PHYS 530

Statistical Mechanics

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(some bits taken from Richard Marchand)

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Contents

Chapter 1

Review of Thermodynamics

1.1 Some Definitions

System We will be considering systems made of a large numbers of particles, or more generally, of a large number of degrees of freedom. In general, the particles or constituents of our systems could all be different, for example, as with individuals in a population. However, our systems will consist of a large numbers of identical particles (distinguishable or not), or a large numbers of just a few different kinds of particles (as in a mixture of H and O in H_2O, for example).

Isolated versus interacting systems A system is isolated if it has no interaction whatsoever with other systems. Such a system can be thought of as being enclosed in a perfectly rigid isolating container. The Hamiltonian describing the system involves the degrees of freedom of the system itself and, possibly, imposed constant external fields (electric, magnetic, gravitational, etc.). A characteristic of such a system is that its total energy is conserved. For systems made of particles such as atoms, the number of particles will also be conserved.

With interacting systems, say A and B, the Hamiltonian describing the evolution of A involves the degrees of freedom of B, and vice versa. Strictly speaking, interacting systems should be treated as a single isolated system in which certain parts would be interacting weakly with others. It is the weakness of the interaction between, say, A and B, which allows us to treat each system as distinct, despite their interaction. Note that conceptually it is possible to make the interaction arbitrarily weak, for example, by placing them farther and farther apart, or by separating them with more and more insolation.

Exchanges For most of this course, the exchanges that will be considered between systems will be energy and particles. Other quantities, such as momentum or angular momentum, can also be exchanged, but those will not be given much emphasis.

Microscopic versus macroscopic description of a system We divide the level of description of a physical systems into two categories: microscopic and macroscopic.

A microscopic description is a very detailed description, involving a very large number of parameters and variables. For a system of N classical point particles, this would involve, for example, the positions $\vec{r}_i$ and momenta $\vec{p}_i$ of each particle, $i = 1, \ldots, N$. For a an N-body system in quantum mechanics, this could involve the specification of the full wavefunction in terms of the N particle coordinates. In the special case where particles would be noninteracting, the full quantum mechanical description of the system would be given in terms of all wave functions $\Psi_i(\vec{r}_i)$ for all individual particles.

A microscopic description may involve all possible information about a system, or a substantial subset thereof. The essential characteristic of microscopic descriptions is that it involves a very large amount of information about the system; an amount that is vastly beyond what we normally consider in everyday life.

A macroscopic description, on the other hand, involves much fewer variables. It involves observables or measurements that can be made with the naked eye. Such observations involve quantities that are averages over spatial scales much larger than typical inter-particle separations. They typically also involve averages over times that are short on a human scale, but long compared to the times that characterise the interaction between particles at the microscopic scale. These averages also involve large numbers of particles, and they are independent of the precise disposition of individual particles in a system. For example, the density of air at normal temperature and pressure is about 0.125 kg/m^3. If we took a sample of 1 cm^3 of air in a large container at equilibrium, we would measure a mass very close to 1.25×10^{-7} kg, and that would be independent of where in the container we took the sample, or how exactly the air molecules were distributed at the microscopic level. A simple example of a macroscopic description of a system would be to specify its density, mass flux, temperature, and pressure as a function of space and time. To any microscopic state of a system, there corresponds a macroscopic state. To a given macroscopic state, on the other hand, there corresponds many – very many – possible microscopic states.

To summarise, the main distinction between the microscopic and macroscopic descriptions of a system is that:

- The former is very detailed. It involves very large amounts of information at the particle scale.

- The latter, on the other hand involves much fewer variables. It relates to averages involving length and time scales that are small for a human observer, but large compared to the scales that characterise interparticle interactions.

Another point worth noting is that a macroscopic state of a system (i.e., a state that corresponds to a given macroscopic description) typically corresponds to – very – many possible microscopic states.

Macroscopic variables or parameters These are divided into two categories: extensive and intensive

Extensive variables or parameters are the ones that scale with the size of the system as that size is varied, while keeping the basic properties of the system the same. Loosely speaking, if a system is made twice as big, say, by appending an identical copy, or if it is reduced in size by inserting an isolating partition and disposing of all but one of the resulting fragments, then extensive variables will vary in proportion to the variation in size. Examples include

- V the volume of a three-dimensional system,
- A the surface area of a two-dimensional system,
- L the length of a one-dimensional system,
- E the energy,
- S the entropy,
- $\vec{P}$ the electric polarisation of a system of particles with electric dipoles,
- $\vec{M}$ the magnetisation of a system of spins.

Intensive variables or parameters remain the same if the size of a system is varied while leaving the basic properties the same. Intensive properties are in fact what is meant by these basic properties, so that the definition is somewhat circular. A good way to understand this concept is with a thought experiment in which a system is increased by appending copies of itself, or reduced by inserting a partition. In such an operation, the parameters that do not change are intensive. Examples include

- the pressure in a three-dimensional system,
- the surface tension in a two-dimensional system,
- the tension in a string (one-dimensional system),
- E/V the energy density in a three-dimensional system (similarly for two-dimensional and one-dimensional systems),
- S/V the entropy per unit volume.

Note that not all parameters fall into these two categories. Some extensive parameters do not scale with the size of a system.

State variables These are the variables that determine the macroscopic state of a system. That state is determined uniquely, and it is independent of how it was prepared. For example if we take 1 as a reference in Fig. 1.1, the state of the system at 2 is uniquely defined in terms of the change in volume $V_2 - V_1$ and in terms of the energy E added to the system. Different amounts of work W and heat Q exchanges will lead to the same final state 2.

Q and W are therefore not state variables, but E and V are state variables. The heat capacity is also a state variable.

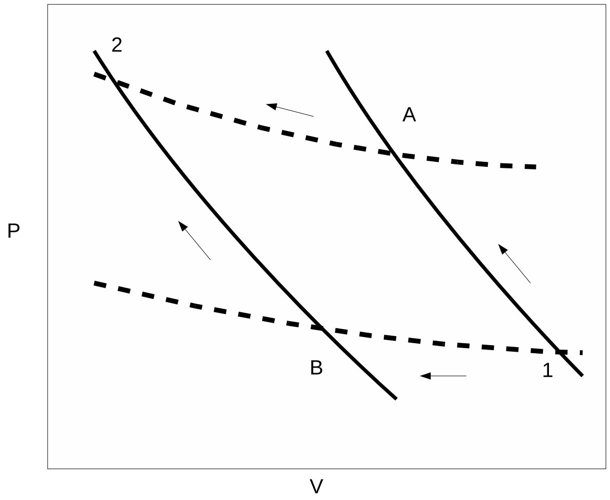


Figure 1.1: Two paths $1A2$ and $1B2$ correspond to different amounts of work done on the system, and to different amounts of heat exchange, but they lead to the same final state 2.

Differentials of state variables are also called **exact** differentials, while differentials of non-state variables are refereed to as **inexact** differentials. Inexact differentials depend on the path taken. Inexact differentials are often distinguished from exact differentials by placing a slash through the d. Thus, one would write dE for the differential in energy, and $đQ$ for a differential in amount of heat. In the following, this notation will not be followed rigorously. Care must therefore be taken in recognising exact and inexact differentials in the mathematical expression that will be presented.

An exact differential of $F = F(x_1, x_2)$ has the following property.

$$\left[\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right]_{x_2} = \left[\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right]_{x_1} . \tag{1.1}$$

We are assuming systems in thermodynamical equilibrium. If a system were not in equilibrium, for example as a result of a rapid heat exchange or external work, then the state of the system would depend on how the system was taken to its final state.

Steady state A system is in steady state if its macroscopic variables are constant in time. Note that the level at which we define macroscopic parameters is somewhat arbitrary. If fine enough – macroscopic – measurements are made, or if the system is close to criticality, some macroscopic variables may fluctuate in time and space. In that case, the system will nonetheless be said to be at steady state if

1. the average over a suitable time scale is constant, and

2. the statistics of the fluctuations around that average is also constant.

Equilibrium A system is in equilibrium if it is at steady state, and if all the macroscopic "forces" acting on it vanish.

Thermodynamical equilibrium A system is in thermodynamical equilibrium if it is in equilibrium and if it satisfies detailed balance.

Detailed balance A system satisfies detailed balance if there is balance between all channels, i.e., between all possible ways a system can exchange with its surrounding. For example, a system of hydrogen atoms in contact with another system can exchange energy via thermal conduction or radiation. If the system receives as much energy through each channel as it loses, then there is detailed balance.

Note that it is possible to have steady state without detailed balance. For example, if the system receives more energy from radiative exchanges than it loses, and loses more from thermal diffusion than it receives, the net amount of energy in the system and all macroscopic variables can be constant. Such a system, however, would not satisfy detailed balance, and it would not be in thermodynamical equilibrium. The remainder of this course will concern system at, or very close to thermodynamical equilibrium. In what follows, we will often refer to thermodynamical equilibrium simply as equilibrium for brevity.

Internal equilibrium Systems can usually store energy in different forms, or different kinds of degrees of freedom. For example, in a gas of helium atoms, energy can be stored in the kinetic motion of the atoms, and in excited states of the atoms. These two kinds of degrees of freedom can exchange energy with one another, for example, in inelastic processes. A system is said to be in internal equilibrium when the different forms in which it can store energy satisfy detailed balance. Thus, for a helium gas, energy (heat) could be deposited in the system by shining a short laser pulse so as to excite a particular energy level. Immediately after shining the laser, the deposited heat would mainly appear in the form of excited electronic states. With time, however, inelastic collisions would transfer part of that energy into kinetic energy, and the system would reach internal equilibrium.

In what follows, unless stated otherwise, systems will also be assumed to be in, or very close to internal equilibrium. Also, when a system is said to be in equilibrium, it will be understood that it is in thermodynamical equilibrium with its surrounding (if it is not isolated), as well as in internal equilibrium.

Equation of State is a relationship between the state variables for a system in equilibrium. It reduces the number of independent degrees of freedom. It can relate a thermal state (S, T) to a mechanical or chemical state.

1.2 Laws of Thermodynamics

The four laws of thermodynamics can be states simply as

- It is possible to build a thermometer.
- Energy is conserved.
- Not all heat can be converted to work.
- We can never reach the coldest temperature using a finte set of reversible steps.

1.2.1 Energy, Work, and Heat

We assume that the energy going in and out of a system, as well as the total energy in a system, can be measured with arbitrary accuracy. We also assume that the energy transfer between systems can take place continuously, i.e., in arbitrarily small amounts.

Work is the amount of energy that is provided to a system by the sole variation of one or more of its extensive – macroscopic – parameters. For example, the differential in the work done by a system on its surrounding is

$$dW = PdV - \sigma dA - \vec{E} \cdot d\vec{P} - \mu_0 \vec{H} \cdot d\vec{M} - \phi d\rho \,. \tag{1.2}$$

The differential of work done on the system is negative that expression.

More generally, the differential work done by a system on its surrounding is written in terms of generalised forces f_i and external variables x_i as

$$dW = -\sum_i f_i dx_i \,. \tag{1.3}$$

The set of variables (f_i, x_i) are called conjugate variables. Note that all generalised forces are intensive, while the external variables are extensive.

Another way of writing this is

$$dU = dQ + YdX + \sum_j \mu_j dN_j \,, \tag{1.4}$$

where the second last term is mechanical and the last term is chemical.

Heat is any energy exchange that is not identified as work. For systems near equilibrium, heat exchanges are assumed to take place sufficiently slowly so as not to be perturbative. For example, if the system can exchange energy through various channels (e.g. radiative and conductive), it is possible that heat is brought only through one of these channels. In any case, we shall assume that the exchange is slow enough that the characteristic time of energy exchange is long compared with the time needed to reach internal equilibrium in the system. Thus, for example, a system could be heated by shining a laser beam through it, or by putting it in contact with a warmer similar system. The end result would only depend on the amount of heat provided, independently of how heating was done.

The distinction between the two forms of energy exchange can be understood by considering the total energy in a system of identical noninteracting particles. If each particle can occupy discrete energy levels labelled i, and we denote the number of particles in level i with n_i, then the total energy in the system is

$$E = \sum_i n_i \epsilon_i \, . \tag{1.5}$$

Infinitesimal variation in E is given by

$$\delta E = \underbrace{\sum_i \delta n_i \epsilon_i}_{\text{heat}} + \underbrace{\sum_i n_i \delta \epsilon_i}_{\text{work}} \, . \tag{1.6}$$

1.2.2 Zeroth Law

Given three macroscopic systems A, B, and C, the zeroth law is as follows. If A and B are in thermodynamical equilibrium, and if A and C are also in thermodynamical equilibrium, then B and C will also be in equilibrium.

An obvious corollary is that if A and B are in thermodynamical equilibrium, and if A and C are not in thermodynamical equilibrium, then B and C will not be in thermodynamical equilibrium.

Thus, there is something universal about thermodynamical equilibrium. That something is independent of the nature of the system, the types of particles or degrees of freedom that it consists of, and the nature of the energy exchange. For example, A and B could interact mainly radiatively, while A and C could interact only via heat diffusion, and the statement would still be true. This follows from the assumption of internal equilibrium as defined previously.

Because of this universality, it is possible to characterise classes of equilibria by a single scalar T such that

- systems that are in equilibrium with one another will have the same value of T, and
- systems with different values of T are not in equilibrium with each another.

1.2.3 First Law

This is nothing but the law of conservation of energy. The variation in the internal energy of a system is negative the work done by the system on the surrounding, plus negative of the heat absorbed, plus any change in energy associated with a possible variation in the number of particles. Mathematically

$$\delta E = -\delta W - \delta Q + \sum_i \mu_i dN_i \, . \tag{1.7}$$

δE is the energy of the system, δW is done by the system on the surroundings, and δQ is the heat absorbed. In this relation, μ_i is the chemical potential and N_i is the number of particles of species i. These quantities will be defined more rigorously later.

1.2.4 Temperature

The definition of temperature and entropy follows from the zeroth law and from two simple observations:

1. When two systems A and B are brought in thermal contact (without doing any work), one of three things will happen:
    - heat is transferred from A to B,
    - heat is transferred from B to A,
    - no heat is exchanged at all. A and B are then in thermal equilibrium.
2. If A and B are in thermal equilibrium and heat is added to A (no work is done on any of the systems), then one of two things will happen:
    - A and B will still be in thermal equilibrium, or
    - heat will be transferred from A to B.

    Heat will never be transferred from B to A.

As a consequence of the second point above, it follows that, in the absence of work done on a system (i.e., when the expression for dW given in Eq. (1.2) vanishes), the universal parameter T introduced above, must be a monotonic (not necessarily strictly monotonic) function of the system energy (see Fig. 1.2. At this point, the definition of T is largely arbitrary. For a given system, it could be either decreasing or increasing as a function of energy.

The temperature T could be defined from an arbitrary reference system, and its definition could be applied to all other systems at equilibrium from the application of the zeroth law. Here we take the temperature T to be an increasing function of energy. At this point, the definition of temperature is still somewhat arbitrary. For a given system, any scalar function of the energy satisfying the properties stated above could be used as a valid thermodynamical temperature. We will eventually introduce the concept of absolute temperature. For the remainder of this chapter, however, the loose concept of temperature will suffice.

