E_i}. \tag{3.28}$$

This is the probability of a microcanonical state with constant energy E_i. The most-probably microstate, or the maximum in $P(E_i)$ can be determined by setting $\mathrm{d}P/\mathrm{d}E_i = 0$. Since in the large system the mean of the distribution $P(E_i)$ is equal to the median, at the maximum of probability one is in equilibrium (which is what we

call the macrostate). Also, in a large system, with many equivalent configurations, $\Omega(E_i)$ increases very rapidly with E_i and therefore $P(E_i)$ is sharply peaked at the mean value $U = \langle E_i \rangle$, as illustrated in Fig. 3.2. The energy distribution for a large system is regarded as Gaussian (according to the Central Limit Theorem of stochastic physics). A short algebra gives the expression for the probability of the microstate with energy E in the following form:

$$P(E) \propto e^{-\beta[E - k_B T \ln \Omega(E)]}. \tag{3.29}$$

Fig. 3.2: The probability, $P(E)$, that a system has energy E is proportional to the product of the statistical weight, $\Omega(E)$, and the Boltzmann factor. $P(E)$ is sharply peaked around the mean value of U, the shaded area regarded as a Gaussian.

Now you see that the maximum-probability microstate (which we also treat as equilibrium, in a large system) is obtained when the expression $E - TS(E)$ is minimal. This macrostate is where we can replace E with its average, and take the equilibrium thermodynamic entropy $S(U)$ to recognise the thermodynamic potential free energy $F = U - TS$. Do not mix $F(E) = E - TS(E)$ with the equilibrium thermodynamic potential $F = U - TS$: it could be called the free energy of the microstate E, but it does not have to be in equilibrium (maximum-probability) state, not until its minimisation.

As we previously showed for the microcanonical ensemble, we can also proceed again through the method of Lagrangian multipliers in order to maximise the entropy S, now subject to the additional constraint for the fixed average energy $\sum_i P_i E_i = U$,

$$\begin{aligned} L(P, \lambda_1, \lambda_2) &= -\sum_i k_B P_i \ln P_i - \lambda_1 \sum_i P_i - \lambda_2 \sum_i P_i E_i \\ \Longrightarrow \quad \frac{\partial}{\partial P_j} L(P, \lambda_1, \lambda_2) &= \frac{\partial}{\partial P_j}\left(-\sum_i k_B P_i \ln P_i - \lambda_1 \sum_i P_i - \lambda_2 \sum_i P_i E_i \right) \\ &= -k_B \ln P_j - k_B - \lambda_1 - \lambda_2 E_j = 0 \\ \Longrightarrow \quad P_i &= e^{-1-\lambda_1/k_B} e^{-\lambda_2 E_i/k_B}. \end{aligned} \tag{3.30}$$

Noticing that $e^{-1-\lambda_1/k_B} = 1/Z$ and defining $\lambda_2 = 1/T$ gives the result

$$P_i = \frac{1}{Z} e^{-E_i/k_B T}, \tag{3.31}$$

as we have already seen in Eq. (3.27). From this, we can again obtain expressions for the partition function from summing these probabilities

$$1 = \sum_i \frac{1}{Z} \Omega_i e^{-E_i/k_B T}, \tag{3.32}$$

thus if we take a sum over the number of microstates then we can obtain the partition function through

$$Z = \sum_{i,\ \text{microstates}} e^{-(E_i - K_B T \ln \Omega)/k_B T}, \tag{3.33}$$

else if we wish to sum over all the states, including those degenerate, we see

$$Z = \sum_{i,\ \text{all states}} e^{-E_i/k_B T}. \tag{3.34}$$

3.5.2 Grand Canonical Ensemble: Gibbs Distribution and Grand Partition Function

We are now going to obtain an expression which parallels the Boltzmann distribution, but for Gibbs' *grand canonical ensemble*, which consists of an infinite number of subsystems each coupled to an identical reservoir with which it can exchange particles as well as energy. We consider a subsystem plus reservoir to have the total (constant) energy U, and the total particle number N. The probability of a given partition of the energy $(E_i, U - E_i)$, and particle number $(N_i, N - N_i)$, such that the system is in a definite energy eigenstate E_i with particle number N_i, is proportional to the number of microstates of the reservoir that are consistent with this partitioning. Again we take E_i and N_i to be small compared with U and N, and expand the logarithm of the accessible states function:

$$\begin{aligned} P_i(E_i, N_i) &\propto e^{\ln \Omega_R(U - E_i, N - N_i)} \\ &\sim \exp\left(\ln \Omega(U, N) - E_i \left(\frac{\partial \ln \Omega_R(U, N)}{\partial U} \right)_N - N_i \left(\frac{\partial \ln \Omega_R(U, N)}{\partial N} \right)_U + \cdots \right) \\ &\sim e^{\ln \Omega_R(U,N)} e^{-\beta(E_i - \mu N_i)}, \end{aligned} \tag{3.35}$$

where, in addition to the entropy $S = k_B \ln \Omega$ and temperature, we have made the identification of the chemical potential using

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_U = -k_B T \left(\frac{\partial \ln \Omega}{\partial N} \right)_U. \tag{3.36}$$

Normalising, we obtain the Gibbs probability distribution:

$$P_i(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i - \mu N_i)}, \tag{3.37}$$

where the new normalisation factor Ξ is called the *Grand partition function*. To obtain it we need to sum over all energy states for each number of particles, as we

did in the canonical partition function (3.26), but also over all possible number of particles the system might have (ultimately, $N_i \in 0 \div N$, where N might be infinity):

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i[N_i]-\mu N_i)} \tag{3.38}$$

The exponential term, $e^{-\beta(E_i-\mu N_i)}$ is called the *Gibbs factor*. The energy eigenstates are in general different for different particle numbers in the system, so this can be a complicated object.

Once more, let us derive some of these results again through the use of Lagrangian multipliers, now with another constraint on the fixed particle average $\sum_i P_i N_i = N$,

$$\begin{aligned} L(P, \lambda_1, \lambda_2, \lambda_3) &= -\sum_i k_B P_i \ln P_i - \lambda_1 \sum_i P_i - \lambda_2 \sum_i P_i E_i - \lambda_3 \sum_i P_i N_i \\ \implies \frac{\partial}{\partial P_j} L(P, \lambda_1, \lambda_2, \lambda_3) &= \frac{\partial}{\partial P_j}\left(-\sum_i k_B P_i \ln P_i - \lambda_1 \sum_i P_i - \lambda_2 \sum_i P_i E_i - \lambda_3 \sum_i P_i N_i\right) \\ &= -k_B \ln P_j - k_B - \lambda_1 - \lambda_2 E_j - \lambda_3 \lambda_3 = 0 \\ \implies \quad P_i &= e^{-1-\lambda_1/k_B} e^{-\lambda_2 E_i/k_B} e^{-\lambda_3 N_i/k_B}. \end{aligned} \tag{3.39}$$

This time, we can fix the additional Lagrange multiplier by defining it in terms of the chemical potential such that

$$P_i \propto e^{-E_i/k_B T} e^{\mu N_i/k_B T}. \tag{3.40}$$

3.6 Solving Problems in Statistical Mechanics

The most general way to approach problems in statistical mechanics is to calculate the partition function, Z, or the grand partition function Ξ. All the thermodynamic potentials can then be obtained from Z or Ξ, as shown below. In problems for large systems one can normally use any of the microcanonical, canonical or grand canonical ensembles, obtaining identical values for the thermodynamic average values. A number of different approaches are often possible, and you should develop experience in choosing a convenient method by tackling problems.

3.6.1 Canonical Ensemble

In the canonical ensemble the probability of a particular microstate is given by the Boltzmann distribution,

$$P_i = \frac{e^{-\beta E_i}}{Z}, \tag{3.41}$$

where the partition function is

$$Z = \sum_{\text{all states } i} e^{-\beta E_i} = \sum_{\text{microstates } E} \Omega(E_i) e^{-\beta E_i} = \sum_{\text{microstates } E} e^{-\beta(E_i - TS(E_i))}, \tag{3.42}$$

where, as before, $S(E) = k_B \ln \Omega(E)$. To find the equilibrium, we minimise $[E_i - TS(E_i)]$, and in a very large system the partition function sum will be dominated by the exponentially large factor describing the macrostate:

$$Z \approx e^{-\beta(U - TS(U))}, \quad \text{hence} \quad F = -k_B T \ln Z. \tag{3.43}$$

Or look at it from the equilibrium Gibbs entropy angle:

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i \Big(-\frac{E_i}{k_B T} - \ln Z \Big) \equiv \frac{U}{T} + k_B \ln Z, \tag{3.44}$$

where we used $U = \langle E \rangle = \sum_i P_i E_i$ and $\sum_i P_i = 1$. From $F = U - TS$ we can make the identification: $F = -k_B T \ln Z$. Once the minimisation of the free energy $F(E)$ of macrostate is done, and we found the equilibrium macrostate, we may treat F as a thermodynamic potential: a function of T and V, and get the entropy from $S = -(\partial F/\partial T)_V$ and the pressure as $p = -(\partial F/\partial V)_T$, and hence U, H and G from analytical thermodynamics.

Another useful formula connecting the partition function to a thermodynamic potential is

$$U = \sum_i E_i P_i(E_i) = -\frac{\partial}{\partial \beta} \ln Z. \tag{3.45}$$

Although, since this gives us $U(T)$, which does not contain all thermodynamic information and so is only really useful for calculating the heat capacity via

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \tag{3.46}$$

3.6.2 Grand Canonical Ensemble

Here the microstate probabilities are given by

$$P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi}, \tag{3.47}$$

where the grand partition function is

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i - \mu N_i)}. \tag{3.48}$$

As in the canonical ensemble, the key is to look at the microstate - a collection of states with the same energy E_i, and count them to $\Omega(E_i)$, the only difference is a

now added summation over the variable number of particles in this microstate, N_i. The probability of such a microstate is

$$P_i = \frac{1}{\Xi}\Omega(E_i, N_i)e^{-\beta(E_i-\mu N_i)} = \frac{1}{\Xi}e^{-\beta(E_i-TS(E_i,N_i)-\mu N_i)}, \tag{3.49}$$

and to find the most-probably = equilibrium macrostate we need to minimise the exponent $E - TS(E, N) - \mu N$, which in equilibrium will become the grand thermodynamic potential $\Phi = U - TS - \mu N$, and $\Xi \approx e^{-\beta\Phi}$.

Or starting from the Gibbs entropy, $S = -k_B \sum_i P_i \ln P_i$, we have

$$\begin{aligned} TS &= -k_B T \sum_i P_i \ln P_i = -k_B T \sum_i P_i\{-(E_i - \mu N_i)/k_B T - \ln \Xi\} \\ &= U - \mu N + k_B T \ln \Xi, \end{aligned} \tag{3.50}$$

where we used the definitions of averages, e.g. $U = \sum_i P_i E_i$. Recalling that the grand potential is given by $\Phi = U - TS - \mu N$, we have $\Phi = -k_B T \ln \Xi$.

From $\mathrm{d}\Phi = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$ we then obtain the entropy, pressure and average particle number from

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}. \tag{3.51}$$

From these quantities we can construct all the other thermodynamic potentials.

3.6.3 Example: Defects in a Solid

Point defects are present in a crystal in thermal equilibrium at finite temperatures. One of the simplest kinds of point defect is the vacancy in which an atom is missing from one of the lattice sites. Suppose that the increase in internal energy on introduction of a vacancy is ϵ. This corresponds to the energy to take an atom from a lattice site and place it at the surface (called a *Schottky defect*). We can calculate the average number of vacancies, n, present in a crystal containing N atoms as follows.

Strictly speaking the system is not at constant volume, because the volume increases with the number of defects, but if the pressure is zero the work term $pV = 0$, and we can find the equilibrium state by minimising the Helmholtz free energy of the microstate with n defects, F rather than G. There are two contributions to F from the vacancies, the internal energy term and the configurational entropy term from the number of ways of choosing n vacant sites out of a total of $N + n$ sites. Therefore

$$F(n) = E(n) - TS(n) = n\epsilon - k_B T \ln\left(\frac{(N+n)!}{N!n!}\right). \tag{3.52}$$

Using the Stirling approximation for the factorials we obtain the free energy of the microstate with energy $E = n\epsilon$:

$$F = n\epsilon - k_B T[(N+n)\ln(N+n) - N\ln N - n\ln n]. \tag{3.53}$$

Minimising with respect to n gives

$$\frac{\partial F}{\partial n} = \epsilon - k_B T \ln\left(\frac{N+n}{n}\right) = 0 \tag{3.54}$$

and therefore the equilibrium (most probable) value of n is given by

$$n_{eq} = \frac{N}{e^{\epsilon/k_B T} - 1} \simeq N e^{-\epsilon/k_B T}. \tag{3.55}$$

Typically ϵ might be about 1 eV, so that at room temperature $n/N \simeq 10^{-17}$, which is very small, but in ionic crystals such as NaCl the vacancies are responsible for the observed electrical conductivity and the colour of the crystals.

The equilibrium thermodynamic free energy is obtained by substitution of the maximum-probability value, $F = F(n_{eq})$, and after some algebra we can obtain:

$$F_{eq}(T, N) = N k_B T \ln\left(1 - e^{-\epsilon/k_B T}\right). \tag{3.56}$$

3.6.4 Example: Vacancies

A crystalline solid contains N identical atoms on N lattice sites, and N interstitial sites to which atoms may be transferred at the energy cost ε_c.

Of the N lattice sites, $N - n$ are occupied by atoms, and n are empty. The corresponding number of configurations is $\Omega_l = N!/(N-n)!n!$. Of the N interstitial sites, n are occupied by atoms, and $N - n$ are empty, and the number of their possible configurations is $\Omega_v = N!/n!(N-n)!$. The configurations of the lattice and the vacancies are independent (once the number of vacancies is fixed), so the total number of configurations is just their product, and the resulting entropy is

$$S_{\text{config}} = \underbrace{k_B \ln \Omega_l \Omega_v}_{(3.7)} = k_B \ln\left(\frac{N!}{(N-n)!n!}\right)^2 = 2k_B \ln\left(\frac{N!}{(N-n)!n!}\right). \tag{3.57}$$

Note that $S_{\text{config}}(n=0) = S_{\text{config}}(n=N) = 0$, so both the states with fully occupied and fully empty interstitial sites have vanishing entropy, and thus are in practice never fully realisable.

Moving an atom from a *particular* lattice site to a *particular* vacancy involves no change in the configurational part of the entropy, hence ε_c is the change in the

non-configurational part of the free energy. Note that this is where we need the requirement of a small number of atoms on vacancy sites: all vacancies can only have the same ε_c if the number of vacancies is so small that there is vanishing probability of finding two vacancies close enough together to interact. The free energy when there are n atoms on vacancy sites is

$$F(n) = F(n=0) + n\varepsilon_c - TS_{\text{config}} = F_0 + n\varepsilon_c - 2k_BT\ln\left(\frac{N!}{(N-n)!n!}\right). \tag{3.58}$$

The terms in the free energy F that depend on n are, after the Stirling approximation,

$$\Delta F(n) = n\varepsilon_c + 2k_BT\Big[N\ln N - n\ln n - (N-n)\ln(N-n)\Big]. \tag{3.59}$$

At temperature T the free energy is minimised to determine the value of its variable (n in this case) at which it takes the equilibrium thermodynamic value. Setting $\partial F/\partial n = 0$ gives

$$\varepsilon_c = 2Tk_B\Big[\ln(N-n) - \ln n\Big], \tag{3.60}$$

i.e. the equilibrium proportion of atoms on interstitial sites n/N is

$$\frac{n}{N} = \frac{1}{1+e^{\varepsilon_c/2k_BT}} \tag{3.61}$$

The low-T limit, as always in systems with an energy gap, has $n = Ne^{-\varepsilon_c/2k_BT}$, and the high-$T$ limit is $n = N/2$.

3.6.5 Example: Point Defect Occupation

A point defect in a solid may be occupied by 0, 1 (spin up or down) or 2 electrons, and the solid provides a reservoir of electrons at chemical potential μ. The energy for occupation by a single electron is ε, and that for 2 electrons is $2\varepsilon + U$, where U is the Coulomb repulsion energy between the electrons.

A table of states, occupancies, and energies may be constructed as in Table 3.1.

$\boldsymbol{i}$	$\boldsymbol{N_i}$	$\boldsymbol{E_i}$
1	0	0
2	$1\uparrow$	ε
3	$1\downarrow$	ε
4	2	$2\varepsilon + U$

Table 3.1: States, occupancies, and energies for a point defect in a solid. The energy for occupation by a single electron is ε, and that for 2 electrons is $2\varepsilon + U$.

The grand partition function (3.38) is

$$\Xi = \sum_i e^{-\beta(E_i - N_i\mu)} = 1 + 2e^{-\beta(\varepsilon-\mu)} + e^{-\beta(2\varepsilon+U-2\mu)}, \tag{3.62}$$

and the grand potential is $\Phi = -k_B T \ln \Xi$. The average electron occupancy of the defect is

$$\begin{aligned} N &= -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \\ &= k_B T \frac{1}{\Xi}\frac{\partial \Xi}{\partial \mu}, \end{aligned} \tag{3.63}$$

where

$$\frac{\partial \Xi}{\partial \mu} = 2\beta e^{-\beta(\varepsilon-\mu)} + 2\beta e^{-\beta(2\varepsilon+U-2\mu)}, \tag{3.64}$$

and therefore

$$N = \frac{2e^{-\beta(\varepsilon-\mu)} + 2e^{-\beta(2\varepsilon+U-2\mu)}}{1 + 2e^{-\beta(\varepsilon-\mu)} + e^{-\beta(2\varepsilon+U-2\mu)}}. \tag{3.65}$$

Alternatively we can write the average directly from the discrete probability

$$N = \frac{\sum_i N_i e^{-\beta(E_i - N_i\mu)}}{\sum_i e^{-\beta(E_i - N_i\mu)}} = \frac{2e^{-\beta(\varepsilon-\mu)} + 2e^{-\beta(2\varepsilon+U-2\mu)}}{1 + 2e^{-\beta(\varepsilon-\mu)} + e^{-\beta(2\varepsilon+U-2\mu)}}. \tag{3.66}$$

Note that if we set $U = 0$, we obtain the familiar Fermi-Dirac distribution (6.3):

$$N = \frac{2e^{-\beta(\varepsilon-\mu)}\left(1 + e^{-\beta(\varepsilon-\mu)}\right)}{\left(1 + e^{-\beta(\varepsilon-\mu)}\right)^2} = \frac{2}{e^{\beta(\varepsilon-\mu)} + 1}, \tag{3.67}$$

which is the average occupancy of the energy level ε (6.3), but multiplied by the degeneracy of 2.

The sketch of N vs. $\mu - \varepsilon$ should show two steps, one when the chemical potential exceeds ε, where the occupancy rises from 0 to 1, then a second one when the chemical potential exceeds $\varepsilon + U$, where the occupancy rises to 2 (Fig. 3.3). This can be obtained by considering the limits of N for $U\beta \to \infty$ for various choices of $\mu - \varepsilon$ such as $\mu - \varepsilon < 0$, $\mu - \varepsilon = 0$, $\mu - \varepsilon > U$, and so on. Note that the wide plateau for which $N = 1$ would correspond physically to a magnetic moment bound to the defect.

3.6.6 Example: Paramagnetic Salt

Consider a paramagnetic salt in which magnetic ions with spin 1/2 and magnetic moment m_0 are arranged on N sites. There is an external magnetic field B, and we assume that the moments do not interact with one another. Calculate the mean magnetic moment per spin, m, and the heat capacity per spin, c.

Fig. 3.3: Caption

Note that each spin makes the same contribution to extensive parameters of the system, and therefore we need consider only quantities per spin, which will be denoted by lower case letters. We have $\mathrm{d}U_1 = T\,\mathrm{d}S_1 + B\,\mathrm{d}m$ (see Subsection 1.1.3), from which we can obtain the relevant free energy F_1, which incorporates the constraints (T, B), by a Legendre transformation: $F_1 = U_1 - TS_1 - mB$:

$$\mathrm{d}F_1 = -S\,\mathrm{d}T - m\,\mathrm{d}B\,. \tag{3.68}$$

A spin can either point up or down and therefore the partition function for a single spin is

$$Z_1 = \sum_i e^{-\beta E_i} = e^{+\beta m_0 B} + e^{-\beta m_0 B} = 2\cosh\left(\frac{m_0 B}{k_B T}\right). \tag{3.69}$$

We have

$$F_1 = -k_B T \ln Z_1 = -k_B T \ln\left(e^{+\beta m_0 B} + e^{-\beta m_0 B}\right) \tag{3.70}$$

and from Eq. (3.68) we obtain

$$m = -\left(\frac{\partial F_1}{\partial B}\right)_T = m_0 \tanh\left(\frac{m_0 B}{k_B T}\right), \tag{3.71}$$

which is the average magnetic moment of a site. We now calculate s. From Eq. (3.68) we have

$$S_1 = -\left(\frac{\partial F_1}{\partial T}\right)_B = k_B \ln\left(1 + e^{-2\beta m_0 B}\right) + \frac{1}{T}\frac{2m_0 B}{e^{2\beta m_0 B} + 1}, \tag{3.72}$$

and we obtain the heat capacity C_1 from

$$C_1 = T\left(\frac{\partial S_1}{\partial T}\right)_B = \frac{(m_0 B)^2}{k_B T^2 \cosh^2(\beta m_0 B)}. \tag{3.73}$$

This form of the heat capacity, called a *Schottky anomaly*, is plotted in Fig. 3.4 along with the average magnetic moment per spin, m and the entropy per spin, s.

Fig. 3.4: The mean magnetisation, m, per spin, the heat capacity per spin, c, and the entropy per spin, s/k_B, for a two-level system.

Note that we did not have to minimise any free energy of a microstate here, since the analysis was done for just one spin: there is no statistics here (except for the two levels).

We could have treated the problem in a different way, to expose the microstates and the maximum-probability condition. We have a lattice of N sites, of which r are up (along the external field B) and $(N-r)$ are down. In the external field B, the energy is $E(r) = -rm_0B + (N-r)m_0B = Nm_0B - 2rm_0B$, where the first term is an additive constant. This is the microstate, with the large number of ways to achieve R out of N: $\Omega(r) = N!/r!(N-r)!$. We now have the free energy of the microstate (which is the exponent of its probability $P(r)$) given by

$$F(r) = -2rm_0B - k_BT\ln\Omega(r) = -2rm_0B - k_BT[N\ln N - r\ln r - (N-r)\ln(N-r)]. \tag{3.74}$$

The most probable microstate (that is, the equilibrium macrostate) is obtained by minimisation of this free energy, in the way you are familiar with. The solution is

$$r_{eq} = \frac{N}{1+e^{-2m_0B/k_BT}}, \tag{3.75}$$

and the average magnetic moment, per spin, takes the form:

$$m_{eq} = \frac{1}{N}\cdot\frac{1}{2}m_0(2r-N) = m_0\tanh\left(\frac{m_0B}{k_BT}\right), \tag{3.76}$$

i.e. identical to the single-spin treatment. By substituting r_{eq} into $F(r)$ we should obtain the same expression for the equilibrium thermodynamic potential $F_{eq}(T,B)$ as in Eq. (3.70).

3.6.7 Example: Zipper

A zipper has N links; each link has a state in which it is closed with energy 0 and open with energy ε. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \cdots$,s-1) are already open.

The partition function is given by the geometric series, since each microstate (with n links open) has only one conformation. You should know, or remember how

to derive the sum:

$$Z = \sum_{n=0}^{N} \left(e^{-\beta\varepsilon}\right)^n = \frac{1 - e^{-(N+1)\beta\varepsilon}}{1 - e^{-\beta\varepsilon}}. \tag{3.77}$$

If $\varepsilon \gg k_B T$ (which is the low-temperature limit) then $e^{-\beta\varepsilon} \ll 1$, and $e^{-(N+1)\beta\varepsilon} \ll e^{-\beta\varepsilon}$, so $Z \simeq 1+e^{-\beta\varepsilon}$ (it is often useful to take the limit early, at the stage of partition function, rather than derive the full result and then simplify it). The average number of broken links can be evaluated directly from the statistical probability:

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{n} n\left(e^{-\beta\varepsilon}\right)^n \simeq e^{-\beta\varepsilon}. \tag{3.78}$$

The same result will follow if you realise that the mean energy $U = \langle n \rangle \varepsilon$ and find U from Z in the usual way.

3.6.8 Example: the Planck Distribution

Consider a single simple harmonic oscillator. The partition function sum has every microstate with just one state. so it's just the geometric series:

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) = \sum_{n=0}^{\infty} \exp\left(-\left(n + \frac{1}{2}\right)\frac{\hbar\omega_0}{k_B T}\right) = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}}, \tag{3.79}$$

$$\implies F_{eq} = -k_B T \ln Z = \frac{\hbar\omega_0}{2} = k_B T \ln\left(1 - e^{-\hbar\omega_0/k_B T}\right), \tag{3.80}$$

$$\implies S = -\left(\frac{\partial F}{\partial T}\right)_V = -k_B \ln\left(1 - e^{-\hbar\omega_0/k_B T}\right) + \frac{\hbar\omega_0}{T}\frac{e^{-\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}}, \tag{3.81}$$

$$\implies U = F + TS = -\frac{\partial}{\partial\beta}\ln Z = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1}. \tag{3.82}$$

This is Planck's formula for the energy of black-body radiation in a mode of frequency ω_0. The mean number of photons with energy $\hbar\omega_0$ is directly related to the energy; $\langle n_{\hbar\omega_0} \rangle = (U - \frac{1}{2}\hbar\omega_0)/\hbar\omega_0 = 1/(e^{\hbar\omega_0/k_B T} - 1)$

3.6.9 The Microscopic Meaning of Heat and Work

We can also use the Boltzmann distribution to gain insight into the meaning of heat and work. Start from the Gibbs entropy, and again substitute the Boltzmann distribution,

$$\begin{aligned} \mathrm{d}S &= -k_B \sum_i \left(\mathrm{d}P_i \ln P_i + \mathrm{d}P_i\right) \\ &= -k_B \sum_i \left(\mathrm{d}P_i \left(-\frac{E_i}{k_B T} - \ln Z\right) + 0\right) \\ &= k_B \sum_i \frac{E_i \, \mathrm{d}P_i}{k_B T}, \end{aligned} \tag{3.83}$$

where we have twice used $\sum_i \mathrm{d}P_i = 0$ (from $\sum_i P_i = 1$). Cancelling the k_B's and multiplying by T, we have

$$T\,\mathrm{d}S = \sum_i E_i\,\mathrm{d}P_i\,. \tag{3.84}$$

This is the reversible heat flow $đQ_{\mathrm{rev}}$. But in general $U = \sum_i E_i P_i$, so from $\mathrm{d}U = T\,\mathrm{d}S + đW$ we conclude that the reversible work is

$$đW_{\mathrm{rev}} = \sum_i P_i\,\mathrm{d}E_i\,. \tag{3.85}$$

Fig. 3.5: We have $U = \sum p_i E_i \implies \mathrm{d}U = \sum E_i\,\mathrm{d}p_i + \sum p_i\,\mathrm{d}E_i$, and also that $\mathrm{d}U = đQ + đW$. Thus the internal energy can conceptually be changed in two ways: moving particles to other states- i.e. transfering energy (heat) to particles; and keeping state occupation the same, but changing state energies – i.e. doing work on the system. Hence, we see that the reversible heat flow, $đQ_{\mathrm{rev}} = \sum_i E_i\,\mathrm{d}P_i$, comes from the change in the probability distribution while the reversible work, $đW_{\mathrm{rev}} = \sum_i P_i\,\mathrm{d}E_i$, comes from the change in the energy levels.

In other words, heat corresponds to a change in the probability distribution with the underlying energy levels unchanged, while work corresponds to shifts in the energy levels with the probability distribution unchanged. Note that the probability distribution may, however, change in a $đW$ process, because energy levels may cross and while they are degenerate their occupancy may shift.

This realisation provides a justification for identifying statistical and thermodynamic entropy, as it leads to a very plausible microscopic interpretation of heat and work. We could also, with hindsight, launch into statistical thermodynamics differently: if we were to start by postulating that heat flow and work must correspond to changes in the probability distribution and in the energy level scheme, respectively, we would find that the Boltzmann probability distribution is the only one consistent with the postulate, and we would arrive, via a back route, at the Gibbs expression for entropy.

Chapter 4

Classical Ideal Gas

4.1 Phase Space

Many problems may be addressed satisfactorily using classical mechanics rather than quantum mechanics, and of course Boltzmann and Gibbs developed statistical mechanics before the advent of quantum mechanics. Here we develop statistical mechanics for use with classical mechanics.

The meaning of the number of states Ω in an expression such as $S = k_B \ln \Omega$ is often clear, e.g., when you have a discrete system where states can be enumerated, as in several examples in Section 3.6. It is often easy to enumerate the states for a quantum system - when the number of microstates corresponding to the macrostate: quantised states are discrete, so we can count them and then calculate the entropy or the partition function. In classical mechanics on the other hand, variables such as the energy, or coordinate-velocity of a particle, are continuous so it isn't immediately clear how to count the states.

In order to think about this issue it will be useful to introduce the notion of the *phase space*. Those of you familiar with Lagrangian and Hamiltonian dynamics would be familiar with this concept: in a normal space, in order to describe the continuous motion we characterise a particle by its coordinate, $\mathbf{r}(t)$. However, just knowing the function $\mathbf{r}(t)$ is not sufficient to fully describe the evolution of the system: you need to simultaneously know the particle velocity $\dot{\mathbf{r}}(t)$ (or, equivalently, its momentum $\mathbf{p} = m\mathbf{v}$) to be able to predict where it will end up at $t+\mathrm{d}t$. The phase space is double in dimensions and represents the particle by a representative point $(\mathbf{r}(t), \mathbf{p}(t))$. In a classical system of N point particles the *precise* microstate of the system is specified by the position of a representative point in the $6N$-dimensional phase space, $X = (\mathbf{r}_1, \cdots, \mathbf{r}_N; \mathbf{p}_1, \cdots, \mathbf{p}_n)$, where $\mathbf{r}_i$ is the position of the ith particle and $\mathbf{p}_i$ is its momentum. The positions and momenta of the particles change with time, and therefore the representative point moves along a trajectory in the phase space, as determined by the classical laws of Newtonian mechanics. This is easy to see if we consider a one-dimensional simple harmonic oscillator, whose "system point" is defined by the position, $x = u \sin \omega t$, and momentum, $p = m\omega u \cos \omega t$, in the two-dimensional phase space. The trajectory in phase space is an ellipse.

To do statistical mechanics, we imagine that we have an ensemble of identical classical systems, which allows us to define a *probability density*, $\varrho(\{\mathbf{r}_i, \mathbf{p}_i\})$, in phase space, which is equal to the fraction of systems located within an infinitesimal

volume $\mathrm{d}\Gamma$ surrounding the point $\{\mathbf{r}_i, \mathbf{p}_i\}$. The infinitesimal volume is given by

$$\boxed{\mathrm{d}\Gamma \equiv \prod_{i=1}^{N} \frac{\mathrm{d}^3 r_i \, \mathrm{d}^3 p_i}{(2\pi\hbar)^3}.} \tag{4.1}$$

Note the appearance of a factor of Planck's constant $\hbar$ for each momentum component, p_i. Clearly this factor could not have arisen from a classical argument! Indeed, there are several ways to demonstrate that the particle position in the phase space is in fact quantised, with the discretisation $\Delta x \Delta p \sim 2\pi\hbar$ for each degree of freedom, and so this factor is necessary when one converts from the (non-dimensional) sum over discrete states to the continuous integral over $\mathrm{d}x \, \mathrm{d}p$. Remarkably, the value of this factor (and thus the "memory" about the underlying quantum nature of the phase space) *cancels* in the differences between thermodynamic functions for different states of a system.

In Appendix A.2 it is shown that ϱ is constant along system trajectories in phase space. This is a very important result, because the trajectories in phase space are lines of constant internal energy of the system, so it tells us that in equilibrium the probability density depends only on the energy, so that states with the same energy have the same probability, i.e., the PEEP.

4.1.1 Classical Partition Function

The definition of quantities in classical statistical mechanics follows in a fashion analogous to the development of quantum statistical mechanics. If we are dealing with a closed system, whose energy is confined to a narrow region between energy E and $E + \mathrm{d}E$, then all states with energy in this interval are equally likely, while those outside have probability zero. The number of states in this energy shell is proportional to $(\mathrm{d}\Gamma \,/\, \mathrm{d}E) \, \mathrm{d}E$, so we define the microcanonical entropy $S(E)$ as

$$S = k_B \ln\left(\frac{\mathrm{d}\Gamma(E)}{\mathrm{d}E} \, \mathrm{d}E\right). \tag{4.2}$$

Moreover we can define the Gibbs entropy as $S = -k_B \int \varrho \ln \varrho \, \mathrm{d}\Gamma$, where we interpret the continuous integration over the phase space as the "sum over all configurations" or all states. The most important consequence is that if we consider a "subsystem" plus a "reservoir" as a larger closed system then, as before, we can derive the Boltzmann distribution for the probability density $\varrho(E)$ and the associated partition function for the subsystem:

$$\varrho = \frac{e^{-\beta E(\{\mathbf{p}_i, \mathbf{q}_i\})}}{Z_{cl}}, \tag{4.3}$$

$$Z_{cl} = \int e^{-\beta E(\{\mathbf{p}_i, \mathbf{q}_i\})} \, \mathrm{d}\Gamma \, . \tag{4.4}$$

We mentioned earlier that the factor of $2\pi\hbar$ in the definition of Γ was not important. From Eqs. (4.3) and (4.4) it is clear that if we multiply Γ by a constant factor A, then $S \Rightarrow S + k_B \ln A$, just a constant added.

Consider a single classical particle in a box of volume V. The classical partition function is

$$\begin{aligned} Z_1 &= \int e^{-\beta E(\mathbf{p},\mathbf{r})}\,\mathrm{d}\Gamma = \int e^{-p^2/2mk_BT}\frac{\mathrm{d}^3r\,\mathrm{d}^3p}{(2\pi\hbar)^3} \\ &= \frac{V}{(2\pi\hbar)^3}\int_0^\infty e^{-p^2/2mk_BT}4\pi p^2\,\mathrm{d}p \\ &= \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} V. \end{aligned} \tag{4.5}$$

Actually, this is not the smartest way to do this integration (twice by parts), given that the Boltzmann exponential factorises in each of the dimensions: $p^2 = p_x^2+p_y^2+p_z^2$ if all three are involved. So in 3D

$$Z_1 = \int \mathrm{d}^3r\left(\int_{-\infty}^{\infty} e^{-p_x^2/2mk_BT}\frac{\mathrm{d}p_x}{2\pi\hbar}\right)^3 = V\left(\sqrt{\frac{mk_BT}{2\pi\hbar^2}}\right)^3 = \frac{V}{\lambda^3}. \tag{4.6}$$

and equally easy to consider 2D or 1D cases. In essence, you only ever need to do one 1D-momentum integral, which is a simple Gaussian, and then take it to the appropriate power.

Let us stop for a second and examine what we have just obtained. Strictly, the free particle in a box has no potential energy and so the standard Boltzmann factor (statistical weight of a given microstate) should be equal to $e^0 = 1$. Hence, by evaluating the partition function according to its definition, $Z = \sum_i \exp[-\beta E_i]$, we should have obtained just the number of states this particle can have in this box, $\Omega = \sum_i$ (the "phase space" arguments are just to help us to count the states in this sum). And we see that this number is:

$$\Omega = V/\lambda^3, \quad \text{where the length scale } \lambda \text{ is:} \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}. \tag{4.7}$$

You may recognise this length scale as the *thermal* de Broglie wavelength of this particle, as you have studied in foundations of quantum physics! By 'thermal' we mean that the mean momentum of the particle is due to the thermal motion ($m\bar{v} = \sqrt{mk_BT}$). So the partition function, or the number of states a free classical particle can take inside the box is just the number of ways you can place the "packet" of size λ^3 inside a fixed V. It's not that surprising, if you look at this result in such a way.

The average energy of the particle is

$$U_1 = -\frac{\partial}{\partial\beta}\ln Z_1 = \frac{3}{2}k_BT. \tag{4.8}$$

The entropy of this single free particle in the box is given by

$$S_1 = -\left(\frac{\partial F_1}{\partial T}\right)_V = -\frac{\partial}{\partial T}(-k_B T \ln Z_1) = k_B \ln Z_1 + \frac{3}{2}k_B = k_B \ln\left(\frac{V}{\lambda^3}e^{3/2}\right). \quad (4.9)$$

4.1.1.1 One-Dimensional Simple Harmonic Oscillator

The one-dimensional simple harmonic oscillator has

$$E(p,x) = \frac{p^2}{2m} + \frac{1}{2}kx^2, \quad (4.10)$$

so, using Eq. (4.4), the classical partition function is

$$Z_{cl} = \int_{-\infty}^{\infty} e^{\beta(-p^2/2m + kx^2/2)} \frac{\mathrm{d}x\,\mathrm{d}p}{2\pi\hbar}, \quad (4.11)$$

which is clearly separable,

$$\begin{aligned} Z_{cl} &= \int_{-\infty}^{\infty} e^{-\beta p^2/2m} \frac{\mathrm{d}p}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-\beta k x^2/2}\,\mathrm{d}x \\ &= \sqrt{\frac{2m}{\beta}}\sqrt{\frac{2}{\beta k}}\frac{1}{2\pi\hbar}\underbrace{\left(\int_{-\infty}^{\infty} e^{-u^2}\,\mathrm{d}u\right)}_{\sqrt{\pi}}^2 \\ &= \frac{1}{\beta\hbar}\sqrt{\frac{m}{k}}. \end{aligned} \quad (4.12)$$

Note that the ratio $k/m = \omega_0^2$, the natural frequency of the oscillator, so in fact $Z = k_B T/\hbar\omega_0$, which is the high-temperature limit of Z of the general quantum oscillator. Obviously, the low-temperature limit of the classical partition function is wrong, the full quantum-oscillator Z will have the limit $Z \to e^{-\beta\hbar\omega/2}$.

This looks very easy, but one should think about the limits of integrals... We chose $\pm\infty$ for the $\int \mathrm{d}x$, but is it correct? If this system did not have any potential energy, only kinetic, then this would be an example of 1-dimensional ideal gas – and there we certainly do not take infinite limits of x-integration (instead we take the interval of the length L for the resulting $Z = L/\lambda$). We are allowed to replace the "proper" limits ($\pm L/2$, say) with infinities only if the exponential integrand decays to zero before the end of the interval is reached, that is, when $kL^2 \gg k_B T$. When this relation is reversed (at a very high T) the limits of $\int \mathrm{d}x$ should be taken finite, and then the ultimate high-T limit of ideal gas will be reached. Note that the momentum integral $\int \mathrm{d}p$ does not have this problem, at least not immediately, because the momentum can go up to infinity (in the relativistic limit of a massive particle $p = mv/\sqrt{1 - v^2/c^2}$).

4.1.1.2 Three-Dimensional Particle in a Uniform Gravitational Field

For a three-dimensional particle moving in a uniform gravitational field, the energy is given by

$$E(p,z) = \frac{p^2}{2m} + mgz. \tag{4.13}$$

The classical partition function is thus given by

$$\begin{aligned} Z_{cl} &= \int e^{-\beta(p^2/2m+mgz)} \frac{\mathrm{d}^3 r\, \mathrm{d}^3 p}{(2\pi\hbar)^3} \\ &= \left(\int_{-\infty}^{\infty} e^{-\beta p^2/2m} \frac{\mathrm{d}p}{2\pi\hbar}\right)^3 \left(\int_0^{\infty} e^{-\beta mgz}\, \mathrm{d}z\right) \underbrace{\int_A \mathrm{d}x\, \mathrm{d}y}_{=A} \\ &= \left(\sqrt{\frac{2m}{\beta}} \frac{1}{2\pi\hbar} \underbrace{\int_{-\infty}^{\infty} e^{-u^2}\, \mathrm{d}u}_{\sqrt{\pi}}\right) \left[\frac{-1}{\beta mg} e^{-\beta mgz}\right]_0^{\infty} A \\ &= \frac{A\sqrt{m}}{(2\pi\hbar)^3 g} (2\pi\hbar)^{3/2} (k_B T)^{5/2}, \end{aligned} \tag{4.14}$$

where A is the area normal to the z-direction. As in the Subsection 4.1.1.1, there is something to think about when deciding on the limits of $\int \mathrm{d}z$ integral. Again, taking the upper limit to infinity is an approximation (when the exponential integrand decays to zero, at $mgL \gg k_B T$) while at a very high temperature (when this inequality is reversed) the integrand is ≈ 1 over the whole z-interval and the integral is equal to L, again recovering ideal gas with little "sedimentation". As for the lower limit taken as zero, this is arbitrary of course – but you should remember that the true gravitational potential is *not* mgz – it is the Newtonian Gm_1m_2/z and it only *looks* like mgz in a narrow interval. So it is important to have a lower limit finite, and zero (the height at the "floor level") is just a simplest value to take.

4.2 Ideal Gas of N Particles

Having derived the partition function for a single particle in a box, which resulted in the expression for its entropy, Eq. (4.9), we now ask about N identical particles in the box. Our initial inclination is to say that the particles of ideal gas can be treated as independent thermodynamic systems, because they don't interact with one another. In that case their entropies would just add, to give

$$S_N^{\text{wrong}} = NS_1 = Nk_B \ln\left(Ve^{3/2}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right), \tag{4.15}$$

which is equivalent to saying that the partition function for N particles is the product of the partition functions for the individual particles,

$$Z_N^{\text{wrong}} = Z_1^N. \tag{4.16}$$

Unfortunately Eq. (4.15) suffers from the major problem that it is not *extensive*: if we double V and N, then S_N should double, but it doesn't! Note that our thermodynamic derivation (see Eq. (2.47)) led to the extensive Sackur-Tetrode formula for the entropy of an ideal gas.

The lack of extensivity of Eq. (4.15) leads to what is known as the "Gibbs paradox". If we allow two gases of identical molecules at the same pressure to mix then Eq. (4.15) predicts that the total entropy changes, which cannot be correct, while Eq. (2.47) predicts that it is unchanged.

All the thermodynamic potentials depend on $\ln Z$, e.g., $U = -\,\partial/\partial\beta \ln Z$, $F = -k_B T \ln Z$, $S = \partial/\partial T\,(k_B T \ln Z)$, etc. To make the thermodynamic potentials extensive we therefore need

$$Z_N = \frac{1}{N!} Z_1^N, \tag{4.17}$$

so that, for large systems, the free energy is

$$F = -k_B T \ln Z_N = -N k_B T (\ln Z_1 - \ln N + 1). \tag{4.18}$$

In particular, the entropy now becomes

$$S = -\frac{\partial F}{\partial T} = N k_B \ln\left(\frac{V}{N} \exp\left(\frac{5}{2}\right)\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}\right), \tag{4.19}$$

which is extensive and is exactly the Sackur-Tetrode formula (2.53) for the entropy of an ideal gas, with all the constants now properly defined.

It was Gibbs who realised that, for the entropy to be extensive, we should only count microstates which are distinguishable from one another. Swapping the positions and momenta of two particles amounts merely to relabelling the two particles, and the microstate is indistinguishable from the original one. Removing all such indistinguishable permutation configurations from the sum over states amounts to dividing Z_N^{wrong} by $N!$.

Eq. (4.19) is consistent with Eq. (2.46), but now we have an explicit formula for the unknown integration constant S_0 which appeared in the earlier derivation. We will derive the Sackur-Tetrode entropy again later using the grand partition function, which automatically takes indistinguishability into account. All this is correct for an ideal classical gas but it is still wrong for the fully quantum regime: you can note that Eq. (4.19) does not satisfy the Third Law of Thermodynamics, as the entropy does not go to zero as $T \to 0$ (when quantum effects would take over).

