

# Part II Statistical Mechanics

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# Abstract

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The abstract (no more than 250 words) makes it possible to assess the interest of a document and makes it easier to identify it in a bibliographic search in databases where the document is referenced.

It is recommended that the summary briefly addresses:

- Main objectives and theme or motivations for the work;
- Methodology used (when necessary for understanding the report);
- Results, analyzed from a global point of view;
- Conclusions and consequences of the results, and link to the objectives of the work.

As this report template is aimed at work that focuses mainly on software development, some of these components may be less emphasized, and information on the work's analysis, design, and implementation may be added.

The abstract should not contain references.

**Keywords:** Keyword 1 · Keyword 2 · Keyword 3 · Keyword 4



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## CHAPTER 1

# The Basics of Thermodynamics

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## 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:

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

where  $m$  is the atomic mass and  $\mathbf{v}_i$  is the velocity of the  $i$ th 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:

$$P(v) dv = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} 4\pi v^2 dv. \quad (1.2)$$

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

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

$$pV = N k_B T \quad \text{Ideal gas law} \quad (1.3)$$

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

where  $p$  is the pressure and  $\gamma$  is the ratio of the heat capacity at constant pressure,  $C_p$ , to that at constant volume,  $C_V$ . Note that we use  $N k_B$ , 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

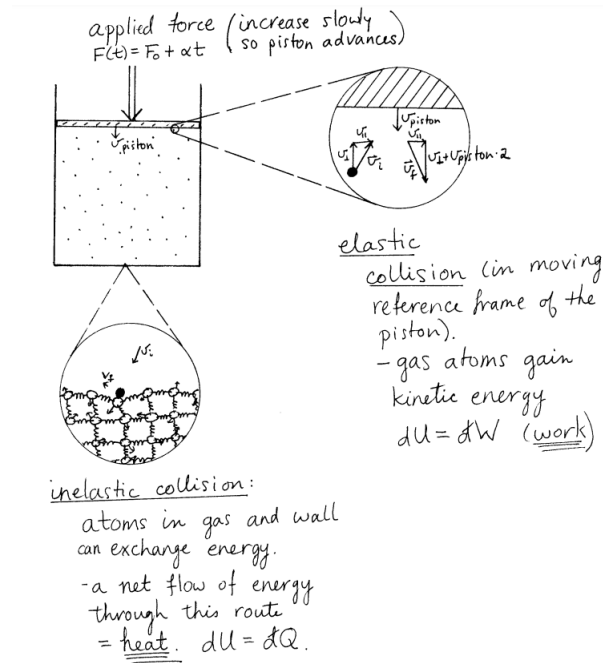
**Macroscopic  $\leftrightarrow$  Microscopic Energy Flow** As illustrated in Fig. (1.1), energy can be transferred to the gas by macroscopic motion of a piston. Atoms colliding with an advancing piston gain kinetic energy (assuming for simplicity elastic collisions), and by this mechanism the gas as 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

$$dU = dW \quad (= -p dV \quad \text{if the compression is reversible}), \quad (1.5)$$

where we have used conservation of energy to state that the work done,  $dW$ , must be equal to the change in the internal energy of the gas.<sup>1</sup> The slash through the symbol  $d$

<sup>1</sup>The sign of  $dW$  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  $dW$  relates to  $dU$ , where  $U$  is the system energy. Positive work means that the system energy goes up, and vice-versa





**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. The arrows in the ball and spring model of the wall denote random thermal motion.

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,  $dW$  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.”

### Microscopic $\leftrightarrow$ 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). 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

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

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

$$dU = \mu dN, \quad (1.7)$$

where  $\mu$  is called the “chemical potential”, defined as the change in energy when you bring an extra particle into the system:

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

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  $\mu$  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

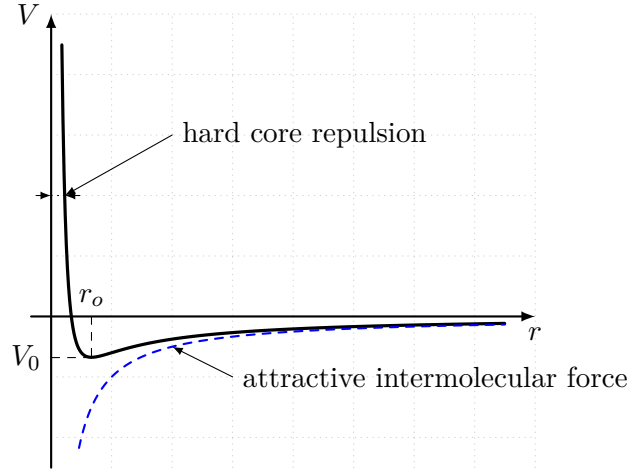
The van der Waals gas is a simple model system incorporating *interactions* between the particles. In this model the ideal gas law,  $pV = Nk_B T$ , is replaced by

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

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  $-N^2 a/V^2$  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.