1.2.5 Entropy

The entropy S is a definition. It is used to relate the increase of energy with a small amount of heat added to the system. Specifically, referring to Eq. (1.7), for a small change in the energy, the element of heat δQ given to a system is written as

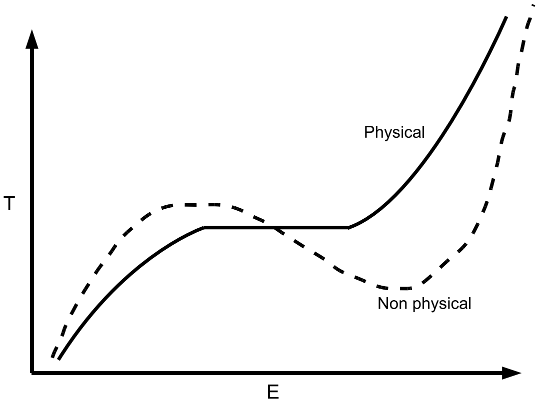


Figure 1.2: Illustration of allowed (solid) and disallowed (dashed) variation of the temperature T as a function of a system energy when energy is varied through heat exchange only (no work).

$$\delta Q = T\delta S\,. \tag{1.8}$$

This simple relation deserves some explanations. First, we note that the differential in the right hand side is in S and not in T. At first, one might expect to see a differential in the temperature T. There are two reasons why this is not the case:

1. All the differentials appearing in Eq. (1.7) are with respect to extensive variables. Taking a differential in T, an intensive parameter, would break the symmetry.
2. More importantly, for systems with phase transitions, it is possible to add heat without increasing the temperature. That is, when a system A is undergoing a phase transition, it is possible for the system to be in equilibrium with another system B; heat is added to A, and A is still in equilibrium with B.

Note that for a given choice of T (the temperature is so far not uniquely defined), Eq. (1.8) defines the entropy. Thus, as T has not yet been uniquely defined, S is also not uniquely defined. The two quantities T and S, however, must be consistent with the expression in Eq. (1.8) for a small heat increment, i.e., if one is defined, then the other is uniquely defined (up to an additive constant).

Also worth noting is the fact that the expression used for the (inexact) heat differential involves the differential in a single variable dS. This is in contrast with the expression used for the (also inexact) work differential, which can involve the product of several generalised forces with their conjugate coordinates, e.g., $-PdV + \sigma dA + ...$ The reason for this simple form comes from the assumptions made in defining the temperature and the assumption of internal equilibrium.

1.2.6 Second Law

The second law of thermodynamics follows directly from the definition of entropy and the second observation mentioned above. With the convention that temperature is monotonically increasing (with the possibility of flat ranges corresponding to phase transitions) as heat is added to a system, it follows from observation 2 that heat always flow from a warmer (higher value of T) to colder (lower value of T), and not vice versa. Thus, if two systems A and B initially in internal equilibrium separately at temperatures T_A and $T_B > T_A$ are placed in thermal contact (no work is done whatsoever), so as to exchange an infinitesimal amount of heat, then heat will flow from B to A. From the definition of entropy, the heat transferred to A is $\delta Q_A = T_A \delta S_A$, while that transferred to B is $\delta Q_B = T_B \delta S_B$ (the latter will be negative because B is loosing energy). From conservation of energy, we then have

$$\delta Q_A + \delta Q_B = T_A \delta S_A + T_B \delta S_B = 0\,. \tag{1.9}$$

It follows that

$$\delta S_B = -\frac{T_A}{T_B} \delta S_A\,. \tag{1.10}$$

Thus, the change in the total entropy of the combined system A and B is

$$\delta S_{AB} = \delta S_A + \delta S_B = \frac{T_B - T_A}{T_B} \delta S_A > 0\,, \tag{1.11}$$

because $\delta S_A > 0$ and $T_B > T_A$. In other words, the second law states that in a thermal interaction between two systems that are initially not in equilibrium with one another, the total entropy of the combined systems always increases.

It is remarkable that this conclusion was obtained with a fairly loosely defined temperature and entropy. The second law applies with any definition of T and S that satisfy the properties stated above.

1.2.7 Third Law

In a nut shell, the third law states that the entropy of any system approaches zero as the energy in, or the absolute temperature of, the system approaches zero. This will be discussed in more detail later.

1.3 Thermodynamic Potentials

It is clear from the exact differential form of the first law of thermodynamics (Eq. (1.7)) that a system energy E is a function of entropy, as well as a number of extensive variables (generalised displacements) that are conjugate to the generalised forces f_i. It is convenient to transform this function so as to have a dependence on selected generalised forces f_i, as well as, on the usual coordinates x_j, where $j \neq i$. This is achieved with a Legendre transformation.

This is the same kind of transformation as used in classical mechanics when constructing the Hamiltonian from the Lagrangian. Specifically, in order to transform $E(x_1, x_2, \ldots, x_N)$ into a function, say, of $x_1, \ldots, x_{k-1}, f_k, x_{k+1}, \ldots, x_N$, it suffices to define $\mathcal{E} = E - f_k x_k$. Indeed, it follows from the exact differential form for E,

$$dE = \frac{\partial E}{\partial x_1} dx_1 + ... + \frac{\partial E}{\partial x_N} dx_N \equiv f_1 dx_1 + \ldots + f_N dx_N \,, \tag{1.12}$$

that the differential in $\mathcal{E}$ is

$$d\mathcal{E} = f_1 dx_1 + \ldots + f_{k-1} dx_{k-1} - x_k df_k + f_{k+1} dx_{k+1} + \ldots + f_N dx_N \,. \tag{1.13}$$

(f_i, x_i) are conjugate variables. For example, S and T are conjugate variables, where S is extensive and T is intensive.

Moreover, it can be shown that this is an exact differential for function $\mathcal{E}$, that is, $\mathcal{E}$ is a state variable. The resulting functions $\mathcal{E}$ are called thermodynamic potentials. The main potentials used in this course are defined below, for a simple fluid made of a single particle species.

From the first law

$$\delta E = -\delta W - \delta Q + \sum \mu N = TdS - PdV + \mu dN \,. \tag{1.14}$$

This is the work done by varying the volume only. The stored energy can do work in analogy to potential energy in mechanics. In thermodynamics the stored energy is the “free energy”.

1.3.1 Internal Energy

For a closed, isochronic, adiabatic assembly,

$$\begin{aligned} \epsilon &= E - 0 && (1.15) \\ U &= E \,, && (1.16) \end{aligned}$$

where E is the total energy and U is the internal energy.. We have

$$dU = TdS - PdV + \mu dN \,, \tag{1.17}$$

so that $U = U(S, V, N)$. This results from a trivial identity Legendre transformation. In the following, we will often use E or U indiscriminately to designate a system internal energy.

1.3.2 Enthalpy

For a closed, isobaric, adiabatic assembly,

$$\begin{aligned} \epsilon &= E - (-PV) && (1.18) \\ H &= E + PV && (1.19) \end{aligned}$$

and

$$dH = TdS + VdP + \mu dN\,, \tag{1.20}$$

so that $H = H(S, P, N)$.

1.3.3 Helmholtz Free Energy

For a closed, isochoric, isothermal assembly,

$$\begin{aligned} \epsilon &= E - TS & (1.21)\\ A &= E - TS & (1.22) \end{aligned}$$

and

$$dA = -SdT - PdV + \mu dN\,, \tag{1.23}$$

so that $A = A(T, V, N)$.

1.3.4 Gibbs Free Energy

For closed, isobaric, isothermal assembly

$$\begin{aligned} \epsilon &= E - (TS - PV) & (1.24)\\ G &= E - TS + PV = A + PV = U - TS + PV = \mu N & (1.25) \end{aligned}$$

and

$$dG = -SdT + VdP + \mu dN\,, \tag{1.26}$$

so that $G = G(T, P, N)$.

1.3.5 Grand Potential

For open, isochoric, isothermal assembly

$$\begin{aligned} \epsilon &= E - (TS + \mu N) & (1.27)\\ \Omega &= E - TS - \mu N & (1.28) \end{aligned}$$

and

$$d\Omega = -SdT - PdV - Nd\mu\,, \tag{1.29}$$

so that $\Omega = \Omega(T, V, \mu)$.

These expressions for the thermodynamic potentials are useful for deriving a number of useful identities among derivatives of thermodynamical variables, as will be seen next with Maxwell's relations. In addition, they can be used to obtain direct expressions for thermodynamical variables in terms of partial derivatives of other variables. For example, from Eq. (1.26), it follows that

$$\left.\frac{\partial P}{\partial T}\right|_{G,N} = \frac{S}{V}\,. \tag{1.30}$$

Similarly, from Eq. (1.20),

$$\left.\frac{\partial P}{\partial N}\right|_{H,S} = -\frac{\mu}{V}\,. \tag{1.31}$$

Such identities will be used later when we calculate quantities such as G or Ω in terms of statistical properties of systems. It should be obvious from these examples that, when taking partial derivatives, it is crucial to keep track of which variables are being held fixed. This point must be remembered in all expressions involving partial derivatives. For that reason when writing partial derivatives, it will be important to indicate explicitely which thermodynamic variables are held constant.

1.4 Maxwell Relations

Maxwell relations follow simply from the fact that the thermodynamic potentials, resulting from the Legendre transformation of state variable E, are also state variables. Thus, the differential forms given for these potentials are exact differentials. For example, from the differential form of the Helmholtz free energy, it follows that

$$\left.\frac{\partial A}{\partial T}\right|_{V,N} = -S \tag{1.32}$$

and

$$\left.\frac{\partial A}{\partial V}\right|_{T,N} = -P \tag{1.33}$$

from which it follows that

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}\,. \tag{1.34}$$

This is known as a Maxwell equation.

Many similar identities can be derived from taking derivatives of the various terms appearing in the thermodynamic potentials. The equations obtained with this procedure are referred to collectively as the Maxwell relations.

1.4.1 Example Application

Consider a system in which heat δQ is added, resulting in a change in temperature δT. The heat capacity is defined as

$$C(T) = \lim_{\delta T \to 0} \left(\frac{\delta Q}{\delta T} \right) = \frac{dQ}{dT} = T \frac{dS}{dT} , \tag{1.35}$$

where the later equality comes from the definition of entropy, $dQ = TdS$. The specific heat c of a substance is the heat capacity per unit mass, or per unit mole.

Let us illustrate the use of Maxwell's relations by deriving a relation between the heat capacity of a system at constant volume C_V (easy to calculate), and the heat capacity at constant pressure C_P (easy to measure). Experimentally, the latter is much easier to measure, while the former is usually easier to calculate. The relation between the two therefore provides a useful tool to connect theory and experiment.

In order to relate C_P to C_V, we need to use the dependence of S on other thermodynamic variables. In general, a number of terms $(-PdV, \sigma dA, \ldots)$ could contribute to work on the system. For simplicity, we assume that work can only be done by a variation in the volume (i.e., via $-PdV$), and the first law has the simple form

$$dE = \underbrace{TdS}_{dQ} - PdV \, . \tag{1.36}$$

It follows that $E = E(S, V)$, from which, in principle, S can be viewed as a function of E and V, $S = \tilde{S}(E, V)$ for some function $\tilde{S}$. Assuming that, when V is fixed, E is a strictly monotonically increasing function of T, i.e., in the absence of phase transition, then E can be considered to be a function of T and V, $E = E(T, V)$. Thus, S can formally be treated to be a function of T and V,

$$S = S(T, V) \, . \tag{1.37}$$

A small variation in S can be written as

$$\delta S = \left. \frac{\partial S}{\partial T} \right|_V \delta T + \left. \frac{\partial S}{\partial V} \right|_T \delta V. \tag{1.38}$$

The heat capacity at constant volume is given by the differential in heat associated with a differential in temperature when the volume is held constant.

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V . \tag{1.39}$$

Now, for C_P, see Eq. (1.37) as being a function of T and P. Let us consider V in the argument of S, that is,

$$V = V(T, P) \, . \tag{1.40}$$

A small variation in V can be written as

$$\delta V = \left.\frac{\partial V}{\partial T}\right|_P \delta T + \left.\frac{\partial V}{\partial P}\right|_T \delta P\,. \tag{1.41}$$

Substituting Eq. (1.41) into Eq. (1.38), we find

$$\delta S = \left.\frac{\partial S}{\partial T}\right|_V \delta T + \left.\frac{\partial S}{\partial V}\right|_T \left[\left.\frac{\partial V}{\partial T}\right|_P \delta T + \left.\frac{\partial V}{\partial P}\right|_T \delta P\right]\,, \tag{1.42}$$

where the last term vanishes when P is constant. We now have

$$\begin{aligned} C_P &= T\left.\frac{\partial S}{\partial T}\right|_P \\ &= C_V + T\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P\,. \end{aligned} \tag{1.43}$$

Let us now concentrate on the second term in the righthand side of Eq. (1.43). From one of Maxwell's relations

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}\,. \tag{1.44}$$

And from Eq. (1.41), it follows for constant V

$$\left.\frac{\partial P}{\partial T}\right|_V = -\frac{\partial V/\partial T|_P}{\partial V/\partial P|_T}. \tag{1.45}$$

Thus, Eq. (1.43) becomes

$$C_P = C_V - T\frac{\left(\partial V/\partial T|_P\right)^2}{\partial V/\partial P|_T}\,. \tag{1.46}$$

With the definition

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P \tag{1.47}$$

for the volume coefficient of expansion and

$$\kappa = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \tag{1.48}$$

for the isothermal compressibility, we obtain

$$C_P = C_V + VT\frac{\alpha^2}{\kappa}\,. \tag{1.49}$$

1.5 Extensive Functions

Consider the first law of thermodynamics (conservation of energy) for a system made of a single type of particle, in which work can only be done by varying the volume (Eq. (1.17)),

$$dE = TdS - PdV + \mu dN \,. \tag{1.50}$$

It follows that E is a function of S, V, and N. Moreover, E being a state variable and dE being an exact differential, we have

$$\begin{aligned} \left.\frac{\partial E}{\partial S}\right|_{V,N} &= T \,, & (1.51)\\ \left.\frac{\partial E}{\partial V}\right|_{S,N} &= -P \,, & (1.52)\\ \left.\frac{\partial E}{\partial N}\right|_{S,V} &= \mu \,. & (1.53) \end{aligned}$$

Making use of the fact that E, S, V, and N are all extensive (and additive) variables, we write

$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N) \,, \tag{1.54}$$

that is, E is a homogeneous function of order one and λ is an arbitrary parameter. Taking the derivative with respect to λ, setting $\lambda = 1$, and making use of Eq. (1.51) to Eq. (1.53), we find

$$\begin{aligned} E &= \left.\frac{\partial E}{\partial \lambda S}\right|_{V,N} \frac{\partial \lambda S}{\partial \lambda} + \left.\frac{\partial E}{\partial \lambda V}\right|_{S,N} \frac{\partial \lambda V}{\partial \lambda} + \left.\frac{\partial E}{\partial \lambda N}\right|_{V,S} \frac{\partial \lambda N}{\partial \lambda} \\ &= \frac{1}{\lambda} TS - \frac{1}{\lambda} PV + \frac{1}{\lambda} \mu N \\ &= TS - PV + \mu N, \quad \text{for} \quad \lambda = 1 \,. \end{aligned} \tag{1.55}$$

$$\boxed{E(S, V, N) = TS - PV + \mu N} \,. \tag{1.56}$$

This relation is known as the "fundamental equation of thermodynamics", and sometime refered to as Euler's equation. The result is readily generalised to systems with conjugate forces f_i and coordinates x_i, and to systems with more than one particle species.