4.2.1 Thermodynamic Properties of Ideal Gas

Once the partition function of a system is found, in effect, you know everything about your system! We just need to learn the route to find these answers. In the

case of ideal gas, the Eq. (4.17) provides:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N. \tag{4.20}$$

We have obtained the entropy, which was essential for the discussion of proper accounting for particle degeneracy. However, the primary aim should always be the appropriate thermodynamic potential. One is the mean energy U, the other is the free energy F:

$$U = -\frac{\partial}{\partial\beta}\ln Z; \qquad F = -k_B T \ln Z. \tag{4.21}$$

To find U you need to differentiate Z with respect to temperature (or its inverse, β) and that is "hiding" under the square-root in the de Broglie wavelength $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$. The logarithm allows factorisation of all other terms in Z, for us not to worry about anything except the proportionality $Z \propto \beta^{-3/2}$, so that $U = \frac{3}{2}Nk_BT$. This is great, but only useful for one thing: to evaluate the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk_B. \tag{4.22}$$

In all other senses the mean energy expressed as a function of temperature is not a good object to work with, because T is not the natural variable of $U = U(S, V)$.

Since by its construction, via the integration of the statistical weight $e^{-\beta E}$ over the phase space, the partition function depends on T and V, the more natural route is to evaluate the free energy $F = F(T, V, N)$:

$$F = -Nk_BT\ln\left(\frac{V}{\lambda^3}\right) + Nk_BT\ln N - Nk_BT = Nk_BT\ln\left(\frac{N\lambda^3}{Ve}\right), \tag{4.23}$$

the last term on the first line arising from the Stirling approximation of the factorial, and part of it contributes to the factor of e in the denominator of Eq. (4.23). The dependence of this thermodynamic potential on its natural variables is explicit and we can reap the benefits. The entropy, $S = -(\partial F/\partial T)_{V,N}$ is already obtained in its Sackur-Tetrode form. The other two conjugate variables are the pressure p and the chemical potential μ:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V}, \tag{4.24}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_BT\ln\left(\frac{N\lambda^3}{V}\right). \tag{4.25}$$

In both cases we benefited from the very convenient property of logarithm factorisation, which allows one to only look at the relevant variable in its argument. The equation of state of the ideal gas is a pleasing, and inevitable result; the expression (4.25) for the chemical potential of classical ideal gas is very important and

will be required several times below. Please compare it with the expression in Eq. (2.54) obtained from entirely thermodynamic arguments: the two are clearly the same, if you think of the ratio $N\lambda^3/V$ as an effective volume fraction of particles (see Section 4.5). This resonates with our old $\mu = k_B T \ln c$ with 'concentration'.

4.2.1.1 Example: Relativistic Gas

Consider an ideal classical gas of volume V and temperature T, consisting of N indistinguishable particles in the extreme relativistic limit where the energy ε and momentum p of a particle are related by $\varepsilon = c|p|$, where c is the speed of light.

For a single particle, the partition function is (4.4),

$$Z_1 = \int e^{-\beta c|p|} \frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} \underbrace{\int \mathrm{d}^3 r}_{V} . \tag{4.26}$$

To calculate this you need to convert $\mathrm{d}^3 p$ into sphericals ($4\pi p^2\,\mathrm{d}p$) since now the factorisation of exponentials will not work (with $c|p|$ in the exponent).

$$\begin{aligned} Z_{cl} &= \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 e^{-\beta c p}\,\mathrm{d}p \\ &= \frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3}. \end{aligned} \tag{4.27}$$

For a classical ideal gas of N ideal particles, the total partition function is given by (4.17), $Z_N = Z_1^N/N!$, and so

$$Z_{cl,N} = \frac{1}{N!}\left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3}\right)^N . \tag{4.28}$$

It is convenient for us to first find F using (4.18),

$$F = -k_B T N \left[\ln\left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3}\right) - \ln N + 1\right]. \tag{4.29}$$

For the equation of state, we recall that $p = -(\partial F/\partial V)_T$ (4.24), from which it follows

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V}, \tag{4.30}$$

the expected equation of state for an ideal gas.

Similarly, we can find the entropy via $S = -(\partial F/\partial T)_V$,

$$S = k_B N \left[\ln\left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3 N}\right)\right], \tag{4.31}$$

and then $F = U - TS$ or $U = -\,\partial \ln Z/\partial\beta$ equivalently give

$$U = 3Nk_BT, \tag{4.32}$$

from which the heat capacity follows as

$$C = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B. \tag{4.33}$$

It seems the equipartition does not work (i.e. it appears we have 6 degrees of freedom)? But of course equipartition only gives $k_BT/2$ when the energy depends on this degree of freedom quadratically, which is only the low-speed limit (the full $E = \sqrt{p^2c^2 + m^2c^4}$). In fact, the generalised equipartition theorem can be used to obtain exactly our result in relativistic case.

Suppose that now, in addition to its translational motion, each of the particles can exist in one of two states of energy Δ and $-\Delta$. A partition function can be factorised into each independent degree of freedom, so the partition function (3.26) just for a two-level system with energy levels $+\Delta$ and $-\Delta$, with no extra degeneracy, is

$$Z_\Delta = e^{\beta\Delta} + e^{-\beta\Delta} = 2\cosh\left(\frac{\Delta}{k_BT}\right). \tag{4.34}$$

The total partition function of the system is then

$$Z = \frac{1}{N!}\underbrace{\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3}\right)^N}_{(4.27)}\underbrace{\left(e^{\beta\Delta} + e^{-\beta\Delta}\right)^N}_{(4.34)} \tag{4.35}$$

The thermodynamic functions depend on $\ln Z$ through the Helmholtz free energy,

$$F = -k_BT\ln Z = \underbrace{-k_BTN\left[\ln\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3N}\right) + 1\right]}_{(4.29)} + \underbrace{-k_BTN\ln\left(e^{\beta\Delta} + e^{-\beta\Delta}\right)}_{NF_\Delta}, \tag{4.36}$$

and therefore to find their values for the ideal gas including the internal states of the particles (Z_Δ in this case) we just have to add N times the contribution from a single particle. These contributions are

$$F_\Delta = -k_BT\ln Z_\Delta = -k_BT\ln\left(e^{\beta\Delta} + e^{-\beta\Delta}\right) \tag{4.37}$$

$$p_\Delta = -\left(\frac{\partial F_\Delta}{\partial V}\right)_T = 0, \quad \text{equation of state remains unchanged} \tag{4.38}$$

$$S_\Delta = -\left(\frac{\partial F_\Delta}{\partial T}\right)_V = k_B\ln\left(e^{\beta\Delta} + e^{-\beta\Delta}\right) + \frac{\Delta}{T}\tanh(\beta\Delta) \tag{4.39}$$

$$U_\Delta = -\frac{\partial}{\partial\beta}\ln Z_\Delta = -\Delta\tanh(\beta\Delta) \tag{4.40}$$

$$C_\Delta = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\Delta^2}{k_BT^2\cosh^2(\beta\Delta)}. \tag{4.41}$$

4.2.1.2 Example: Spherical Trap

Atoms can be held in a spherical trap with the potential energy potential $V(r) = ar$. The single-particle partition function Z_1 (4.4) contains the same momentum integral (4.6) as for a classical ideal gas, which contributes λ^{-3}, but instead of the total volume, we now have a space integral:

$$Z_1 = \frac{1}{\lambda^3}\int_0^\infty \underbrace{4\pi r^2\,\mathrm{d}r}_{\mathrm{d}^3 r}\, e^{-ar\beta} = \frac{8\pi(k_BT)^3}{a^3\lambda^3}. \tag{4.42}$$

This gives the N-particle partition function (4.17) $Z_N = Z_1^N/N!$,

$$F = -k_BTN\left\{\ln\left[\frac{8\pi(k_BT)^3}{N(a\lambda)^3}\right] + 1\right\}, \tag{4.43}$$

and the free energy (4.18) $F = -k_BT\ln Z_N$, from which we obtain an entropy

$$\begin{aligned} S = -\left(\frac{\partial F}{\partial T}\right)_V &= k_BN\left\{\ln\left[\frac{8\pi(k_BT)^3}{N(a\lambda)^3}\right] + 1\right\} \\ &= k_BN\left\{\ln\left[\left(\frac{mk_B}{2\pi\hbar^2}\right)^{3/2}\frac{8\pi k_B^3}{N}\right] + 11/2\right\} + 4.5k_BN\ln T - 3k_BN\ln a \\ &= S_0 + 4.5k_BN\ln T - 3k_BN\ln a, \end{aligned} \tag{4.44}$$

so with decreasing a, we slide from one constant-a curve to another, thereby lowering the temperature, as shown in Fig. 4.1.

Fig. 4.1: Caption

The chemical potential is obtained as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_T = k_BT\ln\left(\frac{Na^3\lambda^3}{8\pi k_B^3T^3}\right). \tag{4.45}$$

Quantum statistics become relevant, when this approaches 0 from below (see Section 5.4), which leads to the inequality $Na^3\lambda(T)^3 > 8\pi k_B^3T^3$ (but keep in mind $\lambda \propto T^{-1/2}$) to get into the quantum regime. Check: the volume explored by the classical gas is of order $(k_BT/a)^3$, so this inequality is similar to that for the standard gas (see Section 4.5), $N\lambda^3/V > 1$.

4.3 Equipartition Theorem

The equipartition theorem is an extremely important result from classical statistical mechanics. It applies to terms in the Hamiltonian which are *separable* and *quadratic* in one of the generalised coordinates or momenta, meaning that they can be written as

$$\mathcal{H} = Aq^2 + \Delta\mathcal{H}(Q), \tag{4.46}$$

where Q represents all of the other $6N - 1$ coordinates of the phase space.

We first examine the consequences of separability. In the canonical ensemble we have

$$\varrho(q)\,\mathrm{d}q = \frac{e^{-\beta Aq^2}\,\mathrm{d}q \int e^{-\beta\Delta\mathcal{H}}\,\mathrm{d}Q}{\int e^{-\beta Aq^2}\,\mathrm{d}q \int e^{-\beta\Delta\mathcal{H}}\,\mathrm{d}Q} = \frac{e^{-\beta Aq^2}\,\mathrm{d}q}{\int e^{-\beta Aq^2}\,\mathrm{d}q} = \frac{e^{-\beta Aq^2}\,\mathrm{d}q}{\sqrt{\pi k_B T/A}}. \tag{4.47}$$

The meaning of this result is that if a coordinate is separable in the Hamiltonian then its probability distribution is independent of all of the other coordinates. So it has its own "private" Boltzmann distribution.

The average internal energy of the system is

$$U = \left\langle Aq^2 \right\rangle + \langle \Delta\mathcal{H}(Q) \rangle\,, \tag{4.48}$$

and, using Eq. (4.47), we obtain

$$\left\langle Aq^2 \right\rangle = \frac{\int Aq^2 e^{-\beta Aq^2}\,\mathrm{d}q}{\int e^{-\beta Aq^2}\,\mathrm{d}q} = \frac{\frac{\sqrt{\pi}}{2\beta^{3/2}}}{\frac{\sqrt{\pi}}{\beta^{1/2}}} = \frac{1}{2}k_B T. \tag{4.49}$$

Hence the average energy for the q degree of freedom is $\frac{1}{2}k_B T$. This is the equipartition theorem: each squared, separable degree of freedom in the Hamiltonian has a mean energy of $\frac{1}{2}k_B T$. This law allows us to write down the internal energy result of Eq. (4.8) without explicit calculation: single free particle in 3-dimensions has three components of its kinetic energy, $(1/2m)(p_x^2 + p_y^2 + p_z^2)$, each averaging to $\frac{1}{2}k_B T$.

Equipartition holds for any term in the Hamiltonian which is separable and squared, but *only in the classical limit*. The precise definition of the classical limit will be left until later, but for a simple harmonic oscillator the condition is $k_B T \gg \hbar\omega_0$.

4.3.1 Kinetic Energy of Particles in Classical Interacting Systems

The kinetic energy degrees of freedom are generally separable and squared. So even when the interaction term is present in the Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(\mathbf{r}_1, \cdots, \mathbf{r}_N), \tag{4.50}$$

in some form of complicated potential energy, our discussion immediately above shows that the probability distribution for the x, y and z components of the velocity of the ith particle in the system still follows the Maxwell-Boltzmann distribution. In each dimension:

$$\varrho(v_{x,i})\,\mathrm{d}v = \sqrt{\frac{m}{2\pi k_B T}}e^{-\beta\frac{1}{2}mv_{x,i}^2}\,\mathrm{d}v_{x,i} \tag{4.51}$$

the corresponding factor in the partition function is $1/\lambda$, and the mean energy is still $\frac{1}{2}k_BT$ per kinetic degree of freedom. These statements are completely independent of the interactions between the particles; they are equally true in gases, liquids and solids, as long as the system is in the classical limit.

4.4 Gas of Diatomic Molecules

In this example we bring together the ideas of quantum statistical mechanics and classical statistical mechanics and the equipartition theorem, and also examine the role of additional degrees of freedom each particle might possess. Consider a diatomic molecule consisting of two different atoms bonded together. As well as the translational motion the molecule can rotate in space and also vibrate along its bond. These internal degrees of freedom contribute to the internal energy and hence the heat capacity of the molecule.

The vibrations can be approximated by those of a harmonic oscillator of frequency ω_0. Following Eqs. (3.79) and (3.81) we have

$$S = -k_B\ln\Big(1-e^{-\hbar\omega_0/k_BT}\Big) + \frac{\hbar\omega_0}{T}\frac{e^{-\hbar\omega_0/k_BT}}{1-e^{-\hbar\omega/k_BT}}. \tag{4.52}$$

Or simply calculate the partition function:

$$Z = \sum_i \exp\Big(-\frac{E_i}{k_BT}\Big) = \sum_{n=0}^{\infty}\exp\Big(-(n+\frac{1}{2})\frac{\hbar\omega_0}{k_BT}\Big) = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_BT}}{1-e^{-\hbar\omega_0/k_BT}}, \tag{4.53}$$

and then find $S = -\,\mathrm{d}F/\mathrm{d}T$, or $U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$.

The vibrational contribution to the heat capacity from N diatomic molecules is given by:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = N\frac{\hbar^2\omega_0^2}{k_BT^2}\frac{e^{\hbar\omega_0/k_BT}}{(e^{\hbar\omega_0/k_BT}-1)^2} = Nk_B\left(\frac{\Theta_\mathrm{v}}{T}\right)^2\frac{e^{\Theta_\mathrm{v}/T}}{(e^{\Theta_\mathrm{v}/T}-1)^2}, \tag{4.54}$$

where we used a shorthand notation for the effective temperature, $k_B\Theta_\mathrm{v} = \hbar\omega_0$. This relation is plotted in Fig. 4.2.

The molecule can also exist in different orbital angular momentum states. The energies of the rotational states are given by

$$\epsilon_J = \frac{\hbar^2 J(J+1)}{2I}, \quad J = 0, 1, 2, \cdots, \tag{4.55}$$

Fig. 4.2: The heat capacity of a harmonic oscillator as a function of temperature.

where I is the moment of inertia of the molecule about an axis through its centre of mass, and the degeneracy of each state is $\Omega_J = 2J + 1$. These again are discrete states, easy to enumerate, and the corresponding partition function is

$$Z = \sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{\hbar^2 J(J+1)}{2Ik_BT}\right). \tag{4.56}$$

The full sum is tedious, but at low temperatures we need only consider the low-energy terms $J = 0$ and $J = 1$, which gives

$$Z \simeq 1 + 3\exp\left(-\frac{\hbar^2}{Ik_BT}\right) + \cdots . \tag{4.57}$$

The Helmholtz free energy at low temperatures is given by

$$F = -k_BT \ln Z \simeq -3k_BT \exp\left(-\frac{\hbar^2}{Ik_BT}\right). \tag{4.58}$$

The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3k_B \exp\left(-\frac{\hbar^2}{Ik_BT}\right) + \frac{3\hbar^2}{IT} \exp\left(-\frac{\hbar^2}{Ik_BT}\right), \tag{4.59}$$

from which we can obtain the rotational contribution to the heat capacity from N diatomic molecules at low temperatures:

$$C_\mathrm{r} = T\left(\frac{\partial S}{\partial T}\right)_V = 12Nk_B\left(\frac{\Theta_\mathrm{r}}{T}\right)^2 \exp\left(-\frac{2\Theta_\mathrm{r}}{T}\right), \tag{4.60}$$

where $k_B\Theta_\mathrm{r} = \hbar^2/(2I)$, a different effective temperature corresponding to the rotational motion. At high temperatures we get the equipartition result,

$$C_\mathrm{r} \simeq Nk_B. \tag{4.61}$$

Fig. 4.3: The rotational heat capacity as a function of temperature.

The full result is shown in Fig. 4.3.

Normally $\Theta_{\rm r} \ll \Theta_{\rm v}$. Experimental results for the heat capacity at constant pressure, C_p, are shown in Fig. 4.4 as a function of temperature for the diatomic gases DT, HT, and HD, where D≡deuterium, H≡hydrogen, T≡tritium. At low T there is only translational motion, then rotational motion is excited, and finally vibrational motion is excited, so the heat capacity should follow:

$$\begin{array}{ccccc} 0 \ll T \ll \Theta_{\rm r} & \text{translational motion:} & C_v = \frac{3}{2}Nk_B, & C_p = \frac{5}{2}Nk_B \\ \Theta_{\rm r} \ll T \ll \Theta_{\rm v} & \text{translational, rotational motion:} & C_v = \frac{5}{2}Nk_B, & C_p = \frac{7}{2}Nk_B \\ \Theta_{\rm v} \ll T & \text{translational, rotational, vibrational motion:} & C_v = \frac{7}{2}Nk_B, & C_p = \frac{9}{2}Nk_B. \end{array} \tag{4.62}$$

Note that in the flat part of the curves, where $\Theta_{\rm r} \ll T \ll \Theta_{\rm v}$, the masses of the atoms are irrelevant - this is when the translational and rotational degrees of freedom can be approximated by their high temperature limits (classical limits) and the vibrations are not excited significantly. Homonuclear molecules, such as H_2, are a bit different at low temperatures - quantum effects due to indistinguishable nuclei!

Fig. 4.4: The rotational-vibrational heat capacities at constant pressure, C_p, for the diatomic gases DT, HT, and HD, as a function of temperature.

4.5 Classical to Quantum Crossover

Let us explore the conditions under which quantum nature of the system (ideal gas in this chapter) becomes important, as opposed to the classical regime where we have just obtained, e.g., Eqs. (4.23) and (4.25) for the free energy and chemical potential. Please note how both these expressions, as in fact the entropy (4.19), depend on the combination of parameters (in a 3-dimensional system):

$$\frac{N\lambda^3}{V} = \frac{N}{V}\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2}. \tag{4.63}$$

You can look at this expression and have a scheme illustrated in Fig. 4.5 in mind. Clearly, the ratio in Eq. (4.63) is related to the effective volume fraction of particles in the box - and the limit when the thermal de Broglie volumes associated with the particles do not clash is when $N\lambda^3/V \ll 1$. This is the limit of classical ideal gas. We can depart from this limit in several ways: by increasing the density of particles (N/V) or by increasing $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$ which, in turn, can be achieved by lowering the temperature $(T \to 0)$, or by considering lighter particles $m \to 0)$. Evidently, when $N\lambda^3/V \geq 1$, we can no longer talk about a classical gas: their wave packets (of the size $\sim \lambda$) will start interfering with each other and we drop into the quantum limit of statistical mechanics.

Fig. 4.5: Particles of "size" λ^3 filling the box of volume V.

The same conclusion can be reached from the "quantum side". Quantum effects become unimportant when the occupancy of each of the energy levels becomes small and therefore the discreteness (quantisation) relevant. This is the reciprocal k-space condition, but there is a corresponding real space condition. The maximum energy of a particle in the gas is around k_BT (ignoring "rare" fluctuations). From $\epsilon_{\mathbf{k}} = \hbar^2k^2/2m$ the wavevector for which the kinetic energy of our classical particles matches k_BT is, therefore:

$$k_{\max} \sim \sqrt{\frac{2mk_BT}{\hbar^2}}. \tag{4.64}$$

This would correspond to a wavelength $\lambda_{\max} = \frac{2\pi}{k_{\max}} = \frac{2\pi\sqrt{\hbar^2}}{\sqrt{2mk_BT}}$, which is close to the *thermal de Broglie wavelength* introduced earlier (Eq. (4.7)), up to a factor of order one. In different textbooks the thermal de Broglie wavelength is given with various factors of π floating around, but the most systematic approach for calculating this important quantity, based on the single-particle partition function $Z_1 = V/\lambda^3$ gives,

as shown earlier (Eq. (4.7)):

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}. \tag{4.65}$$

The wave-packets of the particles will cease to overlap in *real* space when the number of particles per unit volume N/V is less than $n_Q = 1/\lambda^3$, which is sometimes called the quantum concentration. That is, the wave-packets cease to overlap in real space when the inter-particle separation becomes greater than the thermal de Broglie wavelength. How does this correspond to the k-space condition? The average occupation of an accessible energy level is

$$\langle n \rangle = \frac{\text{number of particles}}{\text{number of accessible energy levels}} = \frac{N}{4/3\pi k_{\text{max}}^3}\frac{(2\pi)^3}{V}, \tag{4.66}$$

and the behaviour is classical when $\langle n \rangle \ll 1$. From Eq. (4.66) we see that the crossover occurs at roughly $N\lambda^3/V \sim 1$, so the k-space and real-space criteria agree.

Air at room temperature and pressure is in the classical regime while electrons in a solid are in the quantum regime. A system of Fermions or Bosons is sometimes referred to as *degenerate* if it is within the quantum regime and *non-degenerate* if it is within the classical regime.

Chapter 5

The Grand Canonical Ensemble

5.1 Quantum Mechanics and Indistinguishability

In our discussion of the classical partition function of N particles in Section 4.2 we used the idea that we should only count indistinguishable microstates. Ultimately this arises from the underlying quantum mechanical nature of matter. In quantum mechanics particles are either indistinguishable (identical) or distinguishable (different). In addition, particles come in two types - Fermi particles or fermions which have half-integer spins $(\frac{1}{2}, \frac{3}{2}, \cdots)$ and Bose particles or bosons which have integer spins $(0, 1, 2, \cdots)$. Examples of fermions include protons, neutrons, electrons, muons, neutrinos, quarks, and the ^{3}He atom. Examples of bosons include photons, pions, mesons, gluons, and the ^{4}He atom. The quantum mechanical wave function of a system of identical fermions is *antisymmetric* under the interchange of two particles, while the wave function of a system of identical bosons is *symmetric* under exchange of two particles, that is,

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2) = \pm\Psi(\mathbf{r}_2 s_2, \mathbf{r}_1 s_1) \tag{5.1}$$

where $\mathbf{r}$ is the position of a particle and s is its spin, while the plus sign refers to bosons and the minus to fermions.

To understand the problem more deeply consider two non-interacting quantum particles in a box, in states $|\mathbf{k}_1\rangle$ and $|\mathbf{k}_1\rangle$. If the two particles are distinguishable (say a helium atom and an argon atom), then the state $\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2}$ is different from $\Psi_{\mathbf{k}_2,\mathbf{k}_1}(\mathbf{r}_1, \mathbf{r}_2) = e^{i\mathbf{k}_2\cdot\mathbf{r}_1} e^{i\mathbf{k}_1\cdot\mathbf{r}_2}$, where $\mathbf{r}_1$ and $\mathbf{r}_2$ label the positions of the two particles. But if the particles are indistinguishable then, according to Eq. (5.1), the wave function must be

$$\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big(e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2} |s_1; s_2\rangle \pm e^{i\mathbf{k}_2\cdot\mathbf{r}_1} e^{i\mathbf{k}_1\cdot\mathbf{r}_2} |s_2; s_1\rangle\Big), \tag{5.2}$$

where the plus sign refers to bosons, and the minus to fermions.

So we *don't* have two different states, there is only one state. Also, if $\mathbf{k}_1 = \mathbf{k}_2$, the same-spin fermion wave-function is zero; this state is forbidden by the Pauli exclusion principle, as shown by Eq. (5.1). When we do statistical mechanics of quantum mechanical particles we must count the states correctly.[1]

[1] It is worth noting as an aside that identical particles with different spin states behave like distinguishable particles, i.e., the spin state is a "label" that lets us distinguish particles. Therefore we only have to worry about the effect of wave-function symmetrisation for same-spin particles, and the system can be broken down into same-spin subsystems, whose thermodynamic potentials will add.

As an interesting aside, the plus or minus sign in the wave function leads to profound differences in the physics of fermions and bosons. The particle densities from the wave functions of Eq. (5.2) are uniform. However, consider the joint probability density for the state $\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)$ of finding one particle at $\mathbf{r}_1$ and the other at $\mathbf{r}_2$,

$$\begin{aligned} P_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) &= \Psi^*_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) \\ &= \frac{1}{2}\Big(1+1\pm\delta_{s_1,s_2}\Big\{e^{-i\mathbf{k}_1\cdot(\mathbf{r}_1-\mathbf{r}_2)}e^{-i\mathbf{k}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)}+e^{-i\mathbf{k}_2\cdot(\mathbf{r}_1-\mathbf{r}_2)}e^{-i\mathbf{k}_1\cdot(\mathbf{r}_2-\mathbf{r}_1)}\Big\}\Big) \\ &= (1\pm\delta_{s_1,s_2}\cos\{(\mathbf{k}_1-\mathbf{k}_2)\cdot(\mathbf{r}_1-\mathbf{r}_2)\}). \end{aligned} \tag{5.3}$$

This is called the pair-correlation function, and it is sketched in Fig. 5.1. Note that for same-spin bosons there is an increased probability of finding them close together, while for same-spin fermions this probability is reduced.

Fig. 5.1: The pair-correlation functions for two fermions of the same spin and for two bosons of the same spin.

To evaluate the partition function correctly we should count only microstates corresponding to wave functions of the correct symmetry. It would be a major difficulty if we had to discuss the many-body wave functions of a system every time we wanted to do statistical mechanics. Fortunately it turns out that there is an easy way around this for non-interacting systems; *we stop treating the particles as independent thermodynamic systems, and instead treat the energy levels as independent thermodynamic systems, which contain particles and energy.* The best method for dealing with systems with variable particle number and energy is to use the grand partition function and the grand potential. In the next section we will see how to do this.

5.2 Using the Grand Canonical Ensemble

For a large system we get the same values of quantities such as the mean energy or the entropy whichever ensemble we use. We will of course choose the most

convenient ensemble. Within the canonical ensemble we will want to evaluate the partition function, Z, for a set of N particles. Suppose the particles occupy a set of energy levels $\varepsilon_1, \varepsilon_2, \cdots$, whose occupation numbers we denote by $n_1, n_2, \cdots$. The partition function is then

$$Z(T,V,N) = \sum_{n_1,n_2,\cdots}^{N} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}, \tag{5.4}$$

where the sum is over all sets of occupation numbers, $n_1, n_2, \cdots$, which satisfy $n_1 + n_2 + \cdots = N$. The N above the summation sign reminds us that only sets of occupation numbers obeying this constraint are included. For fermions the occupation numbers of each level can be 0 or 1, and for bosons they can take the values $0, 1, 2, \cdots$. The condition $n_1 + n_2 + \cdots = N$ leads to considerable mathematical difficulties, because it means that the sums over $n_1, n_2, \cdots$ in Eq. (5.4) are not independent.

Suppose we multiply Eq. (5.4) by $e^{\beta\mu N}$, where $\beta = 1/k_B T$ and μ is the chemical potential, and then sum over N,

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} Z(T,V,N)e^{\beta\mu N} = \sum_{N=0}^{\infty} \sum_{n_1,n_2,\cdots}^{N} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots-\mu N)}. \tag{5.5}$$

We recognise Ξ as being the grand partition function, first defined in Eq. (3.38). Noting that $N = n_1 + n_2 + \cdots$, we write

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} \sum_{n_1,n_2,\cdots}^{N} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots-\mu(n_1+n_2+\cdots))}. \tag{5.6}$$

The sums are over all sets of the n_i such that $n_1 + n_2 + \cdots = N$, and over all N. This is equivalent to summing over all $n_1 + n_2 + \cdots$ without the constraint that $n_1 + n_2 + \cdots = N$, because any set of the n_i corresponds to some value of N. We can therefore remove the sum over N if we also remove the constraint that $n_1 + n_2 + \cdots = N$, and write

$$\begin{aligned}
\Xi(T,V,\mu) &= \sum_{n_1,n_2,\cdots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots-\mu(n_1+n_2+\cdots))} \\
&= \sum_{n_1,n_2,\cdots} e^{-\beta(\varepsilon_1-\mu)n_1} e^{-\beta(\varepsilon_2-\mu)n_2} \cdots \\
&= \left[\sum_{n_1} e^{-\beta(\varepsilon_1-\mu)n_1}\right]\left[\sum_{n_2} e^{-\beta(\varepsilon_2-\mu)n_2}\right]\cdots \\
&= \prod_i \Xi_i.
\end{aligned} \tag{5.7}$$

The last line, Eq. (5.7), shows that the grand partition function is just the product of the grand partition functions Ξ_i of the individual energy levels, which is what we would get if we treated the energy levels as independent and distinguishable, each in contact with a reservoir at temperature T and chemical potential μ. All we

need to do is work out the grand partition function for each energy level and multiply them together! Although it is difficult to evaluate the partition function it is much simpler to evaluate the grand partition function! We can obtain all of the required thermodynamic information from the grand partition function. We will see over the coming lectures that the grand partition function leads to a very powerful and elegant approach.

5.3 The Classical Limit

Consider a single energy level, of energy $\varepsilon_{\mathbf{k}}$, in contact with a reservoir with which it can exchange both energy and particles. The grand partition function of the level is

$$\boxed{\Xi_{\mathbf{k}} = \sum_n e^{-\beta(n\varepsilon_{\mathbf{k}} - n\mu)} = \sum_n \left(e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right)^n.} \tag{5.8}$$

If the particles are bosons (i.e., have integer spin) the occupancy of the level is not restricted, so the sum runs from $n = 0$ to ∞. If the particles are fermions (i.e., have half-integer spin), the Pauli exclusion principle dictates that there are only two terms in the sum, $n = 0$ and $n = 1$. We shall turn to these cases soon. If, however, for either fermions or bosons, a limit when the exponent is small is observed,

$$\beta(\varepsilon_{\mathbf{k}} - \mu) \gg 1, \tag{5.9}$$

then the contribution from $n > 1$ is negligible. Note that this is not trivially the "high-temperature limit" where we often expect a relationship like $\beta\varepsilon \ll 1$. Now we have to a good approximation

$$\Xi_{\mathbf{k}}^{\mathrm{cl}} \approx 1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)} + \cdots . \tag{5.10}$$

If the Eq. (5.9) is valid for all energy levels then we have an *ideal classical gas* where the distinction between bosons and fermions is irrelevant to the thermodynamics. Examining the ratio $(\varepsilon_{\mathbf{k}} - \mu)/k_B T$ for an arbitrary value of energy, we can see that this can only be large if the chemical potential is large and negative, as we know is indeed the case in the classical ideal gas where $\beta\mu = \ln(N\lambda^3/v)$.

From Eq. (5.10) we obtain the grand potential for a given level of energy of an ideal classical gas:

$$\Phi_{\mathbf{k}} = -k_B T \ln \Xi_{\mathbf{k}}^{\mathrm{cl}} = -k_B T \ln\left(1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right) \simeq -k_B T e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}, \tag{5.11}$$

where in the last step the logarithm has been expanded to lowest order. The average occupancy of an energy level $\mathbf{k}$ is

$$\langle n_{\mathbf{k}} \rangle = -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial \mu}\right)_{T,V} \simeq e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}, \tag{5.12}$$

which is the *Maxwell-Boltzmann distribution*. From Eq. (5.9) we see that the classical gas corresponds to $\langle n_{\mathbf{k}} \rangle$ being small for all $\mathbf{k}$ including $\mathbf{k} = 0$.

5.4 Sign of Chemical Potential

In the grand canonical ensemble, each state characterised by a particular total energy E and total particle number N, has the probability of appearing

$$p \sim \exp\left[-\beta(E - \mu N)\right]. \tag{5.13}$$

In the exponent, the inverse temperature $\beta = 1/k_B T$ is the coefficient in front of one conserved quantity, the (minus) energy, while another coefficient, βu, is in front of the number of particles N. The chemical potential is therefore the coefficient in front of the number of particles - except for the extra β. The number of particles has to be conserved as well if μ is non-zero.

As long as the sign of N is well-defined, the sign of the chemical potential is well-defined, too.

Now, for bosons, μ can't be positive because the distribution would be an exponentially increasing function of N. Note that in the grand canonical ensemble – which is really the ensemble in which μ is sharply defined – the dual variable to μ, namely N, is not sharply defined. However, the probability for ever larger – infinite N would be larger, so the distribution would be peaked at $N = \infty$. Such a distribution couldn't be well-defined. We want, in the thermodynamic limit, the grand canonical ensemble, while assuming a fixed μ, also generate a finite and almost well-defined N, within an error margin that goes to zero in the thermodynamic limit. That couldn't happen for bosons and a positive μ.

This catastrophe would be possible because $N = \sum_i n_i$, a summation over microstates i, and every n_i can be an arbitrarily high integer for bosons. For fermions, the problem doesn't occur because $n_i = 0$ or 1 for each state i. So for fermions, we can't argue that μ has to be positive. Note that $E - \mu N$ in the exponent is the sum $\sum_i N_i(e_i - \mu)$. For bosons, the problem occurred for states for which $e_i - \mu$ was negative i.e. e_i was low enough. For fermions, however, the number of such states – and therefore the maximum number of fermions in them – is finite, so the divergence doesn't occur if the chemical potential is positive. For fermions, positive μ is OK.

In fact, for fermions, both positive and negative μ is OK. Also, it is easy to see that if both particles and antiparticles exist, μ of the antiparticle has to be minus μ of the particle because only the difference $N_{\text{particles}} - N_{\text{antiparticles}}$ is conserved; this is true both for bosons and fermions.

So if the potential for electrons is positive, the potential for positrons or holes (which play the very same role) has to be negative, and vice versa.

Nothing changes about the meaning of the chemical potential when one switches from classical physics to quantum physics: in fact, above, I was assuming that

there are "discrete states" for the particles, just like in quantum physics – otherwise we wouldn't be talking about bosons and fermions which are only relevant in the quantum setup. Classical physics is a limit of quantum physics in which the number of states is infinite because $\hbar$ goes to zero, so a finite number of particles never ends up in "exactly the same state". In some sense, Ludwig Boltzmann, while working in the context of classical statistical physics, was inherently using the thinking and intuition of quantum statistical physics – he was a truly ingenious "forefather" of quantum physics.

In relativity, one has to be careful how we define the energy of a state. Note that the physically meaningful combination that appears in the exponent is $e_i - \mu$, so if one shifts e_i e.g. by mc^2, the latent energy, one has to shift μ in the same direction by the same amount. The notions of chemical potential obviously work in relativity, too. Relativistic physics is not a "completely new type of physics". It is just a type of the old physics that happens to respect a symmetry – the Lorentz symmetry.

Again, in quantum field theory which combines both quantum mechanics and relativity, statistical physics including the notion of the chemical potential also works but one must be careful that particle-antiparticle pairs may be created with enough energy. That implies $\mu_p = -\mu_{np}$, as previously said.

There can't be any general ban on a negative chemical potential of fermions: fermionic μ can have both signs. However, the text above exhausts all universal facts about the sign of the chemical potential in statistical physics.

Here is a more "simple" answer, only for non-interacting particles to keep it simple:

- When we talk about chemical potential, we are talking about a system in contact with a huge reservoir of particles. These particles can go and come from the reservoir to our system. The reservoir (free) energy per particle is the chemical potential μ.
- We assume equilibrium: the sub-system is in equilibrium with the reservoir. This means the combined system has lowest free energy (or highest entropy), and that is how the particles arrange themselves.
- Now lets' say the lowest energy state of the subsystem is E_0 into which particles can go. We measure chemical potential μ with respect to this number. I mean the value "zero" for chemical potential μ is sort of a convention where we assume the lowest energy state has value zero.
- To lower the total free energy, a particle from the reservoir would happily go into this state if $E_0 < \mu$. For fermions, this just fills the state E_0 and then we would move on to the next state of higher energy E_1; if $E_1 < \mu$, fill it and keep going. So you see that at some point you stop since $E_n > \mu$ for some n. But for bosons there is trouble If $E_0 < \mu$, you can keep putting more

and more particles into E_0 from the reservoir, each transfer lowers total free energy, and you keep going and going... until the reservoir is empty which makes no sense. So basically this situation is not tenable with an actual reservoir. Either $\mu < E_0$ and you have finite number of particles in E_0, or you can't have a reservoir and you get some fixed population of particles in E_0. You can't have a reservoir in contact with a system where $\mu > E_0$. It just is contradictory. In practice what it means, is μ can be quite close to E_0 and one would get macroscopic occupation of the ground-state (Bose condensation) but not exactly equal to or larger in order to have a reservoir with which to exchange particles.

5.5 Grand Thermodynamic Potential

We now calculate the full thermodynamic grand potential $\Phi = -k_B T \ln \Xi$ using Eq. (5.11) and carrying out the summation over all energy states, $\Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}}$. We must appreciate that this is exactly the same summation over the microstates, as in the definition of the canonical partition function Z in Eq. (3.26), because the other aspect of grand statistical summation (over the number of particles) is effectively done for each microstate in Eq. (5.10). So for a continuous classical gas in 3-dimension this summation over the available phase space is the same as in Eq. (4.5):

$$\Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}} = \int \Phi(\varepsilon) \frac{\mathrm{d}^3 r \, \mathrm{d}^3 p}{(2\pi\hbar)^3} = -k_B T \int_0^\infty e^{-\beta(\varepsilon-\mu)} g(\varepsilon) \, \mathrm{d}\varepsilon \,, \tag{5.14}$$

where, after a change of variables, we write the measure of integration as $g(\varepsilon)\,\mathrm{d}\varepsilon$ which is the number of eigenstates with energy between ε and $\varepsilon + \mathrm{d}\varepsilon$. This function is called the density of states. Note that this density of states refers to states of individual particles, not to states of the system as the whole, so that $g(\varepsilon)$ is very different from the function $\Omega(U)$ we used earlier.

To transform the integral over $p(= \hbar k)$ into one over ε we differentiate $\varepsilon = p^2/2m$, which gives

$$\mathrm{d}p = \sqrt{\frac{m}{2\varepsilon}} \, \mathrm{d}\varepsilon \,. \tag{5.15}$$

The density of states depends on the dimensionality of space, and in the case of 3-dimensions the integral the 6-component phase space becomes

$$\int \frac{\sigma \, \mathrm{d}^3 r \, \mathrm{d}^3 p}{(2\pi\hbar)^3} = 4\pi \int_0^\infty \frac{\sigma V}{(2\pi\hbar)^3} p^2 \, \mathrm{d}p = \frac{\sigma V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\varepsilon} \, \mathrm{d}\varepsilon \,, \tag{5.16}$$

where we have also included the spin degeneracy factor $\sigma = 2s + 1$ (the number of

spin states per p-state). Now we conclude:

$$\begin{aligned}\Phi &= -k_BT\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}e^{\beta\mu}\int_0^\infty \sqrt{\varepsilon}e^{-\beta\varepsilon}\,\mathrm{d}\varepsilon \\ &= -k_BT\frac{\sigma V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}e^{\beta\mu}2\int_0^\infty x^2e^{-x^2}\,\mathrm{d}x \\ &= -k_BT\sigma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}e^{\beta\mu} \\ &= -k_BT\frac{\sigma V}{\lambda^3}e^{\beta\mu}, \end{aligned} \tag{5.17}$$

for the classical ideal gas. From the constraint on the total (constant) number of classical particles in the ideal gas we have

$$N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = \frac{\sigma V}{\lambda^3}e^{\beta\mu}, \tag{5.18}$$

where you can note that $Z_1 = \sigma V/\lambda^3$ is the single-particle canonical partition function of this gas. We can invert this equation to obtain the chemical potential:

$$\mu = k_BT\ln\left(\frac{N\lambda^3}{\sigma V}\right). \tag{5.19}$$

This is, of course, the same as the result obtained from the canonical ensemble and differentiating the free energy, Eq. (4.25), apart from the extra spin-degeneracy factor σ accounted for here.

The Maxwell Distribution If we substitute this expression for μ into Eq. (5.12) and multiply by the density of states, $g(\varepsilon)$, we obtain the Maxwell-Boltzmann probability distribution. The probability, $p(\varepsilon)$, that a particular particle has energy ε is given by

$$P(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}\langle n_{\mathbf{k}}\rangle\, g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}e^{-\beta(\varepsilon-\mu)}g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{N\lambda^3}{\sigma V}e^{-\beta\varepsilon}\sqrt{\varepsilon}\,\mathrm{d}\varepsilon\,, \tag{5.20}$$

where we have substituted for $g(\varepsilon)$, from Eq. (5.16), and $e^{\beta\mu}$ from Eq. (5.19). Substituting the classical expression for the kinetic energy, $\varepsilon = \frac{1}{2}mv^2$, and rearranging we obtain

$$P(v)\,\mathrm{d}v = \left(\frac{m}{2\pi k_BT}\right)^{3/2}e^{-\beta mv^2/2}4\pi v^2\,\mathrm{d}v\,, \tag{5.21}$$

which is the Maxwell distribution of speeds. There are obviously more direct ways of getting this, but it is reassuring that our more formal approach works.

The Pressure of an Ideal Gas Our expression for $\Phi(T)$ gives the pressure as the usual thermodynamic derivative:

$$p = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = k_BT\frac{\sigma}{\lambda^3}e^{\beta\mu} = \frac{Nk_BT}{V}, \tag{5.22}$$

which is the usual ideal gas law. We got the last equality by substituting for μ from Eq. (5.19).

The Entropy of an Ideal Gas Finally, let us obtain the entropy from

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} = k_B \frac{\sigma V}{\lambda^3} e^{\mu/k_B T}\left(\frac{5}{2} - \frac{\mu}{k_B T}\right). \tag{5.23}$$

Substituting for μ gives

$$S = k_B N \ln\left(\exp\left(\frac{5}{2}\right)\frac{\sigma V}{N\lambda^3}\right) = k_B N \ln\left(e^{5/2}\frac{\sigma V}{N}\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}\right). \tag{5.24}$$

This is the Sackur-Tetrode expression for the entropy of an ideal classical gas yet again; we derived it in Section 4.2 using the canonical partition function and the principle of indistinguishability.

Grand Partition Function of an Ideal Gas via Z Or we could have done it in a different way, directly from $Z(T, V, N)$ using the definition (5.5). We have already calculated and discussed the canonical partition function

$$Z = \frac{1}{N!} Z_1^N, \quad \text{therefore} \quad \Xi = \sum_{N=0}^{\infty} \frac{1}{N!}\left(Z_1 e^{\beta\mu}\right)^N = \exp\left(Z_1 e^{\beta\mu}\right), \tag{5.25}$$

the sum is evaluated assuming the number of particles in the gas is 'capable' to be very large. Now we recall what Z_1 is, e.g. in 3D:

$$\Xi = \exp\left(\frac{V}{\lambda^3} e^{\beta\mu}\right) = \exp\left(V\left[\frac{m k_B T}{2\pi\hbar^2}\right]^3 e^{\beta\mu}\right), \tag{5.26}$$

$$\Longrightarrow \Phi = -k_B T Z_1 e^{\beta\mu} = -k_B T V \left[\frac{m k_B T}{2\pi\hbar^2}\right]^3 e^{\beta\mu}, \tag{5.27}$$

which is the expression (5.17), with all that followed it.

5.6 Internal Degrees of Freedom and External Potentials

One of the principal results of the previous section was the derivation of the chemical potential of a monatomic ideal gas. It is a simple matter to extend this expression to an ideal gas where there are internal degrees of freedom (for example vibrational and rotational degrees of freedom), or where there is an external potential.