#### 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



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

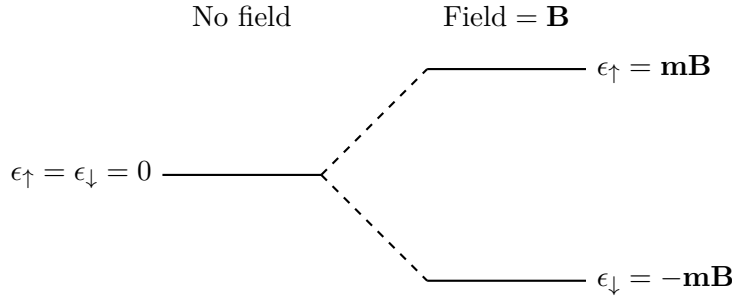
a rarefied gas, the potential energy is small, but if they are condensed to form a liquid it becomes negative. If the system is strongly compressed so that the hard core repulsion is important, the potential energy becomes large and positive. These regimes are reflected in the *isotherms* of the van der Waals gas, which will be discussed in Section ?? (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  $\mathbf{m} + d\mathbf{m}$  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  $(\mathbf{m} \cdot \nabla)\mathbf{H}$ . 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  $W' = -\mu_0 \int_0^{\mathbf{H}_1} \mathbf{m}(\mathbf{H}) d\mathbf{H}$ . 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,  $W_1 = \mu_0 \int \mathbf{m}_1 d\mathbf{H} = \mu_0 \mathbf{m}_1 \mathbf{H}_1$ , giving a net work  $W = \mu \int \mathbf{H} d\mathbf{m}$ . 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:

$$dW = \mu_0 \mathbf{H} d\mathbf{m} \quad (1.10)$$

This contrasts with the work done during the first part of the process only:  $dW' =$



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

$-\mu_0 \mathbf{m} \mathbf{d} \mathbf{H}$ . The difference between the two expressions is the change in the potential energy of the dipole moment in an applied field,  $-\mu_0 \mathbf{d}(\mathbf{m} \mathbf{H})$ , 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).

#### 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  $-\mu_0 \mathbf{m} \mathbf{H}$ , 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  $U_{\text{pot}} = \mu_0 (N_{\uparrow} - N_{\downarrow}) \mathbf{m}_d \mathbf{H}$ , 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  $\leftrightarrow$  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  $dU = -\mu_0 \mathbf{d}(\mathbf{m} \mathbf{H})$ . 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  $dW' = -\mu_0 \mathbf{m} d\mathbf{H}$ . Setting  $dU = dQ + dW'$ , we find that heat is extracted during this process:

$$dQ = dU - dW' = -\mu_0 d(\mathbf{m}\mathbf{H}) + \mu_0 \mathbf{m} d\mathbf{H} = -\mu_0 \mathbf{H} d\mathbf{m}. \quad (1.11)$$

How does this tally with the approach outlined earlier, which gave a work  $dW = \mu_0 \mathbf{H} d\mathbf{m}$ ? 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  $\mu_0 \mathbf{H} d\mathbf{m}$ . This still gives  $dQ = -\mu_0 \mathbf{H} d\mathbf{m}$ , so heat is extracted.

Even if no heat was exchanged between the surroundings and the sample, heat must have left the spin system, because  $dQ$  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  $\leftrightarrow$  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  $n$ th excited state is

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

#### 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  $\omega_0$ , 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.

## CHAPTER 2

# Thermodynamic Equilibrium

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## CHAPTER 3

# The Basics of Statistical Mechanics

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## CHAPTER 4

# Classical Ideal Gas

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## CHAPTER 5

# The Grand Canonical Ensemble

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## CHAPTER 6

# Ideal Fermi Gas

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## CHAPTER 7

# Ideal Bose Gases

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## CHAPTER 8

# Non-ideal Gases and Liquids

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## CHAPTER 9

# Phase Equilibria and Transitions

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## CHAPTER 10

# Fluctuations in Equilibrium

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## CHAPTER 11

# Elements of Stochastic Physics

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## APPENDIX A

# Appendix

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