1.6 Problems

Chapter 2

Statistical Basis of Thermodynamics

2.1 Preliminaries

The systems considered will consist of N identical particles, a given volume V, and a given energy E. For macroscopic systems, N and V will be very large. For example, if the system contains noninteracting particles that can occupy energy levels ε_i, then

$$N = \sum_i n_i \tag{2.1}$$

and

$$E = \sum_i n_i \varepsilon_i \tag{2.2}$$

where n_i is the number of particles of energy ε_i.

The thermodynamic limit is

$$\left.\begin{array}{l} N \to \infty \\ V \to \infty \end{array}\right\} \quad \text{such that} \quad \frac{N}{V} \to \text{finite value.} \tag{2.3}$$

N/V is the particle density. In the thermodynamic limit, systems are large enough that edge effects are negligible. They must be sufficiently small that long-range gravitational forces do not become important. The type of variables describing the system are

$$\begin{array}{rcl} N, V, E & \Rightarrow & \text{macroscopic description} \\ n_i, \varepsilon_i & \Rightarrow & \text{microscopic description} \end{array}$$

Ensembles are like populations from which statistics can be calculated. For a given macroscopic state, an ensemble is a set of all possible microstates that are consistent with the given macrostate.

microcanonical:	E, N, V fixed
canonical:	N, V fixed, E may be exchanged with a heat reservoir
grand canonical:	V fixed, E and N may be exchanged with a reservoir

Question: How should these microstates be distributed?

Answer: Equiprobability assumption. This is a fundamental assumption in statistical mechanics. At equilibrium, a system is equally likely to be in any of its accessible states.

Counting States $\Omega(N,V,E)$ is the number of accessible microstates for a given system. We will also work with the density of states:

$\Gamma(N,V,E)$	is density of accessible microstates for a given system.
$\Gamma(N,V,E)dNdVdE$	is number of microstates in interval. $(N,N+dN)(V,V+dV)(E,E+dE)$

2.2 Thermally Interacting Systems

Consider two physical systems A_1 and A_2, each which are separately in equilibrium, brought into thermal contact with each other.

$$\underbrace{\begin{matrix} A_1 \\ (N_1,V_1,E_1) \end{matrix}}_{\Omega_1(N_1,V_1,E_1)} \leftrightarrow \underbrace{\begin{matrix} A_2 \\ (N_2,V_2,E_2) \end{matrix}}_{\Omega_2(N_2,V_2,E_2)} \tag{2.4}$$

We make the following assumptions.

- A_1 and A_2 exchange energy, but the total energy $E_0 = E_1 + E_2$ is constant.
- V_1, V_2, N_1, N_2 are constant.
- The two systems are statistically independent; the number of states in A_1 for a given macrostate (N_1, V_1, E_1) is independent of the microstate of A_2, and vice versa.

Then

$$\begin{aligned} \Omega_0(E_1,E_2) &= \Omega_1(E_1)\Omega_2(E_2) \\ &= \Omega_1(E_1)\Omega_2(E_0-E_1) \\ &= \tilde{\Omega}_1(E_1)\,. \end{aligned} \tag{2.5}$$

Equilibrium is the most probable macrostate and is given by the maximum value of $\tilde{\Omega}_1(E_1)$. Since E_0 is a constant,

$$E_0 = E_1 + E_2 \Rightarrow 0 = 1 + \frac{\partial E_2}{\partial E_1} \Rightarrow \frac{\partial E_2}{\partial E_1} = -1 \tag{2.6}$$

and

$$\frac{\partial \tilde{\Omega}_1}{\partial E_1} = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0 \tag{2.7}$$

$$\frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2} \tag{2.8}$$

$$\frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2} \, . \tag{2.9}$$

When Eq. (2.9) is satisfied, A_1 and A_2 will most probably not exchange energy, therefore

- they must be in thermal equilibrium,
- they must have the same temperature, and
- $\partial \ln \Omega / \partial E$ must be related to the temperature.

Define

$$\beta = \frac{\partial \ln \Omega}{\partial E} \, . \tag{2.10}$$

For a system getting energy through heat exchange only, $\delta E = \delta Q$ (no work or exchange of particles whatsoever). From Eq. (2.10),

$$\delta E = \delta Q = \frac{\delta(\ln \Omega)}{\beta} \, , \tag{2.11}$$

which is similar to $\delta Q = T \delta S$, with

$$\boxed{S = k \ln \Omega} \, , \tag{2.12}$$

and

$$\beta = \frac{1}{kT} \, , \tag{2.13}$$

where T is the absolute temperature and k is a constant determined experimentally from the choice of the physical units (SI) and theory predictions. Equation (2.12) relates a macroscopic variable S to a microscopic variable Ω.

2.3 More General Interactions

Consider two systems again.

$$\underbrace{\begin{matrix} A_1 \\ (N_1, V_1, E_1) \end{matrix}}_{\Omega_1(N_1,V_1,E_1)} \leftrightarrow \underbrace{\begin{matrix} A_2 \\ (N_2, V_2, E_2) \end{matrix}}_{\Omega_2(N_2,V_2,E_2)} \tag{2.14}$$

Now assume that A_1 and A_2 can exchange heat, volume, and particles subject to the constraints

$$\left. \begin{aligned} E_0 &= E_1 + E_2, \\ V_0 &= V_1 + V_2, \\ N_0 &= N_1 + N_2. \end{aligned} \right\} = \text{constants.} \tag{2.15}$$

Assuming statistical independence as before, the number of states accessible to the combined system is

$$\begin{aligned} \Omega_0 &= \Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2) \\ &= \Omega_1(E_1, V_1, N_1)\Omega_2(E_0 - E_1, V_0 - V_1, N_0 - N_1) \\ &= \tilde{\Omega}_1(E_1, V_1, N_1)\,. \end{aligned} \tag{2.16}$$

The most probable state is the one for which Ω_0 is maximum:

$$\frac{\partial \tilde{\Omega}_1}{\partial E_1} = \frac{\partial \tilde{\Omega}_1}{\partial V_1} = \frac{\partial \tilde{\Omega}_1}{\partial N_1} = 0\,. \tag{2.17}$$

Using the same reasoning as before,

$$\left.\frac{\partial \ln \Omega_1}{\partial E_1}\right|_{V_1,N_1} = \left.\frac{\partial \ln \Omega_2}{\partial E_2}\right|_{V_2,N_2}, \tag{2.18}$$

$$\left.\frac{\partial \ln \Omega_1}{\partial V_1}\right|_{E_1,N_1} = \left.\frac{\partial \ln \Omega_2}{\partial V_2}\right|_{E_2,N_2}, \tag{2.19}$$

$$\left.\frac{\partial \ln \Omega_1}{\partial N_1}\right|_{E_1,V_1} = \left.\frac{\partial \ln \Omega_2}{\partial N_2}\right|_{E_2,V_2}. \tag{2.20}$$

We can interpret these results as follows.

- Using Eq. (2.10) and Eq. (2.18) gives $\beta_1 = \beta_2$. In addition, Eq. (2.13) leads to

$$T_1 = T_2\,. \tag{2.21}$$

- Using Eq. (2.12) and Eq. (2.19) gives $\partial S_1/\partial V_1|_{E_1,N_1} = \partial S_2/\partial V_2|_{E_2,N_2}$. From Eq. (2.21) and the first law of thermodynamics Eq. (1.50), this becomes

$$P_1 = P_2\,. \tag{2.22}$$

- Similarly, given Eq. (2.12) and Eq. (2.20) leads to $\partial S_1/\partial N_1|_{E_1,V_1} = \partial S_2/\partial N_2|_{E_2,V_2}$. From Eq.(2.21) and Eq. (1.50), this is equivalent to

$$\mu_1 = \mu_2 \,. \tag{2.23}$$

Thus, when the two systems A_1 and A_2 are at equilibrium with one another, they must have the same temperature, pressure, and chemical potential. This result is readily extended to systems with an arbitrary number of generalised forces f_i and conjugate external variables x_i: $f_i^{A_1} = f_i^{A_2}$.

Notice that T, P, and μ can be expressed in more way in terms of partial derivatives of thermodynamic quantities.

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V} \quad \Rightarrow \quad T = \left.\frac{\partial E}{\partial S}\right|_{N,V} . \tag{2.24}$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} \quad \Rightarrow \quad P = \left.\frac{\partial S}{\partial V}\right|_{E,N} \left.\frac{\partial E}{\partial S}\right|_{V,N} = - \left.\frac{\partial E}{\partial V}\right|_{S,N} . \tag{2.25}$$

$$\frac{\mu}{T} = - \left.\frac{\partial S}{\partial N}\right|_{E,V} \quad \Rightarrow \quad \mu = - \left.\frac{\partial S}{\partial N}\right|_{E,V} \left.\frac{\partial E}{\partial S}\right|_{V,N} = \left.\frac{\partial E}{\partial N}\right|_{S,V} . \tag{2.26}$$

2.4 Classical Ideal Gas

Consider the following system.

- The particles are point particles with no internal degrees of freedom. In practice, this applies to atomic gases without spin (monatomic molecules).
- The particles are noninteracting.
- The particles are distinguishable.

A good approximation to such a gas is a dilute ^{4}He gas with nuclei of total spin zero. In the limit of high temperature ($T \to \infty$) and low densities ($N/V \to 0$) the ideal-gas behaviour becomes typical of most real systems.

2.4.1 A First Estimate

Assuming the particles are noninteracting

$$\Omega(N, V, E) \approx \prod_{i=1}^{N} \Omega(1, V, \varepsilon) \,, \tag{2.27}$$

that is, the number of states accessible to the system should scale as N products of the number of accessible states for a single particle with representative energy ε. A plausible value of that energy is

$$\varepsilon = \frac{E}{N}\,. \tag{2.28}$$

for no spatial correlations,

$$\Omega(1, V, \varepsilon) \approx V f(\epsilon) \tag{2.29}$$

for some function of energy f. Thus,

$$\Omega(N, V, E) = V^N F(E)\,. \tag{2.30}$$

From this very crude estimate of Ω, it is possible to obtain some useful thermodynamic relations. Since we have an approximate dependence of Ω on V but none on E, we must avoid deriving quantities that rely on the energy dependence of Ω on E, i.e., we do not know $F(E)$. We have

$$S = k \ln \Omega = kN \ln V + \ln F(E)\,. \tag{2.31}$$

From the first law of thermodynamics

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{kN}{V}\,, \tag{2.32}$$

$$PV = NkT \tag{2.33}$$

or

$$PV = nRT\,, \tag{2.34}$$

with $n = N/N_A$ moles of gas and $R = N_A k$ the gas constant per mole. N_A is the Avogadro number. For any classical system composed of noninteracting particles the ideal-gas law holds.

2.4.2 Single Particle in a Box

Assume a cubic box of volume L^3. There are two types of boundary conditions for the wavefunction:

Dirichlet: $\Psi = 0$ at boundaries

$$\Psi(x, y, z) = \sqrt{\frac{8}{V}} \sin\left(\frac{\pi}{L} n_x x\right) \sin\left(\frac{\pi}{L} n_y y\right) \sin\left(\frac{\pi}{L} n_z z\right)\,. \tag{2.35}$$

Neumann: $\nabla\Psi \cdot \hat{n} = 0$ at boundaries

$$\Psi(x,y,z) = \sqrt{\frac{8}{V}}\cos\left(\frac{\pi}{L}n_x x\right)\cos\left(\frac{\pi}{L}n_y y\right)\cos\left(\frac{\pi}{L}n_z z\right)\ . \tag{2.36}$$

Both conditions yield the same results thermodynamically. Assume Dirichlet conditions in what follows.

The single particle energy is given by

$$\varepsilon\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi \tag{2.37}$$

and

$$\begin{aligned}\varepsilon &= \left(\frac{\hbar\pi}{L}\right)^2\frac{1}{2m}\left(n_x^2+n_y^2+n_z^2\right)\\ &= \frac{h^2}{8mL^2}\left(n_x^2+n_y^2+n_z^2\right)\ ,\end{aligned} \tag{2.38}$$

where $h = 2\pi\hbar$.

$\Omega(1, V, \varepsilon)$ is the number of distinct solutions to

$$\varepsilon^* \equiv n_x^2+n_y^2+n_z^2 = \frac{8mL^2}{h^2}\varepsilon = \frac{8mV^{2/3}}{h^2}\varepsilon\,, \tag{2.39}$$

Notice that $\Omega(1, V, \varepsilon^*)$ is a very irregular function of ε^*.

For N particles with a total energy E, $\Omega(N, V, E)$ is the number of distinct solutions of

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2}E \equiv E^*. \tag{2.40}$$

$\Omega(N, V, E^*)$ is an even more irregular function of E^*. Notice that if Ω were the number of states in a finite energy range $(E, E+\delta E)$, then it would become nearly smooth for large enough E.

Now consider the adiabatic ($\delta Q = 0 \Rightarrow \delta S = 0$) compression of an ideal gas. From Eq. 2.40, it is clear that $\Omega = \Omega(V^{2/3}E)$. For reversible[1] ($\delta\Omega$) adiabatic processes, S or Ω must be constant and therefore $V^{2/3}E$ must be constant.

$$V^{2/3}E = V_0^{2/3}E_0 \tag{2.41}$$

for some V_0 and E_0. From Eq. (2.25)

$$P = -\left.\frac{\partial E}{\partial V}\right|_{S,N} = -\frac{\partial}{\partial V}\frac{V_0^{2/3}E_0}{V^{2/3}} = \frac{2}{3}\frac{V_0^{2/3}E_0}{V^{5/3}}$$

and from Eq. (2.41)

---

[1] Reversible means infinitesimally close to equilibrium. Sometimes referred to as quasi-static

$$P = \frac{2}{3}\frac{E}{V}\,. \tag{2.42}$$

From $PV = NkT$, it is clear that

$$E = \frac{3}{2}NkT\,. \tag{2.43}$$

Alternatively, we have

$$\begin{aligned} EV^{2/3} &= \text{constant} \\ &= V^{2/3}\frac{3}{2}PV\,, \end{aligned} \tag{2.44}$$

which implies

$$PV^{5/3} = \text{constant}. \tag{2.45}$$

2.4.3 Detailed Calculation of Ω

$\Omega_N(E^*)$ is very irregular. It is more convenient to work with the cumulative number of states

$$\Sigma_N(E^*) = \sum_{x\le E^*} \Omega(x)\,, \tag{2.46}$$

which is the number of states of energy E^*, or less. This is the number of states in an octant of a sphere of radius $\sqrt{E^*}$, and is much smoother than Ω.