Let's assume that we can write the energy of a molecule in the form $\varepsilon = \varepsilon_{\mathbf{k}} + \varepsilon_{\text{int}} + \varepsilon_{\text{ext}}$, where for a diatomic molecule ε_{int} is (see Section 4.4),

$$\varepsilon_{\text{int}} = \left(n + \frac{1}{2}\right)\hbar\omega_0 + \frac{\hbar^2 J(J+1)}{2I}, \tag{5.28}$$

the first term being the vibrational energy and the second term being the rotational energy (I is the moment of inertia of the molecule). The rotational states have a degeneracy of $(2J+1)$. An example of an external potential is gravity, for which $\varepsilon_{\text{ext}} = mgh$, where m is the mass of the molecule, g is the acceleration due to gravity, and h is the height of the molecule in the gas. A gravitational field does not affect the internal degrees of freedom because the gravitational potential does not vary significantly over the size of the molecule, so the separation of internal and external degrees of freedom is clean. In other cases, such as for an applied magnetic field, the separation is artificial, because the external field changes the sum over the internal degrees of freedom by interacting with the rotational states (via their magnetic moment), lifting their degeneracy, so although the field is external, the energy would be included in ε_{int}. In a given case it should be clear what is meant.

If we consider, for the sake of concreteness, a small volume of gas at height h, then the grand partition function for energy level $\varepsilon_{\mathbf{k}}$ is (in the classical limit)

$$\begin{aligned}\Xi_{\mathbf{k}} &= 1 + \sum_{\text{int}} e^{-\beta(\varepsilon_{\mathbf{k}} + \varepsilon_{\text{int}} + \varepsilon_{\text{ext}} - \mu)} \\ &= 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} e^{-\beta\varepsilon_{\text{ext}}} \sum_{\text{int}} e^{-\beta\varepsilon_{\text{int}}} \\ &\equiv 1 + Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)},\end{aligned} \tag{5.29}$$

where we have defined the partition functions for the internal and external degrees of freedom in the obvious way.

The grand potential of the level is then

$$\Phi_{\mathbf{k}}(h) = -k_B T \ln \Xi_{\mathbf{k}}(h) \simeq -k_B T Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \tag{5.30}$$

where the last equivalence holds in the classical limit only. We have seen this form in Eqs. (5.17) and (5.27) just above. Carrying through the same calculation as in Eq. (5.17) etc., we find the chemical potential for fixed particle number N,

$$\mu = k_B T \left[\ln\left(\frac{N(h)\lambda^3}{\sigma V}\right) - \ln Z_{\text{int}} - \ln Z_{\text{ext}}(h)\right], \tag{5.31}$$

where the possible dependence of particle number on the height h is also emphasised. With $\varepsilon_{\text{ext}} = mgh$ we have $-k_B T \ln Z_{\text{ext}}(h) = mgh$, and we see that this contribution to the chemical potential is a real potential energy.

As a very simple example of the use of these formulae, consider the variation of particle number with height in an ideal classical gas in a gravitational field. In equilibrium the temperature must be independent of height, so that Z_{int} is independent

of height. In equilibrium µ must also be independent of height, and from Eq. (5.31) we can see that $N(h)$ must therefore be of the form

$$N(h) = N(0)e^{-mgh/k_BT}. \tag{5.32}$$

The density therefore drops exponentially with height.

5.7 Equilibrium Constant for Chemical Reactions

In Section 2.4 we derived an expression for the so-called equilibrium constant, $K_c(T)$, for the concentrations of molecules involved in a chemical reaction between ideal gases. Here we derive an expression for the related equilibrium constant $K_N(T)$, defined by

$$K_N(T) \equiv \prod_i N_i^{\nu_i}, \tag{5.33}$$

where ν_i is the number associated with molecules of species i in the reaction equation, and N_i is the number of molecules of species i in the ideal gas.

First we write the chemical potential of Eq. (5.31) for each species as

$$\mu_i = k_BT\Big(\ln N_i - \ln Z_1^i\Big), \tag{5.34}$$

where Z_1^i is the partition function for a single molecule of species i confined to a volume V, including translational, internal, and external degrees of freedom. We now substitute for μ_i in the condition for chemical equilibrium, $\sum_i \nu_i\mu_i = 0$, which gives

$$\sum_i \nu_i\mu_i = \sum_i \nu_i k_BT\Big(\ln N_i - \ln Z_1^i\Big) = 0, \tag{5.35}$$

and therefore

$$K_N(T) = \prod_i N_i^{\nu_i} = \prod_i \left(Z_1^i\right)^{\nu_i}. \tag{5.36}$$

We now have an expression for the equilibrium constant for chemical reactions which involves a quantity that we can calculate, the single-particle partition function which was extensively discussed in Section 4.1. This is called "The Law of Mass Action."

5.7.0.1 Example: Plasma

Show that the equilibrium constant K_N for the ionisation reaction $\mathrm{He} \rightleftharpoons \mathrm{He}^+ + \mathrm{e}^-$ is to a good approximation

$$K_N = \frac{1}{4V}\left(\frac{2\pi\hbar^2}{m_\mathrm{e}k_BT}\right)^{3/2} e^{e\phi/k_BT}, \tag{5.37}$$

where ϕ is the first ionisation potential of He, which is 24.6 V.

The equilibrium constant (5.36) is

$$K_N = \frac{N_{\mathrm{He}}}{N_{\mathrm{He}^+} N_{\mathrm{e}^-}} = \frac{Z_1^{\mathrm{He}}}{Z_1^{\mathrm{He}^+} Z_1^{\mathrm{e}^-}}. \tag{5.38}$$

Remembering that the He^+ and e^- each have two spin states, the single-particle partition functions are

$$Z_1^{\mathrm{He}} = \frac{V}{\lambda_{\mathrm{He}}^3} e^{\beta e \phi} \tag{5.39}$$

$$Z_1^{\mathrm{He}^+} = 2\frac{V}{\lambda_{\mathrm{He}^+}^3} \tag{5.40}$$

$$Z_1^{\mathrm{e}^-} = 2\frac{V}{\lambda_{\mathrm{e}^-}^3} \tag{5.41}$$

Ignoring the mass difference between He and He^+, so that $\lambda_{\mathrm{He}^+} = \lambda_{\mathrm{He}}$, we get

$$K_N = \frac{N_{\mathrm{He}}}{N_{\mathrm{He}^+} N_{\mathrm{e}^-}} = \frac{1}{4V}\left(\frac{2\pi\hbar^2}{m_{\mathrm{e}} k_B T}\right)^{3/2} e^{e\phi/k_B T}. \tag{5.42}$$

Now, we can assume $N_{\mathrm{He}^+} = N_{\mathrm{e}^-}$ so that

$$N_{\mathrm{e}^-}^2 = N_{\mathrm{He}} 4V \lambda_{\mathrm{e}^-}^3 e^{-e\phi/k_B T}. \tag{5.43}$$

From the ideal gas equation, $pV = (2N_{\mathrm{e}^-} + N_{\mathrm{He}})k_B T$, we can write

$$N_{\mathrm{e}^-}^2 = N_{\mathrm{He}} 4(2N_{\mathrm{e}^-} + N_{\mathrm{He}})\frac{k_B T}{p}\lambda_{\mathrm{e}^-}^3 e^{-e\phi/k_B T}, \tag{5.44}$$

giving us a quadratic equation for the ratio of the electron and Helium densities. Solving and substituting the numbers at $T = 10^4$ K gives ratios of 7.3×10^{-5} at 1 atmosphere, and 0.29 at 10^{-2} Pa.

The ratio is pressure dependent because the probability of dissociation only depends on the temperature, while the probability of recombination also depends on the probability of two dissociation products running into each other, so it depends on p. At low pressure recombination becomes much less likely.

5.8 Langmuir Adsorption Isotherm

Suppose a vapour is in thermal equilibrium with a surface, and that a molecule of the vapour may attach itself to the surface at one of N_s surface sites, which lowers its energy by an amount ε. The internal degrees of freedom of the molecule can be neglected in the vapour phase, but when the molecule is attached to the surface it vibrates against it, and the partition function of a single adsorbed molecule is

denoted by $z_s(T)$. Derive the relationship between the fraction of the surface sites occupied by molecules, $\theta = N/N_s$, and the vapour pressure, p.

We proceed by calculating the chemical potential of the adsorbed species, μ_s, and equating it to that of the vapour, μ_v. We can use either the canonical or grand canonical ensembles to calculate the chemical potential of the adsorbed species and here I give both derivations.

- **Canonical Ensemble:** The partition function for N adsorbed molecules is

$$Z_N = \frac{N_s!}{(N_s - N)!N!} z_s^N e^{-\beta(-N\varepsilon)}. \tag{5.45}$$

Using Stirling's approximation we obtain

$$F = -k_B T \ln Z_N = -N\varepsilon - k_B T[N \ln z_s + N_s \ln N_s - (N_s - N)\ln(N_s - N) - N \ln N]. \tag{5.46}$$

The chemical potential is then

$$\begin{aligned} \mu_s = \frac{\partial F}{\partial N} &= -\epsilon - k_B T\left(\ln z_s + \ln\left(\frac{N_s - N}{N}\right)\right) \\ &= -\epsilon + k_B T \ln\left(\frac{N}{(N_s - N)z_s}\right) \\ &= -\epsilon + k_B T \ln\left(\frac{\theta}{(1-\theta)z_s}\right). \end{aligned} \tag{5.47}$$

- **Grand Canonical Ensemble:** The surface sites are independent and therefore we consider a single site. The grand partition function is

$$\Xi = \sum_i e^{-\beta(E_i - \mu_s N_i)} Z_{\text{int}}^{(i)}, \tag{5.48}$$

where each site has two states: $i = 0$ (site is empty so that $N_0 = 0$ and $E_0 = 0$) and $i = 1$ (site is full and $N_1 = 1$ and $E_1 = -\epsilon$). $\sum_{\text{int}}^{(i)}$ denotes the sum over internal degrees of freedom, in this case the vibrational motion, which for $i = 1$ has the partition function z_s. This gives

$$\Xi = 1 + z_s e^{\beta(\epsilon + \mu_s)}. \tag{5.49}$$

The corresponding grand potential is $\Phi = -k_B T \ln \Xi$ and the average occupation of the site is

$$\theta = \frac{N}{N_s} = -\left(\frac{\partial \Phi}{\partial \mu_s}\right)_{T,V} = \frac{z_s e^{\beta(\epsilon+\mu_s)}}{1 + z_s e^{\beta(\epsilon+\mu_s)}}. \tag{5.50}$$

Rearranging we obtain

$$\mu_s = -\epsilon + k_B T \ln\left(\frac{\theta}{(1-\theta)z_s}\right) \tag{5.51}$$

which is, of course, the same as we obtained in the canonical ensemble.

The chemical potential of an ideal gas is given by Eq. (5.19):

$$\mu_v = k_B T \ln\left(\frac{N\lambda^3}{V}\right) = k_B T \ln\left(\frac{p}{k_B T}\lambda^3\right). \tag{5.52}$$

Equating μ_v and μ_s we obtain the Langmuir adsorption isotherm,

$$p = \frac{\theta}{1-\theta}\frac{k_B T}{z_s \lambda^3} e^{-\beta\epsilon}. \tag{5.53}$$

One can also derive the Langmuir adsorption isotherm from a kinetic argument. The rate of change of θ due to adsorption is

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} = k_a p(1-\theta), \tag{5.54}$$

where k_a is the rate constant for adsorption, defined in such a way that the increase of absorption rate with pressure is made explicit. The rate of change of θ due to desorption is just a basic decay:

$$\frac{\mathrm{d}\theta_d}{\mathrm{d}t} = -k_d\theta, \tag{5.55}$$

where k_d is the rate constant for desorption (note that k_a and k_b have different dimensionality, obviously). In equilibrium

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} + \frac{\mathrm{d}\theta_d}{\mathrm{d}t} = 0, \tag{5.56}$$

and therefore

$$p = \frac{\theta}{1-\theta}\frac{k_d}{k_a}, \tag{5.57}$$

which is illustrated in Fig. 5.1. Eq. (5.53) therefore gives an expression for the ratio of the rate constants in terms of microscopic variables. The Langmuir adsorption isotherm often works quite well as long as θ is not too large.

5.8.1 Surface Number Density for Adsorbed Helium Atoms in a 2D Gas

Helium atoms of mass m may be adsorbed from the vapour phase at pressure p onto a solid surface where they can move freely without interaction, behaving as a two-dimensional perfect gas. If the adsorption energy is Δ, then by treating the vapour as a particle reservoir for the helium atoms on the solid surface, and treating both sets of atoms as ideal classical gases, show that the number density per unit area of helium atoms on the surface is

$$n_{\text{ads}} = \left(\frac{p}{k_B T}\right)\left(\frac{2\pi\hbar^2}{m k_B T}\right)^{1/2} e^{\Delta/k_B T}. \tag{5.58}$$

Let us do this example in two ways.

Fig. 5.2: Langmuir isotherms for different ratios of the rate constants, k_d/k_a.

Grand Canonical Ensemble The 3D gas of helium atoms in the vapour acts as a particle reservoir, setting the chemical potential for the helium atoms on the surface.

We need to calculate the grand potential (5.8) of the 2D ideal gas on the surface, and find its chemical potential in that way. We can treat the helium atoms on the surface as a classical gas and, in the corresponding limit (5.9) $\beta(\varepsilon_{\mathbf{k}} - \mu) \gg 1$, retain only the first terms in the grand partition function of a microstate, giving (5.10)

$$\Xi_{\mathbf{k}} = 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} + \cdots , \tag{5.59}$$

since the contribution from $n > 1$ is negligible. The grand potential (5.11) for a microstate with the energy $\varepsilon_{\mathbf{k}}$ is, therefore,

$$\Phi_{\mathbf{k}} = -k_B T \ln \Xi_{\mathbf{k}} \approx -k_B T e^{\beta\mu} e^{\beta\Delta} e^{-\beta p^2/2m}. \tag{5.60}$$

To obtain the full grand potential for the gas (5.14) we need to integrate $\Phi_{\mathbf{k}}$ over the corresponding phase space, which gives for the 2D gas

$$\begin{aligned} \Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}} &= \int \Phi_{\mathbf{k}} \frac{\mathrm{d}^2 x \, \mathrm{d}^2 p}{(2\pi\hbar)^2} \\ &= -k_B T \frac{A}{(2\pi\hbar)^2} e^{\beta\mu} e^{\beta\Delta} \int_0^\infty e^{-\beta p^2/2m} 2\pi p \, \mathrm{d}p \\ &= -k_B^2 T^2 m \frac{A}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \end{aligned} \tag{5.61}$$

The number of particles in this system is

$$N_{\text{ads}} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \frac{m}{2\pi\hbar^2} A k_B T e^{\beta\mu} e^{\beta\Delta}. \tag{5.62}$$

From this we get an expression for the density of adsorbed atoms,

$$n_{\text{ads}} = \frac{N_{\text{ads}}}{A} = \frac{m k_B T}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \tag{5.63}$$

The chemical potential, which is equal to that of the 3D gas (5.19), can then be expressed using the ideal gas equation of state as

$$\mu = k_B T \ln\left(\frac{p\lambda^3}{k_B T}\right), \tag{5.64}$$

where the thermal de Broglie wavelength is $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$. We now substitute the chemical potential into (5.63), and this gives the desired result,

$$n_{\text{ads}} = \frac{p}{k_B T}\left(\frac{2\pi\hbar^2}{mk_BT}\right)e^{\Delta/k_BT}. \tag{5.65}$$

Canonical Ensemble We have two sub-systems in contact: the 3D ideal gas of helium atoms in the vapour, and the 2-dimensional gas of adsorbed particles. The equilibrium between these two sub-systems is when $\mu_{3\text{D}} = \mu_{2\text{D}}$ (of course, along with p and T equality as well). The chemical potential of an ordinary 3D ideal gas is (5.19),

$$\mu_{3\text{D}} = k_B T \ln\left(\frac{N\lambda^3}{V}\right), \tag{5.66}$$

where the de Broglie wavelength $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$.

The gas on the surface, with n_{ads} particles, has two things to consider. First of all, it has lower dimensionality (cf. Eq. (4.7)), giving the basic contribution to the single-particle partition function A/λ^2. There is also the adsorption potential, i.e. the constant potential energy gain $-\Delta$ for each particle, resulting in the extra factor in the partition function:

$$Z_1(2\text{D}) = \frac{A}{\lambda}e^{\beta\Delta}. \tag{5.67}$$

From this, the classical partition function for N particles is given by Eq. (4.17),

$$Z_N(2\text{D}) = \frac{1}{N!}Z_1^N = \frac{A}{\lambda^2 N!}e^{N\beta\Delta}. \tag{5.68}$$

From the Helmholtz free energy,

$$F(2\text{D}) = k_B T N\left[\ln\left(\frac{N\lambda^2}{A}e^{-\beta\Delta}\right) - 1\right], \tag{5.69}$$

it is simple to obtain the chemical potential of the 2D surface,

$$\mu_{2\text{D}} = \left(\frac{\partial F(2\text{D})}{\partial N}\right)_{T,V} = k_B T \ln\left(n_{\text{ads}}\lambda^2 e^{-\beta\Delta}\right), \tag{5.70}$$

where $n_{\text{ads}} = N/A$. Equating the chemical potentials $\mu_{3\text{D}}$ (5.66) and $\mu_{2\text{D}}$ (5.70) then gives

$$n_{\text{ads}} = \frac{N}{V}\lambda e^{\beta\Delta} = \frac{p}{k_B T}\sqrt{\frac{2\pi\hbar^2}{mk_BT}}e^{\beta\Delta}. \tag{5.71}$$

Chapter 6

Ideal Fermi Gas

6.1 Fermi-Dirac Statistics for the Ideal Quantum Gas

The grand partition function for level $\mathbf{k}$ of an ideal gas obeying Fermi-Dirac statistics is

$$\Xi_{\mathbf{k}} = \sum_{n=0}^{1} \left(e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right)^n = 1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}, \tag{6.1}$$

and the grand potential is

$$\Phi_{\mathbf{k}} = -k_B T \ln\left(1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right). \tag{6.2}$$

The average occupation of level $\mathbf{k}$ is

$$\boxed{\langle n_{\mathbf{k}} \rangle = -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial \mu}\right)_{T,V} = \frac{1}{1 + e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}},} \tag{6.3}$$

which is the *Fermi-Dirac distribution*, or the mean particle number for the given microstate in an ideal Fermi-Dirac gas.

In this grand canonical ensemble, the entropy of each level of a Fermi gas can be calculated as

$$\begin{aligned} S_{\mathbf{k}} &= -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial \mu}\right)_{V,\mu} \\ &= k_B \ln\left(1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right) + \frac{k_B \beta(\varepsilon_{\mathbf{k}} - \mu)}{1 + e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}} \\ &= -k_B[\langle n_{\mathbf{k}} \rangle \ln \langle n_{\mathbf{k}} \rangle + (1 - \langle n_{\mathbf{k}} \rangle) + \ln(1 - \langle n_{\mathbf{k}} \rangle)]. \end{aligned} \tag{6.4}$$

The Fermi case is illustrated in Figs. 6.1 and 6.2. Excitations are only significant within roughly $k_B T$ of the Fermi energy. The entropy comes only from those levels whose occupation differs significantly from 0 or 1.

6.2 Quantum States of an Ideal Gas

The quantum states of free particles are solutions of the Schrödinger equation with a constant potential, but they also depend on the boundary conditions. These must be irrelevant for a large system. We have two main choices for the boundary conditions:

Fig. 6.1: The average occupation and entropy of an energy level as a function of energy in a Fermi gas at zero temperature (solid blue line) and at a finite temperature $T \ll T_F$ (dashed dark blue line).

Fig. 6.2: The Fermi-Dirac Distribution function at $T = 0$ and various small T. The distribution differs from the $T = 0$ ground state only for a range of energies $k_B T$ around ε_F as excitations are only significant within roughly $k_B T$ of the Fermi energy.

6.2.1 Hard-Wall Boundary Conditions

The more familiar choice of boundary conditions would "hard walls", which means that the wave-function must vanish at the walls of a three-dimensional box. This produces standing waves. The eigenstates for such a box having dimensions L_x, L_y and L_z are

$$\Psi = \left(\frac{2}{L_x} \frac{2}{L_y} \frac{2}{L_z} \right)^{1/2} \sin(k_x x) \sin(k_y y) \sin(k_z z). \tag{6.5}$$

The associated eigenenergies are

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2). \tag{6.6}$$

In order to satisfy the boundary conditions we need $k_i = n\pi/L_i$, where n is an integer, so that $\psi(x_i = 0) = \psi(x_i = L_i) = 0$. The allowed values of the $\mathbf{k}$-vector form a lattice in k-space, with volume per point

$$\Delta k_x \Delta k_y \Delta k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}, \tag{6.7}$$

Fig. 6.3: The four lowest-energy eigenfunctions for a particle in a box.

Fig. 6.4: The allowed k-values for a box with hard walls.

where V is the volume of the box.

We will transform sums over quantum states into integrals over momentum or energy, in which case we need the density of allowed **k**-vectors in k-space. This is the inverse of the volume per point, multiplied by the spin degeneracy factor $\sigma = 2s+1$ (the number of spin states per k-state):

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{\pi^3}. \tag{6.8}$$

6.2.2 Periodic Boundary Conditions

Less intuitive but more useful in the long term are periodic boundary conditions, by which the wavefunction must be invariant under translations along x, y or z by the respective box sizes L_x, L_y, L_z:

$$\psi(x + L_x, y, z) = \psi(x), \tag{6.9}$$

and similarly for the other two coordinates. The eigenstates in this case are travelling waves

$$\psi = \frac{1}{\sqrt{L_x L_y L_z}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{6.10}$$

where $\mathbf{r} = (x, y, z)$ and the allowed values of the wavevector $\mathbf{k}$ again form a lattice, but now the spacing between lattice points is $2\pi/L_x$ etc., giving a larger volume per lattice point and a lower density:

$$\Delta k_x \Delta k_y \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V} \tag{6.11}$$

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{(2\pi)^3}. \tag{6.12}$$

The density of states in k-space is therefore

$$\mathrm{d}N = g(k)\,\mathrm{d}k = \sigma \frac{[\text{volume of shell at } k]}{[\text{volume of one state}]} = \sigma \frac{4\pi k^2\,\mathrm{d}k}{\frac{(2\pi)^3}{V}} \quad \Longrightarrow \quad g(k) = \sigma \frac{V k^2}{2\pi^2}. \tag{6.13}$$

The factor $\sigma = 2s + 1$ allows for spin-degeneracy (and is equal to 2 for electrons and other spin $s = 1/2$ particles). We can obtain the density of states with energy, $g(\varepsilon)$, using the dispersion relationship for a free particle, $\varepsilon = \hbar^2 k^2/2m$,

$$g(\varepsilon) = \frac{\mathrm{d}N}{\mathrm{d}\varepsilon} = \frac{\mathrm{d}N}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}\varepsilon} = g(k)\frac{\mathrm{d}k}{\mathrm{d}\varepsilon} = \frac{\sigma V k^2}{2\pi^2} \cdot \frac{m}{\hbar^2 k} = \frac{\sigma V k m}{2\hbar^2 \pi^2}$$

$$g(\varepsilon) = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}, \tag{6.14}$$

i.e. $g(\varepsilon) \propto \varepsilon^{1/2}$ in 3D. For electrons,

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}. \tag{6.15}$$

So, compared to the standing-wave, or hard-wall boundary conditions above, are there fewer $k-$points, as there is more volume per $k-$point? No, because we now count wavevectors $\mathbf{k}$ from all eight octants of the three-dimensional wavevector space, whereas for standing wave boundary conditions, states with wavevector $(\pm k_x, \pm k_y, \pm k_z)$ are actually the same, and so we have to limit our sums to one

octant, as shown in Fig. 6.4. This compensates for the lower $k-$space density of allowed states. For this reason, all sums or integrals come out the same whichever of the two boundary conditions we choose.

The advantage in choosing travelling wave boundary conditions is two-fold. Firstly, it is simpler to work with exponentials than with sine and cosine functions. Secondly, and more importantly, transport processes require particles to move. We can picture a moving particle as a wavepacket constructed from travelling wave solutions, but it is much harder to do this in terms of standing wave solutions. So to model transport processes, it is natural to think in terms of travelling wave boundary conditions.

Of course, we could simply recall the integration over the phase space, done in two previous chapters and find it gives the identical result for the measure of integration:

$$\sum_{\text{states}} = \int \mathrm{d}\Gamma = \int \frac{\mathrm{d}^3x\,\mathrm{d}^3k}{(2\pi)^3}. \tag{6.16}$$

Suppose we wish to evaluate a sum over states of the form $\sum_{\text{states}} f(\varepsilon_{\mathbf{k}})$, where $f(\varepsilon_{\mathbf{k}})$ is some function of the energies. Therefore to convert the sum over k into an integral over k or energy ε we use

$$\boxed{\sum_{k_x,k_y,k_z} f(\varepsilon_{\mathbf{k}}) \to \frac{\sigma V}{8\pi^3}\int_0^\infty f(\varepsilon_{\mathbf{k}})4\pi k^2\,\mathrm{d}k = \int_0^\infty g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon\,,} \tag{6.17}$$

where $g(\varepsilon)\,\mathrm{d}\varepsilon$ is the density of states, which is given by Eq. (6.14) in 3-dimensions. However, the nice factorisation of the integrand that we saw in the classical case (with $E = p^2/2m$) is no longer happening here, so it's necessary to switch to the scalar variable ε and face the consequences. We will use Eq. (6.17) for both fermion and boson systems in forthcoming sections and you should familiarise yourself with the method of turning the sum over states into an integral over k or ε (e.g. make sure you have practiced obtaining the corresponding expressions for $g(\varepsilon)$ in $2-$ and $1-$dimensions.)

Consider the partition function of a single particle of mass m in a box of volume V, calculated in the way we develop here:

$$\begin{aligned} Z_1 &= \sum_{k_x,k_y,k_z} e^{-\beta\varepsilon_{\mathbf{k}}} = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty e^{-\beta\varepsilon}\sqrt{\varepsilon}\,\mathrm{d}\varepsilon \\ &= \frac{\sigma V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2} 2\int_0^\infty e^{-x^2}x^2\,\mathrm{d}x \end{aligned} \tag{6.18}$$

where the substitution $x^2 = \varepsilon/k_BT$ has been made. The mon-dimensional integral in infinite limits is always equal to a number of order one... here it is equal to $\sqrt{\pi}/4$, giving

$$Z_1 = \sigma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \frac{\sigma V}{\lambda^3}, \tag{6.19}$$

where $N_Q(T) = 1/\lambda^3$ could be interpreted as the quantum concentration, although we saw and worked with $1/\lambda^3$ in the classical gas already.

Of course, you have noted that Eq. (6.19) is the same as we found earlier in Eq. (4.5), apart from the factor of σ which corresponds to an internal degree of freedom of the particle which we will neglect in this discussion. This means that it gives the classical equipartition result for the energy, i.e., $U_1 = 3/2k_BT$. It is worth considering for a moment why this is so here in the case of quantum particle. The procedure we used for replacing the sum over states by an integral is valid when k_BT is much larger than the maximum separation of the energy levels, ΔE, which have appreciable average occupation. This condition is satisfied if the box is large enough (because the separation of the energy levels gets smaller as the box size increases) and/or the temperature is high enough. It turns out that the condition $k_BT \gg \Delta E$, is the condition for the system to be in the classical regime, where it can be described as a classical gas. When this condition does not apply the system is in the *quantum regime*. For example, the entropy of the particle would also be given by Eq. (4.9), which does not obey the Third Law of Thermodynamics. To obtain the correct result at very low temperatures or very small box sizes one has to take into account the discrete nature of the energy levels. We will have more to say about this issue later.

6.3 Chemical Potential of a Fermi Gas

The total particle number is:

$$N = \int_0^\infty g(\varepsilon)n(\varepsilon)\,\mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{\varepsilon}\,\mathrm{d}\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}, \tag{6.20}$$

using the expression (6.14) for the density of states. As the temperature changes we have to adjust μ so that the integral always gives N. Unfortunately the integral cannot be expressed in a closed form.

In the zero-temperature limit we note that the Fermi-Dirac distribution of Eq. (6.3) becomes a step function,

$$\langle n_{\mathbf{k}}\rangle = 1 \quad \text{for} \quad \varepsilon_{\mathbf{k}} < \mu, \tag{6.21}$$

$$\langle n_{\mathbf{k}}\rangle = 0 \quad \text{for} \quad \varepsilon_{\mathbf{k}} > \mu, \tag{6.22}$$

In this limit we can evaluate the integral in Eq. (6.20) analytically. The chemical potential at zero temperature is called the Fermi energy, ε_F, which is related to the Fermi wave-vector by $\varepsilon_F = \hbar^2 k_F^2/2m$. We have

$$N = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\varepsilon_F}\sqrt{\varepsilon}\,\mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2\varepsilon_F^{3/2}}{3}, \tag{6.23}$$

and therefore

$$\boxed{\mu_F(T \to 0) \equiv \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{V\sigma}\right)^{2/3}.} \tag{6.24}$$

A characteristic Fermi temperature can also be defined as $T_F = \varepsilon_F/k_B$.

As the temperature is increased the chemical potential shifts to lower values, and ultimately becomes negative. In the limit $\beta(\varepsilon - \mu) \gg 1$, which was the classical limit (5.9), we can expand

$$\frac{1}{e^{\beta(\varepsilon-\mu)}+1} \Rightarrow e^{-\beta(\varepsilon-\mu)}, \tag{6.25}$$

and the Fermi-Dirac distribution reduces to the classical (Maxwell-Boltzmann) result, where the chemical potential must be large and negative, see Section 5.3. The variation of the chemical potential with temperature is shown in Fig. 6.5.

Fig. 6.5: Variation of μ with T for non-interacting fermions and bosons at fixed density. [10]

6.4 Ideal Fermi Gas at Low Temperatures

The full grand thermodynamic potential of the system is given by

$$\begin{aligned}\Phi &= \sum_k \Phi_k = \int_0^\infty g(\varepsilon)\Phi(\varepsilon)\,\mathrm{d}\varepsilon \\ &= -k_B T \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{\varepsilon}\ln\left(1+e^{-\beta(\varepsilon-\mu)}\right)\mathrm{d}\varepsilon \\ &= -\frac{2}{3}\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1}\,\mathrm{d}\varepsilon\,,\end{aligned} \tag{6.26}$$

where we have integrated by parts to get the last line. The mean energy can be expressed as the average over all levels with the probability density, given by the product of the mean occupation number of each state ε and the density of these states:

$$U = \int_0^\infty \varepsilon\, n(\varepsilon) g(\varepsilon)\, \mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1}\, \mathrm{d}\varepsilon\,. \tag{6.27}$$

Therefore $\Phi = -\frac{2}{3}U$, but please be mindful of what are the natural variables of these two thermodynamic potentials. From its derivation, we see that $\Phi = \Phi(T, V, \mu)$, that is, expressed in its proper variables (unlike U, which should be a function of N not μ). We also know that $\Phi = -pV$, so this gives us directly:

$$p = \frac{\sigma}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1}\, \mathrm{d}\varepsilon\,. \tag{6.28}$$

This is the equation of state of the ideal Fermi gas, expressed as $p = p(T, V, \mu)$.

6.4.1 Zero Temperature Limit

It is interesting to look at these expressions in the zero-temperature limit. In this case we don't need to evaluate the complicated Fermi integral but simply use the "trick" employed in (6.23). That is, $n(\varepsilon) = 0$ for all values of energy $\varepsilon > \varepsilon_F$ and so

$$U_{T=0} = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2}\, \mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{5}\varepsilon_F^{5/2}. \tag{6.29}$$

Now. this expression no longer depends on T (because it is strictly at $T = 0$), nor on μ (because at $T = 0$ we have $\mu = \varepsilon_F$). Substituting (6.24) and cancelling many factors, we obtain

$$U_{T=0} = \frac{2}{5}\frac{(6\pi^2)^{5/2}}{4\pi^2}\frac{\hbar^2}{2m}\frac{N^{5/3}}{(\sigma V)^{2/3}} = U_0(V, N), \tag{6.30}$$

so now we can find the zero-temperature Fermi pressure in the usual way (ignoring the numerical factor of order one in front):

$$p_F = -\frac{\partial U}{\partial V} \approx \frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{5/3}. \tag{6.31}$$

6.4.2 Low Temperature Limit of the Grand Potential

We now look at the low (but non-zero) temperature behaviour of the grand potential, and the key Fermi-gas variables. It is sometimes useful to expand the integrands in

expressions such as Eq. (6.27) or (6.28) in a series valid at low temperatures.

$$I = \int_0^\infty \frac{f(\varepsilon)\,\mathrm{d}\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} \tag{6.32}$$

$$\approx \int_0^{\varepsilon_F} f(\varepsilon)\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}(k_BT)^2 f'(\varepsilon_F) + \frac{6\pi^4}{360}(k_BT)^4 f'''(\varepsilon_F) + \cdots . \tag{6.33}$$

The detailed derivation of this *Sommerfeld expansion* is a little less trivial (See Appendix A.6 and the next Subsection 6.4.2.2). Our results play off the subtle deviation of $\mu(T)$ from ε_F, which ends up to be:

$$\mu(T) = \varepsilon_F - \frac{\pi^2}{6}(k_BT)^2\frac{g'(\varepsilon_F)}{g(\varepsilon_F)}, \tag{6.34}$$

which leads to the famous (and useful) relations:

$$U = \int_0^{\varepsilon_F} E\,g(E)\,\mathrm{d}E + \frac{\pi^2}{6}(k_BT)^2 g(\varepsilon_F) + \mathcal{O}\Big(T^4\Big); \tag{6.35}$$

$$N = \int_0^{\varepsilon_F} g(E)\,\mathrm{d}E + \left[\frac{\pi^2}{6}(k_BT)^2 g'(\varepsilon_F) + (\mu-\varepsilon_F)g(\varepsilon_F)\right] + \mathcal{O}\Big(T^4\Big). \tag{6.36}$$

Or we could simply go and find the grand potential expanded to second order in k_BT we substitute $f(\varepsilon) = \varepsilon^{3/2}$, to obtain

$$\Phi(T) = \Phi(0) - \frac{\sigma V k_B^2 T^2}{24}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_F^{1/2}, \tag{6.37}$$

and the corresponding expression for the mean energy $U = -\frac{3}{2}\Phi$. The entropy and heat capacity can now be calculated directly. We deal with electrons, for which $\sigma = 2$, so that

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{\mu,V} = \frac{k_B^2 T}{3}\frac{V}{2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon_F} = \frac{\pi^2}{3}g(\varepsilon_F)k_B^2 T. \tag{6.38}$$

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_{V,\mu} = \frac{\pi^2}{3}g(\varepsilon_F)k_B^2 T. \tag{6.39}$$

This linear variation of the heat capacity with temperature is characteristic of the Fermi gas (and indeed of Fermi liquids at very low temperature), and it is often written as $C = \gamma T$, where γ is the linear temperature coefficient of the heat capacity.

Note that all the above expressions retain a symbolic form for the density of states $g(\varepsilon)$. Therefore the conclusions are general, valid for systems of all dimensions (3D, as well as 2D and 1D) in spite of the explicit form of $g(\varepsilon)$ differing in these cases.

6.4.2.1 Example: Heat Capacity of ^{3}He in Dilute Solutions at Low Temperatures

At temperatures below 0.4 K, a dilute solution of ^{3}He in liquid ^{4}He behaves like a gas of ^{3}He atoms moving freely *in vacuo* except that the effective mass of each ^{3}He atom is enhanced by a factor of about 2.4. The concentration of ^{3}He is 5 atomic percent and the density of the solution is 140 kg/m^3.

^{3}He is a fermion, thus can be modelled as an ideal Fermi gas. The heat capacity of a Fermi gas is given by Eq. (6.39), $C_v = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T$, and the dispersion relation is (6.15),

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}, \tag{6.40}$$

where m^* is the effective mass of the fermion "quasiparticles". Substituting the Fermi energy (6.24) for ^{3}He ($\sigma = 2$)

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}, \tag{6.41}$$

it follows that the heat capacity for N particles in volume V is

$$\begin{aligned} C_v &= \frac{\pi^2}{3} k_B^2 T \underbrace{\frac{V}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \overbrace{\left(\frac{\hbar^2}{2m^*}\right)^{1/2}\left(\frac{3\pi^2 N}{V}\right)^{1/3}}^{\varepsilon_F^{1/2}}}_{g(\varepsilon_F),\,(6.40)}, \quad (6.41) \\ &= \underbrace{\frac{2m}{\hbar^2}\left(\frac{V}{3\pi^2 N}\right)^{2/3}}_{1/\varepsilon_F} \frac{\pi^2}{2} N k_B^2 T \\ &= \frac{\pi^2 N k_B^2}{2\varepsilon_F} T. \end{aligned} \tag{6.42}$$

If the density of the mixture is 140 kg m^{-3}, then the average atomic mass of the mixture is 0.05 times the ^{3}He mass plus 0.95 times the ^{4}He mass 6.61×10^{-27} kg per atom. The total number density ($n = N/V$) is then $n_{\text{Tot}} = 2.12 \times 10^{28}$ atoms m^{-3}, and the number density of ^{3}He atoms is $n_{^3\text{He}} = 0.05 n_{\text{Tot}} = 1.06 \times 10^{27}$ atoms m^{-3}.

Considering the ^{3}He atoms as a Fermi gas we obtain

$$\varepsilon_F = 4.60 \times 10^{-24}\ \text{J}, \quad T_F = \frac{\varepsilon_F}{k_B} = 0.33\ \text{K}. \tag{6.43}$$

The heat capacity is written as $C_v = \gamma T$, and from equations for C_v and ε_F we have

$$\frac{\gamma}{N} = 2.0 \times 10^{-22}\ \text{J atom}^{-1}\ \text{K}^{-2}. \tag{6.44}$$

6.4.2.2 Sommerfeld Expansion (*non-examinable*)

In general, the integrals (6.20)

$$N = \int_{-\infty}^{\infty} \mathrm{d}\varepsilon\, g(\varepsilon) n(\varepsilon), \tag{6.45}$$

and (6.27)

$$U = \int_{-\infty}^{\infty} \mathrm{d}\varepsilon\, g(\varepsilon) \varepsilon n(\varepsilon), \tag{6.46}$$

have a rather complex structure. There is, however, a simple systematic expansion that exploits the fact that at almost all temperatures of interest in metals, T is very much smaller than the Fermi temperature. In Fig. 6.2 the Fermi-Dirac distribution function $n(\varepsilon)$ is plotted at $T = 0$, and note that at room temperature for typical metal densities we have $k_B T \approx \frac{1}{100}\mu$. Evidently $n(\varepsilon)$ differs from its zero temperature form only in a small region about μ of width a few $k_B T$. Thus the way in which integral of the form $\int_{-\infty}^{\infty} H(\varepsilon) n(\varepsilon)\, \mathrm{d}\varepsilon$ differ from their zero temperature values, $\int_{-\infty}^{-\varepsilon_F} H(\varepsilon)\, \mathrm{d}\varepsilon$, will be entirely determined by the form of $H(\varepsilon)$ near $\varepsilon = \mu$. If $H(\varepsilon)$ does not vary rapidly in the energy range of the order of $k_B T$ about μ, the temperature dependence of the integral should be given quite accurately by replacing $H(\varepsilon)$ by the first few terms in its Taylor expansion about $\varepsilon = \mu$:

$$H(\varepsilon) = \sum_{n=0}^{\infty} \frac{\mathrm{d}^n}{\mathrm{d}\varepsilon^n} H(\varepsilon)\bigg|_{\varepsilon=\mu} \frac{(\varepsilon - \mu)^n}{n!}. \tag{6.47}$$

This procedure is carried out in Appendix A.6. The result is a series of the form

$$\int_{-\infty}^{\infty} H(\varepsilon n(\varepsilon)\, \mathrm{d}\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\, \mathrm{d}\varepsilon + \sum_{n=1}^{\infty} (k_B T)^{2n} a_n \frac{\mathrm{d}^{2n-1}}{\mathrm{d}\varepsilon^{2n-1}} H(\varepsilon)\bigg|_{\varepsilon=\mu}, \tag{6.48}$$

which is known as the *Sommerfeld expansion*.[1] The a_n are dimensionless constats of the order of unity. The functions H one typically encounters have major variations on an energy scale of the order of μ, and generally $(\mathrm{d}/\mathrm{d}\varepsilon)^n H(\varepsilon)|_{\varepsilon=\mu}$ is of the order of $H(\mu)/\mu^n$. When this is the case, successive terms in the Sommerfeld expansion are smaller by $\mathcal{O}(k_B T/\mu)^2$, which is $\mathcal{O}(10^{-4})$ at room temperature. Consequently, in actual calculations only the first and (*very* occasionally) the second terms are retained in (6.48). The explicit form for these is (Appendix A.6)

$$\boxed{\int_{-\infty}^{\infty} H(\varepsilon) n(\varepsilon)\, \mathrm{d}\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\, \mathrm{d}\varepsilon + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) + \frac{7\pi^4}{360}(k_B T)^4 H'''(\mu) + \mathcal{O}(k_B T/\mu)^6}. \tag{6.49}$$

[1] The expansion is not always exact, but is highly reliable unless $h(\varepsilon)$ has a singularity very close to $\varepsilon = \mu$. If, for example, H is singular at $\varepsilon = 0$ then the exapnsion will neglect terms of the order of $\exp(-\mu/k_B T)$, which are typically of order $e^{-100} \sim 10^{-43}$.

To evaluate the specific heat of a metal at temperatures small compared with T_{F} we apply the Sommerfeld expansion (6.49) to the electronic energy and number densities (Eqs. (6.46) and (6.45))

$$U = \int_0^{\mu} \varepsilon g(\varepsilon)\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}(k_B T)^2[\mu g'(\mu) + g(\mu)] + \mathcal{O}\Big(T^4\Big). \tag{6.50}$$

$$N = \int_0^{\mu} g(\varepsilon)\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}(k_B T)^6 g'(\mu) + \mathcal{O}\Big(T^4\Big). \tag{6.51}$$

Equation (6.51) as we shall presently see in detail, implies that μ differs from its $T = 0$ value, ε_{F}, by terms of order T^2. Thus, correctly to order T^2, we may write

$$\int_0^{\mu} H(\varepsilon)\,\mathrm{d}\varepsilon = \int_0^{\varepsilon_{\mathrm{F}}} H(\varepsilon)\,\mathrm{d}\varepsilon + (\mu - \varepsilon_{\mathrm{F}})H(\varepsilon_{\mathrm{F}}). \tag{6.52}$$

If we apply this expansion to the integrals in Eqs. (6.50) and (6.51), and replace μ by ε_{F} in the terms already of order T^2 in these equations, we find

$$U = \int_0^{\varepsilon_{\mathrm{F}}} \varepsilon g(\varepsilon)\,\mathrm{d}\varepsilon + \varepsilon_{\mathrm{F}}\left[(\mu - \varepsilon_{\mathrm{F}})g(\varepsilon_{\mathrm{F}}) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_{\mathrm{F}})\right] + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_{\mathrm{F}}) + \mathcal{O}\Big(T^4\Big) \tag{6.53}$$

$$N = \int_0^{\varepsilon_{\mathrm{F}}} g(\varepsilon)\,\mathrm{d}\varepsilon + \left[(\mu - \varepsilon_{\mathrm{F}})g(\varepsilon_{\mathrm{F}}) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_{\mathrm{F}})\right]. \tag{6.54}$$

The temperature-independent first terms on the right sides of (6.53) and (6.54) are just the values of U and N in the ground state. Since we are calculating the specific heat at constant density, N is independent of temperature, and (6.54) reduces to

$$0 = (\mu - \varepsilon_{\mathrm{F}})g(\varepsilon_{\mathrm{F}}) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F), \tag{6.55}$$

which determines the deviation of the chemical potential from ε_{F}

$$\mu = \varepsilon_{\mathrm{F}} - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})}. \tag{6.56}$$

Since for free electrons $g(\varepsilon)$ varies as $\varepsilon^{1/2}$, this gives

$$\mu = \varepsilon_{\mathrm{F}}\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_{\mathrm{F}}}\right)^2\right], \tag{6.57}$$

which is, as we asserted above, a shift of the order of T^2 and typically only about 0.01 percent, even at room temperature.

Equation (6.55) sets the term in braces in (6.53) equal to zero, thereby simplifying the form of the thermal energy density at constant electronic density to

$$U = U_0 + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_{\mathrm{F}}), \tag{6.58}$$

where U_0 is the energy density in the ground state. The specific heat capacity of the electron gas is therefore

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_{\mathrm{F}}). \tag{6.59}$$

Comparing this with the classical result for an ideal gas, $C_V = 3Nk_B/2$, we see that the effect of Fermi-Dirac statistics is to depress the specific heat by a factor of $(\pi^2/3)(k_B T/\varepsilon_{\mathrm{F}})$, which is proportional to the temperature, and even at room temperature is only of order 10^{-2}. This explains the absence of any observable contribution of the electronic degrees of freedom to the specific heat of a metal at room temperature.

If one is willing to dispense with the precise numerical coefficient, one can understand this behaviour of the specific heat quite simply from the temperature dependence of the Fermi function itself. The increase in energy of the electrons when the temperature is raised from $T = 0$ comes about entirely because some electrons with energies within $\mathcal{O}(k_B T)$ below ε_{F} have been excited to an energy range of $\mathcal{O}(k_B T)$ above ε_{F}. The number of electrons per unit volume that have been so excited is the width, $k_B T$, of the energy interval times the density of levels per unit volume $g(\varepsilon_{\mathrm{F}})$. Furthermore, the excitation energy is of order $k_B T$, and hence the total thermal energy density is of order $g(\varepsilon_{\mathrm{F}})(k_B T)^2$ above the ground-state energy. This misses the precise result (6.58) by a factor of $\pi^2/6$, but it gives a simple physical picture, and is useful for rough estimates.

6.4.3 Application to Metals

For temperatures much lower than the Fermi temperature, $T_F = \varepsilon_F/k_B$, we can use the low temperature theory described above. In a metal T_F is very large, typically $50,000$K, so the low temperature theory is extremely good under most conditions.

In a metal the electrons give a contribution to the heat capacity proportional to T, while the phonons (as zero-mass bosons) give a contribution to the heat capacity proportional to T^3, which we discuss in Subsection 7.4.1. Remember the same result you have seen for the black-body radiation, since photons are also zero-mass bosons. The total heat capacity can be approximated by

$$C = \gamma T + \alpha T^3. \tag{6.60}$$

At room temperature the phonon contribution is dominant, but at low temperatures the electron contribution is significant. In Fig. 6.6, heat capacity data is plotted against T and fitted with various trends. The values of γ and α may be extracted from the intercept and slope of the line from a plot of C/T against T^2.

Fig. 6.6: Low-temperature heat capacity of copper as an example of a metal that gets not superconducting. The heat capacity is given by the superposition of the linear-in-T heat capacity of the electrons and of the T^3 heat capacity of the phonons. Both functions pass into the origin. [5]

Chapter 7

Ideal Bose Gases

7.1 Bose-Einstein Statistics for the Ideal Quantum Gas

To obtain the grand partition function for the level of energy $\varepsilon_{\mathbf{k}}$ for boson particles we use Bose-Einstein statistics,

$$\Xi_{\mathbf{k}} = \sum_{n=0}^{\infty} \left(e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right)^n = \frac{1}{1-e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}}. \tag{7.1}$$

The grand partition function for the whole system is

$$\Xi = \prod_{\mathbf{k}} \Xi_{\mathbf{k}}, \tag{7.2}$$

and the grand potential is then

$$\Phi = -k_B T \ln \Xi = -k_B T \ln\left(\prod_{\mathbf{k}} \Xi_{\mathbf{k}}\right) = -k_B T \sum_{\mathbf{k}} \ln \Xi_{\mathbf{k}} = \sum_{\mathbf{k}} \Phi_{\mathbf{k}}. \tag{7.3}$$

Each of the energy levels contributes separately to the grand potential and hence separately to other quantities such as the energy and entropy. The mean particle number, entropy and pressure are given by derivatives of the grand potential. All the other thermodynamic potentials can be constructed from these.

For an ideal Bose-Einstein gas the grand potential for level $\mathbf{k}$ is

$$\Phi_{\mathbf{k}} = -k_B T \ln\left(\frac{1}{1-e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}}\right) = k_B T \ln\left(1-e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right). \tag{7.4}$$

The average occupation of level $\mathbf{k}$ is, therefore,

$$\boxed{\langle n_{\mathbf{k}} \rangle = -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial \mu}\right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}-1},} \tag{7.5}$$

which is the *Bose-Einstein distribution*. The Fermi-Dirac and Bose-Einstein distributions are numerically plotted in Fig. 7.1.

The entropy from level $\mathbf{k}$ is

$$\begin{aligned} S_{\mathbf{k}} &= -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial T}\right)_{V,\mu} \\ &= -k_B \ln\left(1-e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right) + \frac{k_B \beta(\varepsilon_{\mathbf{k}}-\mu)}{e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}-1} \\ &= -k_B[\langle n_{\mathbf{k}} \rangle \ln \langle n_{\mathbf{k}} \rangle - (1+\langle n_{\mathbf{k}} \rangle) + \ln(1+\langle n_{\mathbf{k}} \rangle)]. \end{aligned} \tag{7.6}$$

Fig. 7.1: The Fermi-Dirac, $\langle n^{(F)} \rangle$, and Bose-Einstein, $\langle n^{(B)} \rangle$, distributions as a function of $\beta(\varepsilon_{\mathbf{k}} - \mu)$.

7.2 Black-Body Radiation

Black-body radiation can be thought of as a gas of photons, and because the photons do not interact, it is an ideal gas. Moreover, photons have integer angular momentum, so photons obey Bose statistics.

Because photons are non-interacting, to come into equilibrium they have to interact with a reservoir, which is taken to be the walls of the black-body cavity. Thermal equilibrium is reached by absorption and emission of photons by the walls, so we cannot take N, the number of photons in the gas, to be constant. Rather, we take μ to be constant, and find μ from the condition (at constant temperature and volume) that the Helmholtz free energy F must be minimal with respect to variations in the average number of photons,

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0. \tag{7.7}$$

But $(\partial F/\partial N)_{T,V} = \mu$, therefore the chemical potential is zero for black-body radiation. In this case the grand potential and the free energy are the same (recall $\Phi = F - \mu N$).

With $\mu = 0$ the Bose-Einstein distribution becomes

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1}, \tag{7.8}$$

which you recognise as the Planck distribution.

The phase space element for radiation is ($\sigma = 2$, because photons can have two polarisations)

$$\mathrm{d}N = g(\varepsilon)\,\mathrm{d}\varepsilon = \sigma \frac{[\text{volume of shell at } k]}{[\text{volume of one state (6.11)}]} = 2 \cdot \frac{4\pi k^2\,\mathrm{d}k}{\frac{(2\pi)^3}{V}} = \frac{V}{\pi^2 c^3}\omega^2\,\mathrm{d}\omega\,, \tag{7.9}$$

where we have used $\omega = ck$, and c is the speed of light. It is interesting to note how this differs from the density of states of real particles (6.14) (with the rest mass m and $\varepsilon = \hbar^2 k^2/2m$). Photons, as all other elementary excitations, do not have mass and their energy is $\varepsilon = \hbar\omega$. Also it is clear that such "quasiparticles" have no classical limit: you can never make $N\lambda^3/V$ small with $m \to 0$.

From $g(\varepsilon)$ and the Bose-Einstein distribution for photons, we immediately obtain the energy of black-body radiation in a frequency interval $\mathrm{d}\omega$ at energy ω,

$$E_\omega \, \mathrm{d}\omega = \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3 \, \mathrm{d}\omega}{e^{\beta\hbar\omega - 1}}. \tag{7.10}$$

This is the well known Planck radiation law, the result which most clearly marked the beginning of quantum theory. This distribution is shown in Fig 7.2.

Fig. 7.2: Energy density for black-body radiation at 1000 and 2000K (represented here as proportional to the measurable intensity of light). The total energy densities correspond to the areas under the respective curves.

The total energy density is

$$u = \frac{U}{V} = \frac{1}{V} \int_0^\infty E_\omega \, \mathrm{d}\omega = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} T^4. \tag{7.11}$$

This is the full form of the Stefan-Boltzmann law, $u \propto T^4$, which Stefan obtained experimentally in 1879 and Boltzmann derived in 1894 using thermodynamics. Obviously Boltzmann could not get the prefactor as it contains $\hbar$. The corresponding specific heat varies as T^3. Note that as the temperature goes to zero the total energy density, and hence the total number of photons in the black-body cavity, goes to zero.

A quantity which could be useful in understanding how the particles with zero chemical potential behave is the mean number of photons in a frequency interval $\mathrm{d}\omega$ around ω:

$$N(\omega) \, \mathrm{d}\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 \, \mathrm{d}\omega}{e^{\beta\hbar\omega} - 1}. \tag{7.12}$$

Fig. 7.3: Black body spectral radiance curves for various temperatures after Planck, and comparison with the classical theory of Rayleigh-Jeans (in cgs units).

The mean number density, $n_\omega = N(\omega)/V$, can be plotted as a function of ω at various temperatures, similar to the energy density E_ω. Note that as the temperature goes to zero the number of photons in the black-body cavity also goes to zero.

7.2.0.1 Example: Coaxial Cable Spectrum of Excitations

A long air-filled coaxial transmission line, of length L, the outer diameter is 1 cm and the inner diameter 2 mm, is short circuited at each end. At room temperature, consider the electromagnetic waves in this line at a cyclic frequency $\nu = 10^9$ Hz, and at 10^{12} Hz. Show that the mean energy of black body radiation between the conductors in range $\mathrm{d}\omega$ will be approximately

$$\mathrm{d}U\,(10^9\ \mathrm{Hz}) \approx k_B T \frac{L}{\pi c}\,\mathrm{d}\omega \quad \text{but} \quad \mathrm{d}U\,(10^{12}\ \mathrm{Hz}) \approx k_B T \frac{V}{\pi^2 c^3}\omega^2\,\mathrm{d}\omega\,, \tag{7.13}$$

where V is the volume between the conductors.

The example deals with Black-body radiation and, more generally, the relationship between the spectrum of excitations and the dimensionality of the system. The "long air-filled coaxial cable" acts as an EM cavity, at temperature T, with a spectrum of black-body radiation.

At $\nu = 10^9$ Hz, the wavelength, λ, is ≈ 0.3 m, which is greater than the diameter of the cable. Thus the system is essentially one-dimensional. In 1D, the density of states is ($\sigma = 2$, because photons can have two polarisations) **??**

$$\mathrm{d}N = g(\omega)\,\mathrm{d}\omega = 2\frac{\mathrm{d}k}{\left(\frac{2\pi}{L}\right)} = \frac{L}{\pi c}\,\mathrm{d}\omega\,, \tag{7.14}$$

Fig. 7.4: The cosmic background radiation as measured by the Cosmic Background Explorer (COBE), after Mather *et al.* (1990). [7] The continuous curve is a fit to the data using the Planck distribution, which yields a temperature of $T = 2.735 \pm 0.06$K. Since the Big Bang the background radiation has undergone expansion, with its temperature gradually decreasing.

where we have used $\omega = ck$, and c is the speed of light. The internal energy, U, is

$$U = \int \varepsilon_\omega n_\omega g(\omega)\,\mathrm{d}\omega = \int \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}\frac{L}{\pi c}\,\mathrm{d}\omega\,, \tag{7.15}$$

where we have used the Planck distribution Eq. (7.8). We can approximate the Bose factor, $1/(e^{\hbar\omega/k_Bt} - 1) \approx k_BT/\hbar\omega$, since we are in the high-temperature limit at this frequency and $\hbar\omega/k_BT \ll 1$. Thus, the energy in the frequency range $\mathrm{d}\omega$ is $k_BTL\,\mathrm{d}\omega\,/\pi c$.

At a frequency of $\nu = 10^{12}$ Hz, the wavelength $\lambda = 0.3$ mm, which is significantly smaller than the 4 mm radial gap in the cable. It follows that the cable can support radial modes at this frequency alongside the longitudinal ones. Thus the system is approximately three-dimensional. With two polarisations at each **k**-vector, the density of states is (7.9)

$$g(\omega)\,\mathrm{d}\omega = \frac{V\omega^2}{\pi^2c^3}\,\mathrm{d}\omega\,, \tag{7.16}$$

and, as we are still in the high-temperature limit, the Bose factor is still k_BT. The energy in the frequency range $\mathrm{d}\omega$ is, therefore, $k_BTV\omega^2\,\mathrm{d}\omega\,/\pi^2c^3$.

7.3 Bose Condensation at Low Temperatures

For black-body radiation and all quasiparticles (elementary excitations) μ is fixed at zero and N varies, but in a gas of real atoms N is constant and μ varies with

temperature. N is calculated by integrating over the Bose-Einstein distribution,

$$N = \int_0^\infty n(\varepsilon)g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{\varepsilon}\,\mathrm{d}\varepsilon}{e^{\beta(\varepsilon-\mu)}-1}. \tag{7.17}$$

This is a messy integral, but we can see what happens by looking at the integrand as a function of temperature (see Fig. 7.5). We expect the chemical potential to be large and negative at high temperatures, so that $n \ll 1$ for all ε. As the temperature is reduced, in order to keep the area under the curve constant the chemical potential must become less negative. As a result the shape of $n(\varepsilon)g(\varepsilon)$ changes. Note that the chemical potential cannot be zero or positive, because the occupation number at energy $\varepsilon = \mu$ would become infinite, which conflicts with our assumption that N is finite. We see in Fig. 7.5 that below some temperature (between 5 and 10K on the figure), even for $\mu \to 0_-$ the area under the curve cannot be preserved, and at 1K the area is very far from being equal to the area under the 20K curve, even with μ effectively zero. Einstein realised that the atoms which are "disappearing" from the integrand are piling up in the ground state, and the occupation number of the ground state is proportional to the size of the system, which is known as "macroscopic occupation". We have in effect made a mistake in assuming that we can always replace the sum over k-states with an integral over energy.

Fig. 7.5: Integrand of Eq. (7.17). We try to change μ as T changes, to keep the area under the curves constant. At low temperature this becomes impossible, without making μ positive, which causes infinite occupation numbers in some levels (and is thus not allowed).

It is perhaps easiest to understand this situation starting from $T = 0$, where all N particles are in the ground state, that is,

$$\lim_{T\to 0} n_{\varepsilon=0} = \lim_{T\to 0}\frac{1}{e^{-\beta\mu}-1} = N. \tag{7.18}$$

For $N \sim 10^{23}$ this means that $e^{-\beta\mu}$ is equal to 1 to within 10^{23} decimal places (!), and we can Taylor expand to get

$$-\frac{\mu}{k_BT} \sim \frac{1}{N} \quad \text{or} \quad \mu \simeq -\frac{k_BT}{N}. \tag{7.19}$$

For $T = 1$K we have $|\mu| \sim 10^{-46}J$, which is much less than the energy of the lowest excited state of the system. Therefore at low temperatures $\mu \simeq 0$, while at high temperatures μ becomes large and negative, see Fig. 7.6.

Fig. 7.6: The chemical potential as a function of temperature in an ideal Bose gas.

At finite temperatures we treat the particles in the ground state differently from those in the excited states, calculating the number of particles in the excited states by setting $\mu = 0$,

$$N(\varepsilon > 0) = \frac{\sigma V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{x}\,\mathrm{d}x}{e^x - 1} = 2.612\sigma V n_Q(T) \equiv N\left(\frac{T}{T_0}\right)^{3/2}, \quad (7.20)$$

where we have earlier called $n_Q(T) = 1/\lambda^3$ the *quantum concentration*. Remember that $\lambda = \sqrt{2\pi\hbar^2/(mk_BT)}$ is the thermal de Broglie wavelength. The number of particles in the ground state (known as the "condensate") is then

$$N_0 = N\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\right] \quad (7.21)$$

The temperature T_0, above which the ground state is no longer macroscopically occupied, is known as the *Bose condensation temperature*. The occupation numbers of the condensate and of the excited states are shown in Fig. 7.7.

7.3.1 Energy and Heat capacity for Bose-Einstein Condensation

We can calculate the energy and heat capacity of a Bose-Einstein gas straightforwardly. Only the atoms not in the condensate contribute to the energy. Using the standard formula for evaluating sums over phase space, see Eq. (6.17), we have

$$U = \int_0^\infty \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1}\,\mathrm{d}\varepsilon\,. \quad (7.22)$$

Fig. 7.7: The fraction of the particles in the ground state, N_0/N, and in the excited states, $N(\varepsilon > 0)/N$, as a function of temperature.

Below T_0 we can set $\mu = 0$, which gives

$$U = \frac{2\sigma V}{\sqrt{\pi}} n_Q(T) k_B T \int_0^\infty \frac{x^{3/2}\,\mathrm{d}x}{e^x - 1}, \tag{7.23}$$

remember $n_Q(T) = 1/\lambda^3$ is the quantum concentration). The integral is equal to $1.005\sqrt{\pi}$, and we obtain

$$U \approx 2\sigma V n_Q(T) k_B T \propto T^{5/2}. \tag{7.24}$$

The heat capacity is given by

$$C(T) = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2}\frac{\sigma k_B V}{\sqrt{2}} n_Q(T) \propto T^{3/2}. \tag{7.25}$$

Increasing the temperature to well above the Bose-Einstein condensation temperature we move into the classical regime, where the heat capacity is $\frac{3}{2}Nk_B$.

The Bose-Einstein condensate was, for a long time, considered a theoretical oddity. With the discovery of superfluidity in liquid 4He, however, there was evidence that it is a real phenomenon. ^{4}He shows a "λ"-transition at $T_0 = 2.17$K, where the condensate is a superfluid (zero viscosity and entropy). In liquid helium, the atoms are so close to each other that inter-atomic forces are important. These interactions are not included in the calculations for the Bose-Einstein condensate so far, and they produce significant corrections to the theory, which are apparent from Fig. 7.8 (see also Section 7.4).

In 1995 Bose-Einstein condensation was discovered in a very nearly ideal gas, consisting of a dilute supersaturated vapour of rubidium-87 atoms with a density of 2.5×10^{12} atoms per cubic centimetre, at a temperature below about 100 nanokelvin. The measurement is very elegant, and employs some interesting thermodynamic concepts. A simple description is given by C. J. Wieman, *Am. J. Phys.* 64 July 1996, p. 847. The atoms are trapped in a magneto-optic trap, and then cooled

Fig. 7.8: The specific heat in the ideal gas theory of Bose-Einstein particles and in ^{4}He.

by a novel kind of evaporative cooling. The momentum distribution of the cooled gas is probed, again using a very elegant technique. The central finding is that the momentum distribution of the gas consists at "high" temperatures (above about 100nK) of a Maxwell-Boltzmann distribution, while below about 100nK a very sharp peak in the momentum distribution appears, centred on $k = 0$ (the lowest energy eigenstate), which is what we would expect upon formation of a Bose condensate. The 2001 Nobel Prize for physics was awarded to Wolfgang Ketterle, Eric Cornell and Carl E. Wieman for this work.

7.3.2 An Exercise: Bose Condensation in 2D

It is generally believed that Bose-Einstein condensation occurs only in dimensions $d \geq 3$. The argument below is based on number conservation and on peculiarities of the density of states $g(\varepsilon)$ at the band edge ($\varepsilon \to 0$). Specifically, in 2D, we have in the usual way

$$N = A\frac{m}{2\pi\hbar^2}\int_0^\infty \frac{\mathrm{d}\varepsilon}{e^{\beta(\varepsilon-\mu)}-1}. \tag{7.26}$$

Note that we can define the interparticle separation distance r in terms of article density, $N/A = 1/r^2$. To obtain the critical temperature, set $\mu = 0$:

$$N = A\frac{m}{2\pi\hbar^2}k_B T_c\int_0^\infty \frac{\mathrm{d}x}{e^x-1}. \tag{7.27}$$

The integral clearly diverges as $x \to 0$, hence we must correctly conclude that $T_c = 0$. This effect, that we cannot have an "ordered phase" (in this case, the condensate into a special ground state) in the low-dimensional system (2D and 1D) is related to the so-called *Landau-Peierls instability* and you shall meet it a few more times, in this and other courses.

However, the very same feature that causes the integral above to diverge also makes the system unstable against arbitrary weak perturbations and promotes the

appearance of bound states at $\varepsilon \leq 0$. This feature can be demonstrated by introducing a single weak, short-ranged potential well at some fixed (random) position on the plane. If sufficiently short-ranged, it will sustain only a single bound state with finite binding energy $(-\Delta)$. The modified density of states will then include this single bound state:

$$g(\varepsilon) = \frac{1}{A}\delta(\varepsilon + \Delta) + \frac{m}{2\pi\hbar^2}\Theta(\varepsilon) \tag{7.28}$$

(the step function $\Theta(\varepsilon)$ is simply to reflect that only $\varepsilon > 0$ states contribute to the normal phase space element). Now the lowest value that μ can can take is $(-\Delta)$ and if there is a non-vanishing T_c, this has to be determined from the same particle conservation, but with the lowest μ factored in:

$$N = A\frac{m}{2\pi\hbar^2}k_B T_c \int_0^\infty \frac{\mathrm{d}x}{(e^{\Delta/k_B T_c})e^x - 1}. \tag{7.29}$$

Now there is no zero in the denominator at $x \to 0$ and the integral can be evaluated in closed form. The result is an explicit expression for T_c:

$$\frac{2\pi\hbar^2 N}{mA} \equiv \frac{2\pi\hbar^2}{r^2 m} = k_B T_c \ln\left(\frac{1}{1 - e^{-\Delta/k_B T_c}}\right). \tag{7.30}$$

For any $\Delta > 0$ this equation always has a solution for T_c. The r.h.s. increases monotonically with T_c from 0 to ∞, allowing a unique value $T_c(r)$ for any given particle separation $r = \sqrt{A/N}$. Below Tc the number of particles N_0 condensed into the eigenstate at $\varepsilon = -\Delta$ is found by the application of the particle-counting principle (7.20) to the present example of 2D and $\mu = -\Delta$ (and using the same integral again):

$$\begin{aligned} N(\varepsilon > 0) &= A\frac{m}{2\pi\hbar^2}k_B T \int_0^\infty \frac{\mathrm{d}x}{(e^{\Delta/k_B T_c})e^x - 1}, \\ \text{so} \quad N_0 &= N - N(\varepsilon > 0) = A\frac{m}{2\pi\hbar^2}k_B(T_c - T)\ln\left(\frac{1}{1 - e^{-\Delta/k_B T_c}}\right) \\ &= N\left(1 - \frac{T\ln\left(1 - e^{-\Delta/k_B T}\right)}{T_c \ln(1 - e^{-\Delta/k_B T_c})}\right). \end{aligned} \tag{7.31}$$

7.4 Other Elementary Excitations

Many (most, in fact!) physical systems cannot be treated as ideal gas: a large number of particles are interacting with each other and the exact description is very difficult. A common approach in physics is to take a system which is close to its ground state and subject it to a weak external influence, for example we might heat it up a bit - or shine some light on it. In this case we would be interested in the small changes to the system caused the external influence. These can often be described in terms of the excited states or *excitations* of the system. Although the interactions

between elements of the system may be strong, the excitations from the ground state often interact only weakly with one another. In this case we can treat the excitations as *non-interacting* and do the "ideal gas" statistical mechanics with them. We will briefly discuss such systems, interpreting their low temperature properties in terms of approximate normal modes, or "elementary excitations". They are characterised by the zero rest mass (and, therefore, de Broglie wavelength $\lambda \to \infty$, i.e. always in the quantum regime), and they are always bosons (mostly with no spin at all).

7.4.1 Phonons

The atoms of a solid interact very strongly with one another and to calculate the vibrational properties of a solid containing 10^{23} strongly interacting atoms appears at first sight to be a hopeless task. The task is, however, greatly simplified if we note that as long as the magnitude of the vibrations is small, then the interaction potentials between the atoms can be approximated as harmonic. Writing down the equations of motion of the atoms for harmonic interactions, we find eigenstates (normal modes) which are plane waves with a linear dispersion relation at low frequency, flattening off near the Brillouin zone boundary. This is illustrated in Fig. 7.9. These eigenstates are interpreted in terms of a new kind of excitation, called *phonons*. These excitations are non-interacting, so we can use our ideal gas treatment to study their thermodynamics.

Fig. 7.9: Phonon dispersion relationship of a one-dimensional monatomic chain in a simple solid, realistic model in red and the corresponding Debye approximation in blue. [4]

Debye developed a simple model of phonons in a solid. He approximated the dispersion relation as a linear function, $\omega = ck$, with a cutoff at the Debye frequency, ω_D, such that the total number of vibrational modes is correct ($3N$ modes for N atoms). The "effective velocity" parameter c is chosen so as to reproduce the experimental density of states at small ω. This is done by choosing

$$\frac{3}{c^3} = \frac{1}{c_L^3} + \frac{2}{c_T^3}, \tag{7.32}$$

where c_L is the speed of longitudinal waves and c_T is the speed of transverse waves

in the solid. There is one longitudinal mode and two transverse modes at each wave vector.

The condition that the number of vibrational modes is correct is very simple to apply in k-space, it just means that the volume of k-space for the modes should be correct. In frequency space we have

$$3N = \int_0^{\omega_D} g(\omega)\,\mathrm{d}\omega = \int_0^{\omega_D} \frac{3V}{2\pi^2 c^3}\omega^2\,\mathrm{d}\omega = \frac{V\omega_D^3}{2\pi^2 c^3}, \tag{7.33}$$

where the Debye frequency, ω_D, is given by

$$\omega_D^3 = \frac{6\pi^2 c^3 N}{V}. \tag{7.34}$$

The internal energy is

$$U = \int_0^{\omega_D} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega}-1}\,\mathrm{d}\omega\,. \tag{7.35}$$

At low T the occupation of the higher frequency modes is negligible so that the range of integration can be extended to infinity, giving

$$U \approx \int_0^{\infty} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega}-1}\,\mathrm{d}\omega = \frac{3\pi^4}{5}Nk_BT\left(\frac{T}{\Theta_D}\right)^3 \tag{7.36}$$

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta_D}\right)^3, \quad \text{(Low } T\text{)} \tag{7.37}$$

where $k_B\Theta_D = \hbar\omega_D$ defines the Debye temperature. Note that the low T theory is the same as for photons, except that c is now the speed of sound rather than the speed of light. In particular we find that the heat capacity is proportional to T^3.

At high T the cutoff is required but we can expand the denominator in Eq. (7.35) as follows

$$U = \int_0^{\omega_D} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega}-1}\,\mathrm{d}\omega \approx \int_0^{\omega_D} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3}\frac{1}{1+\beta\hbar\omega+\cdots-1}\,\mathrm{d}\omega = 3Nk_BT, \tag{7.38}$$

so that

$$C = 3Nk_B, \quad \text{(High } T\text{)} \tag{7.39}$$

which is the equipartition result. In between things get a bit messy, but conceptually it is clear, we simply have to evaluate Eq. (7.35).

Fig. 7.10 shows that the Debye model works very well for Al, Cu, and Pb, even though the measured density of states is significantly different from the Debye ω^2 dependence (see Fig. 7.11). The Debye theory contains only a single parameter, the velocity c, and it predicts universal behaviour of the heat capacity as a function of T/Θ_D.

Fig. 7.10: The specific heats of Al, Cu and Pb, from experiment and from the Debye model, plotted against T/Θ_D.

Why is the Debye theory so good in spite of its obvious crudeness? The most important reason is that it is actually exact at both high and low temperatures. The high-T behaviour is correctly reproduced because the number of modes is correct. At low frequencies the Debye model correctly reproduces the experimental density of states, which are the only modes excited at low T. A theory which correctly reproduces both the high and low T behaviour and gives a smooth interpolation between them is likely to work at all T if the physics of the phenomenon is smooth (e.g., no phase transitions). The second reason why the Debye theory works so well is related to the Bose occupation factor. The Bose occupation factor is a rapidly decaying function of ω at low T, but the Debye density of states is exact at small ω so the heat capacity is given correctly. At high T the Bose factor is a smooth function of ω and the large discrepancies between the Debye and experimental densities of states at large ω are averaged out by integrating over the frequencies.

Fig. 7.11: The phonon density of states of aluminium (solid line) and of the Debye model (dashed line).

The main point is that the underlying dispersion relation, the dimensionality of the system, and Bose-Einstein statistics, completely define the thermodynamic behaviour. Even though we are dealing with very strongly interacting atoms we are able to apply our ideal gas theory by finding normal modes. If we look more deeply, we find that the phonons are only approximate normal modes (because the inter-atomic potential is only approximately harmonic), so our theory is not perfect. For example, in its simplest form it predicts zero thermal expansion, although this

fault can be rectified very successfully using the "quasi-harmonic approximation" in which the vibrational frequencies are allowed to depend on the volume.

7.4.2 Spin Waves

A similar example is found in the elementary excitations of a ferromagnetic system in which the size of the moments is fixed. These excitations are called "spin waves", and they obey Bose statistics. In the simplest case the dispersion relation is $\varepsilon_{\mathbf{k}} = \alpha k^2$, which is the same form as for ideal gas particles. The density of states is therefore proportional to $\sqrt{\varepsilon}$, and at low temperatures we have, from Eq. (6.17), (note that $\sigma = 1$ for spin waves)

$$U = \frac{V}{4\pi^2\alpha^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2}\,\mathrm{d}\varepsilon}{e^{\varepsilon/k_BT} - 1} = \frac{V}{4\pi^2\alpha^{3/2}} (k_BT)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1}\,\mathrm{d}x\,. \tag{7.40}$$

Using $C = \mathrm{d}U/\mathrm{d}T$ we find that the spin wave heat capacity should be proportional to $T^{3/2}$, which is seen experimentally. Note that we have obtained this result purely from knowing the dispersion relation and that spin waves obey Bose statistics.

Fig. 7.12: Classical picture of a spin wave in a ferromagnet. In the ground state all the spins are parallel, but when a spin-wave excitation is present the spin vectors precess, with successive spins being advanced by a constant phase angle. The line drawn through the ends of the spins in the lower picture shows the wavelength of the excitation.

Historically, most of these results went in the opposite direction, first a certain temperature dependence of the heat capacity was observed, which was interpreted in terms of some underlying "elementary excitation", whose dispersion relation was inferred from $C(T)$. This was the case with phonons, the vanishing of the heat capacity at low temperatures led Einstein to try and interpret the thermal energy of vibration of a lattice in terms of quantised simple harmonic oscillators and, soon after, Debye produced a more accurate theory by finding the normal modes of the entire lattice.

In the case of electrons, the linear temperature dependence of the heat capacity was known long before an adequate theory was found, and both Einstein and Fermi attempted to apply their quantum gas theories to obtain a linear heat capacity (Fermi was successful). It is quite amazing, really, that you can treat electrons in a

metal as being non-interacting particles, given the very strong Coulomb repulsion between them. Indeed, it is rather too good to be true! It turns out that it is often good enough to ignore the interactions between electrons (or include them in an approximate manner using simple concepts such as effective mass) when calculating excitations, but they can *never* be ignored when calculating ground state properties which depend on the chemical bonding between atoms (e.g., the frequencies of atomic vibrations).

Spin waves in many ferromagnets show a gap at low energy, due to coupling of the orbital moments to the crystalline lattice. The resulting dispersion relation curves are typically as shown in Figs. 7.13-7.14.

Fig. 7.13: Dispersion relations for the ferromagnetic and lower antiferromagnetic elementary excitations. The non-interacting and interacting spin-wave calculations are shown by solid and dotted curves respectively, whereas represents the matrix product and the exact diagonalization results (up to $N = 7$). The ground state energy is supposed to be zero. [8]

Fig. 7.14: Spin waves in many ferromagnets show a gap at low energy, due to coupling of the orbital moments to the crystalline lattice. Typically resulting in this dispersion relation curves.

We can treat the elementary excitations as a Bose gas in which N in not conserved (i.e., like black-body radiation, $\mu = 0$), and which has a dispersion relation $\varepsilon_{\mathbf{k}} = \hbar\omega = \Delta + \alpha k^2$, where Δ is the energy gap at the origin. The average energy

is given by

$$
\begin{aligned}
U &= \int \varepsilon_{\mathbf{k}} n_{\mathbf{k}} g(\mathbf{k})\,\mathrm{d}\Gamma \\
&= \int_0^\infty \hbar\omega \underbrace{\frac{1}{e^{\beta\hbar\omega}-1}}_{(7.8)} \frac{4\pi k^2\,\mathrm{d}k}{(2\pi)^3} \underbrace{\int \mathrm{d}^3 r}_{V} \\
&= \frac{V}{2\pi^2}\int_0^\infty \frac{\Delta+\alpha k^2}{e^{\beta(\Delta+\alpha k^2)}-1} k^2\,\mathrm{d}k\,. \qquad (7.41)
\end{aligned}
$$

In the low temperature limit ($k_B T \ll \Delta$) the exponential becomes large compared to unity we can approximate the integral as

$$
\begin{aligned}
U &\simeq \frac{V}{2\pi^2}\int_0^\infty e^{-\beta(\Delta+\alpha k^2)}(\Delta+\alpha k^2)k^2\,\mathrm{d}k \\
&= \frac{V}{2\pi^2} e^{-\beta\Delta}\left[\Delta\int_0^\infty e^{-\beta\alpha k^2}k^2\,\mathrm{d}k + \alpha\int_0^\infty e^{-\beta\alpha k^2}k^4\,\mathrm{d}k\right] \\
&= \frac{V}{2\pi^2} e^{-\beta\Delta}\left[\frac{\Delta}{(\beta\alpha)^{3/2}}\underbrace{\int_0^\infty e^{-y^2}y^2\,\mathrm{d}y}_{\frac{\sqrt{\pi}}{4}} + \frac{\alpha}{(\beta\alpha)^{5/2}}\underbrace{\int_0^\infty e^{-y^2}y^4\,\mathrm{d}y}_{\frac{3}{2}\frac{\sqrt{\pi}}{4}}\right] \\
&= \frac{V}{8}\left(\frac{k_B T}{\alpha\pi}\right)^{3/2} e^{-\beta\Delta}\left[\Delta + \frac{3}{2}k_B T\right] \qquad (7.42)
\end{aligned}
$$

The important temperature dependence is contained in the $e^{-\beta\Delta}$ term, and this would certainly dominate experimental results for the heat capacity. This term is typical of a system with a gap between the ground state and first excited states (and you have seen it in the simple 2-level system already).

At temperatures where $k_B T \gg \Delta$, but still small compared with (say) the Curie temperature, the denominator in the integrand can be approximated as

$$
\begin{aligned}
\frac{1}{e^{\beta(\Delta+\alpha k^2)}-1} &\simeq \frac{1}{e^{\beta\alpha k^2}(1+\beta\Delta)-1} \\
&= \frac{1}{(e^{\beta\alpha k^2}-1)\left(1+\frac{\beta\Delta e^{\beta\alpha k^2}}{e^{\beta\alpha k^2}-1}\right)} \\
&\simeq \frac{1}{(e^{\beta\alpha k^2}-1)}\left(1-\frac{\beta\Delta e^{\beta\alpha k^2}}{e^{\beta\alpha k^2-1}}\right), \qquad (7.43)
\end{aligned}
$$

where the motivation for this rearrangement was to separate the orders in the small quantity $\beta\Delta \ll 1$. U can be rewritten as

$$
\begin{aligned}
U &\simeq \frac{V}{2\pi^2}\int_0^\infty \frac{(\Delta+\alpha k^2)k^2}{e^{\beta\alpha k^2}-1}\left(1-\frac{\beta\Delta e^{\beta\alpha k^2}}{e^{\beta\alpha k^2-1}}\right)\mathrm{d}k \\
&= \frac{V}{2\pi^2}\int_0^\infty \frac{\alpha k^4}{e^{\beta\alpha k^2}-1} + \frac{\Delta k^2}{e^{\beta\alpha k^2}-1} + \mathcal{O}(\beta\Delta) \\
&= \frac{\alpha V}{4\pi^2}\left(\frac{k_B T}{\alpha}\right)^{5/2}\int_0^\infty \frac{x^{3/2}}{e^x-1}\,\mathrm{d}x + \frac{V\Delta}{4\pi^2}\left(\frac{k_B T}{\alpha}\right)^{3/2}\int_0^\infty \frac{x^{1/2}}{e^x-1}\,\mathrm{d}x\,. \qquad (7.44)
\end{aligned}
$$

The first term varies with temperature as $T^{5/2}$; it is the standard ferromagnetic spin wave energy that we would have if there were no gap. The second term, which varies as $T^{3/2}$, comes from the offset of each spin-wave energy by Δ (for example the $k = 0$ spin-wave has no energy if $\Delta = 0$, so it wouldn't contribute to the thermal energy, but when $\Delta > 0$ it does contribute). When $k_B T$ is large compared to Δ, the $T^{5/2}$ term dominates. The next largest term has an integrand which vanishes as $\beta\Delta$ everywhere except near $k \to 0$, where it is finite, but this is a small region of phase space so we can ignore it.

At low temperature the specific heat rises exponentially (signalling that there is a gap in the energy spectrum), then when $k_B T \sim \Delta$ it crosses over to $T^{3/2}$ behaviour characteristic of a quadratic dispersion relation.

7.4.3 Quantum Liquids ^{4}He and ^{3}He

We will now apply these ideas to the behaviour of the quantum liquids ^{4}He and ^{3}He. The first somewhat surprising result is that neither isotope of helium has a solid phase at atmospheric pressure, they liquefy at 4.2 K and 3.2 K, respectively, and remain liquids down to absolute zero (or as close as anyone has been able to take them).

The reason that they remain liquid is that the energy of their zero point motion is comparable to the binding energy of their inter-atomic potential. The inter-atomic potential, which arises from the combination of a van der Waals attractive force and a hard core repulsion, has a depth of about $\varepsilon/k_B \sim 10\,\mathrm{K}$, with the minimum occurring at a separation of 2.9 Å. To understand this we have to calculate the kinetic energy of zero point motion. From the Heisenberg uncertainty principle, the kinetic energy of a particle of mass m confined within a box of volume Δx^3 is roughly

$$\Delta E \sim \frac{\Delta p^2}{2m} \sim \frac{\hbar^2}{2m\Delta x^2}. \tag{7.45}$$

In the liquid phase well below the boiling point and at atmospheric pressure, the average separation of the He atoms is about 3.73 Å. To calculate the kinetic energy we must take into account the hard core of the atom, which reduces the volume, Δx^3, available to the atom for kinetic motion. An appropriate value is $\Delta x = 1.2$ Å, giving $\Delta E/k_B \sim 4\,\mathrm{K}$, which is of the same order as the potential energy. Remaining in the liquid state allows the helium atoms to keep their kinetic energy down, because they are allowed to move around somewhat more. On the other hand, they would have even lower zero point energy at gaseous densities, but then their potential energy would be higher. The liquid represents a compromise between potential and kinetic energy.

The question which then arises is how the entropy of a liquid can go to zero

at $T \to 0$. In fact we already know of one case where this happens, because the electrons in a metal are a kind of liquid at low temperature, and they lose their entropy by condensing into a Fermi gas in which all states below the Fermi energy are occupied.

Fig. 7.15 shows a comparison of the specific heat of pure ^{4}He and ^{3}He at low temperature, where both are in the liquid state. There is a very striking difference. Starting with 3He, we see that below about 0.15K the specific heat is linear in T. This is the behaviour we derived for a Fermi gas. This shows us that the elementary excitations of ^{3}He must correspond to excitations which are linear in k about some Fermi surface. The detailed theory of these excitations was worked out by Landau in his remarkable papers on "Fermi liquid theory" of 1957 and 1958.

Below 0.6K, ^{4}He shows a specific heat proportional to T^3, which is the same behaviour as we found for phonons. Moreover, as the temperature is increased there is an abrupt increase in the specific heat at about 0.6K. Landau postulated that the lowest energy elementary excitations in ^{4}He are phonons (i.e., sound waves in the liquid), while the upturn above 0.6K he ascribed to a dip in the dispersion relation which in effect produces a large number of nearly degenerate states with energy Δ, called rotons. Landau calculated Δ, and his results were later confirmed by neutron scattering experiments (see Fig. 7.15).

7.5 Chemical potential

The chemical potential μ appears as the conjugate variable of N in the thermodynamic potentials U, F, H, G, Φ, etc. From the thermodynamic potentials (e.g., from $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$) we find a number of expressions for μ, such as $\mu = (\partial U/\partial N)_{S,V}$, but these are difficult to interpret intuitively except in special cases. For example, in general we don't know how to change the energy at constant entropy, but for the special case of the Fermi gas, the Gibbs entropy expression for the entropy per energy level,

$$S_k = -k_B\Big(n_k \ln n_k + (1-n_k)\ln(1-n_k)\Big), \tag{7.46}$$

shows us that $(\partial S/\partial N)$ is zero at $n_k = 1 - n_k$, i.e., at ${}_nk = 1/2$, so if we add a particle at the energy level where $n_k = 1/2$, then we are adding energy at constant entropy, and so this energy level must be located at the chemical potential. But this is only possible below the degeneracy temperature, since at high temperatures the chemical potential of a Fermi gas is negative (i.e., there are no states for which $n_k = 1/2$ for a Fermi gas at high temperature). In the limit as $T \to 0$, $n_k = 1/2$ is located at the Fermi energy, so the Fermi energy and the chemical potential coincide at low temperature.

A more intuitive way of writing μ is as discussed in Subsection 2.1.1. The changes leading to equilibrium must be allowed by the Second Law of thermodynamics.

Fig. 7.15: Comparison of the low temperature specific heats of ^{4}He and ^{3}He. This difference arises because ^{3}He is a fermion, while ^{4}He is a boson. The above figure shows ^{3}He exhibits Fermi fluid behaviour at low temperature while ^{4}He shows condensation. Near 1.5 K, $C/N_k = 1$ for both films, indicating 2D ideal gas behavior. [9] The lower figure shows the measured dispersion curve for the elementary excitations in liquid ^{4}He.

Using $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ we get $\mu = -T(\partial S/\partial N)_{U,V}$, that is, the chemical potential is related to the change in entropy of a system when a particle is added at constant energy and volume. To illustrate the appeal of this expression, say we have two systems 1 and 2 in contact so that they can exchange particles, energy and volume.

$$\begin{aligned}\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 &= \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1,V_1}\mathrm{d}U_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{N_1,U_1}\mathrm{d}V_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1,V_1}\mathrm{d}N_1 + \\ &\quad \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2,V_2}\mathrm{d}U_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{N_2,U_2}\mathrm{d}V_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2,V_2}\mathrm{d}N_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\mathrm{d}V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\mathrm{d}N_1\,. \qquad (7.47)\end{aligned}$$

We have used $\mathrm{d}N_1 = -\,\mathrm{d}N_2$, $\mathrm{d}V_1 = -\,\mathrm{d}V_2$ and $\mathrm{d}U_1 = -\,\mathrm{d}U_2$. The Law of Increase of entropy says that $\mathrm{d}S$ must be positive, so the first term tells us that energy flows from hot to cold, and the second term tells us that (for systems at equal temperature) the volume of the high pressure system will increase at the expense of the low pressure system. The last term is the one of interest here. To get it we used the expression for μ in terms of change of entropy with particle number.

It tells us that particles flow from high to low chemical potential (for systems at equal temperature), i.e., $\mathrm{d}N_1$ is negative is $\mu_1 > \mu_2$. The chemical potential controls particle flow just as the temperature controls energy flow.