For a single particle confined to a certain volume, Σ_1 has the properties

- $\Sigma_1(\epsilon^*)$ was tabulated by Gupta (1947).
- Σ_1 depends on the type of boundary conditions (Dirichlet or Neumann).
- Asymptotically

  $$\Sigma_1(\epsilon^*) \to \frac{1}{8}\frac{4\pi}{3}\epsilon^{*3/2}\,, \tag{2.47}$$

  for $\epsilon^* \gg 1$.

Similarly, for a system of N particles, $\Sigma_N(E^*)$, is proportional to the volume of an octant of a $3N$-dimensional sphere of radius $\sqrt{E^*}$.

The volume of a sphere of radius R in n-dimensions, i.e., volume of the region in space that satisfies

$$\sum_{i=1}^{n} x_i^2 \le R^2\,, \tag{2.48}$$

is

$$V = \frac{\pi^{n/2}}{(n/2)!} R^n \,. \tag{2.49}$$

For $n = 3$, $(3/2)! = \Gamma(5/2) = 3\pi^{1/2}/4$, and

$$V = \frac{\pi^{3/2}}{(3\pi^{1/2}/4)} R^3 = \frac{4}{3}\pi R^3 \,. \tag{2.50}$$

Therefore for $3N$

$$\Sigma_N(E^*) \approx \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} \left(\underbrace{\frac{8mV^{2/3}E}{h^2}}_{E*} \right)^{3N/2} . \tag{2.51}$$

Notice that in these expressions use is made of the relation between factorial and the gamma functions

$$x! = \Gamma(x+1) = \int_0^\infty dt\, t^x \exp(-x) \,. \tag{2.52}$$

Also, the calculation of large factorial numbers is made approximately with Stirling's formula. For $n \gg 1$,

$$\ln(n!) \approx n \ln n - n \,, \tag{2.53}$$

from which

$$n! \approx n^n e^{-n}. \tag{2.54}$$

Thus Eq. (2.51) becomes

$$\Sigma \approx \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]^N e^{3N/2}. \tag{2.55}$$

Let us approximate

$$\Omega(E) \approx \frac{\partial \Sigma}{\partial E} \Delta \tag{2.56}$$

for some finite, but macroscopically small energy interval Δ. Then, from Eq. (2.55),

$$\Omega(E) \approx \frac{3N}{2} \frac{\Delta}{E} \Sigma \,. \tag{2.57}$$

As a result

$$\ln \Omega \approx \underbrace{\ln\left(\frac{3N\Delta}{2E}\right)}_{\text{negligible}} + \underbrace{N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3N}{2}}_{\ln \Sigma}. \tag{2.58}$$

Thus, in the thermodynamic limit,

$$\ln \Omega \approx \ln \Sigma \,. \tag{2.59}$$

That is, for practical purposes, the number of states accessible to a system with a given energy E within a small energy interval Δ, is essentially the same as the number of states accessible to that system with any energy not exceeding E.

Why? In high dimensional spaces, the volume of a sphere increases very rapidly with the radius r.

Example: Consider the thickness of the outer shell in a sphere of unit radius in n-dimensions, which contains 99% of the volume. We need to look for the radius $a < 1$, such that 99% of the volume is located in $a \leq r \leq 1$.

$$\begin{aligned} n = \quad 2 &: \; 1 - a^2 &&= 0.99 \rightarrow a = 0.1 \\ n = \quad 3 &: \; 1 - a^3 &&= 0.99 \rightarrow a \approx 0.2 \\ n = \quad 30 &: \; 1 - a^{30} &&= 0.99 \rightarrow a \approx 0.86 \\ n = \; 300 &: \; 1 - a^{300} &&= 0.99 \rightarrow a \approx 0.98 \end{aligned} \tag{2.60}$$

Connection with Thermodynamics

From Eq. (2.58),

$$S(N, E, V) = k \ln \Omega = Nk \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk \tag{2.61}$$

Rearranging gives

$$\boxed{E = \frac{3h^2 N}{4\pi m V^{2/3}} \exp\left(\frac{2S}{3Nk} - 1\right)} \,. \tag{2.62}$$

From this expression and the first law of thermodynamics, Eq. (1.50), it is now possible to derive a number of thermodynamic quantities:

$$T = \left.\frac{\partial E}{\partial S}\right|_{N,V} = \frac{2}{3Nk}E \Rightarrow E = \frac{3}{2}NkT = \frac{3}{2}nRT \,. \tag{2.63}$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \frac{3}{2}Nk = \frac{3}{2}nR \,. \tag{2.64}$$

$$P = - \left.\frac{\partial E}{\partial V}\right|_{N,S} = \frac{2}{3}\frac{E}{V}\,. \tag{2.65}$$

Note that from Eq. (2.63) and Eq. (2.65), this leads to $PV = NkT$, which agrees with our earlier estimate of the ideal-gas law.

From the first law

$$C_P = \left.\frac{\delta Q}{\delta T}\right|_{P,N} = \left.\frac{\delta E}{\delta T}\right|_{P,N} + \left.\frac{\delta W}{\delta T}\right|_{P,N} = \left.\frac{\partial}{\partial T}\left(\frac{3}{2}NkT\right)\right|_{P,N} + P\left.\frac{\partial V}{\partial T}\right|_{P,N}\,. \tag{2.66}$$

We use the equation of state for an ideal gas, $PV = NkT$,

$$V = \frac{NkT}{P} \Rightarrow \left.\frac{\partial V}{\partial T}\right|_{P,N} = \frac{Nk}{P}\,. \tag{2.67}$$

$$C_P = \frac{3}{2}Nk + Nk = \frac{5}{2}Nk\,. \tag{2.68}$$

Alternatively, we can write

$$\begin{aligned} C_P &= \left.\frac{\delta Q}{\delta T}\right|_{P,N} = \left.\frac{\delta E}{\delta T}\right|_{P,N} + P\left.\frac{\delta V}{\delta T}\right|_{P,N} \\ &= \left.\frac{\delta(E+PV)}{\delta T}\right|_{P,N} = \left.\frac{\partial H}{\partial T}\right|_{P,N} \\ &= \left.\frac{\partial}{\partial T}\left(\frac{3}{2}NkT + NkT\right)\right|_{P,N} = \frac{5}{2}Nk\,. \end{aligned} \tag{2.69}$$

Define

$$\gamma = \frac{C_P}{C_V}\,. \tag{2.70}$$

For an ideal gas, $\gamma = 5/3$.

Some Remarks

- For an ideal gas, E depends on T and N, but it is independent of V.
- From the expression for S in Eq. (2.61), constant entropy implies that $VE^{3/2}$ is constant.
  From $E = (3/2)PV$, it follows that

$$\begin{aligned} P^{3/2}V^{5/2} &= \text{constant, or} \\ PV^{\gamma} &= \text{constant}\,. \end{aligned} \tag{2.71}$$

- Notice that the same result can be obtained from the first law of thermodynamics by taking $dS = 0$:

  $$dE = TdS - PdV = -PdV = -\frac{2}{3}\frac{E}{V}dV \tag{2.72}$$

  or, rearranging

  $$\frac{3}{2}\frac{dE}{E} + \frac{dV}{V} \quad = \quad 0$$

  or

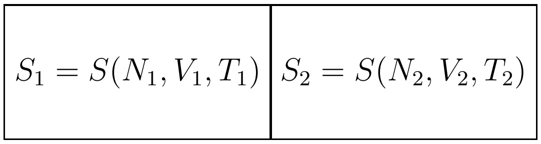
  $$d \ln \left(E^{3/2} V\right) \quad = \quad 0$$

  or equivalently,

  $$E^{3/2} V \quad = \quad \text{constant.} \tag{2.73}$$

2.5 Gibbs Paradox

Consider the mixing entropy of two ideal gases made of the same kind of particles at the same temperature, initially contained in two containers 1 and 2. Initially, the systems are separate, and the entropy in each box is given by Eq. (2.61). Making use of $E = (3/2)NkT$ for an ideal gas, the expression for the entropy in each system before mixing is



$$S_i = \frac{3}{2} N_i k \left[1 + \ln \frac{2\pi m k T}{h^2}\right] + N_i k \ln V_i \,, \tag{2.74}$$

where i stands for 1 or 2. When the boundary between the two systems is removed, the two gases mix, and the entropy of the combined system becomes

$$S_c = \frac{3}{2}(N_1 + N_2) k \left[1 + \ln \frac{2\pi m k T}{h^2}\right] + (N_1 + N_2) k \ln(V_1 + V_2) \,. \tag{2.75}$$

The change in total entropy before and after mixing is then

$$\begin{aligned}
\Delta S &= S_c - (S_1 + S_2) \\
&= (N_1 + N_2)\, k \ln (V_1 + V_2) - N_1 k \ln V_1 - N_2 k \ln V_2 \\
&= N_1 k \ln \frac{V_1 + V_2}{V_1} + N_2 k \ln \frac{V_1 + V_2}{V_2} \geq 0 \,.
\end{aligned} \tag{2.76}$$

The only possibility for having $\Delta S = 0$ is to have one of the systems with zero volume and zero number of particles, say, $N_2 = 0$ and $V_2 = 0$. Any other nontrivial values of N_i and V_j will lead to an increase of entropy. In particular, $\Delta S > 0$ even if $N_1/V_1 = N_2/V_2$; that is, if the two systems initially have the same density, in which case, removing or inserting the partition between the two should not make any macroscopic difference, i.e, no change in entropy. This is a "paradox".

2.5.1 Gibbs' Solution

Modify Eq. (2.61) so as to make S (and E) truly extensive. Specifically, instead of

$$S(N,V,E) = Nk\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk \tag{2.77}$$

use

$$S(N,V,E) = Nk\ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{5}{2}Nk\,. \tag{2.78}$$

With this corrected expression for the entropy, we find

$$E = \frac{3h^2N^{5/3}}{4\pi mV^{2/3}}\exp\left(\frac{2S}{3Nk} - \frac{5}{3}\right)\,. \tag{2.79}$$

It can be seen that these two expressions for S and E are indeed extensive.

In terms of Ω, it amounts to an ad hoc division of the right side of Eq. (2.57) by $N!$

$$\begin{aligned}
\Omega(N,V,E) \quad &\rightarrow \quad \underbrace{\frac{1}{N!}}_{\substack{\text{Gibbs'}\\ \text{correction}}} \quad \underbrace{\frac{3N\Delta}{2E}\left(\frac{1}{2}\right)^{3N}\frac{\pi^{3N/2}}{(3N/2)!}\left(\frac{8mV^{2/3}E}{h^2}\right)^{3N/2}}_{\Omega_N \text{ from Eq. (2.51)}} \\
&\rightarrow \underbrace{\frac{3N\Delta}{2E}\left(\frac{4\pi m}{3h^2}V^{2/3}\frac{E}{N}\right)^{3N/2} e^{3N/2}}_{\text{same as before}}\underbrace{\frac{e^N}{N^N}}_{\sim 1/N!} \\
&\rightarrow \frac{3N\Delta}{2E}\left(\frac{4\pi m}{3h^2}\left(\frac{V}{N}\right)^{2/3}\frac{E}{N}\right)^{3N/2} e^{5N/2}\,.
\end{aligned} \tag{2.80}$$

The corresponding expression for the entropy, $S = k\ln\Omega$, is

$$S = \underbrace{k\ln\left(\frac{3N\Delta}{2E}\right)}_{\text{negligible}} + \underbrace{Nk\ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]}_{\text{extensive}} + \frac{5}{2}Nk\,. \tag{2.81}$$

More Thermodynamics

With the proper dependence of S and E on N, we can now calculate the chemical potential for an ideal gas. Using Eq. (2.79),

$$\begin{aligned}\mu &= \left.\frac{\partial E}{\partial N}\right|_{V,S} \\ &= \frac{5}{3}\frac{E}{N} - \frac{2S}{3k}\frac{E}{N^2} = \frac{1}{N}\left(E + \frac{2}{3}E - \frac{S}{k}\frac{2}{3}\frac{E}{N}\right) . \qquad (2.82)\end{aligned}$$

Let us use the relation $E = (3/2)PV = (3/2)NkT$ in the last equation, to obtain

$$\mu = \frac{1}{N}\left(E + PV - ST\right) = \frac{G}{N} . \qquad (2.83)$$

After some algebra, and making use of $E = (3/2)NkT$, this yields

$$\mu = kT \ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] . \qquad (2.84)$$

Define the volume per unit particle

$$v = \frac{V}{N} \qquad (2.85)$$

and the thermal wavelength of a particle

$$\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2} . \qquad (2.86)$$

With these definitions, the chemical potential becomes

$$\mu = \frac{G}{N} = kT \ln\left(\frac{\lambda^3}{v}\right) . \qquad (2.87)$$

The Helmholtz free energy is

$$A = E - TS = G - PV = NkT\left[\ln\left(\frac{\lambda^3}{v}\right) - 1\right] . \qquad (2.88)$$

The enthalpy is

$$H = E + PV = \frac{5}{2}NkT . \qquad (2.89)$$

2.5.2 Mixing Entropy "encore"

Referring to the same system as before, the entropy of system i before mixing (before the partition between the two systems is removed) is

$$\begin{aligned} S_i &= N_i k \ln\left[\frac{V_i}{N_i h^3}\left(\frac{4\pi m E_i}{3N_i}\right)^{3/2}\right] + \frac{5}{2}N_i k \\ &= \frac{3}{2}N_i k \ln\left(\frac{2\pi m k T}{h^2}\right) + N_i k \ln\frac{V_i}{N_i} + \frac{5}{2}N_i k\,, \end{aligned} \tag{2.90}$$

where we used the relation $E = (3/2)NkT$. The entropy of the combined system after removing the partition is

$$S_c = \frac{3}{2}(N_1+N_2)k\ln\left(\frac{2\pi m k T}{h^2}\right) + (N_1+N_2)k\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) + \frac{5}{2}\left(N_1+N_2\right)k\,. \tag{2.91}$$

As a result, the change in entropy is

$$\begin{aligned} \Delta S &= S_c - (S_1+S_2) \\ &= (N_1+N_2)k\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1 k\ln\frac{V_1}{N_1} - N_2 k \ln\frac{V_2}{N_2} \\ &= N_1 k \ln\left(\frac{V_1+V_2}{N_1+N_2}\frac{N_1}{V_1}\right) + N_2 k\ln\left(\frac{V_1+V_2}{N_1+N_2}\frac{N_2}{V_2}\right)\,. \end{aligned} \tag{2.92}$$

It can be shown that ΔS as given above, is zero when $N_1/V_1 = N_2/V_2$, and that it is greater than zero otherwise.