Another useful way of writing the chemical potential for a pure phase is as the Gibbs free energy per particle, $\mu = G/N$ (2.34). This is useful for describing phase equilibrium, because it can be shown (using the availability or otherwise) that the equilibrium of a system at constant temperature and pressure is determined by minimising the Gibbs free energy, and thus (again) that equilibrium involves equality of the chemical potentials of the phases involved. Among other things, we used this equality of chemical potentials at phase equilibrium to derive the Clausius-Clapeyron equation (Section 2.4.1), from the fact that $\mathrm{d}\mu = v\,\mathrm{d}p - s\,\mathrm{d}T$ (1.34) for each phase as we move along the phase boundary, where v is the volume per molecule, and s is the entropy per molecule, in a given phase. Equating the changes in $\mathrm{d}\mu$ produces the equation (2.43) $\mathrm{d}T/\mathrm{d}p = \Delta v/\Delta s$, where Δv and Δs are the changes in the specific volume and entropy at the phase boundary. The chemical potential plays a similar role in the equilibrium properties of mixtures, where for example the change in chemical potential due to the addition of a solute to a solvent on one side of a semi-permeable membrane produces an osmotic pressure. Moreover, it is also central to chemical equilibrium (see Subsection 2.5.1), where the condition (2.61) $\sum_i \nu_i \mu_i = 0$ can be derived from the minimum Gibbs free energy condition. The ν_i are the number of molecules of species i involved in a unit reaction.

The chemical potential is important in statistical mechanics whenever particles can move between subsystems. In an ideal gas the single-particle energy levels can be treated separate thermodynamic systems, which are in mutual equilibrium and have a common chemical potential. The statistical distribution of the energy eigenstates is then described by the Gibbs distribution: the probability of finding n particles in state i is

$$P(n_i) = \frac{\left(e^{-(\varepsilon_i - \mu)/k_B T}\right)^n}{\Xi}, \tag{7.48}$$

where $\Xi = \sum_n \left(e^{-(\varepsilon_i - \mu)/k_B T}\right)^n$ is the partition function for the state. The chemical potential therefore plays a central role in the occupation number distribution function. It can be set in two ways, either by equilibrium of the gas with a reservoir of particles which sets the chemical potential (this is the case for example in Subsection 5.8.1, where the chemical potential of the two-dimensional gas adsorbed on the surface is set by the chemical potential of the three-dimensional gas, and it is also the case for a photon gas, where the absorption and emission of photons by the cavity walls sets the chemical potential to zero) or it may be set by the requirement that the total number of particles in the gas is N (for closed systems). The latter situation is encountered in standard treatments of Fermi and Bose gases, and of classical gases.

It should be noted that as well as containing terms that are related to the entropy, the chemical potential also contains terms that look like genuine potential energies, and in general particle equilibrium involves both kinds of terms. So for a classical

ideal gas the chemical potential is (5.31)

$$\mu = k_B T \left[\ln \left(\frac{N\lambda^3}{\sigma V} \right) - \ln Z_{\text{int}} \right] + \phi. \tag{7.49}$$

The first two terms, which come from the translational degrees of freedom of a classical gas and the internal degrees of freedom of the molecules, respectively, have to do with entropy, whereas the latter term is a potential energy per molecule, ϕ, which could for example be an electric potential if the molecules are charged, or a gravitational potential. General equilibrium involves particles flowing from high to low chemical potential. If the potential term is due to gravity, then this term tends to "want" all the molecules to collect at the bottom of the system. However the entropic terms "want" the molecules to spread out as much as possible. The final equilibrium represents a compromise between these two tendencies.

Fig. 7.16: Caption

The sketch in Fig. 7.16 of μ plotted against N/V has the classical regime at small $(N\lambda^3/V) \ll 1$ where $\mu = k_B T \ln(N\lambda^3/\sigma V)$, hence for low values of N/V, μ is negative and diverges as $(N/V) \to 0$. When $N\lambda^3/V \sim 1$, quantum effects become important (see Subsection 4.5). There is, of course, a difficult crossover region – and then in the deep quantum regime at $N\lambda^3/V \gg 1$ we have: the Bose-Einstein condensation in Bose-particles case, which results in $\mu \simeq 0^-$; it stays there as the density increases further. In the Fermi case we get a degenerate Fermi gas, for which $\mu \approx \varepsilon_F$, the Fermi energy, which is positive and grows with density as $(N/V)^{2/3}$ in 3D.

Chapter 8

Non-ideal Gases and Liquids

In the previous chapters we dealt with particles or excitations which were (approximately) noninteracting. This is a very useful approach, but if one wants to know the equation of state of a material there is no alternative to dealing with the interactions between the particles. In general a quantum mechanical approach is necessary to describe these interactions accurately. In this section we deal with liquids and imperfect gases, describing the interactions by a simple central inter-atomic potential. We can then use classical statistical mechanics to calculate the equation of state.

8.1 Virial Theorem

This approach offers a neat way to arrive at an equation of state. The classical virial $\mathcal{V}$, introduced by Clausius in 1870, is defined as

$$\mathcal{V} = -\frac{1}{2}\sum_i \mathbf{r}_i \cdot \mathbf{f}_i, \tag{8.1}$$

where $\mathbf{r}_i$ and $\mathbf{f}_i$ are, respectively, the position of, and the force acting on, the ith particle. From Newton's second law we find that

$$\mathcal{V} = -\frac{1}{2}\sum_i \mathbf{r}_i \cdot m_i \frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} = -\frac{1}{2} m_r \frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{r}_i \cdot \mathbf{v}_i) + \frac{1}{2}\sum_i m_i \mathbf{v}_i^2. \tag{8.2}$$

Consider a liquid consisting of N particles in a container of volume V. The value of $\mathbf{r}_i \cdot \mathbf{v}_i$ can only fluctuate between finite limits. Over a long period, its time derivative must therefore average to zero, which leads to

$$\langle \mathcal{V} \rangle = \sum_i \frac{1}{2} m_i \left\langle v_i^2 \right\rangle = \langle \text{K.E.} \rangle = \frac{3}{2} N k_B T. \tag{8.3}$$

The mean virial is equal to the mean kinetic energy. This is Clausius' *virial theorem.*

For our system in its container the force on each particle, and hence the mean virial, is the sum of two parts, the external virial due to the pressure forces exerted on the particles by the walls, and the internal virial due to forces acting between particles, i.e.,

$$\langle \mathcal{V} \rangle = \langle \mathcal{V}_{\text{ext}} \rangle + \langle \mathcal{V}_{\text{int}} \rangle . \tag{8.4}$$

We will calculate these two contributions separately.

To calculate the external virial we note that the force on an element of the wall is $p\,\mathrm{d}\mathbf{A}$. The force on the particles acts inwards and $\mathrm{d}\mathbf{A}$ is directed outwards, so that we have

$$\langle \mathcal{V}_{\mathrm{ext}} \rangle = \left\langle -\frac{1}{2}\sum_i \mathbf{r}_i \cdot \mathbf{f}_{\mathrm{ext},i} \right\rangle = \frac{1}{2}\iint_A \mathbf{r}\cdot p\,\mathrm{d}\mathbf{A} = \frac{p}{2}\iint_A \mathbf{r}\cdot \mathrm{d}\mathbf{A}\,, \tag{8.5}$$

where the integral is over the surface of the container. Using the divergence theorem we find

$$\langle \mathcal{V}_{\mathrm{ext}} \rangle = \frac{p}{2}\iint_A \mathbf{r}\cdot \mathrm{d}\mathbf{A} = \frac{p}{2}\iiint_V \boldsymbol{\nabla}\cdot\mathbf{r}\,\mathrm{d}V = \frac{3}{2}pV. \tag{8.6}$$

As a quick "sanity check" we note that for an ideal gas this is the total virial, and combining Eqs. (8.3), (8.4), and (8.6) we obtain the ideal gas law, $pV = Nk_BT$.

Fig. 8.1: A plot of the Lennard-Jones potential, (solid red line) exhibiting the repulsive and attractive contributions (dotted blue lines). [3]

To calculate the internal virial, we model the interactions between particles via a potential, $\phi(r)$ (Fig. 8.1), which for simplicity we assume depends only on the separation of the point-like particles: $\phi(r_{ij}) = \phi(|\mathbf{r}_i - \mathbf{r}_j|)$. An example of an interaction potential is the Lennard-Jones $6-12$ inter-atomic potential,

$$\phi(r) = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]. \tag{8.7}$$

This potential consists of a short ranged hard-core repulsion and a long ranged van der Waals attraction, which decays as $1/r^6$. As an aside, consider an object moving in a potential of the form

$$\phi(r) = \frac{A}{r}. \tag{8.8}$$

In this case the contribution to the internal virial $-\frac{1}{2}\mathbf{r}\cdot\mathbf{f}$ is

$$\frac{1}{2}r\frac{\mathrm{d}\phi}{\mathrm{d}r} = -\frac{1}{2}\phi, \tag{8.9}$$

and as there is no external virial and hence no pressure,

$$\langle \mathcal{V} \rangle = \langle \text{K.E.} \rangle = \langle \mathcal{V}_{\text{int}} \rangle = -\frac{1}{2} \langle \text{P.E.} \rangle \,. \tag{8.10}$$

This result often comes up in the context of orbits in classical dynamics. As a simple example of the quantum virial theorem you might like to verify for yourself that Eq. (8.10) also holds for the ground state of the hydrogen atom, when the proton mass is taken to be infinite.

Now back to our gas. We consider first just two molecules. The virial for such a pair is

$$\mathcal{V}_{ij} = -\frac{1}{2}(\mathbf{f}_{ij} \cdot \mathbf{r}_i + \mathbf{f}_{ji} \cdot \mathbf{r}_j) = \frac{\mathrm{d}\phi}{\mathrm{d}r_{ij}} \frac{r_{ij}}{2}, \tag{8.11}$$

because $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$. We can then get the contribution to the virial from the forces between the single molecule at $\mathbf{r}_i$ and all the other molecules j by integrating over all space:

$$\langle \mathcal{V}_i \rangle = \frac{1}{2} \sum_{j \neq i} \frac{\mathrm{d}\phi}{\mathrm{d}r_{ij}} \frac{r_{ij}}{2} = \frac{1}{2} \int_0^\infty n\, g(r) r \frac{\mathrm{d}\phi}{\mathrm{d}r} 4\pi r^2 \,\mathrm{d}r \,, \tag{8.12}$$

where $g(r)$ is the *radial distribution function* (Fig. 8.2). This function is dimensionless, and it goes to 1 for large r, when no correlation between the particle at $\mathcal{O}$ and at r is expected (this needs to be revised in an ideal infinite crystalline lattice, where such correlation does persist). The the probability density that given a particle at the origin you would find a second particle at distance r is given by $n\, g(r)$, i.e. the product of particle density $n = N/V$ and radial distribution function $g(r)$.

Fig. 8.2: Radial distribution functions $g(r)$ for Lennard-Jones $6-12$ potential in a simple liquid of argon in different thermodynamic states. Note that the potential always tends to 1 for large r, as expected due to the lack or correlation between the particle at $\mathcal{O}$ and at r. [6]

To get the total virial, we need to multiply by N, because each molecule in the gas makes the same contribution to the virial, and then divide by 2, because each contribution to the virial $\mathcal{V}_{ij}$ is traced back to a pair of molecules. Thus

$$\langle \mathcal{V}_{\text{int}} \rangle = \frac{N}{2} \langle \mathcal{V}_i \rangle = \frac{N}{4} \int_0^\infty 4\pi r^2 n\, g(r) r \frac{\mathrm{d}\phi}{\mathrm{d}r} \,\mathrm{d}r \,. \tag{8.13}$$

Combining this expression for the internal virial with the virial theorem (Eq. 8.3) and with our earlier result for the external virial (Eq. (8.6)),

$$\langle \mathcal{V} \rangle = \frac{3}{2} N k_B T = \langle \mathcal{V}_{\text{ext}} \rangle + \langle \mathcal{V}_{\text{int}} \rangle = \frac{3}{2} pV + \frac{N}{4} \int_0^\infty 4\pi r^2 n\, g(r) r \frac{\mathrm{d}\phi}{\mathrm{d}r} \,\mathrm{d}r \,, \tag{8.14}$$

we obtain the *virial equation of state*:

$$\boxed{p = nk_BT - \frac{n^2}{6}\int_0^\infty r\frac{\mathrm{d}\phi}{\mathrm{d}r}g(r)4\pi r^2\,\mathrm{d}r\,.} \tag{8.15}$$

8.1.1 More on the Pair Distribution Function

The Hamiltonian of the system is

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{j>i}\phi(r_{ij}), \tag{8.16}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and the symbol $\sum_{j>i}$ denotes a sum over all pairs of particles.

The classical partition function is

$$Z = \sum_{\text{microstates}} e^{-\beta\mathcal{H}(\mathbf{r},\mathbf{p})} = \frac{1}{N!}\int e^{-\beta\mathcal{H}}\,\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N\,\frac{\mathrm{d}^3p_1\cdots\mathrm{d}^3p_N}{(2\pi\hbar)^{3N}}. \tag{8.17}$$

The momentum integrals can be done straight away, as always with the quadratic kinetic energy part, giving the $3N$-th power of quantum concentration

$$Z = \frac{1}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2} Z_\phi, \tag{8.18}$$

where the factor is our familiar ideal-gas partiction function arising from the momentum integration, while the complicated sum over potential-energy terms gives

$$Z_\phi = \int e^{-\sum_{j>i}\beta\phi(r_{ij})}\,\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N\,, \tag{8.19}$$

which is called the configurational partition function. Unfortunately, Z_ϕ involves very difficult integrals over the interaction potential.

One way to deal with averages involving the interaction energy is to use the two-particle distribution function,

$$P_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{N(N-1)}{Z_\phi}\int e^{-\sum_{j>i}\beta\phi(r_{ij})}\,\mathrm{d}^3r_3\cdots\mathrm{d}^3r_N\,, \tag{8.20}$$

which is the probability density of finding a particle at $\mathbf{r}_1$ and another particle at $\mathbf{r}_2$. For a liquid or gas (with no orientational symmetry breaking as in a crystalline lattice), P_2 depends only on the distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. It has dimensions of density squared, $n^2\,(= N^2/V^2)$. We can divide through by n^2 to obtain the *radial distribution function*, which is dimensionless:

$$g(r_{12}) = \frac{V^2}{N^2}P_2(\mathbf{r}_1,\mathbf{r}_2). \tag{8.21}$$

A typical $g(r)$ for a liquid is shown in Fig. 8.2. The radial distribution function is small at short distances because of the hard-core repulsion between the atoms. It rises to a peak at the distance of the first shell of neighbours. There is a smaller peak at the second shell but at large distances $g(r)$ goes to unity, which is the value it would have in the absence of interactions (so that $P_2(r) \to (N/V)^2$). We can understand roughly how $g(r)$ will change when T and V are altered. If the system is compressed we expect the peaks of $g(r)$ to move to smaller separations, and if T is increased we expect the peaks to become less pronounced as the thermal motion smears them out.

We can find a very useful approximation to the radial distribution function which is accurate at low densities. We rewrite the two-particle distribution function of Eq. (8.20) as

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1)e^{-\beta\phi(r_{ij})} \frac{\int e^{-\sum'_{j>i} \beta\phi(r_{ij})} \, \mathrm{d}^3 r_3 \cdots \mathrm{d}^3 r_N}{\int e^{-\sum_{j>i} \beta\phi(r_{ij})} \, \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N}, \tag{8.22}$$

where the primed summation indicates that we have removed the $\phi(r_{ij})$ term. At very low densities the integrals over particles $3, 4, \cdots, N$ in the numerator mostly involve configurations in which these particles are distant from each other and from particles 1 and 2, and therefore we can set all the $\phi(r_{ij})$ inside the integral to zero. In the denominator particles 1 and 2 are also far apart for almost all configurations, so we can again set all the $\phi(r_{ij})$ inside the integral to zero. Therefore

$$P_2(\mathbf{r}_1, \mathbf{r}_2) \simeq \frac{N(N-1)}{V^2} e^{-\beta\phi(r_{ij})}, \tag{8.23}$$

and, as N is large,

$$g(r) \simeq g_0(r) = e^{-\beta\phi(r_{ij})}, \tag{8.24}$$

where we use the term $g_0(r)$ to express the fact that in this approximation $g(r)$ is explicitly independent of density – more on the virial expansion in Section 8.2. We can see that this form has the right sort of behaviour; $\phi(r = 0) = \infty$, so that $g_0(r = 0) = 0$, and $\phi(r = \infty) = 0$, so that $g_0(r = \infty) = 1$. Also $g_0(r)$ takes its maximum value at the minimum in $\phi(r)$, which seems sensible.

The key quantities in the classical statistical mechanics of liquids are the inter-molecular potential and the radial distribution function. For simple liquids such as those of the noble gases Ne, Ar, etc., the Lennard-Jones potential works very well. The Lennard-Jones potential also works well for He, but in this case the effects of quantum statistics are important. The Lennard-Jones potential normally gives a poor description of systems with strong ionic, covalent or metallic bonding. For ionic bonding one should include the long-range Coulomb forces, for covalent materials one needs directional bonding forces, and in metals the interaction energy is not well described by a sum of pairwise terms. Also, if the molecules are far from spherical or have significant dipole moments the inter-molecular potentials will depend on the relative orientation of the molecules.

Radial distribution functions can be measured using x-ray or neutron diffraction techniques. They can also be calculated using Monte Carlo or Molecular Dynamics methods. Monte Carlo methods are statistical techniques for generating ensembles of configurations, $\{\mathbf{r}_1, \cdots, \mathbf{r}_N\}$, distributed according to a known probability distribution. In classical Molecular Dynamics methods the molecules are moved according to Newton's laws in what amounts to a "computational experiment". An important modern development is the use of computational quantum mechanical techniques to calculate the interaction energy, which can readily be combined with the classical theory of liquids developed here.

8.1.2 Internal Energy

Calculating the internal energy, we find

$$U = -\frac{\partial}{\partial\beta}\ln Z = \frac{3}{2}Nk_BT - \frac{\partial}{\partial\beta}\ln Z_\phi. \tag{8.25}$$

The Z_ϕ term gives

$$\begin{aligned} -\frac{\partial}{\partial\beta}\ln Z_\phi &= \frac{1}{Z_\phi}\int\sum_{j>i}\phi(r_{ij})e^{-\sum_{j>i}\beta\phi(r_{ij})}\,\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N \\ &= \frac{N(N-1)}{2Z_\phi}\int\phi(r_{12})e^{-\sum_{j>i}\beta\phi(r_{ij})}\,\mathrm{d}^3r_1\cdots\mathrm{d}^3r_N\,, \end{aligned} \tag{8.26}$$

where the last line follows because there are $N(N-1)/2$ terms in the sum. Substituting from Eqs. (8.19), (8.20) and (8.21) we find

$$U = \frac{3}{2}Nk_BT + \frac{1}{2}\int\phi(r_{12})P_2(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2 = \frac{3}{2}Nk_BT + \frac{N^2}{2V}\int_0^\infty\phi(r)g(r)4\pi r^2\,\mathrm{d}r\,. \tag{8.27}$$

In retrospect this result is obvious; the internal energy is the sum of the kinetic energy, which follows from equipartition, and the potential energy that is evaluated here in some average manner.

Unfortunately, even if we knew $\phi(r)$ and had $g(r)$ as a function of T, V and N we wouldn't have enough information to do the complete thermodynamics of liquids, because T, V and N are not the natural variables of U. This is why we had to employ the virial theorem earlier on to arrive at the equation of state,

$$p = nk_BT - \frac{n^2}{6}\int_0^\infty r\frac{\mathrm{d}\phi}{\mathrm{d}r}g(r)4\pi r^2\,\mathrm{d}r\,. \tag{8.28}$$

The expression for $U(T,V,N)$ and the equation of state give a great deal of equilibrium thermodynamic information. For a complete description we also need a "non-mechanical" quantity such as the chemical potential. The chemical potential can also be written in terms of the radial distribution function, although the dependence is more complicated.

Although we now have nice expressions for the equation of state and for the internal energy, we would need to know the radial distribution function to calculate anything. We now turn to a series expansion of the equation of state, which enables us to go a bit further, still:

8.2 Virial Expansion

If we start off with a very dilute gas, interactions are unimportant, and the equation of state will approach the ideal gas law. As density increases, we may expect increasing corrections to the ideal gas law. This is the motivation for the *virial expansion*, which expresses the equation of state in terms of increasing powers of density:

$$\boxed{\frac{p}{k_B T} = n + B_2(T)n^2 + B_3(T)n^3 + \cdots .} \tag{8.29}$$

The mth virial coefficient, $B_m(T)$, reflects the m-body correlations in the equation of state. Mayer developed a diagrammatic recipe which (in principle) allows each coefficient to be calculated.

The radial distribution function $g(r)$ likewise depends on the density. If we expand it in powers of $n = N/V$,

$$g(r) = g_0(r) + g_1(r)n + g_2(r)n^2 + \cdots , \tag{8.30}$$

and substitute into the virial equation of state of Eq. (8.28), we can link the coefficients B_m in the virial expansion to coefficients g_{m-2} in the expansion of the radial distribution function.

The virial expansion is not useful at liquid densities because it only converges when the distance between molecules is much greater than their size. However, the virial expansion gives an excellent description of imperfect gases at low densities, when only pair interactions between particles are relevant. To calculate $B_2(T)$, we can use our earlier approximate result for the leading order contribution to $g(r)$ (Eq. (8.24)): $g_0(r) = e^{-\beta\phi(r)}$.

We substitute $g_0(r)$ into Eq. (8.15), and integrate by parts:

$$\begin{aligned}
\frac{p}{k_B T} &= n - \frac{n^2}{6k_B t}\int_0^\infty 4\pi r^3 \frac{\mathrm{d}\phi}{\mathrm{d}r} e^{-\phi/k_B T}\,\mathrm{d}r \\
&= n + \frac{n^2}{6}\left[4\pi r^3 e^{-\phi/k_B T}\Big|_0^\infty\right] - \int_0^\infty 12\pi r^2 e^{-\phi/k_B T}\,\mathrm{d}r && (8.31)\\
&= n + \frac{n^2}{6}\left[\int_0^\infty 12\pi r^2\,\mathrm{d}r - \int_0^\infty 12\pi r^2 e^{-\phi/k_B T}\,\mathrm{d}r\right] && (8.32)\\
&= n + n^2\left[\int_0^\infty 2\pi r^2\left(1 - e^{-\phi/k_B T}\right)\mathrm{d}r\right], && (8.33)
\end{aligned}$$

where to get Eq. (8.32) from Eq. (8.31) we have used the fact that $e^{-\phi/k_BT}$ is equal to 1 at $r = \infty$. Comparing with Eq. (8.29) we see that the second virial coefficient is

$$B_2(T) = \int_0^\infty 2\pi r^2 \left(1 - e^{-\phi/k_BT}\right) \mathrm{d}r \,. \tag{8.34}$$

Fig. 8.3 shows the second virial coefficient for a gas of particles interacting via the Lennard-Jones $6-12$ potential, compared with data for some real gases. At high temperatures the second virial coefficient is dominated by hard core repulsion, and is positive and roughly constant. At low temperatures it is dominated by the van der Waals attraction, and is negative and roughly proportional to $1/T$. Experimental values have been determined by careful measurements of p as a function of density, and the agreement with theory is excellent except where quantum effects are important, when more sophisticated calculations are necessary.

The *Boyle temperature* is defined as the temperature at which the second virial coefficient $B_2(T)$ passes through zero, see Fig. 8.3. At this point, the gas is nearest to the ideal gas equation, $pV = Nk_BT$, essentially because the contribution from the long-range particle attraction on average exactly compensates the short-range repulsion - leaving effectively "non-interacting" particles. At higher temperature the gas is *harder* to compress than an ideal gas (effect of the hard core repulsion), and at lower T it is *easier* (effect of long-range attraction, pulling the pairs of particles together).

Fig. 8.3: The second virial coefficient in reduced units for a Lennard-Jones gas (solid line) as a function of the reduced temperature, $T* = k_BT/\epsilon$, compared with experimental data. Note that at low $T*$ the He data does not fit the classical result because of quantum effects.

We can motivate the general Eq. (8.34) by a simple argument, finding the mean potential energy of the N-particle system by counting the interacting pairs:

$$U_{\text{pair}} = \sum_{i>j} \phi(r_{ij}) \approx \frac{N^2}{2}\frac{1}{V}\int \phi(r)\,\mathrm{d}^3r = \frac{N^2}{2}\bar{\phi} \tag{8.35}$$

where $\frac{1}{2}N^2$ is the number of distinct pairs in the system and we have replaced the pair potential by its average over space, $\bar{\phi}$, which is obviously a very crude approximation. This is only meaningful if the potential is weak and slowly-varying,

Fig. 8.4: The form of the density-independent part of the radial distribution function versus r for $k_BT \gg \varepsilon$ and $k_BT \gg \varepsilon$.

in which case the limit $\beta\phi(r) \ll 1$ in Eq. (8.34) produces $B_2 \approx \frac{1}{2}\int \beta\phi(r)\,\mathrm{d}^3r$ and we can make the connection:

$$U_{\text{pair}} \approx \frac{N^2}{V} k_B T B_2(T). \tag{8.36}$$

This is a "poor man's" form of the second term in Eq. (8.27). It is also important to note that the average potential energy density of a system of particles with pair interactions, $u = U/V$, is proportional to the square of the particle density.

8.2.1 Example: Virial Coefficient and Radial Distribution Function

An inter-molecular potential takes the form

$$\phi(r) = \begin{cases} \infty & r < a \\ -\varepsilon & a < r < 2a \\ 0 & r > 2a \end{cases}. \tag{8.37}$$

Within the virial expansion the radial distribution function is expanded in powers of the density. We can use Eq. (8.24) to express the density-independent part of the radial distribution function $g_0(r)$,

$$g_0(r) = e^{-\beta\phi(r)}. \tag{8.38}$$

8.3 The Van der Waals Equation of State

Typical inter-atomic potentials can be written as the sum of a short-range repulsive part, $\phi_r(r)$, and an long range attractive part, $\phi_a(r)$,

$$\phi(r) = \phi_r(r) + \phi_a(r), \tag{8.39}$$

so that the partition function becomes

$$Z = \frac{1}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2} \int e^{-\sum_{j>i}\beta[\phi_r(r_{ij})+\phi_a(r_{ij})]}\,\mathrm{d}^3r_1 \cdots \mathrm{d}^3r_N\,. \tag{8.40}$$

Each particle will feel the long range attractive potential from many others and therefore we can write

$$\sum_{j>i}\phi_a(r_{ij}) = \frac{1}{2}\sum_{j\neq i}\sum_i \phi_a(r_{ij}) \simeq \frac{N(N-1)}{2}\frac{1}{V}\int \phi_a(r)\,\mathrm{d}^3r \simeq -\frac{aN^2}{V}, \tag{8.41}$$

where

$$a = -\frac{1}{2}\int \phi_a(r)\,\mathrm{d}^3 r\,. \tag{8.42}$$

The effect of the short range repulsive part is to exclude the particles from a volume around each of them, and so we can write

$$\int e^{-\sum_{j>i}\beta\phi_r(r_{ij})}\,\mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N \simeq (V - Nb)^N. \tag{8.43}$$

We now have

$$Z \simeq \frac{1}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2}(V - Nb)^N e^{\beta a N^2/V}. \tag{8.44}$$

Calculating the Helmholtz free energy we obtain

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln\left[\frac{1}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2}\right] - k_B T \ln(V - Nb) - \frac{aN^2}{V}. \end{aligned} \tag{8.45}$$

The pressure is given by

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V - Nb}\frac{aN^2}{V^2}, \tag{8.46}$$

which is the van der Waals equation of state. The second virial coefficient of a van der Waals gas is $B_2^{\mathrm{VdW}} = b - a/k_B T$, and the Boyle temperature is $k_B T_B^{\mathrm{VdW}} = a/b$. One of the advantages of this derivation is that we have the full partition function, from which we can calculate all equilibrium thermodynamic information. As we know, the van der Waals equation of state contains a description of a liquid-vapour transition, although it is a rather poor one.

The constant a captures the effect of the attractive interaction at large distances. We see that its role is to reduce the pressure of the gas. The reduction in pressure is proportional to the density squared because this is, in turn, proportional to the number of *pairs* of particles which feel the attractive force. In contrast, b arises due to the hard-core repulsion in the potential. Its effect is the reduce the effective volume of the gas because of the space taken up by the particles.

Chapter 9

Phase Equilibria and Transitions

A phase transition is the occurrence of an abrupt change in the physical properties of a system when a thermodynamic variable, such as the temperature or pressure, is changed by a small amount. In Section 2.4 we have examined the coexistence and transitions between the three basic phases of a pure substance: gas, liquid and solid. Fig. 2.10 gives an example of what is called the *phase diagram*, or a map that shows where the different phases occur. In that particular case, the map was drawn in the variables p, T where the transition between the gas and the liquid was a sharp line, in contrast with the same transition represented in p, Vvariables in Fig. 2.9 where we find a broad region of coexistence (along V) for any fixed p and T.

As explained in thermodynamics, with changing thermodynamic parameters such as temperature, pressure, etc., the system can undergo phase transitions. In the first-order phase transitions, the chemical potentials μ of the two competing phases become equal at the phase transition line, while on each side of this line they are unequal and only one of the phases is thermodynamically stable. The first-order transition is switching between two different phases (as, for instance, between water and ice in Fig. 2.10) and is thus abrupt. To the contrast, second-order transitions are gradual: The so-called order parameter continuously grows from zero as the phase-transition line is crossed. Thermodynamic quantities are singular at second-order transitions

Phase transitions are complicated phenomena that arise due to interaction between particles in many-particle systems in the thermodynamic limit $N \to \infty$. It can be shown that thermodynamic quantities of finite systems are non-singular and, in particular, there are no second-order phase transitions. Including systems with interaction demands use of the familiar grand canonical ensemble, where one has to calculate partition functions over the energy levels of the whole system that, in general, depend on the interaction. In some cases these energy levels are known exactly but they are parametrized by many quantum numbers over which summation has to be carried out. In most of the cases, however, the energy levels are not known analytically and their calculation is a huge quantum-mechanical problem. In both cases calculation of the partition function is a very serious task. There are some models for which thermodynamic quantities had been calculated exactly, including models that possess second-order phase transitions. For other models, approximate numerical methods had been developed that allow calculating phase transition temperatures and critical indices. It was shown that there are no phase transitions in one-dimensional systems with short-range interactions.

System	Order Parameter
Fluid	Density difference $n_l - n_g$
Binary mixture	Concentration difference $\phi = c - c_X$
Nematic liquid crystal	Degree of alignment $\frac{1}{2}\langle 3\cos^2\theta - 1\rangle$
Ferromagnet	Magnetisation $\mathbf{M}$
Ferroelectric	Polarisation $\mathbf{P}$
Superconductor	Complex field ψ, which relates to
	the density of super-electrons $n_s = \lvert\psi\rvert^2$

Table 9.1: Examples of systems with phase transitions and their order parameters.

9.1 Examples of Phase Transitions

Earlier we have already met another example of a phase transition, namely Bose-Einstein condensation. Further examples are the ferromagnetic/paramagnetic phase transition in magnetic materials and the separation of components from a homogeneous mixture. Both examples will be discussed below. A more subtle example is the superconducting phase transition in metals. Phases must be distinguished by an order parameter. The idea is to identify a macroscopic quantity which changes abruptly at the phase transition. Some examples of order parameters are given in Table 9.1.

9.1.1 Magnetism and the Ising Model

Consider N spins, σ_i, which can either point up ($\sigma = 1$) or down ($\sigma = -1$), arranged on a one-, two-, or three-dimensional lattice. The energy (Hamiltonian) for this model is

$$H = -m_0 B \sum_i^N \sigma_i - J \sum_{ij,nn} \sigma_i \sigma_j, \tag{9.1}$$

where B is an external magnetic field, m_0 is the magnetic moment of the spin, J is the interaction energy between nearest-neighbour spins, and $\sum_{ij,nn}$ means the sum over all pairs of spins which are nearest neighbours. $J > 0$ favours parallel spins and can lead to the phenomenon of *spontaneous magnetisation*, that is, a non-zero magnetisation, M, which occurs even when $B = 0$, due to the potential energy of interaction between the spins. At $T = 0$ we expect all the spins to be aligned. If the temperature is increased we expect the spins to become progressively more disordered, so that M will decrease. At this stage one can raise the objection that if $B = 0$ then for each configuration of the spins there is another configuration of equal energy in which the direction of every spin is reversed. These two states are of equal energy and have equal weight in the partition function, and therefore the average magnetisation must be zero. This is correct, but at low temperatures the system is likely to be stuck with a net magnetisation of either $+M$ or $-M$, and it is extremely unlikely to jump between the two equivalent macrostates because of the

high energy barrier between them. Spontaneous magnetisation is observed in real systems.

The Ising model of Eq. (9.1) has been solved analytically for spins in one-dimension (by Ernst Ising) and in two-dimensions (a mathematical tour de force by Lars Onsager). The three-dimensional model has not been solved analytically although accurate numerical results have been obtained.

9.1.1.1 Ising Model in 1D

For a one-dimensional chain of interacting spins and with $B = 0$ it is straightforward to evaluate the partition function. We do it here for the enthusiasts, but this indented section is not essential for the rest of the course and it is not examinable:

Using periodic boundary conditions (where the $N + 1$ spin is the first spin), we have

$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} \exp\left[\beta J \sum_{ij,nn} \sigma_i \sigma_j\right] = \sum_{\{\sigma_i\}} \exp\left[\beta J \sum_{i=1}^{N} \sigma_i \sigma_{i+1}\right] \\ &= \left(\sum_{X=\pm 1} \exp\left[\beta J X\right]\right)^N \\ &= \left[2\cosh(\beta J)\right]^N. \end{aligned} \tag{9.2}$$

This relies on the fact that the sum in the exponent can be reduced to a sum over a single index, $X = \pm 1$ depending whether the two neighbours are parallel or antiparallel. Unfortunately this trick doesn't work in higher dimensions. In the presence of external field the calculation is a little more difficult, and we simply quote the result originally obtained by Ernst Ising in 1925:

$$Z = \left[e^{\beta J}\cosh(\beta m_0 B) + \sqrt{e^{-2\beta J} + e^{2\beta J}\sinh^2(\beta m_0 B)}\right]^N. \tag{9.3}$$

The free energy $F(T, N, B) = -k_B T \ln Z$ and the macroscopic magnetisation is given by

$$M = -\left(\frac{\partial F}{\partial B}\right)_{T,N} = \frac{N m_0 \sinh(m_0 B/k_B T)}{\sqrt{e^{-4J/k_B T} + \sinh^2(m_0 B/k_B T)}}. \tag{9.4}$$

For $T = 0$, $M = N m_0$, as expected, but as $B \to 0$, for any $T > 0$, Eq. (9.4) gives $M = 0$.

The one-dimensional Ising model shows a phase transition, but only at the exact $T = 0$. The reason for this is that it costs very little energy to reverse the direction

of a large block of spins on a line. For dimensions greater than one, the Ising model shows a real phase transition as $B \to 0$ at a temperature proportional to J, into a ferromagnetic phase with non-zero magnetisation, while the high-temperature disordered paramagnetic phase has $M = 0$. When $B \neq 0$, the equilibrium value of M is finite and varies smoothly with temperature, and therefore no phase transition occurs.

9.1.1.2 The Ising Model within Mean Field Theory

While a rigorous solution of the problem of phase transition is very difficult, there is a simple approximate solution that captures the physics of phase transitions as described above and provides qualitatively correct results in most cases, including three-dimensional systems. The idea of this approximate solution is to reduce the original many-spin problem to an effective self-consistent one-spin problem by considering one spin (say i) and replacing other spins in the interaction by their average thermodynamic values.

We now solve the Ising model within a *mean field approximation* known in this case as the Weiss theory. The idea is to focus on a particular spin and assume that the interactions with the other spins can be represented by their average effect. This particular spin is then $\sigma_i = \langle\sigma\rangle + \delta\sigma_i$ and we assume the fluctuation is small. Now let's replace the pair-interaction term in the Hamiltonian of Eq. (9.1):

$$\begin{aligned} H &= -m_0 B \sum_i^N \sigma_i - J \sum_{ij} (\langle\sigma\rangle + \delta\sigma_i)(\langle\sigma\rangle + \delta\sigma_j) \\ &= -m_0 B \sum_i^N \sigma_i - J \sum_{ij} \Big(\langle\sigma\rangle^2 + \langle\sigma\rangle (\delta\sigma_i + \delta\sigma_j) + \delta\sigma_i \delta\sigma_j \Big). \end{aligned} \tag{9.5}$$

Now drop the small term quadratic in fluctuations, and assume that fluctuations are site-independent:

$$\begin{aligned} H &= -m_0 B \sum_i^N \sigma_i - J \sum_{ij} \Big(\langle\sigma\rangle^2 + 2 \langle\sigma\rangle \delta\sigma_i \Big) \\ &= -m_0 B \sum_i^N \sigma_i - \frac{1}{2} z J \sum_i \Big(\langle\sigma\rangle^2 + 2 \langle\sigma\rangle [\sigma_i - \langle\sigma\rangle] \Big), \end{aligned} \tag{9.6}$$

where z, the coordination number, is the number of nearest neighbours and the $\frac{1}{2}$ prefactor avoids double-counting, since each bond participates in two spins. Thus we now have an *effective Hamiltonian* which is linear in the variable σ_i, that is, a single-particle two-state system which we certainly know how to solve!

$$H_{\text{eff}} = \frac{1}{2} z J N \langle\sigma\rangle^2 - \Big(m_0 B z J \langle\sigma\rangle \Big) \sum_i \sigma_i. \tag{9.7}$$

The partition function for a spin is easily evaluated, just like in the case of paramagnetic salt, Eq. (3.69). The only difference is that the external field value is "shifted" by the term representing the mean effect of pair interactions.

$$\begin{aligned} Z_1 &= \sum_{\sigma=\pm 1} \exp\left[-\frac{zJ\langle\sigma\rangle^2}{2k_BT} - \frac{m_0B\sigma + zJ\sigma\langle\sigma\rangle}{k_BT}\right] \\ &= 2\cosh\left[\frac{m_0B\sigma + zJ\langle\sigma\rangle}{k_BT}\right] e^{-\frac{1}{2}\beta zJ\langle\sigma\rangle^2}. \end{aligned} \tag{9.8}$$

Note that we carry through the constant term in Eq. (9.7); this is not needed for now, but will play a role in the next section. The Helmholtz free energy per spin is

$$F_1 = -k_BT\ln\left(2\cosh\left[\frac{m_0B\sigma + zJ\langle\sigma\rangle}{k_BT}\right]\right) + \frac{1}{2}J\langle\sigma\rangle^2. \tag{9.9}$$

The mean magnetic moment per spin (which is related to the mean value of spin) we obtain in the usual way:

$$m = m_0\langle\sigma\rangle = -\left(\frac{\partial F_1}{\partial B}\right)_T = m_0\tanh\left(\frac{m_0B + zJ\langle\sigma\rangle}{k_BT}\right). \tag{9.10}$$

Eq. (9.10) is the *self-consistency equation.* This is a transcendental equation, so we cannot solve for $\langle\sigma\rangle$ analytically. However, we can solve for $\langle\sigma\rangle$ graphically by plotting $\langle\sigma\rangle$ and $\tanh\left(\frac{m_0B+zJ\langle\sigma\rangle}{k_BT}\right)$ (for fixed values of T, m_0B, z, and J).

Let's consider the special case of $B = 0$. In Fig. 9.1 we plot $\langle\sigma\rangle$ and $\tanh(zJ\langle\sigma\rangle/k_BT)$ on the same plot for various values of zJ/k_BT. We can graphically see that the solutions are qualitatively different when $zJ/k_BT \leq 1$ and $zJ/k_BT > 1$.[1]These two cases can be understood as follows:

- $zJ/k_BT \leq 1$: There is only one solution: $\langle\sigma\rangle = 0$. This corresponds to the system being in a *paramagnetic* state.
- $zJ/k_BT > 1$: There are three solutions: $\langle\sigma\rangle = 0$ and $\langle\sigma\rangle = \pm\langle\sigma\rangle_0$, where $\langle\sigma\rangle_0 \leq 1$. The $\langle\sigma\rangle = \pm\langle\sigma\rangle_0$ solutions correspond to the system being in a *ferromagnetic* state (the system is magnetised). As we will discuss later, the $\langle\sigma\rangle = 0$ solution turns out to be unstable, so we physically only observe either $\langle\sigma\rangle = +\langle\sigma\rangle_0$ or $\langle\sigma\rangle = -\langle\sigma\rangle_0$ at these temperatures.

[1]We can also reach this conclusion a bit more rigorously by noting that there are three solutions when

$$\left.\frac{\mathrm{d}\tanh\left(\frac{zJ\langle\sigma\rangle}{k_BT}\right)}{\mathrm{d}\langle\sigma\rangle}\right|_{\langle\sigma\rangle=0} > 1, \tag{9.11}$$

and one solution otherwise. Evaluating the derivative gives

$$\left.\frac{\mathrm{d}\tanh\left(\frac{zJ\langle\sigma\rangle}{k_BT}\right)}{\mathrm{d}\langle\sigma\rangle}\right|_{\langle\sigma\rangle=0} = \left[\frac{zJ}{k_BT}\frac{1}{\cosh^2\left(\frac{zJ\langle\sigma\rangle}{k_BT}\right)}\right] = \frac{zJ}{k_BT}, \tag{9.12}$$

so we find that we have three solutions solution when $zJ/k_BT > 1$, and one solution otherwise.

The *critical temperature* T_c below which the system becomes spontaneously magnetised without any external magnetic fields is therefore given by

$$k_B T_c = zJ. \tag{9.13}$$

It should be noted that for the 1D case, mean field theory thus predicts a magnetic phase transition at $k_B T_c = 2J$; however, solving this system exactly we find that there is in fact no phase transition in 1D. Thermal fluctuations turn out to be strong enough to destroy the system's magnetic ordering in 1D, so mean field theory provides a qualitatively incorrect result in this specific case.

As mentioned earlier, mean field theory is more accurate in higher dimensions. For example, for the 2D square lattice, it predicts $k_B T_c = 4J$, whereas solving the system exactly we find that $k_B T_c = 2J/\ln\left(2+\sqrt{2}\right) \approx 2.27J$. Also note that since mean field theory assumes fluctuations are small, it generally overestimates the system's tendency to order and thus overestimates the value of T_c.

To obtain the spontaneous magnetisation we set $B = 0$, which gives

$$\langle\sigma\rangle = \tanh\left(\frac{zJ\langle\sigma\rangle}{k_B T}\right), \tag{9.14}$$

and rearranging the exponentials we obtain

$$\frac{T_c}{T} = \frac{1}{2\langle\sigma\rangle}\ln\left(\frac{1+\langle\sigma\rangle}{1-\langle\sigma\rangle}\right), \tag{9.15}$$

where the shorthand notation $T_c = zJ/k_B$. To find $\langle\sigma\rangle$ as a function of temperature we can substitute values of $\langle\sigma\rangle$ in the right hand side ($0 \leq \langle\sigma\rangle \leq 1$). A plot of $\langle\sigma\rangle$ against T/T_c is given in Fig. 9.2, showing that all the spins are aligned at $T = 0$ but, as the temperature is increased, $\langle\sigma\rangle$ decreases and goes to zero at $T = T_c$, which is the critical temperature.

The exact and mean field results for T_c are compared in Table 9.2. Note that the mean field value depends on the number of nearest neighbours, but is otherwise independent of the dimensionality, which is incorrect. The mean field theory is qualitatively incorrect in one dimension because, we have seen, there is no transition in this case for $T > 0$. Note, however, that the mean field theory becomes more accurate as the dimensionality increases. In spite of its many limitations, the mean field approach has one great advantage: the physical problem can usually be solved, while the exact solution is often impossibly difficult.

9.1.2 Mixing and Phase Separation

An important and generic situation of phase coexistence and separation occurs in the problem of mixing. Let us consider a mixture of just two species, so that the

Fig. 9.1: Solving the self-consistent equation (9.10) graphically for $B = 0$ and various values of zJ/k_BT. The yellow plot is at $T > T_c$, the orange plot is at $T = T_c$, and the dark red bottom plot is at $T < T_c$.

Lattice	Mean field k_BT_c	Exact k_BT_c
One-dimensional line	$2J$	No transition for $T > 0$
Two-dimensional square lattice	$4J$	$0.567 \times 4J$
Three-dimensional simple cubic lattice	$6J$	$0.752 \times 6J$

Table 9.2: Critical temperatures for the Ising model in one, two, and three dimensions.

total number of particles is $N = N_A + N_B$. The entropy of mixing (2.48) has been derived for an arbitrary number of species, now we just have

$$S_{\text{mix}} = -k_B N \sum_i c_i \ln c_i = -k_B N[c_A \ln c_A + (1 - c_A)\ln(1 - c_A)], \tag{9.16}$$

where the concentration (fraction) of species is $c_i = N_i/N = p_i/p$, and for just two components $c_B = 1 - c_A$. If the system is a non-interacting ideal gas, then the discussion of the earlier Section 2.5 applies. An ideal gas of different species will always remain homogeneously mixed, because this maximises the entropy and there is no potential energy to benefit from. When particles of our system interact, then – at least for low particle densities – we can estimate the mean energy in terms of the virial expansion. Limiting ourselves to the pair interactions only, the second virial coefficient contribution to the average potential energy of the system (8.36)

Fig. 9.2: The average value of the spin on a site, $\langle\sigma\rangle$, as a function of T/Tc within the Weiss theory.

now gives for each combination of species:

$$U_{AA} \approx \frac{N_A^2}{V} k_B T B_2(AA), \tag{9.17}$$

$$U_{AB} \approx \frac{N_A N_B}{V} k_B T B_2(AB), \tag{9.18}$$

$$U_{BB} \approx \frac{N_B^2}{V} k_B T B_2(BB), \tag{9.19}$$

where each of the B_2 coefficients corresponds to the interaction of the given pair of species, and the factor of 2 in Eq. (9.18) arises from the distinguishability of species A and B: there is only one way to have an A, A or B, B pair, but there are two A, B pairs, namely $A - B$ and $B - A$.

Using the species concentrations c_A and $c_B = 1 - c_A$, Eqs. (9.17-9.19) can be recast as:

$$U_{AA} \approx N\epsilon_{AA} c_A^2, \tag{9.20}$$

$$U_{AB} \approx 2N\epsilon_{AB} c_A (1 - c_A), \tag{9.21}$$

$$U_{BB} \approx N\epsilon_{BB} (1 - c_A)^2, \tag{9.22}$$

where each energy coefficient ϵ_{ij} is related to the corresponding virial coefficient by $\epsilon_{ij} = k_B T B_2(ij)/v_0$ for a molecular volume v_0. The ϵ_{ij} are more straighforwardly interpreted in terms of a bond energy E_{ij} and coordination number z, so that $\epsilon_{ij} = z2E_{ij}$. In this picture, Nc_A A-particles now each have zc_A A-type neighbours. We therefore have in total $Nzc_A^2/2$ A-A bonds (divide by two to avoid double-counting), each with energy E_{AA}, leading to Eq. (9.20) and, likewise, the other two internal energy expressions above. We find for the internal energy of the mixture:

$$U_{\text{int}} = U_{AA} + U_{AB} + U_{BB} = N\Big[\epsilon_{AA} c_A^2 + 2\epsilon_{AB} c_A (1 - c_A) + \epsilon_{BB} (1 - c_A)^2\Big]. \tag{9.23}$$

A negative ϵ_{ij} means an effective attraction between molecules of species "i" and "j", so that the corresponding contribution to the overall potential energy is

less than the non-interacting ideal-gas value of zero; positive ϵ_{ij} means an effective repulsion and the increase in energy. What is being done here is a "mean field" approximation, that is, the average field (concentration of monomers in this case) is being used instead of the spatially dependent value of concentration.

The energy of the un-mixed (or phase-separated) state is also non-zero. Putting all the species "A" to one side, each A-particle now has z A-neighbours, giving in total $zNc_A/2$ A-A bonds and an interaction energy $U_{AA} = N\epsilon_{AA}c_A$, and similar for the species "B". Neglecting the energy of the interface between separated species, we have:

$$U_{\text{unmixed}} = N[\epsilon_{AA}c_A + \epsilon_{BB}(1 - c_A)]. \tag{9.24}$$

If we subtract the energy of the unmixed state from Eq. (9.23), and pull out the common concentration-dependent factor, we get the average internal energy of mixing:

$$\begin{aligned} U_{\text{mix}} = U_{\text{int}} - U_{\text{unmixed}} &= N[2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})]c_A(1 - c_A) \\ &\equiv Nk_BT\chi c_A(1 - c_A), \end{aligned} \tag{9.25}$$

where the shorthand non-dimensional parameter χ is defined as a measure of the average interaction energy, $k_BT\chi = [2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})]$, or

$$\chi = \frac{1}{k_BT}[2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}]. \tag{9.26}$$

A positive ϵ_{AB} (i.e. species "A" and "B" repelling each other) and negative ϵ_{AA}, ϵ_{BB} (each species attracting their like) would result in a large and positive parameter χ, leading to the trend for the two species to separate from each other. Evidently, the opposite case of small, or even negative χ would promote mixing of species. Combining the mixing entropy and energy terms leads to the free energy for the mixture (or solution of concentration $c_A = N_A/N \equiv c$), expressed in its proper variables T, V, N (Fig. 9.3):

$$F_{\text{mix}} = Nk_BT[c\ln c + (1 - c)\ln(1 - c) + \chi c(1 - c)]. \tag{9.27}$$

9.1.2.1 Spinodal and Binodal Lines

Fig 9.3 tells us the answer to an attempt to find a minimum of the free energy of mixing. Differentiating w.r.t. concentration gives

$$\frac{\partial F_{\text{mix}}}{\partial c} = \chi(1 - 2c) - \ln\left(\frac{1 - c}{c}\right) = 0. \tag{9.28}$$

This equation is difficult to solve analytically, but we can see from the plot of free energy that it should have one solution, at $c = 1/2$ for small and negative χ (when we expect the good mixing of species), and three roots at large and positive χ (when

Fig. 9.3: Plots of the free energy of mixing (9.27) for different values of the χ-parameter. The figure illustrates that the mixture for $\chi = 3$ is energetically unfavourable compared to the fully phase separated arrangement, whereas for small χ values (higher temperatures), it is favourable for the two species to remain fully mixed

we might expect demixing to occur), one of which (at $c = 1/2$) is now the maximum. The line of solutions for the minimum of the mixing free energy, $c^*(\chi)$, is called the binodal line and is plotted in Fig. 9.4 as the function $\chi(c^*)$.

The stability of the mixture at concentration c against small fluctuations is given by the sign of second derivative:

$$\frac{\partial^2 F_{\text{mix}}}{\partial c^2} = \frac{1}{(1-c)c} - 2\chi. \tag{9.29}$$

The set of inflection points given by the solution of $\partial^2 F_{\text{mix}}/\partial c^2 = 0$ is called the spinodal line, $c_s(\chi)$. It represents the boundary of stability and is plotted in Fig. 9.4 as a dashed line for $\chi(c_s)$.

The plot of $\chi(c)$ in Fig. 9.4 is the phase diagram that maps the regions of different behaviour. Below the binodal line, at any concentration the mixture is stable: the mixing free energy is convex at any value of c. Above the spinodal line, the values of c and χ are such that the mixture is absolutely unstable and its components separate immediately. The region between the two lines is more complicated, it is the region of *metastability* where one of the phases (mixed or separated) may have a higher free energy than the other, but is prevented from reaching the ground state by an energy barrier; we shall discuss this feature of *first order* phase transitions shortly. Fig. 9.4 also highlights the *critical point* where the region of metastability shrinks to zero as its two boundaries coincide. It is easy to find the coordinates of

Fig. 9.4: [Left] The sketch of $F_{\rm mix}(c)$ illustrating stability of the mixture against separation of species. In the convex ($F'' > 0$) region, at any concentration c, any small fluctuation leading to two nearby regions $c \pm \Delta c$ leads to the overall free energy increase. A similar fluctuation in the concave ($F'' < 0$) region leads to the decrease of free energy on any small fluctuation and, therefore, instability of the mixture against macroscopic separation. The boundary of stability (labelled by χ on this sketch) gives the spinodal line on the phase diagram. [Right] Plots of the binodal and spinodal lines, as $\chi(c)$ variation.

this critical point, from Eq. (9.29) we can find the minimum of the spinodal line:

$$\chi_s = \frac{1}{2c(1-c)} \quad \text{hence} \quad \frac{\partial \chi_s}{\partial c} = \frac{2c-1}{2c^2(1-c)^2} = 0. \tag{9.30}$$

This gives the critical point at $c_0 = 1/2$ and $\chi_0 = 2$, as seen on the plot.

The conclusion is that the least stable mixture is at concentration $c = 1/2$ (this is obtained assuming that the molecular size of both species was approximately the same, v_0, otherwise there would be corrections to the above analysis). This mixture has to separate at the lowest value of the effective (repulsive) interaction χ.

Since χ is inversely proportional to temperature, the phase diagram can be replotted in more accessible coordinates T, c (see Fig. 9.5). Suppose we prepare a good mixture, at some concentration c_A and temperature T_A (in the stable region of phase diagram). The easiest way to change the balance between the mixing entropy and potential energy is by reducing the temperature: this corresponds to the point A' on the phase diagram in Fig. 9.5. This is the absolutely unstable region, corresponding to the convex region on the corresponding high-χ curve for $F_{\rm mix}(c)$ in Fig. 9.3, so the mixture will separate (at constant temperature) into the two regions, each rich in one of the two species. The final state will be given by the minima of the free energy for the value χ that corresponds to this temperature $T_{A'}$.

Fig. 9.5: The phase diagram of a mixture plotted in T, c coordinates, with the binodal, spinodal and critical point labelled. An initial mixture, prepared at concentration c_A at temperature T_A, after cooling to a temperature inside the demixing region (point A' on the diagram) will phase separate into the fractions, one rich in "1" (high c) and one rich in "2" (low c) minima of the mixing free energy.

9.2 First Order Phase Transition

Let us consider the process of quenching and demixing analytically. We start with a system at equilibrium at concentration c_X (see Fig. 9.5) and allow the concentration to fluctuate, so that a value $c = c_X + \phi$ is reached. Before going further, we need to consider a subtlety about the free energy of the mixture. It would seem at first that an arbitrary concentration away from $c = 0.5$ could never be present in equilibrium, because the slope of the free energy versus concentration in Fig. 9.3 is nonzero for most values of c. In contrast to, for instance, the case of ferromagnetism, in which magnetic moments can flip and thereby convert from one type to another, the total number of A and B particles is still conserved as the system finds stable equilibrium. To consider the practically relevant case when in the mixture the concentration of species A is fixed at some value $c_X \neq 0.5$, we need to implement a constraint on c by using a Lagrange multiplier α, defining a modified free energy $F_\alpha(c,T) = F_{\rm mix}(c,T) - \alpha c$ such that $\partial F_\alpha/\partial c\,|_{c_X} = 0$, i.e. $\alpha = \partial F_{\rm mix}/\partial c\,|_{c_X}$ and the free energy, thus transformed, becomes $F_{c_X}(c,T) = F_{\rm mix}(c,T) - \partial F_{\rm mix}/\partial c\,|_{c_X}$. This means that a straight line is subtracted from the mixing free energy shown in Fig. 9.3 to produce zero slope at the concentration dictated by the external constraint, namely by the amount of the species actually put into the mixture. This is the free energy we would need to consider when analysing phase separation in a mixture with arbitrary starting concentrations.

Assuming ϕ is small we can expand Eq. (9.27) and obtain

$$\frac{F_{c_X}(c) - F_{c_X}(c_X)}{Nk_BT} = -\frac{1-2\chi c_X(1-c_X)}{2c_X(1-c_X)}\phi^2 - \frac{1-2c_X}{6c_X^2(1-c_X)^2}\phi^3 + \frac{1-3c_X+3c_X^2}{12c_X^3(1-c_X)^3}\phi^4 + \cdots . \tag{9.31}$$

Note that the linear term $\propto \phi = c = c_X$ has disappeared due to the equilibrium condition mentioned above. Fig. 9.6 plots this free energy difference as function

of ϕ for an arbitrary $c_X = 0.4$ and several values of χ-parameter, starting from the critical point value $\chi = 2$ upwards. You can see how on increasing χ (or equivalently – decreasing temperature) we pass through the region of metastability. At first, it is clear that any fluctuation $\phi \neq 0$ increases the free energy and is therefore unfavourable. Starting from $\chi \geq 2.02$ we see a new minimum developing; this corresponds to crossing the binodal line on the phase diagram. Eventually there is a point ($\chi \approx 2.035$ for the chosen c_X value) when there is a new free energy minimum at a finite ϕ^*; this curve is highlighted. However, there is an energy barrier separating this new state of increased c from the original c_X. The barrier persists even when the new "A"-rich state has a significant preference in free energy, preventing the actual separation. Only at a substantially higher χ the barrier finally disappears and the state $\phi = 0$ (or the initial c_X) becomes absolutely unstable: this corresponds to crossing the spinodal line. At higher χ (or lower T) the mixture immediately separates into the "A"-rich state (and the associated "A" poor state, to conserve the total number of particles). When this happens, the concentration changes discontinuously, with a jump from $\phi = 0$ to $\phi = \phi^*$. This scenario is the essence of the *First order phase transitions*, the other example familiar to you is the liquid-gas transformation.

Fig. 9.6: : [Left] The change in the free energy, $\Delta F = F_{\text{mix}}(c) - F_{\text{mix}}(c_X)$ plotted against the fluctuation amplitude $\phi = c - c_X$ for several values of χ-parameter above the critical point. [Right] The values of $\Delta F(\phi)$ at the point of minimum $\phi = \phi^*$, as function of χ or T, showing the region of coexistence with the mixed state $\phi = 0$, $\Delta F = 0$.

What happens at the critical point? If the starting concentration c_X was chosen at the exact value $c_X = c_0 = 1/2$, then on cooling the mixture (or on increasing χ) we will cross the critical point on the phase diagram. In that case Eq. (9.31) takes the form which looks much simpler:

$$\frac{F_{c_X}(c) - F_{c_X}(c_X)}{Nk_BT} = (2-\chi)\phi^2 + \frac{4}{3}\phi^4 + \cdots . \tag{9.32}$$

The new, phase-separated value ϕ^* now emerges in a continuous manner, which is easy to obtain by minimisation, $\partial \Delta F / \partial \phi = 0$ gives

$$\phi^* = \sqrt{\frac{3}{8}(\chi - 2)}. \tag{9.33}$$

9.2.0.1 General Classification of Phase Transitions

Fig. 2.8 shows the Gibbs free energies of liquid and vapour phases, same as Fig. 9.6 showed the free energies of the mixed and phase-separating states. At the transition the free energy of the equilibrium (that is, lowest in energy) phase has a discontinuity in its first derivative. From the thermodynamic relation, e.g. for the Gibbs free energy,

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \tag{9.34}$$

we see that the entropy is discontinuous at the transition, and there is a latent heat, $L = T\Delta S$. In Ehrenfest's classification scheme, phase transitions were labelled by the lowest derivative of the free energy which is discontinuous at the transition. Under this classification scheme the transitions shown in Figs. 2.8 and 9.6 are *first order* transitions. A second order transition has a discontinuity in the second derivative of the free energy, for example, the liquid/vapour transition or demixing phase separation at the critical point. Third and higher order transitions could be similarly defined. However, in a ferromagnet the heat capacity (proportional to the second derivative of the free energy) diverges as $|T_c - T|^{-\alpha}$ at the critical temperature T_c, which means that there are no discontinuities in any of the derivatives of the Gibbs free energy. Unfortunately, this case cannot be classified satisfactorily within Ehrenfest's scheme. In the modern classification phase transitions are divided into just two categories: First-order or *discontinuous* transitions are those which involve a latent heat, while all other transitions are referred to as second order or *continuous* phase transitions. Critical behaviour and *continuous, or second order, phase transitions* are the subject of the rest of this chapter.

9.3 Landau Theory of Phase Transitions

We illustrate the ideas of Landau theory using a simple magnetic system which is essentially equivalent to the Ising model discussed above. In this case the order parameter is the magnetisation M. Near the phase transition the order parameter is small and the idea is to expand the free energy as a power series in the order parameter. Remember, we have done something similar in the problem of mixing, see Eqs. (9.31) and (9.32). Expanding $F(T, M)$ in a Taylor series about $M = 0$, and truncating after a few terms, we have

$$F(T, M) = F_0(T) + \mathcal{A}(T)M + \mathcal{B}(T)M^2 + \mathcal{C}(T)M^3 + \mathcal{D}(T)M^4 + \cdots . \tag{9.35}$$

At this stage we use the symmetry of the system and note that, in the absence of an applied magnetic field, F must be unchanged if we reverse the magnetisation, $M \to -M$. Therefore the coefficients of the odd powers of M must be zero and the free energy reduces to

$$F(T, M) = F_0(T) + \mathcal{B}(T)M^2 + \mathcal{D}(T)M^4. \tag{9.36}$$

This expression, similar to (9.32), determines the thermodynamics of the second-order phase transition within the Landau theory.

The Landau theory is in fact equivalent to the mean field theory in the vicinity of the transition. To demonstrate this we expand the Helmholtz free energy of Eq. (9.9) in powers of m around $m = 0$. If you do this algebra yourself, you will see that the constant term that we kept in that expression now plays an important role in determining the transition point (the change of sign of the Landau coefficient $\mathcal{B}$). We obtain the series expansion:

$$F_1 \simeq -k_B T \ln 2 + \frac{zJ}{2k_B T m_0^2}(k_B T - zJ)m^2 + \frac{1}{12}\frac{(zJ)^4}{(k_B T)^3 m_0^4}m^4, \tag{9.37}$$

which is exactly the form obtained in the Landau theory. To see this, we must realise that in the vicinity of $T = T_c$ only the term in square brackets has any relevant temperature dependence: in all other instances we can reliably replace $k_B T$ with $k_B T_c = zJ$. Then the Landau coefficient $\mathcal{B}(T)$ takes the form $\mathcal{B} = (k_B/2m_0^2)[T - T_c]$, while $\mathcal{D} = k_B T_c/12m_0^4 \approx$ const. Note that the only ingredients required to obtain Eq. (9.36) were a suitable order parameter and the symmetry of the system.

9.3.1 Magnetic Phase transition within Landau Theory

The equilibrium state of the system described by Eq. (9.36) is found by minimising $F(M)$,

$$\left(\frac{\partial F}{\partial M}\right)_T = 2\mathcal{B}(T)M + 4\mathcal{D}(T)M^3 = 0, \tag{9.38}$$

which has three solutions,

$$M_0 = 0 \quad \text{or} \quad M_0 = \pm\sqrt{\frac{-\mathcal{B}}{2\mathcal{D}}}. \tag{9.39}$$

Suppose that $\mathcal{D} > 0$ so that F increases at large M. The behaviour depends on the sign of $\mathcal{B}$, if $\mathcal{B} > 0$ the only solution is $M = 0$, which corresponds to a minimum in F, but if $\mathcal{B} < 0$ there are three solutions, although only the two with $M = \pm\sqrt{-\mathcal{B}/(2\mathcal{D})}$ are minima in F. The phase transition must therefore occur at $\mathcal{B} = 0$.

Expanding $\mathcal{B}(T)$ and $\mathcal{D}(T)$ in powers of $T - T_c$ and truncating after the first term we obtain

$$\mathcal{B}(T) = b(T - T_c), \tag{9.40}$$
$$\mathcal{D}(T) = d, \tag{9.41}$$

where b and d are positive constants. The free energy becomes

$$F(T, M) = F_0(T) + b(T - T_c)M^2 + dM^4, \tag{9.42}$$

Fig. 9.7: The free energy F of a simple magnetic system as a function of magnetisation M when no magnetic field is present, for a value of $T > T_c$ in dark blue and a value of $T < T_c$ in dark red.

which is plotted in Fig. 9.7 for $T < Tc$ and $T > Tc$. The order parameter is continuous at T_c and therefore this is a second order or continuous phase transition. The equilibrium values of M and T are related by

$$M_0(T) = \begin{cases} \pm\sqrt{\dfrac{b}{2d}(T_c - T)} & T < T_c \\ 0 & T > T_c \end{cases}. \tag{9.43}$$

To complete the thermodynamic description, let us find the entropy from the equilibrium free energy $F_{\text{eq}}(T) = F(T, M_0(T))$. Assuming $\mathcal{D}(T)$ is temperature independent, at least near the transition, we have:

$$S = -\left(\frac{\partial F(M_0, T)}{\partial T}\right) = S_0(T) - bM_0(T)^2. \tag{9.44}$$

Using Eq. (9.43) for equilibrium magnetisation we obtain

$$S = \begin{cases} S_0(T) - \dfrac{b^2}{2d}(T_c - T) & T < T_c \\ S_0(T) & T > T_c \end{cases}. \tag{9.45}$$

The entropy is continuous at T_c, but the heat capacity is not; there is a finite jump in heat capacity at T_c:

$$C = T\left(\frac{\partial S}{\partial T}\right)_{B=0} = \begin{cases} C_0(T) + \dfrac{b^2}{2d}T & T < T_c \\ C_0(T) & T > T_c \end{cases}. \tag{9.46}$$

With an applied magnetic field, B, the free energy becomes

$$F(T, M, B) = F_0(T) + b(T - T_c)M^2 + dM^4 - BM. \tag{9.47}$$

Fig. 9.8: The free energy F as a function of magnetisation M with a symmetry-breaking magnetic field $B > 0$, for one value of $T > T_c$, and three values of $T < T_c$.

The $-BM$ term breaks the symmetry between the states with $+M$ and $-M$. The equilibrium state at temperature T is found by minimising $F(T, M, B)$ with respect to M,

$$\left(\frac{\partial F}{\partial M}\right)_{T,B} = 2b(T - T_c)M + 4dM^3 - B = 0. \tag{9.48}$$

Plots of F as a function of M are shown in Fig. 9.8, at fixed T, with a symmetry-breaking magnetic field $B > 0$. For $T > T_c$ a single minimum exists with small positive M, while for $T < T_c$ there are two unequal minima, a deeper one at a positive value of M and a shallower one at a negative value. There is an analytic expression for the roots of a cubic equation such as Eq. (9.48), but it is a bit messy. However, if we restrict ourselves to the region close to T_c with B extremely small we can neglect the M_3 term, so that

$$M = \frac{B}{2b(T - T_c)} \tag{9.49}$$

The phase diagram is shown in Fig. 9.7. If we start with a magnetic field $B < 0$ and follow the path labelled 1 where $T < T_c$ then, as the system passes through $B = 0$, the equilibrium value of the magnetisation flips from a negative value to an equal and opposite positive value. At this phase transition the order parameter changes discontinuously and, although there is no latent heat, we classify it as a first order phase transition. Landau conceived his theory for continuous phase transitions, but it can also be applied to many discontinuous ones. If we set $B = 0$ and increase the temperature from below T_c, following path 2, then a second order continuous phase transition occurs at the critical point where $T = T_c$.

Landau conceived his theory for continuous phase transitions, but it can also be applied to many discontinuous, first-order transitions - the example of such analysis was shown in the problem of mixing and phase separation. In general, the Landau expansion of the free energy in powers of the appropriate order parameter, such as (9.35), can always be done (although its accuracy depends on how small the

Fig. 9.9: Phase diagram for a simple magnetic system.

order parameter is near the transition: that's why Landau has originally developed this approach for the continuous transitions). In ferromagnetic system, with the order parameter being a vector $\mathbf{M}$, the symmetry has excluded odd-power terms in the expansion, leading to Eq. (9.36). However, in a different system symmetry this might not be the case, e.g. the concentration difference ϕ is a scalar and we had a cubic term present in Eq. (9.31), except at an isolated critical point. The same would apply to the (scalar) density in a liquid-gas transition, or a degree of alignment in a nematic liquid crystal. All these are first-order transition systems, which could be generically described by the Landau expansion

$$F(T,\phi) = F_0(T) + b(T-T_c)\phi^2 - c\phi^3 + d\phi^4, \tag{9.50}$$

where ϕ is the order parameter corresponding in a given system ($\phi = 0$ in the high-temperature phase), and we followed the assumption (9.40) that only the leading square-power term has a relevant temperature dependence. The discussion of the resulting transition is essentially that we have already had at the end of Subsection 9.1.2.

9.3.2 Example: Liquid Crystal

The order parameter for a fluid of rod shaped molecules is their degree of alignment, Q, with $Q = 0$ corresponding to a disordered fluid, and $Q \neq 0$ corresponding to a nematic liquid crystal. The free energy can be written as

$$F(Q,T) = a(T-T_c)Q^2 - bQ^3 + cQ^4, \tag{9.51}$$

where a, b, c and T_c are positive constants. This system shows a first order phase transition, at a temperature T^*, between two states with $Q = 0$ and $Q = Q^*$.

The free energy expansion suggests the 1st order transition since the cubic term is present. The first step is to identify free energy minima:

$$\begin{aligned}\frac{\partial F}{\partial Q} &= 2a(T-T_c)Q - 3bQ^2 + 4cQ^3 \\ &= \left[2a(T-T_c) - 3bQ + 4cQ^2\right]Q = 0.\end{aligned} \tag{9.52}$$

The disordered phase corresponds to $Q = 0$, $F = 0$. The condition that the free energies of the ordered and disordered phases are equal at the transition point $T = T^*$ leads to

$$a(T^* - T_c) - bQ^* + cQ^{*2} = 0. \tag{9.53}$$

The condition that the free energy is stationary (i.e. has a minimum at Q^*) leads to

$$2a(T^* - T_c) - 3bQ^* + 4cQ^{*2}0. \tag{9.54}$$

Solving these equations for Q^* and T^* leads to

$$Q^* = \frac{b}{2c} \qquad \text{the jump of the order parameter} \tag{9.55}$$

$$T^* = T_c + \frac{b^2}{4ac} \qquad \text{point of equilibrium transition} \tag{9.56}$$

The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_Q = -aQ^2. \tag{9.57}$$

You might be concerned that $Q = Q(T)$ itself, so why is there only the partial derivative here? The full expression is, of course, $S = (\frac{\partial F}{\partial T})_{V,N} = (\partial F/\partial T)_Q + (\partial F/\partial Q)(\partial Q/\partial T)$. But the derivative $(\partial F/\partial Q) = 0$ in equilibrium, so the second (unpleasant) term drops out always.

For the disordered phase $S = 0$, while for the ordered phase $S = -ab^2/4c^2$, and therefore the latent heat of this phase transition is

$$L = T^*\Delta S = -\left(T_c + \frac{b^2}{4ac}\right)\frac{ab^2}{4c^2}. \tag{9.58}$$

The entropy of the ordered state is negative, but this should not worry us as there will be other contributions to the entropy which will ensure that the total entropy is positive. The fact that the jump in entropy is negative on entering the more ordered phase is, on the other hand, a natural expectation: the extra heat is released from the system (in contrast to requiring the heat, and thus cooling the vicinity environment, on entering the high-temperature disordered phase).

9.3.3 Example: Coupled Order Parameters

The free energy of a ferroelectric crystal can be written as

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6 + D\varepsilon P^2 + E\varepsilon^2, \tag{9.59}$$

where P is the polarisation of the crystal and ε is the elastic strain. The coupling εP^2 can be found in most materials (in contrast to the linear "piezoelectric" coupling εP that requires polar symmetry breaking). In spite of the even-power expansion

required to make the scalar energy out of the vector P, the crystal will undergo a first order phase transition when $D^2/4E > b$.

It looks like the free energy expansion in powers of P is in even powers only, i.e. there is no cubic term and thus one expects the second-order transition. However, this depends on the sign of the coefficient of the 4th-order term. If this coefficient is positive then, in fact, we don't need the 6th-order term at all because at small $P \ll 1$ (which is the basis for the Landau series expansion) $bP^4 \gg cP^6$ and they both have the similar qualitative effect of increasing F at higher P.

Since we now have the free energy a function of two variables, but are only interested in one (the transition in P), we should equilibrate this microstate in the ε variable. That is:

$$\frac{\partial F}{\partial \varepsilon} = DP^2 + 2E\varepsilon = 0 \quad \text{so} \quad \varepsilon^* = -\frac{DP^2}{2E}. \tag{9.60}$$

Now let's write the effective free energy

$$F(P, \varepsilon^*) = \alpha(T - T_c)P^2 + bP^4 + cP^6 - \frac{D^2P^4}{4E} \tag{9.61}$$

(note that the renormalisation is always negative: the "best" configuration $\varepsilon^*(P)$ will surely lower the free energy of this microstate with respect to zero when both $\varepsilon = 0$, $P = 0$).

Fig. 9.10: Caption

If the 4th order coefficient $(b - D^2/4E)$ is negative, the first order transition may occur depending on the relative magnitude of parameters. The plot in Fig. 9.10 (made at $b = -3$, $c = 3$, a= 1) illustrates the point: the solution is symmetric for $\pm P$ (as expected for even-power series), but has all the features of the ordinary 1st order transition.

The analysis follows the standard steps: first identify free energy minima:

$$\frac{\partial F}{\partial P} = 0 \quad \text{so} \quad \Big[2a(T - T_c) - 4b\Big|b - D^2/4E\Big|P^2 + 6cP^4\Big]P = 0 \tag{9.62}$$

(taking the renormalised 4th order coefficient to be explicitly negative). The disordered phase corresponds to $P = 0$, $F = 0$, as always. Solving the bi-quadratic equation gives

$$P^2 = \frac{b \pm \sqrt{(b - D^2/4E)^2 - 3ac(T - T_c)}}{3c}, \tag{9.63}$$

so the beginning of hysteresis region is when $(b - D^2/4E)^2 - 3ac(T - T_c) = 0$ or at $T_B = T_c + (b - D^2/4E)^2/3ac$.

At the thermodynamic equilibrium transition point $T = T^*$ the free energies of the ordered and disordered phases are equal, so

$$a(T^* - T_c) - \left|b - D^2/4E\right| P^{*2} + cP^{*4} = 0. \tag{9.64}$$

Solving this, together with the $\frac{\partial F}{\partial P}$ equation, for P^* and T^* leads to

$$P^* = \pm\sqrt{\frac{|b - D^2/4E|}{2c}} \qquad \text{the jump of the order parameter} \tag{9.65}$$

$$T^* = T_c + \frac{(b - D^2/4E)^2}{4ac} \qquad \text{equilibrium transition point.} \tag{9.66}$$

The entropy is, as in Eq. (9.57) in the previous example 9.3.2, $S = -aP^2$. For the disordered phase $S = 0$, while for the ordered phase $S = -ab/2c$ and therefore the latent heat of this transition is

$$L = T^*\Delta S = -\left(T_c + \frac{(b - D^2/4E)^2}{4ac}\right)\frac{ab}{2c}. \tag{9.67}$$

9.4 Critical Exponents and Universality

Continuous phase transitions are easier to study than first-order transitions due to the absence of latent heat, and they have been discovered to have many interesting properties. The phenomena associated with continuous phase transitions are called critical phenomena, due to their association with critical points. Returning back to the case of ferromagnetic transition, let us define the magnetic susceptibility:

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{B\to 0}. \tag{9.68}$$

We can calculate χ from differentiating Eq. (9.48), which gives

$$\chi = \frac{1}{2b(T - T_c) + 12dM^2}. \tag{9.69}$$

We should treat the cases $T > T_c$ and $T < T_c$ separately because M, which is given by Eq. (9.43), is different in the two cases. For $B \to 0$ and $T > T_c$, we obtain

$$\chi_+ = \frac{1}{2b(T - T_c)}, \tag{9.70}$$

	β	γ	δ
Landau Theory	1/2	1	3
Two-dimensional Ising model	1/8	7/4	15
Three-dimensional Ising model	0.33	1.24	4.77
Three-dimensional ferromagnets	0.30-0.36	1.24-1.4	4.2-4.8

Table 9.3: Values of critical exponents within mean field theory, for the two- and three-dimensional Ising model, and experimental values for three-dimensional ferromagnets.

which is the Curie-Weiss law, while for $B \to 0$ and $T < T_c$,

$$\chi_- = \frac{1}{4b(T_c - T)}. \tag{9.71}$$

Also, if we set $T = T_c$ in Eq. (9.48), we obtain at the critical point:

$$B = 4dM^3. \tag{9.72}$$

Let us write

$$M \propto (T_c - T)^\beta \qquad T < T_c, B = 0 \tag{9.73}$$

$$\chi \propto |T - T_c|^{-\gamma} \qquad B \to 0 \tag{9.74}$$

$$B \propto M^\delta \qquad T = T_c. \tag{9.75}$$

The numbers β, γ, and δ are examples of critical exponents where, for the simple magnetic system, Landau theory predicts

$$\beta = 1/2; \quad \gamma = 1; \quad \delta = 3. \tag{9.76}$$

It turns out that Landau theory predicts these values to be *universal*, that is, the same for all phase transitions, irrespective of underlying physical interactions. Unfortunately the critical exponents for real systems don't always take these values! Some values of critical exponents are given in Table 9.3.

Experimental and theoretical investigations have led to the idea that very different physical systems show precisely the same values of the critical exponents, in which case they are said to belong to the same *universality class*. Three factors determine the universality class:

1. the dimensionality of the physical space;
2. the number of components in the order parameter;
3. whether the interaction is short ranged or long ranged.

For example, in the Ising model, the order parameter has one component and the interaction is short ranged.

Landau theory is not adequate for describing the precise detail of critical behaviour that occurs close to a continuous phase transition. Landau theory assumes that the free energy can be expanded about the transition point in a power series in the order parameter, but this assumption is actually invalid at $T = T_c$ because the free energy is *singular* at a continuous phase transition. Crucially, Landau theory ignores *fluctuations in the order parameter*. To understand what this means, think about the Weiss theory in which each spin feels the average effect of the others. This cannot be correct because in reality the partition function includes contributions from different arrangements of the nearest neighbour spins. As shown by the example of critical opalescence, very large fluctuations occur near a critical point, which can be thought of as strong correlations between the behaviour at distant points in space. Landau theory neglects these correlations.

We have examined failures of mean field theories at some length. One must not conclude that mean field theories are useless. In fact they are *very useful* for describing and understanding phase transitions. They give the wrong critical behaviour, but can still give useful insights into the nature of the phases involved and reasonable numerical estimates of when a phase transition will occur.

What is the origin of this universality? To give a crude answer we return to the example of critical opalescence. In a fluid the long ranged correlations produce variations in the density on length scales many times larger than the molecular dimensions. This suggests that the details of what happens on the molecular length scale should be irrelevant to the critical behaviour.

Chapter 10

Fluctuations in Equilibrium

So far we have mostly been concerned with the average values of thermodynamic quantities, such as the internal energy U or magnetisation M. Even in equilibrium the actual value of the internal energy of a system in contact with a heat reservoir fluctuates in time around the average value.

10.1 Fluctuations

Although they are an inherent part of the equilibrium state, under normal conditions fluctuations of macroscopic thermodynamic quantities are unmeasurably small. There are, however, situations in which fluctuations are important. At second-order phase transitions fluctuations in some thermodynamic quantities diverge, and in that case fluctuations *dominate* the physics. Even far from critical points, spatial fluctuations in the density (e.g., number density, magnetisation density) scatter particles such as photons or neutrons, although it is again at critical points that these effects become most spectacular. Another important example is the scattering of conduction electrons in metals from density fluctuations of the positively charged ions on the lattice (electron-phonon scattering). At normal temperatures in reasonably pure metals such scattering is usually the main source of electrical resistivity. We won't treat scattering from fluctuations here. We will, however, look at some general properties of fluctuations, calculating the fluctuations in the magnetisation of a paramagnet, and generic fluctuations in energy, particle number and volume.

10.1.1 Fluctuations and the Boltzmann-Gibbs Distribution

We can, if we know the energy eigenstates of a system, directly obtain from the Boltzmann or Gibbs distributions not only the average value of a quantity x but its error $\Delta x = x - \langle x \rangle$. The expectation value $\langle \Delta x \rangle$ manifestly vanishes, but the variance, a measure of the magnitude of fluctuations of x:

$$\left\langle \Delta x^2 \right\rangle \equiv \left\langle x^2 \right\rangle - \langle x \rangle^2 = \frac{1}{Z} \sum_i x_i^2 e^{-E_i(x_i)/k_B T} - \left(\frac{1}{Z} \sum_i x_i e^{-E_i(x_i)/k_B T} \right)^2, \qquad (10.1)$$

where x_i is the value of variable x when the system is in state i. This is a useful method of calculating fluctuation magnitude, which becomes even more attractive if there is a simple dependence of the microstate energy on the variable. E.g. if such

dependence is linear, $E_i = -fx_i$, then a generic trick applies:

$$\langle x \rangle = \frac{1}{Z}\sum_i x_i e^{fx_i\beta} = \frac{1}{\beta Z}\frac{\partial Z}{\partial f} = k_B T \frac{\partial(\ln Z)}{\partial f}, \tag{10.2}$$

$$\left\langle x^2 \right\rangle = \frac{1}{Z}\sum_i x_i^2 e^{fx_i\beta} = \frac{1}{Z\beta^2}\frac{\partial^2 Z}{\partial f^2}. \tag{10.3}$$

But if we take one more derivative of $\langle x \rangle$, we note:

$$k_B T \frac{\partial \langle x \rangle}{\partial f} = (k_B T)^2 \left[-\frac{1}{Z^2}\left(\frac{\partial Z}{\partial f}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial f^2} \right] \equiv -\langle x \rangle^2 + \left\langle x^2 \right\rangle, \tag{10.4}$$

which is exactly the same as $\langle \Delta x^2 \rangle$.

Alternatively, we can notice that substituting Eqs. (10.2-10.3) into the variance (10.1) gives what looks like the derivative of a product,

$$\begin{aligned} \left\langle \Delta x^2 \right\rangle &= \frac{1}{Z\beta^2}\frac{\partial^2 Z}{\partial f^2} - \frac{1}{Z^2\beta^2}\left(\frac{\partial Z}{\partial f}\right)^2 \\ &= \frac{1}{\beta^2}\frac{\partial}{\partial f}\left(\frac{1}{Z}\frac{\partial Z}{\partial f}\right) \\ &= \frac{1}{\beta}\frac{\partial}{\partial f}\underbrace{\left(\frac{\partial \ln Z}{\partial f}\right)}_{\langle x \rangle,\,(10.2)}, \end{aligned} \tag{10.5}$$

thus we again see the result identical to Eq. (10.4),

$$\boxed{\frac{1}{\beta}\frac{\partial \langle x \rangle}{\partial f} = \left\langle \Delta x^2 \right\rangle.} \tag{10.6}$$

For example, consider the fluctuations in the magnetisation of a subsystem consisting of a paramagnet in an external field B, and in contact with a reservoir at temperature T.

Applying the Boltzmann distribution with $E_i = -M_i B$ we have

$$\langle M \rangle = \frac{1}{Z}\sum_i M_i e^{M_i B/k_B T} = \frac{k_B T}{Z}\left(\frac{\partial Z}{\partial B}\right)_T. \tag{10.7}$$

Following the method above, the mean square fluctuation in M is (NB. change of sign)

$$\left\langle \Delta M^2 \right\rangle \equiv \left\langle M^2 \right\rangle - \langle M \rangle = k_B T \left(\frac{\partial \langle M \rangle}{\partial B}\right)_T. \tag{10.8}$$

We showed earlier (see Section 3.6 and Eq. (3.76)) that for a system of non-interacting spins

$$\langle M \rangle = N m_0 \tanh\left(\frac{m_0 B}{k_B T}\right). \tag{10.9}$$

Substituting this into our expression for the mean square fluctuation in M we obtain

$$\left\langle \Delta M^2 \right\rangle = \frac{N m_0^2}{\cosh^2(m_0 B/k_B T)}. \tag{10.10}$$

This is an interesting result, because it shows that the root mean square fractional fluctuation is proportional to the square-root of the number of particles, $\sqrt{\langle \Delta M^2 \rangle} \propto N^{1/2}$, so the relative size of the fluctuation to the magnetisation value is:

$$\frac{\sqrt{\langle \Delta M^2 \rangle}}{\langle M \rangle} \propto \frac{1}{\sqrt{N}}. \tag{10.11}$$

The dependence on $1/\sqrt{N}$ is a characteristic that will emerge repeatedly.

Another useful example using the same approach involves asking about the fluctuations of mean energy of the system. Although U is not a thermodynamic variable, we can still write the same sequence of steps:

$$U = \langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}; \quad \left\langle E^2 \right\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}, \tag{10.12}$$

and the mean square fluctuation in U is

$$\left\langle \Delta E^2 \right\rangle \equiv \left\langle E^2 \right\rangle - \langle E \rangle = \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right] = k_B T \underbrace{\frac{\partial U}{\partial T}}_{C_V}. \tag{10.13}$$

10.1.1.1 Example: Fluctuations of Particle Number

We want to calculate the fluctuations in particle number, N, at constant temperature, T, and volume, V,

$$\left\langle \Delta N^2 \right\rangle = \left\langle N^2 \right\rangle - \langle N \rangle^2. \tag{10.14}$$

Using the grand partition function (3.48) we have

$$\langle N \rangle = \frac{\sum_i N_i e^{-\beta(E_i - \mu N_i)}}{\sum_i e^{-\beta(E_i - \mu N_i)}} = \frac{k_B T}{\Xi}\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V} \tag{10.15}$$

(Note that we are using the single index i to denote the microstates). From the expression for $\langle N \rangle$ we have

$$\begin{aligned}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} &= -\frac{k_B T}{\Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)^2_{T,V} + \frac{k_B T}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,V} \\ &= -\frac{\langle N \rangle^2}{k_B T} + \frac{\langle N^2 \rangle}{k_B T} = \frac{\langle \Delta N^2 \rangle}{k_B T},\end{aligned} \tag{10.16}$$

so that

$$\left\langle \Delta N^2 \right\rangle = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V}. \tag{10.17}$$

Of course, this expression is an example of fluctuation-dissipation relation that one can derive directly from the general probability of fluctuation, see equation (10.27).

10.2 Connection with Thermodynamics

In our discussion of availability theory in Section 2.2 it may have occurred to you as odd that we only ever used the condition $\mathrm{d}A = 0$. This enabled us to locate the equilibrium conditions for thermodynamic systems in contact with various kinds of reservoirs. But we might ask if there isn't some meaning to the entire availability function, not just its extremal value. The answer is that for finite systems, the *curvature* of the availability function is related to the size of the fluctuations. We now proceed to find out what this relationship is.

Consider a system that can exchange energy and particles with a large reservoir. We wish to calculate the probability distribution, $P(x)$, for variable x of the system, when the total internal energy of the system+reservoir is U_{tot}. It is easy to see that

$$P(x) \propto \Omega_{\mathrm{tot}}(x, U_{\mathrm{tot}}), \tag{10.18}$$

where $\Omega_{\mathrm{tot}}(x, U_{\mathrm{tot}})$ is the number of microstates of the system + reservoir in which the variable of the system is equal to x. The entropy of the system + reservoir is given by

$$S_{\mathrm{tot}}(x, U_{\mathrm{tot}}) = k_B \ln \Omega_{\mathrm{tot}}(x, U_{\mathrm{tot}}), \tag{10.19}$$

so that

$$P(x) \propto e^{S_{\mathrm{tot}}(x, U_{\mathrm{tot}})/k_B} \tag{10.20}$$

This formula is inconvenient as it contains the entropy of the system + reservoir. However, we found out how to get around this in Section 2.2 by using the availability,

$$A = U - T_R S + p_R V - \mu_R N, \tag{10.21}$$

where the subscript R refers to the reservoir, and the other variables are for the system. Because the reservoir is large T_R, p_R, and μ_R are constant. A change in the total entropy of the system+reservoir is related to a change in the availability by

$$\mathrm{d}S_{\mathrm{tot}} = -\frac{\mathrm{d}A(x)}{\mathrm{d}T_R}, \tag{10.22}$$

where T_R is the temperature of the reservoir. Therefore

$$P(x) = \aleph e^{-A(x)/k_B T_R}, \tag{10.23}$$

where $\aleph$ is a normalisation constant. In this formula the availability is calculated in equilibrium with the system variable of interest constrained to take the value x.