2.5.3 Corrected Counting of States

Let $(i_1, i_2, \ldots, i_N)$ represent the microstate of an N-particle system. In this notation, i_1 is the energy level occupied by particle 1, etc. In counting states previously, we treated particles as distinguishable. For example, for a system of three particles, there would be only one state corresponding to all three particles being in level 2:

$$(2,2,2)\ \}\ \text{single state.}$$

However, there would be three distinct states corresponding to two particles in level 2 and one in level 4:

$$\left.\begin{array}{c}(2,2,4)\\(2,4,2)\\(4,2,2)\end{array}\right\}\ \text{three distinct states.} \tag{2.93}$$

Now consider another microscopic description of the system in terms of

- single particle energy levels ε_i, and
- populations n_i of the different energy levels.

In this description, only the populations of the various energy levels are specified, rather than the energy levels occupied by each individual particle. This approach may appear to be a less detailed microscopic picture than the previous one. It is actually more suitable to describe systems of indistinguishable particles.

In order to illustrate this point, let us represent the populations of the various energy levels by the set of numbers $\{n_1, n_2, \ldots\}$. If the system has a finite number of energy levels, then the set of occupation numbers would be finite, otherwise, it would be infinite. Whether finite or infinite, these numbers must be constrained by the total number of particles

$$\sum_i n_i = N \tag{2.94}$$

and the total energy

$$\sum_i n_i \varepsilon_i = E\,. \tag{2.95}$$

Thus, in example (2.93), the system configuration $\{0, 2, 0, 1, \ldots\}$ is treated as three distinct states if particles are treated as distinguishable. For indistinguishable states, however, that configuration must be counted as a single state.

Considering this, when particles are treated as distinct, the number of states corresponding to a configuration $\{n_1, n_2, \ldots\}$ is

$$\frac{N!}{n_1!n_2!\ldots}\,. \tag{2.96}$$

It follows that, when treating particles as indistinguishable, our estimate of the number of states Ω must divided by Eq. (2.96).

Notice that this correction factor is different from the one introduced by Gibbs (who divided by $N!$). Our correction factor agrees with that of Gibbs when essentially all n_i are either 0 or 1. In other words, Eq. (2.96) is a good approximation of $N!$ when the system is sufficiently energetic that the probability for two particles to be in the same quantum state is negligible.

2.6 Problems

Chapter 3

Microcanonical Ensembles

Recall the following.

- An ensemble is a set of all possible microstates corresponding to a macrostate.
- All microstates in a given ensemble, are equally probable (equiprobability).
- The probability of a macrostate is proportional to number of microstates consistent with that macrostate.
- A given microstate of an actual system may be changing constantly in time.
- An ensemble may also change in time. In other words, the macrostate corresponding to an ensemble may change in time if that macrostate does not correspond to an equilibrium.

A stationary distribution is one that does not change in time. The ensemble corresponding to a system at equilibrium must be made of a stationary distribution of microstates. Note that in a stationary distribution, microstates may still migrate to other possible microstates, but the distribution of these states remains unchanged.

3.1 Classical Systems with Continuous Variables

To be specific, let us consider a system of point particles in the context of classical mechanics. For simplicity, let us assume that the particles are nonrelativistic, and they do not radiate.

Particles may interact with one another, but retardation fields and radiation are ignored. If radiation were included, then the degrees of freedom associated with the radiation field would have be taken into account. The microstate of the system is determined by the coordinates and velocities $(q_i, \dot{q}_i)$, or the coordinates and conjugate momenta (q_i, p_i).

Some definitions follow.

- Lagrangian: $L = T - U =$ kinetic $-$ potential energy.

- Hamilton's action principle
$$S = \int_a^b dt\, L \tag{3.1}$$
is an extremum if $\delta q = 0$ at the end points a and b. This gives rise to Euler-Lagrange equations
$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0\,. \tag{3.2}$$
Examples are
$$L = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2 \tag{3.3}$$
for a harmonic oscillator and
$$L = -\frac{mc^2}{\gamma} - q\left(\phi - \vec{v}\cdot\vec{A}\right) \tag{3.4}$$
for a relativistic particle in an electromagnetic field.

- Canonical momentum:
$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \tag{3.5}$$

- Hamiltonian: obtained from a Legendre transformation
$$H = \sum_i p_i \dot{q}_i - L\,. \tag{3.6}$$
This changes from the independent variables $(q_i, \dot{q}_i)$ for L to (q_i, p_i) for H:
$$\begin{aligned} dH &= \sum_i \left(dp_i\dot{q}_i + p_i d\dot{q}_i - \underbrace{\frac{\partial L}{\partial q_i}}_{\dot{p}_i} dq_i - \underbrace{\frac{\partial L}{\partial \dot{q}_i}}_{p_i} d\dot{q}_i \right) \\ &= \sum_i \left(dp_i\dot{q}_i - \frac{\partial L}{\partial q_i} dq_i \right) \\ &= \sum_i \left(\left.\frac{\partial H}{\partial p_i}\right|_{\substack{q_k \\ p_k, k\neq i}} dp_i + \left.\frac{\partial H}{\partial q_i}\right|_{\substack{p_k \\ q_k, k\neq i}} dq_i \right)\,. \end{aligned} \tag{3.7}$$
From this last equality, we find Hamilton's equations of motion
$$\dot{q}_i = \left.\frac{\partial H}{\partial p_i}\right|_{\substack{q_k \\ p_k, k\neq i}} \quad \text{and} \quad \dot{p}_i = -\left.\frac{\partial H}{\partial q_i}\right|_{\substack{p_k \\ q_k, k\neq i}}. \tag{3.8}$$

3.2 Phase Space

Phase space is a multi-dimensional space with coordinates $(q_i, p_i), i = 1, \ldots, N$, where q_i and p_i are canonical variables. That is, these are the independent variables of a Hamiltonian of the system, and their equations of motion are given by the Hamilton's equations, Eq. (3.8).

Some observations can be made.

- The microstate of a system is a point in phase space.
- Evolution of a system in time corresponds to the motion of a point in phase space.
- Ensemble: Distribution of points in phase space. If $\rho(q_i, p_i, t)$ is the probability density, $\rho(q, p, t)dqdp$ is the probability of finding a system in volume element $(q, q{+}dq)(p, p{+}dp)$ at time t. Here, q stands for q_i, and similarly for p.
- Canonical transformation: $(q_i, p_i) \to (Q_i, P_i)$ such that if (q_i, p_i) are canonical variables, then (Q_i, P_i) are also canonical.
- The evolution of ρ in time is determined by the dynamics of the system.
- Average of a physical quantity: If $f(q, p, t)$ represents a physical observable, then its average over an ensemble with a given probability density is

$$\langle f \rangle = \int dqdpf(q, p, t)\rho(q, p, t)\,. \tag{3.9}$$

An ensemble is stationary if $\partial\rho/\partial t = 0$. This is a necessary condition for a system to be at equilibrium.

Example: The harmonic oscillator Hamiltonian in one dimensions is

$$H = \frac{kq^2}{2} + \frac{p^2}{2m}. \tag{3.10}$$

For a microcanonical ensemble (E constant) the probability density is on an ellipse in (q, p) space.

Theorem: For an infinitesimal energy range (a thin shell in phase space),

- there exist a stationary distribution ρ,
- this distribution is unique, and
- ρ is constant in that shell (equiprobability).

3.3 Liouville's Theorem

Liouville's Theorem says the probability density ρ for a given ensemble (stationary or not) is constant along a system trajectory in phase space.

Proof: Consider the number of systems, or points in a fixed volume ω delimited by a boundary σ in phase space:

$$N = \int_\omega d\omega\ \rho = \int_\omega \prod_i dq_i dp_i\ \rho\,. \tag{3.11}$$

The rate at which N changes in time is

$$\frac{dN}{dt} = \int_\omega d\omega\ \left.\frac{\partial \rho}{\partial t}\right|_{q,p}. \tag{3.12}$$

Also, from the conservation of systems or points in phase space,

$$\frac{dN}{dt} = -\oint_\sigma \vec{F}\cdot\hat{n} da\,, \tag{3.13}$$

where $\vec{F}$ is the flux of points (or systems) in phase space:

$$\vec{F} = \rho\vec{v}, \tag{3.14}$$

where $\vec{v} = (\dot{q}_i, \dot{p}_i)$ is the velocity of points in phase space. From the divergence theorem,

$$\oint_\sigma F_\alpha n_\alpha da = \int_\omega \partial_\alpha F_\alpha d\omega\,. \tag{3.15}$$

Thus, in terms of the generalised phase space velocity $(\dot{q}_i, \dot{p}_i)$,

$$\begin{aligned} \frac{dN}{dt} &= -\int_\omega d\omega \sum_i \left[\frac{\partial}{\partial q_i}(\dot{q}_i\rho) + \frac{\partial}{\partial p_i}(\dot{p}_i\rho)\right] \\ &= -\int_\omega \sum_i \left[\left(\underbrace{\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}}_{\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0}\right)\rho + \dot{q}_i\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i}\right]. \end{aligned} \tag{3.16}$$

From Eq. (3.12) and Eq. (3.16), if follows that

$$\int_\omega d\omega \left[\frac{\partial \rho}{\partial t} + \sum_i \left(\dot{q}_i\frac{\partial \rho}{\partial q_i} + \dot{p}_i\frac{\partial \rho}{\partial p_i}\right)\right] = 0\,. \tag{3.17}$$

Because this equality holds for arbitrary (fixed) volumes ω in phase space, we conclude that the integrand must vanish almost everywhere:

$$\frac{\partial \rho}{\partial t} + \sum_i \left(\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) \equiv \frac{D\rho}{Dt} = 0\,. \tag{3.18}$$

In this expression, $D\rho/Dt$ is the convective derivative of ρ along a trajectory followed by a system in phase space. Thus, Eq. (3.18) implies that the probability density of an ensemble in phase space is constant along any system trajectory.

3.4 Some Definitions

Microcanonical ensemble This has been introduced in the context of quantum systems with discrete eigenstates. We extend the concept to classical continuous systems.

- In the context of classical systems described in continuous phase space, the microcanonical ensemble is a (continuous) set of accessible states in (high dimensional) phase space.
- The population of this ensemble is described in terms of a continuous probability distribution function, or density of states $\rho(q, p, t)$. The ensemble is restricted to values of the energy in a narrow interval $(E, E+\Delta)$. This corresponds to a thin shell (a surface in the limit $\Delta \to 0$) in phase space.
- The volume of domain ω in phase space is calculated as

$$V_\omega = \int_\omega d^{3N}q\, d^{3N}p\,. \tag{3.19}$$

Equilibrium Assume any state of the system can get arbitrarily close to any other state if we wait long enough. This is the concept of ergodicity. At equilibrium, the density of states, or probability density $\rho(q, p, t)$, must be constant. Why?

- At equilibrium, ρ is stationary.
- From Liouville's theorem, and from the assumption above, ρ must be the same at every point of the microcanonical ensemble. This means that equiprobability appears as a consequence of the condition for equilibrium and the assumption of ergodicity.

Averages We distinguish between two types of averages:

- Ensemble average:

$$\langle f \rangle = \int dq\, dp\, f(q, p) \rho(q, p)\,, \tag{3.20}$$

  where we assume no explicit time dependence in f or ρ.

- Time average:

$$\{f\} = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt f(q,p)\,. \tag{3.21}$$

- Ergodicity is when the ensemble average and time average are the same. This follows from the assumption of ρ being stationary and the assumption that, with time, a system in any given state can get arbitrarily close to any other state.

Measurements

- Physical measurements involve averages over time and space. The averages are typically over short macroscopic temporal and spatial scales.

- Measurements should correspond to the most probable macrostates.

- The ensemble average is the most probable macrostate if that state is much more probable than all the others.

Connection with statistics

- Number of states

$$\begin{aligned} \Omega &= \text{number of accessible states} \\ &\propto \text{volume } \omega \\ &= \omega/\omega_0 \end{aligned} \tag{3.22}$$

  for some elemental phase space volume ω_0.

- What is ω_0?

- Answer: consider the following examples.

3.5 Connection with Quantum Counting

3.5.1 Ideal Gas: N noninteracting particles in a Box

For a system of N distinguishable particles, we have

$$
\begin{aligned}
\omega &= \int_{\text{energy}\leq E} dq^{3N} dp^{3N} \\
&= V^N \underbrace{\int_{\sum_{i=1}^{3N} \frac{p_i^2}{2m} \leq E} dp^{3N}}_{\substack{\text{volume of a sphere of radius} \\ \sqrt{2mE} \text{ in } 3N\text{-dimensions}}} \\
&= V^N \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2}. \qquad (3.23)
\end{aligned}
$$

But previously (see Eq. (2.51)), we found the number of quantum states accessible to a system of N distinguishable particles with total energy E or less is

$$\Sigma_N(E) = V^N \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{2mE}{h^2}\right)^{3N/2}, \qquad (3.24)$$

$$\Rightarrow \omega_0 = \frac{\omega}{\Sigma} = h^{3N}, \qquad (3.25)$$

where h (Planck's constant) is the elemental phase-space volume per degree of freedom.

3.5.2 Harmonic Oscillator

The classical expression for the Hamiltonian of the system is

$$H = \frac{1}{2}\left(kq^2 + \frac{p^2}{m}\right) = E = \text{constant}. \qquad (3.26)$$

With $\bar{\omega} = \sqrt{k/m}$, this becomes

$$\frac{q^2}{2E/(m\bar{\omega}^2)} + \frac{p^2}{2Em} = 1, \qquad (3.27)$$

which is the equation for an ellipse.

The volume in phase space, within energy E (for energy E or less) is given by the area of an ellipse;

$$V = \frac{\pi^N}{N!} a^N b^N, \quad \text{for } N = 1 \text{ and } a, b \text{ half lengths}, \qquad (3.28)$$

with semi-major axes $\sqrt{2E/(m\bar{\omega}^2)}$ and $\sqrt{2Em}$:

$$\omega = \pi \sqrt{\frac{2E}{m\bar{\omega}^2}} \sqrt{2Em} = \frac{2\pi E}{\bar{\omega}}. \qquad (3.29)$$

From quantum mechanics, however,

$$E_n = \hbar\bar{\omega}\left(n + \frac{1}{2}\right) , \tag{3.30}$$

$$\Rightarrow \Sigma_1(E) \approx \frac{E}{\hbar\bar{\omega}} , \tag{3.31}$$

$$\Rightarrow \omega_0 = \frac{\omega}{\Sigma} = \frac{2\pi E}{\bar{\omega}}\frac{\hbar\bar{\omega}}{E} = h\,. \tag{3.32}$$

Again, h is the elemental volume in phase space per degree of freedom.

3.5.3 Uncertainty Principle

The uncertainty principle is

$$\Delta x \Delta p \geq \hbar/2 \tag{3.33}$$

for conjugate variables x and p. Within a region of size $\sim h$ in phase space, per degree of freedom, different points do not actually represent different states of the system.

3.6 Problems

Chapter 4

Canonical Ensembles

It is easier to speak of the temperature of a system than its total energy. The canonical ensemble is determined by the following.

- Systems may exchange energy with their surrounding.
- We assume thermodynamic equilibrium.
- The macrostate is determined by (N, V, T) instead of (N, V, E) for microcanonical ensembles.