As discussed in Subsection 2.3.3, for an isothermal, constant volume system, $\mathrm{d}A$ reduces to $\mathrm{d}F$, so $P(x) \propto e^{-F(x)/k_B T_R}$, while for constant T and p, $\mathrm{d}A = \mathrm{d}G$, and the fluctuation probability is $P(x) \propto e^{-G(x)/k_B T_R}$, and for $đQ = 0$ and $\mathrm{d}p = 0$ the fluctuation probability is $P(x) \propto e^{-H(x)/k_B T_R}$.

Eq. (10.23) is the general formula, but for a large system the probability distribution is almost Gaussian and one can extract the mean square fluctuation by simply expanding about the equilibrium value of x, which we denote by x_0

$$A(x) = A(x_0) + (x - x_0) \underbrace{\left.\frac{\partial A}{\partial x}\right|_{x=x_0}}_{=0} + \frac{1}{2}(x - x_0)^2 \left.\frac{\partial^2 A}{\partial x^2}\right|_{x=x_0} + \cdots . \tag{10.24}$$

The second term on the right hand side is zero because we are expanding about a minimum. Combining Eqs. (10.23) and (10.24) we obtain the probability distribution within the Gaussian approximation

$$P(x) = \frac{1}{\sqrt{2\pi \left\langle \Delta x^2 \right\rangle}} \exp\left(-\frac{\Delta x^2}{2\left\langle \Delta x^2 \right\rangle}\right), \tag{10.25}$$

where

$$\boxed{\left\langle \Delta x^2 \right\rangle = \left\langle (x - x_0)^2 \right\rangle = \frac{k_B T_R}{\partial^2 A/\partial x^2 \,|_{x=x_0}}.} \tag{10.26}$$

There is an important and simple message emerging from this discussion. You may recall (from Section 2.2) that the small increment of availability, such as $\Delta A(x) = A(x) - A(x_0)$ here, is actually equal to a corresponding thermodynamic potential (in which x is the proper variable). Therefore the first derivative $\partial A/\partial x$, evaluated in equilibrium, is in fact equal to the thermodynamic force f conjugate to the variable x. Let's say that the corresponding thermodynamic potential (not specifying its name to any of the familiar ones) is $\Pi(x)$, so that $\mathrm{d}\Pi = f\,\mathrm{d}x + \cdots$. Then we see from Eq. (10.26) that

$$\left\langle \Delta x^2 \right\rangle = \frac{k_B T_R}{\partial f/\partial x \,|_{x=x_0}} = k_B T \left.\frac{\partial x}{\partial f}\right|_{x=x_0}. \tag{10.27}$$

If you think of the arbitrary conjugate pair of thermodynamic variables (x, f) as a force and the corresponding displacement which are related by the *linear response* relation $x = \alpha f$, then we conclude that the mean square fluctuation of a thermodynamic variable is given by $k_B T$ times the linear response coefficient: $\langle \Delta x^2 \rangle = k_B T \alpha$ in our notations. This is the first example of *Fluctuation Dissipation Theorem* we discover in this course.

Let us now derive the probability distribution for fluctuations in the internal energy U of a system held at constant volume and particle number but thermally coupled to a reservoir. This is an example when the fluctuating object is not the basic thermodynamic variable, and so we have to be cautious with the conclusions reached above. We will use the thermodynamic approach, although if the eigenstates were known we could use statistical mechanics.

A change in the availability (Eq. (10.21)) is given by

$$\mathrm{d}A = \mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N\,, \tag{10.28}$$

which for constant V and N reduces to

$$\mathrm{d}A = \mathrm{d}U - T_R\,\mathrm{d}S = \mathrm{d}F\,. \tag{10.29}$$

Therefore

$$\left(\frac{\partial F}{\partial U}\right)_V = 1 - T_R\left(\frac{\partial S}{\partial U}\right)_V, \tag{10.30}$$

and using $\left(\frac{\partial S}{\partial U}\right)_V = 1/T$, we obtain

$$\left(\frac{\partial F}{\partial U}\right)_V = 1 - \frac{T_R}{T}, \tag{10.31}$$

which must be zero in equilibrium so that, as expected, $T = T_R$ is the equilibrium condition. Differentiating again we obtain

$$\left(\frac{\partial^2 F}{\partial U^2}\right)_V = \frac{T_R}{T^2}\left(\frac{\partial T}{\partial U}\right)_V. \tag{10.32}$$

Using $\left(\frac{\partial U}{\partial U}\right)_V = C_V$, and setting $T = T_R$, we obtain

$$\left(\frac{\partial^2 F}{\partial U^2}\right)_V = \frac{1}{T_R C_V}, \tag{10.33}$$

so that using Eq. (10.26) we obtain the same expression as we have seen earlier, in Eq. (10.13)

$$\left\langle \Delta E^2 \right\rangle = \frac{k_B T}{\left(\frac{\partial^2 F}{\partial U^2}\right)_V} = k_B T^2 C_V, \quad \text{for} \quad \langle E \rangle = U, \tag{10.34}$$

and

$$P(E) = \frac{1}{\sqrt{2\pi k_B T^2 C_V}} \exp\left[-\frac{[E - \langle E \rangle]^2}{2 k_B T^2 C_V}\right]. \tag{10.35}$$

Fig. 10.1: The Helmholtz free energy is a minimum at the mean value of U, and the probability distribution for U is a sharply peaked Gaussian centred on the mean value.

Let's consider, for example, $1\,\mathrm{cm}^3$ of monatomic ideal gas:

$$N = \frac{pV}{k_B T} \sim 2.5 \times 10^{19}\,\text{atoms}. \tag{10.36}$$

Equipartition gives $U = 3/2Nk_BT = 0.15\text{J}$, and the heat capacity at constant volume is $C_V = 3/2Nk_B = 5.2 \times 10^{-4}\text{J}\,\text{K}^{-1}$, so the root mean square fluctuation is

$$\sqrt{\langle \Delta E^2 \rangle} \sim T\sqrt{k_B C_V} \sim 2.5 \times 10^{-11}\text{J}. \tag{10.37}$$

The fractional fluctuation is

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{U} \sim 1.6 \times 10^{-10}. \tag{10.38}$$

Thus the fluctuations in energy would be unmeasurably small. Note from the formulae that the fractional fluctuation is again proportional to $1/\sqrt{N}$

Before considering other examples of fluctuations we should think a little more carefully about what is going on.

1. Some variables, for example T, S, μ, are not well defined for each microstate, they are only defined as averages over them. Can such variables be considered to fluctuate at all? This is related to the discussion of the law of increase of entropy in Appendix A.1, which implies that the answer is "yes". However this is a subtle question which I will not address further.

2. Some variables cannot be fixed in practical situations, such as the pressure of a gas, or the magnetisation of a paramagnet. However, this does not prevent us from calculating the fluctuations in the pressure or magnetisation. You can read about this on pages 207-208 of Waldram, but this issue is not examinable.

3. You should beware that in general it is *incorrect* to take the formula for the probability distribution of one variable and substitute for another one. As a trivial example, consider an isolated cylinder of ideal monatomic gas held at constant volume. As the system is isolated U is constant, and in equilibrium $U = \frac{3}{2}pV$. If V is constant one might conclude that because U does not fluctuate neither can p. This is nonsense because the usual equilibrium relations between functions of state do not hold during the course of fluctuations.

10.2.1 Energy Fluctuations

For a system of N free electrons the statistical weight, $\Omega(E)$, is proportional to $\exp\left[(NE/\epsilon_0)^{1/2}\right]$, where ϵ_0 is about 10^{-19} J. The statistical weight is

$$\Omega(E) \propto \exp\left[(NE/\epsilon_0)^{1/2}\right] \quad \text{with} \quad S = k_B \ln \Omega, \tag{10.39}$$

and we effectively have $U = U(S, N)$, i.e. in correct variables. In this case we can evaluate the usual thermodynamic derivative

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E} k_B \ln \Omega(R) = \frac{k_B}{2}\left(\frac{N}{\epsilon_0}\right)^{1/2} E^{-1/2}, \tag{10.40}$$

and therefore

$$T = \frac{2}{k_B}\left(\frac{\epsilon_0 U}{N}\right)^{1/2}, \tag{10.41}$$

where U in this expression is the average internal energy $\langle E\rangle$. The specific heat capacity C (per particle) is given by

$$\begin{aligned} C &= \frac{1}{T}\frac{\partial\langle E\rangle}{\partial N} = \frac{\partial}{\partial T}\frac{T^2 k_B^2}{4\epsilon_0} = \frac{k_B^2 T}{2\epsilon_0} \\ &= 2.8\times 10^{-25}\ \mathrm{J\ K^{-1}}. \end{aligned} \tag{10.42}$$

The probability distribution of the internal energy is given by the Boltzmann distribution,

$$P(E) = \frac{1}{Z}\Omega(E)e^{-E/k_B T}. \tag{10.43}$$

It is often easier to work with $\ln P$,

$$\ln P(E) = -\frac{E}{k_B T} + \ln\Omega(E) + \text{const.} \tag{10.44}$$

The maximum in $\ln P(E)$ occurs at the same value of E as the maximum in $P(E)$. Expand $\ln P(E)$ about its maximum value which occurs at $\langle E\rangle$, defining $\Delta E = E - \langle E\rangle$:

$$\ln P(E) = \ln P|_{\langle E\rangle} + \frac{\Delta E^2}{2}\left.\frac{\partial^2 \ln P}{\partial E^2}\right|_{\langle E\rangle} + \cdots, \tag{10.45}$$

because the term linear in ΔE must vanish. Hence at constant T,

$$\left.\frac{\partial \ln P}{\partial E}\right|_{\langle E\rangle} = -\frac{1}{k_B T} + \left.\frac{\partial \ln\Omega}{\partial E}\right|_{\langle E\rangle} = 0 \quad \text{so} \quad \left.\frac{\partial \ln\Omega}{\partial E}\right|_{\langle E\rangle} = \frac{1}{k_B T} \tag{10.46}$$

(in a sense, we have just re-defined the entropy). Note that $\Omega(E)$ is not a function of T, but the average energy $\langle E\rangle$ is. Solving for $\langle E\rangle$ we obtain

$$\langle E\rangle = \frac{k_B^2 T^2 N}{4\epsilon_0}. \tag{10.47}$$

The width of the distribution, $\langle \Delta E^2\rangle$, can be obtained from

$$\begin{aligned} \left.\frac{\partial^2 \ln P}{\partial E^2}\right|_{\langle E\rangle} &= \left.\frac{\partial^2 \ln\Omega}{\partial E^2}\right|_{\langle E\rangle} = \left.\frac{\partial^2}{\partial E^2}\left(\frac{NE}{\epsilon_0}\right)^{1/2}\right|_{\langle E\rangle} \\ &= -\frac{1}{4}\left(\frac{N}{\epsilon_0}\right)^{1/2}\langle E\rangle^{-3/2}, \end{aligned} \tag{10.48}$$

and

$$\left\langle \Delta E^2\right\rangle - \frac{1}{\left.\frac{\partial^2 \ln P}{\partial E^2}\right|_{\langle E\rangle}} = \frac{k_B^3 T^3 N}{2\epsilon_0}. \tag{10.49}$$

Therefore

$$\frac{\langle \Delta E^2\rangle}{\langle E\rangle^2} = \frac{8\epsilon_0}{k_B T N} = 4.5\times 10^{-11}\text{at} \quad T = 290\ \text{k}. \tag{10.50}$$

The probability distribution of the energy of the system is therefore approximately a Gaussian of width $\langle \Delta E^2\rangle$ and mean $\langle E\rangle$. This alternate but long-winded derivation is given to illustrate several points made previously in Section 10.2. If you want a simple shortcut, then see how Eq. (10.13) was derived.

10.2.2 Anharmonic Oscillator

A system is governed by the anharmonic potential energy $E(x) = ax^2 + bx^4$, which makes evaluating the partition function and the thermodynamic equilibrium difficult. An approximate solution could be obtained using the *Gaussian Variation Method* by considering a model harmonic energy $E_\alpha = \alpha x^2$ with the adjustable parameter α, and finding the best α that approximates the equilibrium properties of a system governed by $E(x)$.

First of all, let's write down the definitions and do the algebra. For the energy $E(x) = ax^2 + bx^4$, the equilibrium free energy is determined by its partition function: $F = -k_BT \ln [\int \exp(-(ax^2 + bx^4)/k_BT)\,\mathrm{d}x]$. Let's add and subtract E_α in the exponent, and then Taylor-expand to the leading order in $(E - E_\alpha)$, which we assume is small:

$$\begin{aligned}
F &= -k_BT \ln \left[\int \exp\left(-\frac{E(x) - E_\alpha}{k_BT}\right) \exp\left(-\frac{E_\alpha}{k_BT}\right) \mathrm{d}x\right] \\
&\approx -k_BT \ln \left[e^{-E_\alpha/k_BT}(1 - [E(x) - E_\alpha]/k_BT + \cdots)\,\mathrm{d}x\right] \\
&= -k_BT \ln \underbrace{\left[\int e^{-E_\alpha/k_BT}\,\mathrm{d}x\right]}_{Z_\alpha} - k_BT \ln \left[1 - \frac{\int e^{-E_\alpha/k_BT}(E(x) - E_\alpha)/k_BT\,\mathrm{d}x}{\int e^{-E_\alpha/k_BT}\,\mathrm{d}x}\right] \\
\tilde{F} &\approx -k_BT \ln Z_\alpha + \langle E(x) - E_\alpha \rangle_\alpha\,, \qquad (10.51)
\end{aligned}$$

after another Taylor expansion of the logarithm, and the average is evaluated with the probability distribution $\rho_\alpha(x) = Z_\alpha^{-1} \exp(-\alpha x^2/k_BT)$.

Since all the integrals here are Gaussian, we can evaluate both terms:

$$\begin{aligned}
\tilde{F} &= -k_BT \ln \left[\sqrt{\frac{\pi k_BT}{\alpha}}\right] + (a - \alpha)\left\langle x^2 \right\rangle_\alpha + b\left\langle x^4 \right\rangle_\alpha \\
&= -k_BT \ln \left[\sqrt{\frac{\pi k_BT}{\alpha}}\right] + (a - \alpha)\frac{k_BT}{2\alpha} + 3b\left(\frac{k_BT}{2\alpha}\right)^2, \qquad (10.52)
\end{aligned}$$

where we used the variance of the Gaussian in the first term, and the Wick's theorem relation $\langle x^4 \rangle = 3\langle x^2 \rangle^2$, which can easily be shown for Gaussian distributions.

In equilibrium, the system adjusts its probability distribution $\rho(x)$ in such a way that the free energy of the microstate $E(x)$ is minimised. Calculating the average (or the most probably) $E - TS$ for a *different* probability distribution will produce a larger value than the true F. $\tilde{F}$ is such a case, namely the free energy for the anharmonic system is approximated by using the probability distribution for the harmonic system. This can at best be equal to F, but in reality one cannot exactly match the anharmonic $E(x)$ with a harmonic E_α, so $F > \tilde{F}$.

All we need to do now is to find α for which $\tilde{F}$ is minimal:

$$\frac{\partial \tilde{F}}{\partial \alpha} = 0 = \frac{k_B T}{2\alpha} - a\frac{k_B T}{2\alpha^2} - 3b\frac{(k_B T)^2}{2\alpha^3} \quad \text{or} \quad \alpha^2 - a\alpha - 3bk_B T = 0, \tag{10.53}$$

which you can alternatively write as: $\alpha = a + 6b\,\langle x^2\rangle_\alpha$. This already suggests that the system becomes less responsive at higher T, when the variance goes up and the system explores the anharmonic part of the potential more and more.

In detail, the solution of the quadratic gives $\alpha = a/2 + \sqrt{(a/2)^2 + 3bk_B t}$. For low T, α starts out as a, as expected for the system fluctuations to be confined at small x where E and E_α can coincide. At high T it rises $\alpha \propto \sqrt{T}$, as the system spends more time at large x-values, where the true potential rises more steeply and the model parameter α needs to reflect that by increasing its value. Conversely, the variance $\langle x^2\rangle$ starts off at low T as $\propto T$, as would be expected from the equipartition theorem, but with increasing T, when the response of the system becomes stiffer, the variance increases sublinearly.

10.3 Fluctuations near Critical Points

Fig. 10.2: Volume fluctuations at constant T and N.

The first example of critical point we have encountered, back in Fig. 1.5, was for the van der Waals gas. In $p - V$ coordinates the critical isotherm has a single point where $\mathrm{d}p/\mathrm{d}V = 0$ (at lower temperatures there are two such points on each isotherm, but the liquid-gas transition occurs outside their range.

Let us calculate the fluctuation of thermodynamic variable V in the vessel shown in Fig. 10.2, at constant T and N. This is similar to what we have done for U, but requires a little more thought about which variables are fixed and which ones fluctuate. In this problem U is free to fluctuate but T is fixed and equal to its equilibrium value of T_R. Applying the first law to the system we have

$$\mathrm{d}U = T_R\,\mathrm{d}S - p\,\mathrm{d}V\,, \quad \text{so that} \quad \mathrm{d}A = (p_R - p)\,\mathrm{d}V\,. \tag{10.54}$$

Differentiating w.r.t. $\mathrm{d}V$ and taking T to be constant we have

$$\left(\frac{\partial A}{\partial V}\right)_T = p_R - p, \tag{10.55}$$

which must be zero in equilibrium so that, as expected, $p = p_R$ is the equilibrium condition. Differentiating again we obtain

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T \equiv \frac{1}{\kappa_T V}, \tag{10.56}$$

where we have defined the parameter κ_T - the isothermal compressibility, which is effectively the linear response coefficient for the conjugate pair of thermodynamic variables p, V. Therefore

$$\left\langle \Delta V^2 \right\rangle = k_B T V \kappa_T, \quad \text{and} \quad P(V) = \frac{1}{\sqrt{2\pi k_B T V \kappa_T}} \exp\left[-\frac{\Delta V^2}{2 k_B T V \kappa_T}\right]. \tag{10.57}$$

The fractional volume fluctuation is

$$\frac{\sqrt{\langle \Delta V^2 \rangle}}{V} = \sqrt{\frac{k_B T \kappa_T}{V}}. \tag{10.58}$$

Fig. 10.3: The fluctuations grow as one approaches the critical point, where they diverge.

In line with our other findings, the fractional fluctuation is proportional to $1/\sqrt{V}$. Note that $\kappa_T \propto \frac{\mathrm{d}V}{\mathrm{d}p}$ diverges at the liquid-vapour critical point (see Fig. 10.3), and hence the magnitude of the volume fluctuations. This effect has the name of 'critical opalescence' and you can see it every time when slowly boiling water in a pan: as the critical point is approached, the volume of density fluctuations (microscopic bubbles of vapour in the liquid) increases so that they start scattering light.

Two other examples of critical points we examined in *phase transitions* were the isolated critical point at the end of the demixing region of a phase-separating mixture, and the continuous second order phase transition in ferromagnets at zero external B-field. The first critical point is fully analogous to the van der Waals critical point, only represented in variables T, c. It is convenient to look at both these transition with the help of Landau expansion(s) of the corresponding thermodynamic potential, Eq. (9.32) for the critical mixture and Eq. (9.42) for the magnet. For instance, taking the magnetic case at T_c, we can write the mean square fluctuation of magnetisation as

$$\left\langle \Delta M^2 \right\rangle = k_B T \frac{\partial M}{\partial B}. \tag{10.59}$$

Evaluated at $B \to 0$ and in equilibrium ${}_M0 = 0$ at $T > T_c$, the derivative is equal to the susceptibility χ, that is, the corresponding linear response coefficient of the M, B pair. As we have seen in Eq. (9.70), this susceptibility diverges at the critical point and so must the magnitude of fluctuation in magnetisation. Note that this divergence occurs on both sides of the critical point.

10.3.1 Critical Fluctuations at Ferromagnetic Phase Transition

Find the mean square fluctuation of magnetisation, $\langle \Delta M^2 \rangle$, as a function of temperature on both sides of the critical point T_c of the ferromagnetic phase transition, which can be described by the Landau free energy expansion

$$F = a(T - T_c)M^2 + bM^4. \tag{10.60}$$

This is a simplest form of Landau model of 2nd order transition. Evaluating the derivative of free free energy, we find the solution for the equilibrium magnetisation $M^*(T)$

$$\frac{\partial F}{\partial M} = 2M\Big[a(T - T_c) + 2bM^2\Big] = 0 \quad \text{gives} \quad M^* = \pm\sqrt{\frac{a(T_c - T)}{2b}}. \tag{10.61}$$

The non-zero solution only exists below the critical point $T = T_c$.

Now, speaking about fluctuations, we have the generic expression (10.26) valid on both sides of the transition,

$$\Big\langle \Delta M^2 \Big\rangle = \left.\frac{k_B T}{\frac{\partial^2 F}{\partial M^2}}\right|_{M=M_{\text{eq.}}}. \tag{10.62}$$

This gives different results above and below the phase transition:

$$T > T_c : \Big\langle \Delta M^2 \Big\rangle = \frac{k_B T}{2a(T - T_c)} \tag{10.63}$$

$$T < T_c : \Big\langle \Delta M^2 \Big\rangle = \frac{k_B T}{2a(T - T_c) + 12bM^{*2}} = \frac{k_B T}{4a(T_c - T)}. \tag{10.64}$$

This is an important result showing that the mean square amplitude of the order parameter fluctuations (magnetisation in this case) diverges on approaching the critical point. However, there is a constant factor between the two expressions, making the fluctuations in the disordered phase always bigger than in the ordered phase. If you plot both curves against T, the result will look like the Greek letter λ, hence the name for this effect: "lambda-point".

Fig. 10.4: Specific heat of liquid ^{4}He obtained with the PIMC method around the normal-to-superfluid λ phase transition. The line corresponds to experimental results. [11] The point's name derives from the graph that results from plotting the specific heat capacity as a function of temperature, which resembles the Greek letter lambda λ. The specific heat capacity has a sharp peak as the temperature approaches the lambda point. [2]

Chapter 11

Elements of Stochastic Physics

11.1 Brownian Motion

The origin of all thermodynamic fluctuations is, of course, the underlying thermal motion of particles in matter. It is most explicitly represented in the phenomenon of *Brownian motion*: the perpetual irregular motions exhibited by small grains or particles of colloid size immersed in a liquid. A botanist Robert Brown is credited with the formal discovery of this effect in 1827, when he observed in the microscope tiny particles within the vacuoles of the pollen grains executing a jittery motion. By repeating the experiment with particles of dust, he was able to rule out that the motion was due to pollen particles being 'alive'.

Brownian motion is one of the simplest phenomena where we need the new approach - called the *stochastic physics*. As in the equilibrium statistical physics, one cannot predict the outcome on the basis of solving the dynamic (Newton) equations, and yet a lot of knowledge about the system can be acquired via the probability distributions and average properties. It is a common case when the characteristic length scales of the problem are well separated, as it is with a relatively large Brownian particle experiencing collisions and exchanging the momentum with very small molecules of liquid. Under normal conditions, in a liquid, a particle will suffer about 10^{21} collisions per second. So we cannot - and really should not speak of separate events, or attempt to follow the particle trajectory in any detail.

The theory of the Brownian motion of a free particle (i.e. Brownian motion in the absence of external field or force) starts with the *Langevin equation* for the particle dynamics:

$$m\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} = -\gamma\mathbf{u} + \xi(t), \tag{11.1}$$

where $\mathbf{u}$ denotes the vector of particle velocity. According to this equation, the influence of the surrounding medium on the motion of the particle can be split up into two parts: first, a systematic part $-\gamma\mathbf{u}$ representing the kinetic friction experienced by the particle (with γ the corresponding friction coefficient). It is assumed that this is governed by fluid dynamics, e.g., the Stokes law which states that the frictional force decelerating a spherical particle of radius a and mass m in a liquid with a viscous coefficient η is given by $\gamma = 6\pi a\eta$.

The second contribution to the force acting on the Brownian particle in Eq. (11.1) is fluctuating part $\xi(t)$, which is the force provided by collisions with molecules of surrounding liquid, which are in thermal motion. If we had a purely 1-dimensional motion, then an example of such a force might be seen in Fig. 11.1. This type of force

is called the stochastic force and it is clear that any solution $\mathbf{u}(t)$ of the Langevin equation would also have the same unpredictable nature at any instance of time. Note that if we have a fluctuating part $\xi(t)$, then we *need* a dissipative term $-\gamma\mathbf{u}$, such to balance the gain and dissipative loss of the particles energy.

Fig. 11.1: An example of stochastic force acting on the Brownian particle from the surrounding medium in thermal motion.

This problem is, in fact, very general. For instance in an electric (L, R) circuit, $L\,\mathrm{d}I/\mathrm{d}t + RI = V(t)$, the thermal noise acting on electrons generates the stochastic contribution to the voltage; using the charge as variable: $L\ddot{q} = -R\dot{q} + V_\xi(t)$ we reproduce Eq. (11.1). In general, the Langevin equation for any given system is the corresponding classical dynamical equation (2nd Newton law, if we talk about moving particles) with the stochastic force added to any other forces present.

What can we say about the properties of stochastic force $\xi(t)$? The simplest approach would be to consider the 1-dimensional motion and assume the "white noise" properties, that is

$$\langle\xi(t)\rangle = 0; \quad \text{but} \quad \left\langle\xi(t)^2\right\rangle \neq 0 \quad \text{and} \quad \langle\xi(t_1)\xi(t_2)\rangle = 0 \quad \text{if} \quad t_1 \neq t_2. \tag{11.2}$$

The complete lack of correlations between its pulses can be described by the shorthand notation $\langle\xi(t)\xi(t')\rangle = \Gamma\delta(t-t')$, with Γ denoting the intensity of the flat spectrum white noise, although one can show that a little spreading of the delta-function will not change the properties of Brownian motion on long time scales. Here the parameter Γ is the measure of intensity of the stochastic force. We demand that $\langle\xi\rangle = 0$, as any net drift can be incorporated into the effect of the macroscopic force the particle experiences instead.

11.1.1 Fluctuation-Dissipation Relation

The homogeneous dynamical equation $m\dot{u} = -\gamma u$ has the obvious solution, $u = u_0 \exp\left[-(\gamma/m)t\right]$, which represents the decay of the initial condition: the particle having velocity u_0 at $t = 0$. With the added stochastic force, the formal solution of Eq. (11.1) is

$$u(t) = u_0 e^{-(\gamma/m)t} + \int_0^t e^{-(\gamma/m)[t-t']}\frac{\xi(t')}{m}\,\mathrm{d}t'\,, \tag{11.3}$$

which you can readily verify by evaluating the derivative $m(\mathrm{d}u/\mathrm{d}t)$. The instantaneous value of $u(t)$ cannot be predicted, but its mean square value is easy to

determine:

$$\begin{aligned}
\left\langle u^2 \right\rangle &= \left\langle u_0^2 e^{-2(\gamma/m)t} + 2u_0 e^{-(\gamma/m)t} \int_0^t e^{-(\gamma/m)[t-t']} \frac{\xi(t')}{m} \, \mathrm{d}t' \right. \\
&\quad \left. + \int_0^t \int_0^t e^{-(\gamma/m)[2t-t_1-t_2]} \frac{\xi(t_1)\xi(t_2)}{m^2} \, \mathrm{d}t_1 \, \mathrm{d}t_2 \right\rangle \\
&= u_0^2 e^{-2(\gamma/m)t} + \frac{1}{m^2} \int_0^t \int_0^t e^{-(\gamma/m)[2t-t_1-t_2]} \left\langle \xi(t_1)\xi(t_2) \right\rangle \mathrm{d}t_1 \, \mathrm{d}t_2 \qquad (11.4) \\
&= u_0^2 e^{-2(\gamma/m)t} + \frac{\Gamma}{m^2} e^{-2(\gamma/m)t} \int_0^t e^{2(\gamma/m)t_1} \, \mathrm{d}t_1 \\
&= u_0^2 e^{-2(\gamma/m)t} + \frac{\Gamma}{2m\gamma} \left(1 - e^{-2(\gamma/m)t}\right). \qquad (11.5)
\end{aligned}$$

The cross term, linear in $\langle \xi \rangle$ dropped out in writing the second line (11.4). In the long-time limit[1] the decaying exponential disappears, $e^{-2t/\tau} \to 0$, and we are left with the value of the mean kinetic energy of the particle:

$$\left\langle \frac{1}{2} m u^2 \right\rangle = \frac{\Gamma}{4\gamma} = \frac{1}{2} k_B T, \qquad (11.6)$$

where the equipartition was used for this 1-dimensional free motion. The important conclusion we have now reached is that the intensity of stochastic force is proportional to temperature (which is expected, in retrospect), but also to the friction constant of the particle in this medium: $\Gamma = 2k_B T\gamma$; the two effects initially might have appeared independent. This is a representation of the fluctuation-dissipation theorem, relating the fluctuation of the energy input, $\langle \xi^2 \rangle$, to the linear response coefficient of energy dissipation (friction constant) via $k_B T$.

11.2 Diffusion of Free and Confined Particles

If we persist with the notion that, after a long time of observation, $t \gg m/\gamma$, no memory of the initial particle velocity u_0 must remain and the current velocity must be distributed according to the Maxwell distribution (Eq. (1.2) gave its 3-dimensional form), the next step of the coarse-graining would be to say that the inertial effects are irrelevant on long time scales of interest and the particle acceleration $\dot{u}$ must average out of Eq. (11.1). We have to maintain the balance of forces:

$$0 = -\gamma u + \xi(t), \quad \text{or} \quad \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{\gamma} \xi(t). \qquad (11.7)$$

[1] E.g. for small (1µm size) organic particles in water the time scale of this decay, $\tau = m/\gamma \sim 10^{-8}$s

Continuing our example of the simplest 1-dimensional example, the current position of the Brownian particle is evolving according to

$$x(t) = \frac{1}{\gamma}\int_0^t \xi(t')\,\mathrm{d}t'\,, \tag{11.8}$$

$$\text{hence} \quad \left\langle x^2 \right\rangle = \frac{1}{\gamma^2}\int_0^t\int_0^t \langle \xi(t_1)\xi(t_2)\rangle\,\mathrm{d}t_1\,\mathrm{d}t_2\,,$$

$$\text{i.e.} \quad \left\langle x^2 \right\rangle = \frac{\Gamma}{\gamma^2}t \equiv 2Dt \quad \text{with} \quad D = \frac{k_B T}{\gamma}. \tag{11.9}$$

This is the famous law of diffusion (Einstein 1905), meaning that the r.m.s. displacement of the free particle from its position at $t = 0$ increases $\propto \sqrt{t}$, that is, slower than for the free motion with constant velocity. The fact that $\langle x^2\rangle = 2Dt$ is a very basic property of any Gaussian stochastic process and you have no doubt seen this before. In 3-dimensions, without any constraints, we only need to repeat the same analysis in all directions to end up with

$$\left\langle \mathbf{r}^2 \right\rangle = \left\langle x^2 \right\rangle + \left\langle y^2 \right\rangle + \left\langle z^2 \right\rangle = 6Dt. \tag{11.10}$$

In 1909, Jean Perrin has completed quantitative microscopic observations of Brownian diffusion, which confirmed the Einstein's theory and earned him the 1926 Nobel prize. The theory based on the Langevin equation has been applied to many diffusion phenomena: mixing of gases or liquids, atom motion in solids, spread of the black plague, spread of agriculture in Neolithic times, spread of clothing fashions, spread of africanised-bees, etc.

Fig. 11.2: Mean square displacement of labelled impurities, diffusing in pure and distorted crystalline lattices.

11.2.1 Brownian Particle in a Potential Well

What is the effect of stochastic (thermal) noise on a system that is not free, but is confined by a potential energy to be near its equilibrium. A mechanical analogy

of this is the Brownian particle that is moving in a quadratic potential $V = \frac{1}{2}kx^2$ - essentially, the particle tied to an origin by an elastic spring exerting a force $f = -kx$.

Fig. 11.3: Particle moving under thermal noise in a potential well.

At time scales of observation which are much longer than the velocity relaxation time $\tau = m/\gamma$, inertial effects are again irrelevant and the acceleration averages to zero in the equation of motion for the average position. In this limit, the Langevin equation takes the *overdamped* form:

$$\gamma \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = -k\mathbf{x} + \xi(t), \tag{11.11}$$

which is exactly the same as the equation for the free particle with the inertial term present, Eq. (11.1). Therefore the algebra of solving this problem of confined Brownian particle is exactly the same as what led us to the expression (11.5) for the mean square velocity. Once again, assuming 1-dimensional motion, for simplicity of argument, the stochastic solution for $x(t)$ is

$$x(t) = x_0 e^{-(k/\gamma)t} + \int_0^t e^{-(k/\gamma)[t-t']} \frac{\xi(t')}{\gamma} \, \mathrm{d}t' \,. \tag{11.12}$$

The instantaneous value of $x(t)$ cannot be predicted, but its mean square value is easy to determine:

$$\begin{aligned} \left\langle x^2 \right\rangle &= x_0^2 e^{-2(k/\gamma)t} + \frac{1}{\gamma^2} \int_0^t \int_0^t e^{-(k/\gamma)[2t-t_1-t_2]} \left\langle \xi(t_1)\xi(t_2) \right\rangle \mathrm{d}t_1 \, \mathrm{d}t_2 && (11.13) \\ &= x_0^2 e^{-2(k/\gamma)t} + \frac{\Gamma}{\gamma^2} e^{-2(k/\gamma)t} \int_0^t e^{2(k/\gamma)t_1} \, \mathrm{d}t_1 \\ &== x_0^2 e^{-2(k/\gamma)t} + \frac{\Gamma}{2k\gamma} \left(1 - e^{-2(k/\gamma)t}\right). && (11.14) \end{aligned}$$

There is a new time scale emerging, $\tau_x = k/\gamma$, which essentially determines how long does the memory of the initial condition x_0 persists in such a system. Without thermal noise $\xi(t)$, the particle released at $x = x_0$ would come to a rest at the point of its equilibrium $x = 0$ in approximately this length of time.

In the long time limit, at $t \gg \tau_x$ we obtain the result, that the mean square displacement of the particle from its equilibrium is constant:

$$\left\langle x^2 \right\rangle = \frac{\Gamma}{2k\gamma} = \frac{k_B T}{k}, \tag{11.15}$$

if we recall the value for the intensity of the stochastic force, $\Gamma = 2k_BT\gamma$. This conclusion is interesting for two reasons. First of all, this is yet another example of the formula for general thermodynamic fluctuations in equilibrium, Eq. (10.27): the conjugate variable to the particle displacement is force, $f = kx$, and what we see above is just $\langle x^2\rangle = k_BT\,\partial x/\partial f$. Secondly, this expression has a wide significance in a variety of real physical systems (well outside Brownian motion). For instance, consider atoms experiencing thermal motion in a crystalline lattice: their mean square displacement is proportional to k_BT - and inversely proportional to the strength of their confining lattice potential.

11.2.2 Brownian Particles Escaping Sink

Consider free Brownian particles diffusing along the axis $x \geq 0$, so that there is a reflecting wall at $x = 0$. Also there is a "sink" at $x = L$ where the particles can escape from the system, so that the probability at that point is $P(L,t) = 0$ at any time.

This requires solving the free diffusion equation for $P(x,t)$ with the boundary conditions $P(x = L) = 0$ and $\mathrm{d}P/\mathrm{d}x = 0$. Separating variables, we have:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \tag{11.16}$$

taking $P(x,t) = T(t)X(x)$,

$$\dot{T} = -\lambda T \quad \text{and} \quad X'' + \frac{\lambda}{D}X = 0. \tag{11.17}$$

The time dependence gives a simple exponential, $T(t) = e^{-\lambda t}$. The x-dependence is best described by the harmonic functions (since we see the oscillator equation), $X(x) = A\sin\left(\sqrt{\lambda/D}x\right) + B\cos\left(\sqrt{\lambda/D}x\right)$. The reflecting wall at $x = 0$ means that $X'(0) = \sqrt{\lambda/D}\cdot A\cos 0 = 0$, that is, the constant $A = 0$. The particle "sink" at the end of our range demands: $X(L) = B\cos\left(\sqrt{\lambda/D}L\right) = 0$. This gives the discrete values ("quantisation") of the parameter λ:

$$\sqrt{\frac{\lambda}{D}}L = \pi\left(n + \frac{1}{2}\right) \quad \text{so} \quad P(x,t) = \sum_n B_n \exp\left(-\frac{\pi^2 D}{L^2}\left(n + \frac{1}{2}\right)^2 t\right)\cos\left(\frac{\pi x}{L}\left(n + \frac{1}{2}\right)\right). \tag{11.18}$$

One could analyse this solution, and the evolution of particle distribution in this system, in much greater detail (especially if an initial condition $P(t = 0)$ would be given, of which B_n are the Fourier coefficients). But it is clear that the relevant time scale of particles escaping is $\tau = 4L^2/\pi^2 D$, which is the life time of the longest-surviving mode.

11.3 Damped Harmonic Oscillator

So far, we have started with a white-noise (uncorrelated) Langevin force and deduced the properties of Brownian motion in certain scenarios from it. But how do we know that the Langevin force has a the form which has been postulated? We will investigate the properties of the Langevin force in detail by considering the more general example of a damped harmonic oscillator: a mass on a spring surrounded by a fluid at temperature T. We have seen that the position of the mass fluctuates, so as a function of time it follows some random curve. We know that if we push down on the mass and then release it, its position will oscillate, but the oscillations decay with some time constant m/γ, where friction against the fluid is given by γv, and the mass will eventually return to its original behaviour of fluctuation around its average position. If we imagine that we had an *ensemble* of identical mass-spring systems, and we displaced each mass by an amount x, and then released it, the *average* displacement would obey a damped harmonic oscillator equation:

$$m\ddot{x} + \gamma\dot{x} + kx = 0. \tag{11.19}$$

We call γ the damping constant.

More generally, if we apply a time dependent sinusoidal force $f(t) = f_\omega e^{-i\omega t}$ to the system, and observe the displacement it observes, $x(t) = x_\omega e^{-i\omega t}$, then we define the response function as

$$\begin{aligned}\alpha_\omega = \langle x_\omega / f_\omega \rangle &= \frac{1}{-m\omega^2 - i\gamma\omega + k} \\ &= \frac{m(\omega_0^2 - \omega^2) + i\gamma\omega}{m^2(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \\ &\equiv \alpha'_\omega + i\alpha''_\omega,\end{aligned} \tag{11.20}$$

where $\omega_0^2 = k/m$ and α', α'' are the real and imaginary part of α. Because the mass behaves like a damped simple harmonic oscillator, it must be possible to write down a potential energy $\frac{1}{2}kx^2$ associated with displacement x. The principle of equipartition of energy tells us that this must have an average energy of $\frac{1}{2}k_BT$. We immediately deduce that the mean square displacement of the mass must be

$$\left\langle x^2 \right\rangle = k_BT/k = k_BT\alpha'_{\omega=0}. \tag{11.21}$$

11.3.0.1 Langevin equation

Using Langevin's idea that the fluctuating system obeys the damped simple harmonic oscillator equation but on top of the applied force $f(t)$ also has a *random force* $\xi(t)$ acting on it, we formulate the equation

$$m\ddot{x} + \gamma\dot{x} + kx = \xi(t), \tag{11.22}$$

which is what we already saw in Eqs. (11.1) and (11.11).

Within the Langevin equation, we see that there must be some connection between the random force and the damping term γ, because the mean square displacement in Eq. (11.21) is independent of γ, whereas the response to the force which causes the displacement gets smaller as the damping gets stronger: *as the damping gets larger, the random force must also get stronger.* To calculate the properties of the Langevin force, we can use the form of classical fluctuation dissipation theorem (FDT), explored in Appendix A.3:

$$\left\langle \delta x_\omega^2 \right\rangle = \frac{2k_B T}{\omega} \alpha_\omega''. \tag{11.23}$$

Here, $\delta x = x - \bar{x} = x$, as $\bar{x} = 0$ for our damped oscillator, and the difference with the earlier constant forms of FDT is that here we retain the time/frequency dependence of retarded parameters.

We can now apply this powerful relation to our damped oscillator, taking the Langevin force as an applied force $f(t)$:

$$x_\omega = f_\omega \alpha_\omega = \frac{f_\omega}{-m\omega^2 - i\gamma\omega + k} \tag{11.24}$$

$$\left\langle x_\omega^2 \right\rangle = \left\langle |x_\omega|^2 \right\rangle = \left\langle |\xi_\omega|^2 \right\rangle |\alpha_\omega|^2 = \frac{2k_B T}{\omega} \alpha_\omega'' \tag{11.25}$$

$$\implies \left\langle |\xi_\omega|^2 \right\rangle = \frac{2k_B T}{\omega} \frac{\alpha_\omega''}{|\alpha_\omega|^2} = 2k_B T \gamma. \tag{11.26}$$

This shows that, as postulated in the previous examples, the fluctuating Langevin force indeed has a uniform power spectrum, like white noise, and that the intensity of the Langevin force is given by the damping constant.

11.4 Working with Probability Distributions

One would like to have a more universal approach to stochastic processes which could, for instance, have a different friction law or a different form of external force. Let us re-formulate the theory of Brownian motion in a different manner, via the probability distribution.

11.4.1 1D Random Walk

For simplicity, we start with 1-dimensional motion: a particle moving in back and forth along a line, $x(t)$. Such a motion is analogous to the 1-dimensional *random walk*, a problem which you have seen several times in this and last year's courses. If

the particle may hop from one point to one of its two neighbouring points with equal probability, we then ask what is the probability that after N such steps the particle reaches a certain distance, x, from the point where it had started. By labelling the moves to the right as N_+ and to the left as N_- (with $N_+ + N_- = N$) and the length of an elementary step as a, the distance x can be expressed as

$$x = a(N_+ - N_-) = a(2N_+ - N), \tag{11.27}$$

from which the number of steps to the right, say, is equal to $N_+ = \frac{1}{2}N + \frac{1}{2}(x/a)$. Denoting the transition time per elementary step by τ, the total time of motion is $t = N\tau$. The probability of finding the configuration with N trials out of which N_+ are "successful" is, as usual,

$$P(N_+, N) = \frac{N!}{N_+!(N - N_+)!}\left(\frac{1}{2}\right)^N, \tag{11.28}$$

because both possibilities, steps to the right and to the left, have the same probability of 1/2. Now, the necessary simplifying assumption, equivalent to the assumption made in the previous section about the sufficiently long time since the beginning of motion, is that the numbers of steps (both N and N_+) are large. Using the Stirling formula $N! \approx e^{-N}N^N\sqrt{2\pi N}$ we obtain

$$P(N_+, N) = \sqrt{\frac{N}{2\pi N_+(N - N_+)}}\, e^{N\ln N - N_+\ln N_+ - (N-N_+)\ln(N-N_+) - N\ln 2}. \tag{11.29}$$

Now one should get rid of unimportant N+ in favour of the displacement x, using Eq. (11.27), and expand the probability $P(N_+, N)$ in powers of the parameter $\epsilon = (x/aN) = (x\tau/at)$, which we assume to be small for a free random walk of many steps. Do the algebra as an exercise to obtain, keeping only terms up to second order in exponential,

$$\begin{aligned} P(N_+, N) &= \sqrt{\frac{2}{\pi N}}\sqrt{\frac{1}{1 - (x/aN)^2}}\exp\left[-\frac{x^2}{2a^2N}\right] \\ &= 2a\sqrt{\frac{1}{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right] \equiv 2aP(x,t), \end{aligned} \tag{11.30}$$

where the abbreviation $D = a^2/2\tau$ is used. Note, that we should have in mind letting τ and a go to zero, recovering the continuum description, but keeping fixed the ratio D. This is already looking familiar, reminding about the diffusion profiles evolving with time, or the problem of 1-dimensional rubber elasticity from 1*B* *Thermodynamics*. But let us make a few more steps. First, changing from the summation over the number of discrete steps to the integration is, taking into account Eq. (11.27),

$$\sum_{N_1}^{N_2}\cdots = \int_{N_1}^{N_2}\cdots \mathrm{d}N_+ = \int_{x_1}^{x_2}\cdots\frac{\mathrm{d}x}{2a}$$

$$\text{so that}\quad \sum_{N_1}^{N_2} P(N_+, N) = \int_{x_1}^{x_2} P(x,t)\,\mathrm{d}x\,, \tag{11.31}$$

where $P(x,t)$ is the proper continuous probability density defined in Eq. (11.30): $P(x,t)\,\mathrm{d}x$ gives the probability of finding the particle after time t in the interval $x \to x + \mathrm{d}x$ (having started at $x = 0$ at $t = 0$ in our picture). We now recover the key result about the 1-dimensional Brownian motion: $\langle x(t)^2 \rangle = 2Dt$. It is clear that the ratio of microscopic parameters of random walk motion, $D = a^2/2\tau$ plays the role of the diffusion constant, compare with Eq. (11.9).

The consideration in more than one dimension is analogous and, in fact, the results can be deduced immediately. Dividing this into three separate random walks, along x, y and z directions, one multiplies the probabilities of statistically independent processes, and thus obtains as before $\langle \mathbf{r}^3 \rangle = 3\,\langle x^2 \rangle = 6Dt$.

11.4.2 Diffusion Equation

Clearly the random walk resembles the diffusion process and it is time we establish an explicit connection. Let us return to the 1-dimensional discrete representation of a random walk the free Brownian particle is performing. Assign a number m to the current position the particle occupies after $N+1$ steps (simply define $m = x/a$ so that $m = 0, \pm 1, \pm 2, \cdots$) and denote the probability of this occurrence as $P(m, N+1)$. In order to arrive at this point m, the particle must have been at either $m+1$ or $m-1$ after N steps; there it arrived with probabilities $P(m+1, N)$ or $P(m-1, N)$. Thus the probability $P(m, N+1)$ consists of two parts stemming from two possibilities for the particle to jump into m with corresponding *transition probabilities*, denoted as $w(m, m+1)$ and $w(m, m-1)$:

$$P(m, N+1) = w(m, m-1)P(m-1, N) + w(m, m+1)P(m+1, N). \tag{11.32}$$

Fig. 11.4: The scheme of 'detailed balance' - the change in probability $P(m)$ is due to the difference between the *rate in*, Eq. (11.32), and the *rate out*: $-(w_+ + w_-)P(m)$.

Of course, $w(m, m+1) = \frac{1}{2}$ and $w(m, m-1) = \frac{1}{2}$ for our 1-dimensional free Brownian motion. Note that Eq. (11.32) is actually valid for the general case, provided $w(m, m+1) + w(m, m-1) = 1$, that is, the particle is certain to hop out of the position m on the next time-step. Now, subtract $P(m, N)$ from both sides of Eq. (11.32), see Fig. 11.4, and then divide it by the elementary time interval $\tau = t/N$. We have then

$$\begin{aligned}
\frac{P(m, N+1) - P(m, N)}{\tau} &= \frac{1}{\tau} w(m, m-1)P(m-1, N) + \frac{1}{\tau} w(m, m+1)P(m+1, N) \\
&\quad - \frac{1}{\tau}[w(m-1, m) + w(m+1, m)]P(m, N) \\
\frac{\partial P(m, t}{\partial t} &= \frac{1}{2\tau}[P(m-1, t) - 2P(m, t) + P(m+1, t)],
\end{aligned} \tag{11.33}$$

where in our case all w's $= 1/2$, which is implemented in Eq. (11.33). Now, let us rewrite this equation again, this time paying attention to the fact that the expression in square brackets is the discrete representation of second derivative:

$$\frac{\partial P(m,t)}{\partial t} = \frac{1}{2\tau}\frac{\partial^2 P(m,t)}{\partial m^2}. \tag{11.34}$$

Now, replacing the index m by a continuous variable, $m = x/a$, we have at last

$$\frac{\partial P(x,t)}{\partial t} = \frac{a^2}{2\tau}\frac{\partial^2 P(x,t)}{\partial x^2} \tag{11.35}$$

(because the discrete probability and the continuous probability density are linearly related: $P(m,t)\Delta m = P(x,t)\Delta x$, where $\Delta m = 1$ and $\Delta x = a$). This is the 1-dimensional diffusion equation with the diffusion constant $D = a^2/\tau$ defined, as before, as the constant limit at $a \to 0$, $\tau \to 0$. We already know its fundamental solution, which is given by Eq. (11.30)!

By analogy, we can deduce the corresponding equation for a 3-dimensional diffusion process (by considering separately the process along the three Cartesian coordinates)

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t) \tag{11.36}$$

The diffusion equation has an immense importance in physics in general. One has only to look at a direct analogy with heat transfer (which is just the diffusion of "fast" molecules in the medium), and at the Schr¨odinger equation, which is exactly Eq. (11.36) only with imaginary time, or $D = i\hbar/m$.

11.5 Diffusion in External Potentials

We have already examined the Brownian motion in external potential, but it was done from the Langevin equation, at a microscopic level. Now we are dealing with the probability function of the whole process, $P(\mathbf{r},t)$ and the kinetic equation that governs it. The simplest physical example of diffusion under external force is the problem of particle sedimentation in solution. In this case, the force acting on the particles is constant (just mg) and we can readily modify the earlier analysis of probability flow. Go back to Eq. (11.32) and Fig. 11.4, and now assume that the transition probabilities are not equal: independently of where the particle is on the x-scale, we take

$$w(m,m-1) = \frac{1}{2} - \epsilon \quad \text{and} \quad w(m,m+1) = \frac{1}{2} + \epsilon, \tag{11.37}$$

so that there is a preference for the particles to drift 'down' (from $m+1$ to m) as opposed to move 'up'. Repeating the procedure that led to Eq. (11.34) we now have

$$\frac{\partial P(m,t)}{\partial t} = \frac{1}{2\tau}\frac{\partial^2 P(m,t)}{\partial m^2} + \frac{2\epsilon}{\tau}\frac{\partial P(m,t)}{\partial m}, \tag{11.38}$$

$$\text{or} \quad \frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(mx,t)}{\partial x^2} + C\frac{\partial P(x,t)}{\partial x}, \tag{11.39}$$

with the results shown in Fig. 11.5, but we can reach a better understanding of this phenomenon if we just look at the steady state of this process. In the limit of $t \to \infty$ we expect no time-dependence left in the probability distribution (or the concentration of particles), so that Eq. (11.39) becomes

$$0 = D\frac{\partial^2 P(x)}{\partial x^2} + C\frac{\partial P(x)}{\partial x}. \tag{11.40}$$

We can integrate this up w.r.t. t and obtain $0 = D\,\partial P(x)/\partial x + CP(x) + K$, with K a constant of integration. However, this constant of integration can be fixed, because we know that for some very large x, both P and P' have to be $= 0$. Hence K must be $= 0$ as well, giving.

$$0 = D\frac{\partial P(x)}{\partial x} + cP(x), \quad \text{i.e.} \quad P_{\text{eq}}(x) = P_0 e^{-(C/D)x}. \tag{11.41}$$

If we recall the other definition of the diffusion constant, $D = k_B T/\gamma$, then the steady state distribution of particles in the gravity potential will take the form

$$P_{\text{eq}}(x) = P_0 \exp\left(-\frac{mgx}{k_B T}\right), \tag{11.42}$$

as long as we assign $C = mg/\gamma$, or the earlier parameter $\varepsilon = mg\tau/2\gamma a$. This is the equilibrium Boltzmann distribution with the gravitational potential energy mgx, which we could have guessed from the outset.

The requirement that the equilibrium probability distribution (in the steady state, at $t \to \infty$) reproduces the Boltzmann form, $P_{\text{eq}} \propto \exp[-E(x)/k_B T]$, with $E(x)$ the corresponding potential energy of the particle at point x, helps us understand the form of the generalised diffusion equation. Reproducing the argument in Eq. (11.41) we can say:

$$0 = D\frac{\partial P(x)}{\partial x} + \frac{1}{\gamma}\frac{\mathrm{d}E}{\mathrm{d}x}P(x), \tag{11.43}$$

$$\text{so that} \quad \frac{\mathrm{d}P}{P} = -\frac{1}{\gamma D}\,\mathrm{d}E \quad \text{and} \quad P_{\text{eq}}(x) = P_0 e^{(}-E(x)/k_B T), \tag{11.44}$$

where the negative derivative $f = \mathrm{d}E/\mathrm{d}x$ is the external force acting on the particle. This means that the full, time-dependent, generalised diffusion equation can be written as

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{1}{\gamma}\frac{\mathrm{d}E}{\mathrm{d}x} + D\frac{\partial}{\partial x}\right)P(x,t) \tag{11.45}$$

$$\text{or} \quad \frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{1}{\gamma}f(x)P(x,t)\right] + D\frac{\partial^2 P(x,t)}{\partial x^2}, \tag{11.46}$$

Fig. 11.5: The time-evolution of particle concentration $c(x,t)$, proportional to the probability, during sedimentation. The left panel shows particles "sinking" from an initial delta-function distribution at $x = x_0$, and the right panel shows particles being "lifted" by the thermal excitation having started from a delta-function distribution at $x = 0$.

which go by the name of the *Fokker-Planck equation*. Note that its steady-state limit solution reproducing the equilibrium Boltzmann distribution is only valid when the external potential energy $E(x)$ has a minimum: the free Brownian particle (at $f = 0$) has no equilibrium position to act as reference point and follows the classical diffusion behaviour described by Eqs. (11.9) and (11.30).

The generalised diffusion equation (11.46) can also be written in a form that reproduces the continuity equation that you have seen in the context, e.g., of charge density in electromagnetism:

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}, \tag{11.47}$$

$$\text{with} \quad J(x,t) = -D\frac{\partial P(x,t)}{\partial x} + \frac{1}{\gamma} f(x)P(x,t) = -De^{-\beta E(x)}\frac{\partial}{\partial x}\left[e^{\beta E(x)}P(x,t)\right], \tag{11.48}$$

where $J(x,t)$ represents the net current for the probability $P(x,t)$, or equivalently, the particle concentration $c(x,t)$. This net current arises as the sum of the *diffusion current* $-D\frac{\partial P(x,t)}{\partial x}$, which is driven by a probability (or concentration) gradient – as in Fick's law – and the *drift current* $\frac{1}{\gamma}f(x)P(x,t)$, which is driven by the applied force. The equivalent second form of writing the total current can be checked by differentiation, and implementing $D = k_B T/\gamma$. For the force-free Brownian motion, the total current is just the diffusion current, i.e. the negative gradient of concentration: $J = -D\nabla c(x,t)$.

11.5.1 The Kramers Problem: Escape over a Potential Barrier

As a final illustration of the application of principles of Brownian motion we shall consider the problem of the escape of particles over potential barriers. The solution to this problem has important implications on a variety of physical, chemical and astronomical problems, known as the *thermal activation*.

Fig. 11.6: The potential energy profile of the Kramers problem. The key parameter is the height of the energy barrier, ΔE, at a position x_0.

As usual, for simplicity limiting ourselves to a 1-dimensional problem, consider a particle moving in a potential field (x) shown in Fig. 11.6. We suppose that the particles are initially caught in the *metastable* state at A, and we wish to find the rate at which the particles will escape from this state over the potential, as a result of thermal motion.

Let us concentrate on the long-time limit of this process, when the steady current of particles is established. Eq. (11.48) tells us that, at constant current J, integration between points A and B along the x-axis gives:

$$J \int_A^B e^{\beta E(s)}\,\mathrm{d}s = -D\Big[e^{\beta E(x)} P(x)\Big]_A^B, \tag{11.49}$$

where on the right-hand side the integral of the full derivative $\mathrm{d}/\mathrm{d}x$ just gives us the difference between the initial and final values of the argument. Let us now approximate the potential near the metastable equilibrium point A as $E(x) \approx E_A + \frac{1}{2}K_A x^2$. The number of particles in the vicinity of A can be estimated from taking

$$\mathrm{d}N_A = P(x_A) e^{-\beta E_A}\,\mathrm{d}x \tag{11.50}$$

and integrating the Gaussian exponential $e^{-\beta E_A}$ to obtain:

$$N_A \approx P(x_A) \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_A x^2}\,\mathrm{d}x = P(x_A)\sqrt{\frac{2\pi k_B T}{K_A}}. \tag{11.51}$$

Considering point B, we can safely neglect its contribution to Eq. (11.49) if we assume the potential well $E_B(x)$ is deep enough (the end-point being an "infinite sink" of particles). Then (since $E(x_A) = 0$) the steady state current takes the form

$$J \approx \frac{DP(x_A)}{\int_A^B e^{\beta E(s)}\,\mathrm{d}s}; \qquad \text{rate} = \frac{J}{N_A} D\sqrt{\frac{K_A}{2\pi k_B T}} \frac{1}{\int_A^B e^{\beta E(s)}\,\mathrm{d}s}. \tag{11.52}$$

The principal contribution to the integral in denominator arises only from the very small region near the potential barrier C. Although the exact solution of Kramers problem may depend on the particular shape of the potential $E(x)$, a very good estimate may be obtained by simply assuming the parabolic form near the maximum: $E_C \approx \Delta E - \frac{1}{2}K_C(x-x_0)^2$. On this assumption, with a sufficient degree of accuracy we have

$$\int_A^B e^{\beta E(s)}\,\mathrm{d}s \approx e^{\Delta E/k_BT}\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_C(x-x_0)^2}\,\mathrm{d}x = e^{\Delta E/k_BT}\sqrt{\frac{2\pi k_BT}{K_C}}. \tag{11.53}$$

Combining Eqs. (11.52) and (11.53) we obtain the rate of particles transit over the barrier (equivalent to the rate of leaving the metastable state A):

$$\text{rate} = \frac{J}{N_A} = De^{-\Delta E/k_BT}\frac{\sqrt{K_AK_C}}{2\pi k_BT} = \frac{\sqrt{K_AK_C}}{2\pi\gamma}e^{-\Delta E/k_BT}. \tag{11.54}$$

This expression gives the probability, per unit time, that a particle originally in the potential hole A, will escape to B by crossing the barrier at C. The prefactor fraction is determined by various microscopic features of the system, but the most important fact to pay attention to is the exponential. This is the form representing the *thermal activation*, often known as the empirical Arrhenius law which one encounters in a variety of physical situations.

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Appendix A

Appendix

A.1 Microscopics of Irreversibility

Can we derive the law of increase of entropy from the underlying microscopic laws such as Newtonian mechanics or quantum mechanics? This is a difficult question and I will discuss it in terms of a simple model, an isolated container (U constant) of gas consisting of N point particles obeying Newtonian mechanics. It is very important in physics to start with the simplest possible model which is relevant to the problem at hand. It is possible to derive the PEEP for such a system from Newtonian mechanics, and the proof is given in Appendix A.2. This is helpful but it doesn't tell us about the approach to equilibrium and the law of increase of entropy.

If we write the jump rate between two microstates, i and j, as ν_{ij}, and assume that the jump rates for the processes $i \to j$ and $j \to i$ are the same, then $\nu_{ij} = \nu_{ji}$. If the probability of being in microstate i is p_i then the probability of jumping from i to any other microstate is $\sum_j \nu_{ij} p_i$ and the probability of jumping from any other microstate into state i is $\sum_j \nu_{ji} p_j$, so that overall we obtain Fermi's "master equation",

$$\begin{aligned} \frac{\mathrm{d}p_i}{\mathrm{d}t} &= \sum_j \left(-\nu_{ij} p_i + \nu_{ji} p_j\right) \\ &= \sum_j \nu_{ij}(p_j - p_i). \end{aligned} \tag{A.1}$$

In dynamic equilibrium $\mathrm{d}p_i/\mathrm{d}t = 0$ so that, as long as none of the ν_{ij} are zero (accessibility), equilibrium must correspond to $p_i = p_j$, i.e., the postulate of equal equilibrium probabilities (PEEP). The master equation not only predicts the PEEP, it also shows *irreversibility*. The master equation predicts that if the probabilities, p_i, are not equal to their equilibrium values then processes occur which drive them towards equilibrium. The master equation correctly shows how systems approach equilibrium. All that remains is to derive the master equation from the underlying microscopic physical laws! Here comes the disappointment, unfortunately it is *not possible* to derive the master equation in this way.

Consider a classical gas of molecules in an isolated container. The molecules obey Newton's laws, which have time reversal symmetry, so if we start off with all the molecules at one end of the container, make a film of the subsequent motion in which the molecules spread out over the container and play it backwards (equivalent to reversing all the velocities) nothing looks wrong, they are still obeying Newton's

Fig. A.1: Four snapshots of a gas in a box approaching equilibrium.

laws. The Schrödinger equation of quantum mechanics also obeys *time reversal symmetry* and therefore it is not possible to derive the master equation from classical or quantum mechanics without some additional assumptions. Some of the equations of physics are irreversible, such as the diffusion equation and the Navier-Stokes equation, but these describe macroscopic phenomena and they already have the Second Law of Thermodynamics built into them. The success of these equations can be used as evidence that the Second Law is correct, but they cannot be invoked to derive it.

A.1.1 Law of Increase of Entropy

This leads us to the greatest paradox of thermal and statistical physics, which Boltzmann sought to answer. How can irreversibility arise from the underlying time-reversible equations of motion? This problem is still not resolved to everyone's satisfaction. I will present a view which I hope is not too controversial, but certainly some will argue with it.

Consider a gas of N particles obeying Newtonian mechanics within an isolated container ($U =$ constant) which has upper and lower chambers joined by a hole. A sequence of snapshots of the gas is shown in Fig. A.1. The first snapshot on the left shows a low entropy non-equilibrium state with all the gas in the lower chamber. If we start the system off from this state then we expect gas to move through the hole into the upper chamber so that equilibrium is approached where the gas is evenly distributed between the upper and lower chambers. The final state is then one of high entropy. Why does the gas prefer to be in the equilibrium state shown in the last snapshot on the right of Fig. A.1?

To answer this question we use arguments based on the phase space introduced in Section 4.1.[1] Each snapshot in Fig. A.1 shows a microstate of the system (I haven't shown the velocities of the particles) which is a member of a *macrostate* $\Gamma(X)$ consisting of very many microstates which *"look like"* the snapshot. Let me try and make this notion more precise. Suppose the gas contains 10^{23} molecules and we divide up the system into 10^9 small boxes. In equilibrium each box contains on

[1]Note that because we are assuming that the energy of our system is constant the trajectory of the point representing the system's microstate is confined to a constant energy surface of the phase space.

average $10^{23}/10^9 = 10^{14}$ molecules. In equilibrium the number of molecules in each box fluctuates about the mean value, but fluctuations of the size of the snapshot on the left of Fig. A.1 are never seen. We can define a macrostate by specifying the number of particles in each box, to within some range. One can associate a Boltzmann entropy with each macrostate,

$$S_B(X) = k_B \ln |\Gamma(X)|, \tag{A.2}$$

where $|\Gamma(X)|$ is the volume of phase space occupied by the *macrostate* $\Gamma(X)$.

The different macrostates occupy different volumes of the phase space and the equilibrium macrostate occupies a much greater volume of phase-space than any other macrostate. The ratio of the phase space volumes, $|\Gamma(X)|$, for the macrostates on the right and left snapshots in Fig. A.1 is roughly $2^N = 2^{10^{23}}$. We expect that if the system starts off in the macrostate corresponding to the snapshot on the left it will move with a probability of essentially unity into the much larger region of phase space corresponding to the equilibrium macrostate. In other words, the macrostate on the right of A.1 is immensely more probable than the one on the left.

Many objections were raised to these ideas. Loschmidt noted that the form of Newton's laws means that the time-reversed solution is also valid. Zermelo noted that according to the Poincaré recurrence theorem almost all microstates will return to their initial microstate after a long enough period of time (which, however, for macroscopic systems turns out to be longer than the age of the universe). These objections illustrate the fact that there are points in phase space which do not have proper thermodynamic behaviour, but in fact they form a vanishingly small fraction of the total number of points.

Let us revisit the idea of watching a classical gas move towards equilibrium and then playing the film backwards. If we reverse all the velocities when the gas has attained equilibrium then obviously it just returns to its original state, which was far from equilibrium. The important point to realise is that this is totally irrelevant to the argument! We would not notice anything unphysical when we watched the film played backwards because Newton's laws are still obeyed, but starting conditions such that the system quickly moves far away from equilibrium are highly improbable, as once more I assert that most points in phase space just don't behave like that!

Modern computers have made it possible to simulate the time evolution of a gas of particles obeying Newton's laws. The number of particles and the simulation time must be kept fairly small so that the evolution is (almost) reversible. However, the results fully support Boltzmann's arguments.

Another important thing to notice is what Boltzmann's arguments *don't* involve. There was no mention of the precise nature of the dynamics, we only said that the molecules obeyed Newtonian mechanics. We have not used the PEEP. Nor have we mentioned quantum mechanics, which Boltzmann didn't know about. Of course matter obeys quantum mechanics rather than classical mechanics, but the

introduction of quantum mechanics into the problem of the gas in a container only obscures the central issues. We *ought* to be able to explain this phenomenon within classical mechanics. Nor have we invoked "our limited knowledge of the microscopic state of the system", which is clearly irrelevant within a classical framework. Finally we have also not invoked residual interactions with the surroundings, although in practice these can never be entirely removed.

A.1.2 The Arrow of Time

We have explained why entropy increases with time. Now comes the difficult part of the argument. Why should there be an "arrow of time" in our universe which says that time moves forwards, if the microscopic laws of physics are reversible? This is a rather controversial topic and a proper discussion of it is outside the scope of this course. The basic idea is that just after the Big Bang the universe was in a low entropy state; the arrow of time that we experience may simply be the continuing tendency of the universe to move away from this special state.[2]

A.2 Liouville's Theorem

The state of a classical system at some given time is determined by its position in the $6N$-dimensional phase space. The trajectory of the system in the phase space is determined by the equations of motion which, in the Hamiltonian formulation, are:

$$\frac{\partial q_i}{\partial t} = \frac{\partial \mathcal{H}}{\partial p_i} \quad \text{and} \quad \frac{\partial p_i}{\partial t} = -\frac{\partial \mathcal{H}}{\partial q_i}, \tag{A.3}$$

where $\mathcal{H}$ is the Hamiltonian function giving the system energy: $E = \mathcal{H}(\{q_i, p_i\})$. The classical equivalent of the quantum probability distribution is obtained by defining a *probability density* $\varrho(\{q_i, p_i\})$ in the $6N$ dimensional phase space.[3]

To obtain *Liouville's equation* we use the continuity relation, which states that probability is conserved,

$$\frac{\partial \varrho}{\partial t} + \boldsymbol{\nabla} \cdot (\varrho \mathbf{v}) = 0. \tag{A.4}$$

The divergence term gives

$$\begin{aligned} \boldsymbol{\nabla} \cdot (\varrho \mathbf{v}) &= \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}\left(\varrho \frac{\partial q_i}{\partial t}\right) + \frac{\partial}{\partial p_i}\left(\varrho \frac{\partial p_i}{\partial t}\right) \right\} \\ &= \sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t}\frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t}\frac{\partial \varrho}{\partial p_i} \right\} + \sum_{i=1}^{3N} \left\{ \varrho \frac{\partial^2 q_i}{\partial q_i \partial t} + \varrho \frac{\partial^2 p_i}{\partial p_i \partial t} \right\}. \end{aligned} \tag{A.5}$$

[2] For a more detailed discussion see J. Lebowitz, *Physics Today*, Sept. 1993, p.32

[3] *Probability density* means what it says: you have to multiply by a volume element to get a probability.

The second term in brackets is identically equal to zero, from Hamilton's equations, so Liouville's equation is

$$\frac{\partial \varrho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t} \frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t} \frac{\partial \varrho}{\partial p_i} \right\} = 0. \tag{A.6}$$

We now derive *Liouville's Theorem*, which states that in equilibrium the probability density ϱ is constant along the trajectories of the system in phase space. We are interested in the equilibrium ensemble, so $\partial \varrho / \partial t = 0$, and we obtain

$$\sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t} \frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t} \frac{\partial \varrho}{\partial p_i} \right\} = 0. \tag{A.7}$$

In other words, as we travel along the trajectory in phase space the probability density doesn't change.

This is a very important result, because the trajectories in phase space are lines of constant internal energy of the system, so it tells us that in equilibrium the probability density depends only on the energy, so states with the same energy have the same probability, which is the PEEP.

A.3 Fluctuation-Dissipation Theorem and Wiener-Khinchin Theorem

Following on from Section 11.3 11.3, we can obtain a very useful and general result about the relation between the frequency spectrum of fluctuations in a dynamic system and the response function of this system. First, we operate in the time-domain and argue that the expectation value of the fluctuating variable $x(t)$ is given by the history of forces that have acted on it:

$$\langle x(t) \rangle = \langle x \rangle_0 + \int_{-\infty}^{t} f(t') \alpha(t - t') \, \mathrm{d}t' \,, \tag{A.8}$$

where $\langle x \rangle_0$ is the average value x assumes in the absence of the applied force f, and $\alpha(t - t')$ gives the response of the dynamical system we are modelling at time t, provided it was exposed to a δ-function force at time t'. This is the Fourier transform of the frequency-dependent response function α_ω, mentioned above, and it is also called Green's function.

We now choose a specific form for $f(t)$, namely an infinitesimal perturbation that switches on at $t = -\infty$ and switches off at $t = 0$:

$$f(t) = f_0 \theta(-t) \tag{A.9}$$

where $\theta(t)$ is the Heaviside step function.

We can express the expectation value of x at time t by integrating over all possible values that x may have at time t, weighted with their corresponding likelyhood. These likelyhoods, in turn, are obtained by integrating over all values x' at time 0, weighted with their likelyhoods and multiplied further by the probability that these values of x' would evolve into x at time $t > 0$:

$$\langle x(t)\rangle = \iint \mathrm{d}x'\,\mathrm{d}x\, x P(x,t;x',0) W(x',0). \tag{A.10}$$

Here, $P(x,t;x',0$ is the conditional probability that the system will evolve to value x at time t, if it had value x' at time $t=0$, and $W(x',0)$ is the probability that the system had value x' at time $t=0$. This is a special case of the more general result

$$\langle g(x(t))h(x(0))\rangle = \iint \mathrm{d}x'\,\mathrm{d}x\, g(x)h(x')P(x,t;x',0)W(x',0). \tag{A.11}$$

We can find $W(x',0)$ in equilibrium from statistical mechanics:

$$\begin{aligned} W(x',0) &= \frac{e^{-\beta(E_0(x')-f_0x')}}{\int e^{-\beta(E_0(x'')-f_0x'')}\,\mathrm{d}x'} \underbrace{\simeq}_{\text{Taylor expand}} \frac{e^{-\beta E_0(x')}(1+\beta f_0 x')}{\int e^{-\beta E_0(x'')}(1+\beta f_0 x'')\,\mathrm{d}x''} \\ &= \frac{e^{-\beta E_0(x')}(1+\beta f_0 x')}{\int e^{-\beta E_0(x'')}(1+\beta f_0 \langle x'\rangle_0)\,\mathrm{d}x''} = W_0(x')(1+\beta f_0(x'-\langle x'\rangle_0)). \end{aligned} \tag{A.12}$$

Here, $\langle\cdots\rangle_0$, which we abbreviate in the following with $\bar{\cdots}$, denotes an average with respect to the unperturbed system, without applied force $f(t)$. This average is determined by the unperturbed energy $E_0(x)$, which produces the unperturbed probability distribution $W_0(x)$.

Putting this expression for $W(x',0)$, which is accurate for infinitesimal perturbations f – and our test perturbation was designed to be infinitesimal – back into Eq. (A.10) then gives the expectation value for $x(t)$ as

$$\begin{aligned} \langle x(t)\rangle &= \iint \mathrm{d}x'\,\mathrm{d}x\,(x-\bar{x}+\bar{x})P(x,t;x',0)W_0(x',0)(1+\beta f_0(x'-\bar{x})) \\ &= \langle (x(t)-\bar{x}+\bar{x})(1+\beta f_0(x'-\bar{x}))\rangle_0 \\ &= \bar{x} + \beta f_0 \langle (x(t)-\bar{x})(x(0)-\bar{x})\rangle_0 \\ &= \bar{x} + \beta f_0 A(t), \end{aligned} \tag{A.13}$$

where $A(t) = \langle (x(t)-\bar{x})(x(0)-\bar{x})\rangle_0$ is called the *autocorrelation function* of the variable $x(t)$.

Earlier on, when first considering the effect of a perturbing force $f(t)$ on our system, namely in Eq. (A.8), the expectation value of $x(t)$ was related to the response function of the system. We can now combine that equation with our most recent result to obtain:

$$\langle x(t)\rangle - \bar{x} = \beta f_0 A(t) = \int_{-\infty}^{t} f(t')\alpha(t-t')\,\mathrm{d}t' \underbrace{=}_{\tau=t-t'} f_0 \int_0^\infty \theta(\tau-t)\alpha(\tau)\,\mathrm{d}\tau = f_0 \int_t^\infty \alpha(\tau)\,\mathrm{d}\tau\,. \tag{A.14}$$

Taking the derivative w.r.t. t on both sides, we obtain the key result

$$\frac{\mathrm{d}A}{\mathrm{d}t}\theta(t) = -\frac{1}{\beta}\alpha(t). \tag{A.15}$$

The step function $\theta(t)$ ensures that $\alpha(t) = 0$ for $t < 0$, which is required by causality. We find that the time derivative of the autocorrelation function is determined by the response function

A.3.1 Wiener-Khinchin Theorem

To take this further, we need to study the behaviour of our system in the frequency domain. We use the following conventions for the treatment of Fourier series for a variable $y(t)$:

$$y(t) = \frac{1}{\sqrt{t_0}} \sum_\omega y_\omega e^{-i\omega t}, \tag{A.16}$$

$$y_\omega = \frac{1}{\sqrt{t_0}} \int_{-t_0/2}^{t_0/2} y(t) e^{-\omega t}\, \mathrm{d}t\,, \tag{A.17}$$

$$\omega = \frac{2\pi}{t_0} \quad \text{with} \quad n \in \mathbb{Z}, \tag{A.18}$$

$$\sum_\omega \xrightarrow[t_0\to\infty]{} \frac{t_0}{2\pi} \int \mathrm{d}\omega\,, \tag{A.19}$$

where the Fourier integrals are carried out over a time interval t_0, producing a grid of allowed frequencies spaced $2\pi/t_0$. Because the physical variable $y(t)$ is real-valued, we can use y^* instead of y, when convenient.

We find that for two frequencies ω, Ω and for correlation functions that are invariant under translation, $\langle y(t+\tau)y(t)\rangle = \langle y^*(t+\tau)y(t)\rangle = \langle y^*(\tau)y(0)\rangle$:

$$\begin{aligned}
\left\langle y^*_{\omega+\Omega} y_\omega \right\rangle &= \frac{1}{t_0} \int_{-t_0/2}^{t_0/2} \int_{-t_0/2}^{t_0/2} \langle y^*(t_1)y(t_2)\rangle\, e^{i(\omega+\Omega)t_1} e^{i\omega t_2}\, \mathrm{d}t_1\, \mathrm{d}t_2 \\
(\text{setting}\, t_1 = t_2 + \tau) \quad &= \frac{1}{t_0} \int \mathrm{d}\tau\, \mathrm{d}t_2\, \langle y^*(t_2+\tau)y(t_2)\rangle\, e^{-i(\omega+\Omega)(t_2+\tau)} e^{i\omega t_2} \\
&= \frac{1}{t_0} \underbrace{\int \mathrm{d}t_2\, e^{-i\Omega t_2}}_{=t_0 \quad \text{for} \quad \Omega=0} \int \mathrm{d}\tau\, \langle y^*(\tau)y(0)\rangle\, e^{-i\omega\tau} e^{-i\Omega\tau} \\
&= \delta_{\Omega,0} \int \mathrm{d}\tau\, \langle y^*(\tau)y(0)\rangle\, e^{-i\omega\tau}.
\end{aligned} \tag{A.20}$$

We see two results: firstly, the frequency components of our fluctuating variable $y(t)$ are uncorrelated: a finite result is only obtained for the average $\left\langle y^*_{\omega_1} y_{\omega_2}\right\rangle$, when $\omega_1 = \omega_2$. This is a consequence of the translational invariance of the correlation function. Secondly, the power spectrum $\langle y^*_\omega y_\omega\rangle$ of our process turns out to be given by the Fourier transform of the autocorrelation function. This is the essence of the Wiener-Khinchin theorem.

A.3.2 Power Spectrum of Fluctuations Given by Imaginary Part of the Response Function

We can use the Wiener Khinchine theorem to revisit the earlier result Eq. (A.15):

$$\begin{aligned}
\alpha(t) &= -\beta \frac{\mathrm{d}A}{\mathrm{d}t}\theta(t) \\
\alpha_\omega &= \int_{-\infty}^{\infty} \alpha(t) e^{i\omega t}\,\mathrm{d}t \\
&= -\beta \int_0^{\infty} \dot{A} e^{i\omega t}\,\mathrm{d}t \\
&= i\omega\beta \int_0^{\infty} A(t) e^{i\omega t}\,\mathrm{d}t + \beta A(0) \quad \text{(integration by parts)} \\
&= \frac{1}{2} i\omega\beta \int_{-\infty}^{\infty} A(t) e^{i\omega t}\,\mathrm{d}t - \omega\beta \int_0^{\infty} A(t)\sin(\omega t)\,\mathrm{d}t + \beta A(0),
\end{aligned} \tag{A.21}$$

where the rearrangement in the last step follows from the fact that $A(t)$ is a real and even function. We can now relate the real and imaginary parts of the response function α_ω to properties of the fluctuation spectrum:

$$\alpha'_{\omega=0} = \beta \left\langle |x(0) - \bar{x}|^2 \right\rangle = \beta \left\langle |\delta x|^2 \right\rangle, \qquad \alpha''_\omega = \frac{1}{2}\omega\beta \left\langle |\delta x_\omega|^2 \right\rangle. \tag{A.22}$$

The last step follows from the Wiener-Khinchin theorem, and we write $\delta x = x - \bar{x}$. Rearranging this slightly, we obtain the power spectrum of fluctuations around the mean, $\left\langle |\delta x_\omega|^2 \right\rangle$, from the imaginary part of the response function. The variance of the fluctuations, in turn, is given by the real part of the response function:

$$\left\langle |\delta x|^2 \right\rangle = k_B T \alpha'_{\omega=0}, \qquad \left\langle |\delta x_\omega|^2 \right\rangle = \frac{2k_B T}{\omega}\alpha''_\omega. \tag{A.23}$$

The first of these two expressions already followed from the equipartition theorem and was introduced in Eq. (11.21), but the second is new; this is the classical version of the fluctuation-dissipation theorem.

A.4 Stirling's Approximation

Stirling's approximation gives an approximate value for the factorial function $n!$ for $n \gg 1$. The approximation can most simply be derived for $n \in \mathbb{Z}$ by approximating

the sum over the terms of the factorial with an integral, so that

$$\begin{aligned}
\ln(n!) &= \ln\left(\prod_{i=1}^{n} i\right) \\
&= \sum_{i=1}^{n} \ln i \\
&\approx \int_1^n \ln x \, \mathrm{d}x \\
&= [x \ln x - x]_1^n \\
&= n \ln n - n + 1 \\
&\approx n \ln n - n. \qquad \text{(A.24)}
\end{aligned}$$

The equation can also be derived using the integral definition of the factorial,

$$n! = \int_0^\infty e^{-x} x^n \, \mathrm{d}x \, . \qquad \text{(A.25)}$$

Note that the derivative of the logarithm of the integrand can be written

$$\frac{\mathrm{d}}{\mathrm{d}x} \ln\left(e^{-x} x^n\right) = \frac{\mathrm{d}}{\mathrm{d}x}(n \ln x - x) = \frac{n}{x} - 1. \qquad \text{(A.26)}$$

The integrand is sharply peaked with the contribution important only near $x = n$. Therefore, let $x = n + \xi$ where $\xi \ll n$, and write

$$\begin{aligned}
\ln\left(e^{-x} x^n\right) &= n \ln x - x \\
&= n \ln(n + \xi) - (n + \xi). \qquad \text{(A.27)}
\end{aligned}$$

Now,

$$\begin{aligned}
\ln(n + \xi) &= \ln[n\left(1 + \frac{\xi}{n}\right)] \\
&= \ln n + \ln\left(1 + \frac{\xi}{n}\right) \\
&= \ln n + \frac{\xi}{n} - \frac{1}{2}\frac{\xi^2}{n^2} + \cdots \, , \qquad \text{(A.28)}
\end{aligned}$$

so

$$\begin{aligned}
\ln\left(e^{-x} x^n\right) &= n \ln(n + \xi) - (n + \xi) \\
&= n \ln n + \xi - \frac{1}{2}\frac{\xi^2}{n} - n - \xi + \cdots \\
&= n \ln n - n - \frac{\xi^2}{2n} + \cdots \, . \qquad \text{(A.29)}
\end{aligned}$$

Taking the exponential of each side then gives

$$\begin{aligned}
x^n e^{-x} &\approx e^{n \ln n} e^{-n} e^{-\xi^2/2n} \\
&= n^n e^{-n} e^{-\xi^2/2n}. \qquad \text{(A.30)}
\end{aligned}$$

Plugging into the integral expression for $n!$ then gives

$$\begin{aligned} n! &\approx \int_{-n}^{\infty} n^n e^{-n} e^{-\xi^2/2n}\,\mathrm{d}\xi \\ &= n^n e^{-n} \int_{-\infty}^{\infty} e^{-\xi^2/2n}\,\mathrm{d}\xi\,. \end{aligned} \tag{A.31}$$

Evaluating the integral gives

$$\begin{aligned} n! &\approx n^n e^{-n}\sqrt{2\pi n} \\ &= \sqrt{2\pi} n^{n+1/2} e^{-n}. \end{aligned} \tag{A.32}$$

Taking the logarithm of both sides then gives

$$\begin{aligned} \ln(n!) &\approx n\ln n - n + \frac{1}{2}\ln(2\pi n) \\ &= \left(n + \frac{1}{2}\right)\ln n - n + \frac{1}{2}\ln(2\pi). \end{aligned} \tag{A.33}$$

This is Stirling's series with only the first term retained and, for large n, it reduces to Stirling's approximation

$$\boxed{\ln(n!) \approx n\ln n - n.} \tag{A.34}$$

Note, this is a *lower* limit!

A.5 Lagrange Multipliers

A.6 The Sommerfeld Expansion

The sommerfeld expansion is applied to integrals of the form

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon\, H(\varepsilon) n(\varepsilon), \quad n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}, \tag{A.35}$$

where $H(\varepsilon)$ vanishes as $\varepsilon \to -\infty$ and diverges no more rapidly then some power of ε as $\varepsilon \to +\infty$. If one defines

$$K(\varepsilon) = \int_{-\infty}^{\varepsilon} H(\varepsilon')\,\mathrm{d}\varepsilon'\,, \tag{A.36}$$

so that

$$H(\varepsilon) = \frac{\mathrm{d}K(\varepsilon)}{\mathrm{d}\varepsilon}, \tag{A.37}$$

the one can integrate by parts[4] in (A.35) to get

$$\int_{-\infty}^{\infty} H(\varepsilon) n(\varepsilon)\,\mathrm{d}\varepsilon = \int_{-\infty}^{\infty} K(\varepsilon)\left(-\frac{\partial n}{\partial \varepsilon}\right)\mathrm{d}\varepsilon\,. \tag{A.38}$$

[4]The integrated term vanishes at ∞ because the Fermi function vanishes more rapidly than K diverges, and at $-\infty$ because the Fermi function approaches unity while K approaches zero.

Since n is indistinguishable from zero when ε is more than a few k_BT greater than μ and indistinguishable from unity when ε is more than a few k_BT less than μ, its ε-derivative will be appreciable only within a few k_BT of μ. Provided that H is non-singular and not too rapidly varying in the neighbourhood of $\varepsilon = \mu$, it is very reasonable to evaluate (A.38) by expanding $K(\varepsilon)$ in a Tay lor series about $\varepsilon = \mu$, with the expectation that only the first few terms will be of importance

$$K(\varepsilon) = K(\mu) + \sum_{n=1}^{\infty} \left[\frac{(\varepsilon-\mu)^n}{n!}\right] \frac{\mathrm{d}^n K(\varepsilon)}{\mathrm{d}\varepsilon^n}\bigg|_{\varepsilon=\mu}. \tag{A.39}$$

When we substitute (A.39) in (A.38), the leading term gives just $K(\mu)$, since

$$\int_{-\infty}^{\infty} -\frac{\partial n}{\partial \varepsilon}\,\mathrm{d}\varepsilon = 1. \tag{A.40}$$

Furthermore, since $\partial n/\partial\varepsilon$ is an even function of $\varepsilon - \mu$, only terms with even n in (A.39) contribute to (A.38), and if we reexpress K in terms of the original function through (A.36), we find that

$$\int_{-\infty}^{\infty} \mathrm{d}\varepsilon\, H(\varepsilon) n(\varepsilon) = \int_{-\infty}^{\mu} H(\varepsilon)\,\mathrm{d}\varepsilon + \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{(\varepsilon-\mu)^{2n}}{(2n)!}\left(-\frac{\partial n}{\partial\varepsilon}\right)\mathrm{d}\varepsilon\, \frac{\mathrm{d}^{2n-1}}{\mathrm{d}\varepsilon^{2n-1}} H(\varepsilon)\bigg|_{\varepsilon=\mu}. \tag{A.41}$$

Finally, making the substitution $(\varepsilon-\mu)/k_BT = x$, we find that

$$\int_{-\infty}^{\infty} H(\varepsilon) n(\varepsilon)\,\mathrm{d}\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\,\mathrm{d}\varepsilon + \sum_{n=1}^{\infty} a_n (k_BT)^{2n} \frac{\mathrm{d}^{2n-1}}{\mathrm{d}\varepsilon^{2n-1}} H(\varepsilon)\bigg|_{\varepsilon=\mu}, \tag{A.42}$$

where the a_n are dimensionless numbers given by

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!}\left(-\frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{e^x+1}\right)\mathrm{d}x\,. \tag{A.43}$$

By elementary manipulations one can show that

$$a_n = 2\left(1 - \frac{1}{2^{2n}} + \frac{1}{3^{2n}} - \frac{1}{4^{2n}} + \frac{1}{5^{2n}} - \cdots\right). \tag{A.44}$$

This is usually written in terms of the Riemann zeta function, $\zeta(n)$, as

$$a_n = \left(2 - \frac{1}{2^{2(n-1)}}\right)\zeta(2n), \tag{A.45}$$

where

$$\zeta(n) = 1 + \frac{1}{2^n} + \frac{1}{3^n} + \frac{1}{4^n} + \cdots\,. \tag{A.46}$$

For the first few n, $\zeta(2n)$ has the values

$$\zeta(2n) = 2^{2n-1}\frac{\pi^{2n}}{(2n)!}B_n, \tag{A.47}$$

where the B_n are known as Bernoulli numbers, and

$$B_1 = \frac{1}{6}, \quad B_2 = \frac{1}{30}, \quad B_3 = \frac{1}{42}, \quad B_4 = \frac{1}{30}, \quad B_5 = \frac{5}{66}. \tag{A.48}$$

In most practical calculations in metals physics, one rarely needs to know more than $\zeta(2) = \pi^2/6$, and never goes beyond $\eta(4) = \pi^4/90$. Nevertheless, if one should wish to carry the Sommerfeld expansion (6.49) beyond $n = 5$ (and hence past the values of B_n listed in (A.48)), by the time $2n$ is as large as 12, the a_n can be evaluated to five-place accuracy by retaining only the first two terms in the alternating series (A.44).

Appendix B

Appendix: Equations

B.1 The Basics of Thermodynamics 1

B.2 Thermodynamic Equilibrium 2

B.3 The Basics of Statistical Mechanics 3

B.4 Classical Ideal Gas 4