Question: What is the probability of finding the system in a given state of energy E_r?

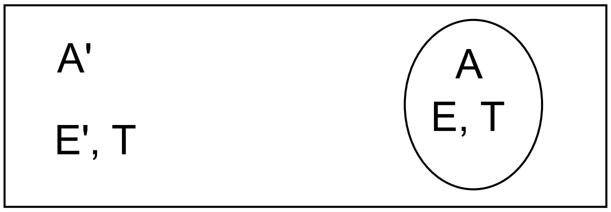
Answer: Two possible approaches:

1. Consider the system in contact with a heat reservoir (very large system at a given temperature).
2. Consider the system as part of a canonical ensemble, with a total number $\mathcal{N}$ of systems and given total energy

$$\mathcal{E} = \sum_{i=1}^{\mathcal{N}} \varepsilon_i = \mathcal{N} U \,, \tag{4.1}$$

   where U is the mean system energy.

In the thermodynamic limit 1. and 2. are equivalent.



4.1 Approach 1: Contact with a Heat Reservoir

Assume

$$E^0 = E' + E_r = \text{constant} \tag{4.2}$$

with $E_r \ll E^0$. The probability for A to be in quantum state r is proportional to the total number of states accessible to the combined system

$$P_r \propto \Omega_0 = \Omega'(E^0 - E_r)\Omega(E_r)\,, \tag{4.3}$$

where $\Omega(E_r) = 1$ because A is assumed to be in a precise quantum state r:

$$P_r \propto \Omega'(E^0 - E_r)\,. \tag{4.4}$$

Make use of the fact that $E_r \ll E^0$ to do a Taylor series expansion. More specifically, we write

$$P_r \propto e^{[\ln \Omega'(E^0 - E_r)]}, \tag{4.5}$$

and

$$\ln[\Omega'(E^0 - E_r)] \approx \ln \Omega'(E^0) - E_r \frac{\partial \ln \Omega'}{\partial E'} + \frac{1}{2} E_r^2 \frac{\partial^2 \ln \Omega'}{\partial E'^2}\,. \tag{4.6}$$

Making use of

$$\begin{aligned} \frac{\partial \ln \Omega'}{\partial E'} &= \frac{1}{kT}\,, && (4.7) \\ \frac{\partial^2 \ln \Omega'}{\partial E'^2} &= -\frac{1}{kT^2 C_V}\,. && (4.8) \end{aligned}$$

gives

$$\begin{aligned} P_r &\propto \Omega' \equiv \Omega'(E^0) \exp\left[-\frac{E_r}{kT}\left(1 + \frac{E_r}{2TC_V}\right)\right] \\ P_r &\propto \Omega' \exp\left(-\frac{E_r}{kT}\right)\,. && (4.9) \end{aligned}$$

where the last term in the exponential is negligible for a heat reservoir. The normalised probability is

$$P_r = \frac{\exp(-E_r/kT)}{\sum_s \exp(-E_s/kT)} \,. \tag{4.10}$$

4.2 Approach 2: In a Canonical Ensemble

This ensemble is similar to the microcanonical ensemble introduced earlier. It also acts as a fictitious population from which statistics can be calculated. Remember that the microcanonical ensemble consisted of all possible microstates of a system with a given energy.

With the canonical ensemble, we consider ensembles of $\mathcal{N}$ systems sharing a total energy $\mathcal{E}$. Let E_r be the various energy levels of the systems and n_r be the number of systems with energy E_r. Any ensemble satisfying the constraints

$$\mathcal{N} = \sum_r n_r \,, \tag{4.11}$$

$$\mathcal{E} = \sum_r n_r E_r \equiv \mathcal{N} U \tag{4.12}$$

can be an element of the canonical ensemble.

Thus, the canonical ensemble is actually an ensemble of ensembles of systems in all possible microscopic configurations subject to the constraints Eq. 4.11 and Eq. 4.12. In these ensembles, individual systems do not necessarily have a given energy. It is the ensembles within the canonical ensembles, that are constrained to have a given total number of systems $\mathcal{N}$ and energy $\mathcal{E}$. In such an ensemble, an individual system can be thought of as exchanging energy with other elements of the ensemble, as it would with a heat reservoir.

The state of a given ensemble of systems is described by the distribution

$$\{n\} \equiv \{n_0, n_1, \ldots\} \,,$$

where n_i represents the number of systems in state i in that ensemble.

Treating systems in each ensemble as distinguishable, the number of distinct combinations corresponding to a state $\{n\}$ is

$$W\{n\} = \frac{\mathcal{N}!}{n_0! n_1! \ldots} \propto P_{\{n\}} \,, \tag{4.13}$$

where $P_{\{n\}}$ is the probability of encountering configuration $\{n\}$. Thus, the normalised probability is

$$P_{\{n\}} = \frac{W\{n\}}{\sum_{\{n\}} W\{n\}} \,. \tag{4.14}$$

With an explicit expression for the probability, it is then possible to do some statistics. For example,

$$\langle n_r \rangle = \frac{\sum_{\{n\}} n_r W\{n\}}{\sum_{\{n\}} W\{n\}}\,, \tag{4.15}$$

where the sum is over all distribution sets that conform to the constraints.

There are two possible approaches to the calculation: 1) maximum probability and 2) detailed calculation of the probability with a generating function.

4.2.1 Maximum Probability

We need to maximise

$$W\{n\} = \frac{\mathcal{N}!}{n_0! n_1! \ldots}$$

subject to the constraints Eq. 4.11 and Eq. 4.12.

Assume that $\mathcal{N}, n_0, n_1, \cdots \to \infty$. Use Stirling's formula to evaluate factorials.

$$\begin{aligned} \ln W\{n\} &\approx (\mathcal{N} \ln \mathcal{N} - \mathcal{N}) \\ &- (n_0 \ln n_0 - n_0) \\ &- (n_1 \ln n_1 - n_1) \\ &- \ldots \\ &\approx \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r\,. \end{aligned} \tag{4.16}$$

The first term is a constant. We see that maximising $W\{n\}$ is equivalent to minimising $\sum_r n_r \ln n_r$ subject to constraints Eq. (4.11) and Eq. (4.12). We use Lagrange multipliers. Find the extremum of

$$\sum_r n_r \ln n_r + \alpha \left(\sum_r n_r - \mathcal{N} \right) + \beta \left(\sum_r n_r E_r - \mathcal{E} \right) \tag{4.17}$$

with respect to n_r, α, and β.

$$\begin{aligned} \frac{\partial}{\partial n_r} = 0 \quad &\Rightarrow \quad \ln n_r + 1 + \alpha + \beta E_r = 0 \\ &\Rightarrow \quad n_r \propto e^{-\beta E_r}\,, \end{aligned} \tag{4.18}$$

The $1 + \alpha$ has been absorbed into the overall constant.

$$\frac{\partial}{\partial \alpha} = 0 \Rightarrow \sum_r n_r = \mathcal{N} \tag{4.19}$$

or, making use of Eq. 4.18,

$$\frac{n_r}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}\,. \tag{4.20}$$

Setting the derivative with respective to β to zero reproduces constraint Eq. (4.12).

Eq. (4.20) gives the probability of having a given quantum state r in an ensemble. Let us now use this to write an expression for the probability of having a system in a given energy level E_i. Let g_i be the degeneracy of energy level E_i. The probability of finding energy E_i is

$$P_i = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}\,. \tag{4.21}$$

This is the probability of energy E_i. But, $g_i = \Omega(E_i)$ so $P_i \propto \exp[-\beta E_i + \ln \Omega(E_i)]$. The most probable energy E_i is the one for which P_i is maximum; i.e., for which $\partial P_i/\partial E_i = 0$:

$$\Rightarrow -\beta + \frac{\partial \ln \Omega}{\partial E} = 0 \Rightarrow \beta = \frac{1}{kT}\,. \tag{4.22}$$

4.2.2 Detailed Calculation of the Probability – Mean Values

Our goal is to evaluate

$$\langle n_r \rangle = \frac{\sum'_{\{n\}} n_r W\{n\}}{\sum'_{\{n\}} W\{n\}} \tag{4.23}$$

subject to constraints. This is the meaning of prime in summation.

$$\sum_r n_r = \mathcal{N}\,, \tag{4.24}$$

$$\sum_r n_r E_r = \mathcal{N} U\,. \tag{4.25}$$

Let us define

$$\tilde{W}\{n\} \equiv \frac{\mathcal{N}!\, \omega_0^{n_0} \omega_1^{n_1} \ldots}{n_0! n_1! \ldots} \tag{4.26}$$

and

$$\Gamma(\mathcal{N}, U) \equiv {\sum_{\{n\}}}' \tilde{W}\{n\} \tag{4.27}$$

with the understanding that all the ω_r will be set equal to unity in the end. The average value of n_r can be calculated formally from (see Eq. (4.23))

$$\langle n_r \rangle = \omega_r \left.\frac{\partial \ln \Gamma}{\partial \omega_r}\right|_{\text{all } \omega_r = 1}\,. \tag{4.28}$$

Notice that Γ can be rewritten as

$$\Gamma = \mathcal{N}! \sum_{\{n\}}{}' \left(\frac{\omega_0^{n_0}}{n_0!} \frac{\omega_1^{n_1}}{n_1!} \cdots \right) . \tag{4.29}$$

If we only had constraint Eq. (4.24), we could use the multinomial expansion and write

$$(\omega_0 + \omega_1 + ...)^{\mathcal{N}} .$$

That is not possible, however, because of the additional constraint Eq. (4.25).

As an aside, the multinomial expansion is

$$(x_1 + x_2 + \ldots + x_m)^n = \frac{n!}{\sum_{k_1+k_2+\ldots k_m} k_1! k_1! \cdots k_n!} \prod_{1 \le t \le n} x_t^{k_t} . \tag{4.30}$$

Solution of Darwin and Fowler (1922, 1923). Introduce a generating function

$$G(\mathcal{N}, z) = \sum_{U=0}^{\infty} \Gamma(\mathcal{N}, U) z^{\mathcal{N} U} , \tag{4.31}$$

$$\begin{aligned} G(\mathcal{N}, z) &= \sum_{U} \sum_{\{n\}}{}' \frac{\mathcal{N}!}{n_0! n_1! \ldots} \left(\omega_0 z^{E_0}\right)^{n_0} \left(\omega_1 z^{E_1}\right)^{n_1} \cdots \\ &= \sum_{\{n\}}{}' \frac{\mathcal{N}!}{n_0! n_1! \cdots} \left(\omega_0 z^{E_0}\right)^{n_0} \left(\omega_1 z^{E_1}\right)^{n_1} \cdots , \end{aligned} \tag{4.32}$$

where the constraint is now only on Eq. (4.24). The constraint Eq. (4.25) has been eliminated because of the summations over all possible energies U. Thus, from the multinomial theorem

$$\begin{aligned} G(\mathcal{N}, z) &= \left(\omega_0 z^{E_0} + \omega_1 z^{E_1} + \ldots\right)^{\mathcal{N}} \\ &\equiv [f(z)]^{\mathcal{N}} . \end{aligned} \tag{4.33}$$

From Eq. (4.31), we see that the functions Γ needed to calculate averages (see Eq. 4.28) are simply the coefficients of the power series expansion of G in z.

Assumptions made in the proof (see the original articles for details):

- E_i are integers,
- $E_i \le E_{i+1}$,
- E_i have no common dividers,
- $E_0 = 0$,

- $G = f^{\mathcal{N}}$ is analytic at $z = 0$,

The solution is

$$\Gamma(\mathcal{N}, U) = \frac{1}{2\pi i} \oint dz \frac{f^{\mathcal{N}}(z)}{z^{\mathcal{N}U+1}} \,. \tag{4.34}$$

Consider the integrand along the real z-axis.

- When $z \to 0 : f \to 1$ (remember $E_0 = 0$).
- When $z \to 0 : 1/z^{\mathcal{N}U+1} \to \infty$.
- When $z > 0 : 1/z^{\mathcal{N}U+1}$ is a decreasing function.
- For $z \to \infty$: $f^{\mathcal{N}}$ increases faster than $1/z^{\mathcal{N}U+1}$ decreases $\Rightarrow$ the integrand goes to infinity.

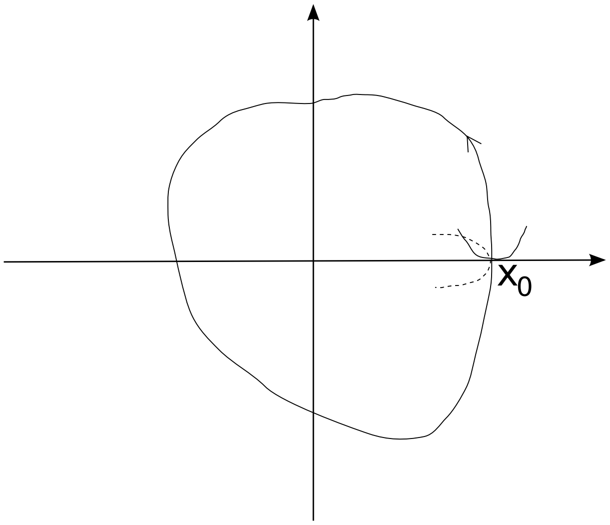
$\Rightarrow f^{\mathcal{N}}/z^{\mathcal{N}U+1}$ has a minimum along the real z-axis.

Recall that analytic functions cannot have absolute maxima or minima in the complex plane. They can only have saddle points.

Proof: If $f = f(z) = f(x, iy)$ and f is analytic, then

$$\frac{\partial}{\partial x}\frac{\partial}{\partial x} f = \frac{\partial}{\partial iy}\frac{\partial}{\partial iy} f = -\frac{\partial}{\partial y}\frac{\partial}{\partial y} f \,. \tag{4.35}$$

If f has a maximum in x, it will have a minimum in y, and vice versa.



Let x_0 be the position of the minimum of the integrand along the real z-axis.

Choose $\oint dz$ so that it goes through $z = x_0$. If the maximum is sharp, most of the contribution is near x_0.

$$\frac{1}{2\pi i}\oint dz \frac{f^{\mathcal{N}}(z)}{z^{\mathcal{N}U+1}} \approx \frac{1}{2\pi i}\int_{-a}^{a} idy \frac{f^{\mathcal{N}}}{z^{\mathcal{N}U+1}} \tag{4.36}$$

for some small but finite a

Let

$$\frac{f^{\mathcal{N}}}{z^{\mathcal{N}U+1}} = \exp[\mathcal{N}g(z)] \tag{4.37}$$

with

$$g(z) = \ln f - \left(U + \frac{1}{\mathcal{N}}\right)\ln z \approx \ln f - U\ln z\,. \tag{4.38}$$

Saddle point is given by

$$\frac{\partial g}{\partial z} = \frac{1}{f(x_0)}f'(x_0) - \frac{U}{x_0} = 0 \Rightarrow U = \frac{x_0 f'(x_0)}{f(x_0)}\,. \tag{4.39}$$

Recall $f(z) = \sum_s w_s x_0^{E_s}$ from Eq. (4.33).

$$U = \frac{\sum_s w_s E_s x_0^{E_s}}{\sum_s w_s x_0^{E_s}}\,. \tag{4.40}$$

Recall that we will take $w = 1$. Similar to $U = \sum_s E_s P_s$ with

$$P_s = \frac{x_0^{E_s}}{\sum_s x_0^{E_s}}\,. \tag{4.41}$$

Take $x_0 = e^{-\beta}$ gives

$$U = \frac{\sum_s w_s E_s e^{-\beta E_s}}{\sum_s w_s e^{-\beta E_s}} \tag{4.42}$$

Notice that for U given, this defines a dependence of β on w_r.

Calculation of $\boldsymbol{\Gamma}$

$$\frac{f^{\mathcal{N}}}{z^{\mathcal{N}U+1}} = e^{\mathcal{N}g}. \tag{4.43}$$

Taylor expansion around x_0

$$\begin{aligned} g &\approx f(x_0) + \frac{1}{2}[(x_0 + iy) - x_0]^2 g''(x_0) && (4.44)\\ &\approx f(x_0) - \frac{y^2}{2}\left[\frac{f''}{f} - \frac{f'f'}{f} + \frac{U}{z^2}\right] && (4.45)\end{aligned}$$

$$\Rightarrow \frac{f^{\mathcal{N}}}{z^{\mathcal{N}U+1}} \approx \frac{f^{\mathcal{N}}(x_0)}{x_0^{\mathcal{N}U+1}} e^{-1/2\mathcal{N}g''y^2} \tag{4.46}$$

$$\Gamma(\mathcal{N}, U) \approx \frac{1}{2\pi i}\int_{-\infty}^{\infty} idy \frac{f(x_0)^{\mathcal{N}}}{x_0^{\mathcal{N}U+1}} e^{-\mathcal{N}/2g''y^2} \tag{4.47}$$

$$\approx \frac{f^{\mathcal{N}}(x_0)}{x_0^{\mathcal{N}U+1}} \frac{1}{\sqrt{2\pi g''(x_0)\mathcal{N}}} \tag{4.48}$$

$$\ln\Gamma = \mathcal{N}[\ln f(x_0) - U\ln x_0] - \frac{1}{2}\ln 2\pi g''(x_0) \tag{4.49}$$

g'' negligible as $\mathcal{N} \to \infty$.

Recall

$$f(x_0) = \sum_r w_r x_0^{E_r} = \sum_r w_r e^{-\beta E_r} \tag{4.50}$$

Therefore

$$\ln\Gamma = \mathcal{N}\ln\left(\sum_s w_s e^{-\beta E_s}\right) + \mathcal{N}\beta U \tag{4.51}$$

Statistics

$$\langle n_r \rangle = w_r \frac{\partial \ln\Gamma}{\partial w_r}\bigg|_{\text{all } w=1} \tag{4.52}$$

$$\frac{\langle n_r \rangle}{N} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \left[-\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + U\right]\frac{\partial \beta}{\partial w_r}\,. \tag{4.53}$$

This is consistent with

$$p_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{4.54}$$

seen in Eq. (4.42).

Standard Deviation in n_r

By definition

$$\langle \Delta n_r^2 \rangle = \langle n_r^2 \rangle - \langle n_r \rangle^2\,. \tag{4.55}$$

Recall

$$\Gamma(\mathcal{N}, U) = \sum_{\{n\}}^{\prime} \mathcal{N}! \frac{w_0^{n_0} w_1^{n_1} \ldots}{n_0! n_1! \ldots} \tag{4.56}$$

$$\begin{aligned} \Rightarrow w_r \frac{\partial \Gamma}{\partial w_r} &= \sum_{\{n\}} \frac{\mathcal{N}! w_r^{n_r} n_r}{n_0! n_1! \ldots} = \Gamma \langle n_r \rangle && (4.57) \\ w_r \frac{\partial}{\partial w_r} \left(w_r \frac{\partial \Gamma}{\partial w_r} \right) &= \sum_{\{n\}} \frac{\mathcal{N}! w_0^{n_0} w_0^{n_0} \ldots}{n_0! n_1! \ldots} n_r^2 = \Gamma \langle n_r^2 \rangle \,. && (4.58) \end{aligned}$$

$$\begin{aligned} \langle \Delta n_r^2 \rangle &= \frac{1}{\Gamma} w_r \frac{\partial}{\partial w_r} \left(w_r \frac{\partial \Gamma}{\partial w_r} \right) - \left(\frac{\partial \ln \Gamma}{\partial w_r} \right)^2 && (4.59) \\ &= w_r \frac{\partial}{\partial w_r} \left(w_r \frac{\partial}{\partial w_r} \ln \Gamma \right) \Bigg|_{w=1} \,. && (4.60) \end{aligned}$$

Use

$$\ln \Gamma = \mathcal{N} \left(\ln \sum_s w_s e^{-\beta E_S} + \beta U \right) \tag{4.61}$$

$$w_r \frac{\partial \ln \Gamma}{\partial w_r} = \frac{w_r e^{-\beta E_r}}{\sum_s w_s e^{-\beta E_s}} + \left\{ - \frac{\sum_s w_s E_s e^{-\beta E_S}}{\sum_s w_s e^{-\beta E_S}} + U \right\} w_r \frac{\partial \beta}{\partial w_r} \tag{4.62}$$

$\partial\beta/\partial w_r$ is obtained from

$$U = \frac{\sum_s w_s E_s e^{-\beta E_s}}{\sum_s w_s e^{-\beta E_s}} = x_0 \frac{f'(x_0)}{f(x_0)} \tag{4.63}$$

$$\Rightarrow \left(\frac{\partial \beta}{\partial w_r} \right)_U = \frac{E_r - U}{\langle E_r^2 \rangle - U^2} \frac{\langle n_r \rangle}{\mathcal{N}} \tag{4.64}$$

$$\Rightarrow \langle \left(\frac{\Delta n_r}{\langle n_r \rangle} \right)^2 \rangle = \frac{1}{\langle n_r \rangle} - \frac{1}{\mathcal{N}} \left[1 + \frac{(E_r - U)^2}{\langle (E_r - U)^2 \rangle} \right] \tag{4.65}$$

As $\mathcal{N} \to \infty$ (also $\langle n_r \rangle \to \infty$)

$$\left\langle \left(\frac{\Delta n_r}{\langle n_r \rangle} \right)^2 \right\rangle \to 0 \tag{4.66}$$

and the “maximum probability” approach is justified.

4.3 Physical Interpretation

The canonical distribution is

$$P_r = \frac{\langle n_r \rangle}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \,. \tag{4.67}$$

β is given by

$$U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = -\frac{\partial}{\partial \beta} \ln Q \,, \tag{4.68}$$

where Q is the partition function

$$Q = \sum_r e^{-\beta E_r}. \tag{4.69}$$

Consider the Helmholtz free energy $A = U - TS$. The differential is $dA = -SdT - PdV + \mu dN$.

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial A}{\partial V}\right)_{T,N} = -P, \quad \left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu \,. \tag{4.70}$$

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V} = -T^2 \frac{\partial}{\partial T}(A/T)\bigg|_{N,V} = \frac{\partial (A/T)}{\partial (1/T)}\bigg|_{N,V} \,. \tag{4.71}$$

Comparing Eq. (4.68) and Eq. (4.71) gives

$$\beta = \frac{1}{kT} \tag{4.72}$$

and

$$\frac{A}{kT} = -\ln Q \quad \Rightarrow \quad A = -kT \ln \sum_r \exp(-E_r/kT) \,. \tag{4.73}$$

Notice that A and $\ln Q$ are extensive.

$$P_r = Q^{-1} e^{-\beta E_r} \,, \tag{4.74}$$

$$\langle \ln P_r \rangle = -\beta \langle E_r \rangle - \ln Q = -\frac{U}{kT} + \frac{A}{kT} = -\frac{S}{k} \tag{4.75}$$

$$\Rightarrow S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r \,. \tag{4.76}$$

4.3.1 Consequences

- From the third law of thermodynamics $S \to 0$ as $T \to 0$, i.e., as the system approaches the ground state.
- For a microcanonical ensemble, $P_r = 1/\Omega$ and

  $$S = -k \sum_r \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) = k \ln \Omega \tag{4.77}$$

  as expected.

4.4 Partition Function

$$\sum_r e^{-\beta E_r} \to \sum_{E_i} g_i e^{-\beta E_i} \,, \tag{4.78}$$

where g_i is the degeneracy of energy level i. The probability is

$$P_i = \frac{g_i \exp(-\beta E_i)}{\sum_i g_i \exp(-\beta E_i)} \,. \tag{4.79}$$

For dense energy spectra, $g(E)dE$ is the number of states in the interval $(E, E + dE)$. $g(E)$ is density of states

$$g(E) = \sum_r \delta(E - E_r) = \sum_i g_i \delta(E - E_i) \,, \tag{4.80}$$

$$P(E)dE = \frac{g(E) \exp(-\beta E) dE}{\int_0^\infty dE g(E) \exp(-\beta E)} \,. \tag{4.81}$$

For a physical observable f,

$$\langle f \rangle = \sum_r f_r P_r \,. \tag{4.82}$$

If f only depends on the energy

$$\langle f \rangle = \frac{\sum_i g_i \exp(-\beta E_i) f(E_i)}{\sum g_i \exp(-\beta E_i)} = \frac{\int_0^\infty dE g(E) \exp(-\beta E) f(E)}{\int_0^\infty dE g(E) \exp(-\beta E)} \,. \tag{4.83}$$

Clearly,

$$Q(\beta) = \int_0^\infty dE g(E) e^{-\beta E} \,. \tag{4.84}$$

$Q(\beta)$ is Laplace transform of $g(E)$.

$$g(E) = \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta e^{\beta E} Q(\beta)\,, \tag{4.85}$$

for $\beta' > 0$.

4.5 Classical Systems

The ensemble average is

$$\langle f \rangle = \frac{\int dq dp \rho(q,p) f(q,p)}{\int dq dp \rho(q,p)}\,. \tag{4.86}$$

For the microcanonical ensemble $\rho(q,p)$ is a constant in the accessible phase space $1/(N! h^{3N})$.

For the canonical ensemble

$$\rho(q,p) = \frac{e^{-\beta H(q,p)}}{N! h^{3N}} \tag{4.87}$$

and

$$Q_N(V,T) = \frac{1}{N! h^{3N}} \int dq dp e^{-\beta H(q,p)}\,. \tag{4.88}$$

This produces the same results as seen previously for an ideal gas. Read Pathria Sec. 3.5 for more details.

4.6 Energy Fluctuations

(Sec. 3.6 Pathria)

Mean energy

$$U \equiv \langle E \rangle = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}\,. \tag{4.89}$$

$$\begin{aligned} \frac{\partial U}{\partial \beta} &= -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{(\sum_r E_r e^{-\beta E_r})^2}{(\sum_r e^{-\beta E_r})^2} & (4.90) \\ &= -\langle E^2 \rangle + \langle E \rangle^2\,. & (4.91) \end{aligned}$$

The mean squared deviation, or variance, is given by

$$\langle (\Delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2\,. \tag{4.92}$$

Therefore

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= -\frac{\partial U}{\partial \beta} = kT^2 \frac{\partial U}{\partial T} \\ &= kT^2 C_V \,. \end{aligned} \tag{4.93}$$

The relative root mean squared is

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{U} \ll 1 \,, \tag{4.94}$$

For macroscopic systems, microcanonical ensemble is approximately the same as the canonical ensemble. The final thermo properties should be the same for both ensembles: microcanonical $E + \Delta E$ and canonical $0 < E < \infty$. The most probably energy E^* is approximately the mean energy U, i.e. $E^* \approx U$. For a canonical ensemble the energy is almost equal to the mean enegy U.

Distribution in Energy

Treat E as a continuous variable.

$$P(E) \propto g(E) e^{-\beta E} = e^{S/k} e^{-\beta E} = e^{-\beta(E - TS)} \,, \tag{4.95}$$

where $g(E)$ is the density of states $S = k \ln g$ and $e^{-\beta E}$ is the Boltzman distribution. Taylor expand around the most probable energy $E^* \approx U$.

$$S(E) \approx S(U) + (E - U)\left(\frac{\partial S}{\partial E}\right) + \frac{(E-U)^2}{2} \frac{\partial^2 S}{\partial E^2} \,. \tag{4.96}$$

Notice that

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{4.97}$$

and

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial E} = -\frac{1}{T^2}\frac{\partial T}{\partial S}\frac{\partial S}{\partial E} = -\frac{1}{T^2}\frac{T}{C_V}\frac{1}{T} = -\frac{1}{C_V T^2} \,. \tag{4.98}$$

Taylor expanding around U gives

$$E = U + (E - U) \tag{4.99}$$

$$E - TS \approx U - TS(U) + (E - U)\left[1 - \frac{T}{T}\right] + \frac{(E-U)^2}{2TC_V} \tag{4.100}$$

$$P(E) \propto \exp(-\beta[U - TS(U)]) \exp\left[-\frac{\beta(E-U)^2}{2TC_V}\right] . \tag{4.101}$$

This is a guassian function with mean U. As $N \to \infty$ the guassian will approach a delta function.

The partition function is

$$\begin{aligned} Q_N(U,T) &= \sum_r e^{-\beta E_r} \\ &= \int dE g(E) e^{-\beta E} \\ &= \int dE P(E) \\ &\approx \int dE e^{-\beta(U-TS)} \exp\left[\frac{-(E-U)^2}{2kT^2C_V}\right] \\ &\approx e^{-\beta(U-TS)} \sqrt{2\pi kT^2 C_V} \end{aligned} \tag{4.102}$$

$$A \equiv -kT \ln Q \approx (U - TS) - \frac{1}{2} kT \ln(2\pi kT^2 C_V) \approx U - TS\,, \tag{4.103}$$

where the last term is negligible.

4.7 Equipartition

Let $x_i = q_i$ or p_i, and consider

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int dw x_i \frac{\partial H}{\partial x_j} \exp(-\beta H)}{\int dw \exp(-\beta H)} \tag{4.104}$$

$$= -\frac{1}{\beta} \frac{\int dw x_i \frac{\partial}{\partial x_j} \exp(-\beta H)}{\int dw \exp(-\beta H)} \tag{4.105}$$

$$= -\frac{1}{\beta} \frac{\int dw x_i \exp(-\beta H)\big|_{x_{j1}}^{x_{j2}} - \int dw \frac{\partial x_i}{\partial x_j} \exp(-\beta H)}{\int dw \exp(-\beta H)} \tag{4.106}$$

$$= \frac{1}{\beta} \delta_{ij}\,. \tag{4.107}$$

For the special cases:

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = -\langle q_i \dot{p}_i \rangle = kT\,, \tag{4.108}$$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \langle p_i \dot{q}_i \rangle = kT\,. \tag{4.109}$$

Special case $H = \sum_i A_i P_i^2 + B_i Q_i^2$, where P_i, Q_i are transformed canonically conjugate coordinates, and A_i and B_i are coefficients.
Since

$$\frac{\partial H}{\partial P_i} = 2A_i P_i \quad \text{and} \quad \frac{\partial H}{\partial Q_i} = 2B_i Q_i \,, \tag{4.110}$$

$$\sum_i \left(P_i \frac{\partial H}{\partial P_i} + Q_i \frac{\partial H}{\partial Q_i} \right) = 2H \tag{4.111}$$

$$\Rightarrow 2\langle H \rangle = N_P kT + N_Q kT \equiv fkT \tag{4.112}$$

(N_P, N_Q) is the number of non-zero terms in (A_i, B_i).
Equipartition theorem is

$$\langle H \rangle = \frac{f}{2} kT \,. \tag{4.113}$$

This is a classical result. In quantum systems, some degrees of freedom may be frozen when $\Delta E > kT$.

4.8 Virial Theorem

The virial of the system is

$$\begin{aligned} \mathcal{V} &= \left\langle \sum_i q_i \dot{p}_i \right\rangle = -\left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle && (4.114) \\ &= -3NkT \,. && (4.115) \end{aligned}$$

Notices that

$$\left\langle \sum_i q_i \dot{p}_i \right\rangle = \left\langle \sum_i q_i F_i \right\rangle = \mathcal{V} \,. \tag{4.116}$$

For an ideal gas, the only forces acting on the gas are due to the pressure of the walls of container.

$$\begin{aligned} \mathcal{V}_0 &= \sum_{n=1}^{N} \vec{r}_n \cdot \vec{F}_n && (4.117) \\ &= -P \oint da \vec{r} \cdot \hat{n} && (4.118) \\ &= -P \int d^3 r \nabla \cdot \vec{r} && (4.119) \\ &= -3PV \,. && (4.120) \end{aligned}$$

From Eq. (4.115) and Eq. (4.120): $PV = NkT$.

Also from Eq. (4.113), with $3N$ degrees of freedom, the average kinetic energy of an ideal gas is $K \equiv \langle H \rangle = \frac{3}{2}NkT$, and from Eq. (4.115) $\mathcal{V} = -2K$.

4.8.1 Two-Body Potential Interaction

Consider a classical system of point particles. The N-particle distribution function is

$$\rho(q,p) = f_N(\vec{r}_1, \vec{p}_1, \ldots) \,. \tag{4.121}$$

Equation of motion for f_N. From Liouville's theorem

$$\frac{\partial f_N}{\partial t} + \sum_i \frac{\vec{p}_i}{m} \cdot \frac{\partial f_N}{\partial \vec{r}_i} + \sum_i \vec{F}_i \cdot \frac{\partial f_N}{\partial \vec{p}_i} = 0 \,, \tag{4.122}$$

where

$$\begin{aligned} \vec{F}_i &= \vec{F}_i^{\text{ext}} + \sum_{i \neq j} \vec{F}_{ij} && (4.123) \\ &= \vec{F}_i^{\text{ext}} - \sum_{i \neq j} \left(-\frac{\partial U(r_{ij})}{\partial \vec{r}_i} \right) \,. && (4.124) \end{aligned}$$

with $U = U(r_{ij}) = U(|\vec{r}_i - \vec{r}_j|)$

An aside on reduced distribution functions. Let $f_N(1, 2, \ldots, N, t)$ be the N-particle probability density function for a system with N identical but distinguishable classical particles. f_N is normalised such that

$$\int d1 d2 \cdots dN f_N = 1 \,. \tag{4.125}$$

The n-particle ($n \leq N$) reduced distribution function is defined as

$$f_n(1, 2, \ldots, n, t) = \frac{N!}{(N-n)!} \int d(N+1) \cdots dN f_N \,. \tag{4.126}$$

Physically, f_n is proportional to the probability density of finding "any n" particles at position $1, 2, \ldots, n$ in the reduced n-dimensional phase space.

Reduced distribution function

$$f_n(\vec{r}_1, \vec{p}_1, \ldots, \vec{r}_n, \vec{p}_n) \equiv \int d^3 r_{n+1} d^3 p_{n+1} \ldots f_N \tag{4.127}$$

Equation for f_n can be obtained from Eq. 4.122 by applying

$$\int \frac{d^3 r_{n+1}}{V} d^3 p_{n+1} \ldots \frac{d^3 r_N}{V} d^3 p_N \,. \tag{4.128}$$

Special cases:
$f_1(\vec{r}, \vec{p}, t)$ single particle distribution function.
$f_1(1, 2, t)$ two-particle distribution function.

The virial for such a gas is

$$\begin{aligned}
\mathcal{V} &= \mathcal{V}_0 + \sum_i q_i F_i && (4.129)\\
&= \mathcal{V}_0 + \frac{1}{2}\sum_{i\neq j}\left[\vec{r}_i \cdot \left(-\frac{\partial U}{\partial \vec{r}_i}\right) + \vec{r}_j \cdot \left(-\frac{\partial U}{\partial \vec{r}_j}\right)\right] && (4.130)
\end{aligned}$$

where $\mathcal{V}_0$ is the kinetic piece.

$$\begin{aligned}
\sum_{i\neq j} &\to -\sum_{i\neq j}\left(\vec{r}_i \cdot \frac{\partial r_{ij}}{\partial \vec{r}_i} + \vec{r}_j \cdot \frac{\partial r_{ij}}{\partial \vec{r}_j}\right)\frac{\partial U}{\partial r_{ij}} && (4.131)\\
&\to -\sum_{i\neq j} r_{ij}\frac{\partial U}{\partial r_{ij}} && (4.132)
\end{aligned}$$

where $r_{ij} = |r_i - r_j|$.

Consider

$$\langle \mathcal{V} \rangle = \mathcal{V}_0 - \frac{1}{2}\sum_{i\neq j}\left\langle r_{ij}\frac{\partial U}{\partial r_{ij}}\right\rangle . \qquad (4.133)$$

Define $g(1, 2)$ as the pair distribution function. Relative probability of finding a particle at 2 if there is a particle at 1.

Isotropy: $g(1, 2) = g(r_{12})$.

Normalisation: $g(r) \to 1$ as $r \to \infty$. Notice that $g(r \to \infty) \to 1$ means that distant particles are uncorrelated. The actual probability of finding a particle at 2 if there is one at 1 is $g(r_{12})N/V$.

$$\begin{aligned}
\frac{1}{2}\sum_{i\neq j}\langle r_{ij}\frac{\partial U}{\partial r_{ij}}\rangle &= \frac{N^2}{2}\int d^3r_1 \int d^3r_2 r\frac{\partial U}{\partial r}g(r_{12})\frac{1}{V^2}\\
&= \frac{N^2}{2V^2}V\int_0^\infty dr r^2 4\pi r\frac{\partial U}{\partial r}g(r)\\
&= 2\pi n N\int_0^\infty dr r^3\frac{\partial U}{\partial r}g(r) . && (4.134)
\end{aligned}$$

Using Eq. (4.133) and Eq. (4.120)

$$\mathcal{V} = -3PV - 2\pi n N \int_0^\infty dr r^3 \frac{\partial U}{\partial r} g(r)\,. \tag{4.135}$$

Also, from Eq. (4.115)

$$PV = NkT\left[1 - \frac{2\pi n}{3kT}\int_0^\infty dr r^3 \frac{\partial U}{\partial r} g(r)\right]\,. \tag{4.136}$$

The internal energy is

$$\begin{aligned}
U &= \langle K\rangle + \langle U_{\text{interaction}}\rangle \\
&= \frac{3}{2}NkT + \frac{1}{2}\sum_{i\neq j}\langle U(r_{ij})\rangle \\
&= \frac{3}{2}NkT + \frac{N^2}{2}\int \frac{d^3r_1 d^3r_2}{V^2} g(r_{12})U(r_{12}) \\
&= \frac{3}{2}NkT + \frac{N^2}{V}2\pi \int dr r^2 U(r) g(r) \\
&= \frac{3}{2}NkT\left[1 + \frac{4\pi n}{3kT}\int dr r^2 U(r) g(r)\right]\,. \qquad (4.137)
\end{aligned}$$

4.9 Harmonic Oscillators

Consider N practically independent harmonic oscillators.

4.9.1 Classical

In one dimension

$$H = \sum_i^N \left[\frac{1}{2} m w^2 q_i^2 + \frac{p_i^2}{2m}\right]\,. \tag{4.138}$$

Single-oscillator partition function

$$Q_1 = \frac{1}{h}\int_{-\infty}^{\infty} dq dp \exp\left[-\beta m w^2 \frac{q_1^2}{2} - \beta\frac{p_1^2}{2m}\right] = \frac{1}{h}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{1}{\beta\hbar\omega}\,. \tag{4.139}$$

For N oscillators

$$Q_N(\beta) = \left(\frac{1}{\beta\hbar w}\right)^N\,. \tag{4.140}$$

Notice that oscillators (representing the energy levels) are distinguishable for now.

Helmholtz free energy is

$$A = -kT \ln Q_N = NkT \ln(\beta \hbar w) = NkT \ln \left(\frac{\hbar \omega}{kT} \right) . \tag{4.141}$$

Derived quantities are

$$\begin{aligned} \mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V} = kT \ln \left(\frac{\hbar w}{kT} \right) . & (4.142) \\ P &= -\left(\frac{\partial A}{\partial V} \right)_{T,N} = 0 \, . & (4.143) \\ S &= -\left(\frac{\partial A}{\partial T} \right)_{V,N} = -\left[Nk \ln \left(\frac{\hbar w}{kT} \right) - Nk \right] = Nk \left(1 + \ln \frac{kT}{\hbar w} \right) . & (4.144) \\ U &= A + TS \\ &= NkT \ln \left(\frac{\hbar w}{kT} \right) + NkT \left(1 + \ln \frac{kT}{\hbar w} \right) = NkT \, , & (4.145) \end{aligned}$$

which agrees with equipartion

$$\frac{U}{N} = 2 \times \frac{1}{2} kT = kT \, . \tag{4.146}$$

Also, the specific heat is

$$C_V = C_P = \frac{\partial U}{\partial T} = Nk \, . \tag{4.147}$$

Density of states

$$Q(\beta) = \int dE g(E) e^{-\beta E} \tag{4.148}$$

$$\begin{aligned} g(E) &= \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} d\beta Q(\beta) e^{\beta E} & (4.149) \\ &= \frac{1}{2\pi i} \int d\beta \frac{e^{\beta E}}{(\beta \hbar w)^N} & (4.150) \end{aligned}$$

$$g(E) = \begin{cases} \frac{E^{N-1}}{(\hbar w)^N (N-1)!} & E > 0 \\ 0 & E \leq 0 \end{cases} \tag{4.151}$$

Check by calculating the entropy.

$$
\begin{aligned}
S = k\ln g(E) &= k\ln\left(\frac{E^{N-1}}{(\hbar w)^N}\frac{e^{N-1}}{(N-1)^{N-1}}\right) && (4.152)\\
&\approx Nk\left(\ln\frac{E}{\hbar w N}+1\right) && (4.153)
\end{aligned}
$$

$$
T = \left(\frac{\partial S}{\partial E}\right)^{-1} = \frac{\partial E}{\partial S} = \frac{E}{Nk} \Rightarrow E = NkT \qquad (4.154)
$$

$$
\Rightarrow S = Nk\left(\ln\frac{kT}{\hbar w}+1\right) \qquad (4.155)
$$

as before.

4.9.2 Quantum Mechanical

$$
\varepsilon_n = \hbar w\left(n+\frac{1}{2}\right) \qquad (4.156)
$$

$$
Q_1 = \sum_n e^{-\beta\varepsilon_n} = \frac{e^{-\beta\hbar w/2}}{1-e^{-\beta\hbar w}} = \left[2\sinh\frac{\beta\hbar w}{2}\right]^{-1}. \qquad (4.157)
$$

$$
Q_N = Q_1^N = \frac{e^{-N\beta\hbar w/2}}{[1-e^{-\beta\hbar w}]^N} = \left[2\sinh\frac{\beta\hbar w}{2}\right]^{-N}. \qquad (4.158)
$$

Helmholtz free energy

$$
\begin{aligned}
A &= -kT\ln Q && (4.159)\\
&= NkT\ln\left[2\sinh\frac{\beta\hbar w}{2}\right] && (4.160)\\
&= \frac{N}{2}kT\beta\hbar w + NkT\ln[1-e^{-\beta\hbar w}] && (4.161)\\
&= \frac{N}{2}\hbar w + NkT\ln[1-e^{-\beta\hbar w}]\,. && (4.162)
\end{aligned}
$$

Derived quantities

$$
\mu = \frac{\partial A}{\partial N} = \frac{A}{N} \qquad (4.163)
$$

$$
P = -\frac{\partial A}{\partial V} = 0 \qquad (4.164)
$$

$$\begin{aligned}
S &= -\frac{\partial A}{\partial T} \\
&= -Nk\ln[1-e^{-\beta\hbar w}] - \frac{NkT(-)(-)(-)}{1-e^{-\beta\hbar w}}\frac{\hbar w}{kT^2}e^{-\beta\hbar w} \\
&= Nk\left[\frac{\beta\hbar w}{e^{\beta\hbar w}-1} - \ln(1-e^{-\beta\hbar w})\right] . \qquad (4.165)
\end{aligned}$$

$$\begin{aligned}
U &= A+TS \\
&= \frac{N\hbar w}{2} + NkT\ln(1-e^{-\beta\hbar w}) + NkT\left[\frac{\beta\hbar w}{e^{\beta\hbar w}-1} - \ln(1-e^{-\beta\hbar w})\right] \\
&= N\hbar w\left[\frac{1}{2}+\frac{1}{e^{\beta\hbar w}-1}\right] . \qquad (4.166)
\end{aligned}$$

Notice that $U \neq NkT$ (classical) and this does not follow equal partition.

$$\begin{aligned}
C_V = C_P &= \frac{\partial U}{\partial T} \\
&= \frac{N\hbar w}{(e^{\beta\hbar w}-1)^2}e^{\beta\hbar w}\frac{\hbar w}{kT^2} \\
&= Nk(\beta\hbar w)^2\frac{e^{\beta\hbar w}}{(e^{\beta\hbar w}-1)^2} . \qquad (4.167)
\end{aligned}$$

Now calculate $g(E)$ density of states

$$Q_N(\beta) = \frac{e^{-N\beta\hbar w/2}}{(1-e^{-\beta\hbar w})^N} . \qquad (4.168)$$

Factor out the $e^{-\beta E}$ piece and use the binomial expansion

$$(a+b)^N = \sum_{r=0}^{N}\frac{N!}{r!(N-r)!}a^r b^{N-r} = \sum_{r=0}^{N}\left(\begin{array}{c} N \\ r \end{array}\right) a^r b^{N-r} \qquad (4.169)$$

$$\begin{aligned}
\left.\frac{1}{(1-b)^N}\right|_{|b|<1} &= 1 + Nb + \frac{N(N+1)}{2!}b^2 + \frac{N(N+1)(N+2)}{3!}b^3\cdots \qquad (4.170) \\
&= \sum_{r=0}^{\infty}\left(\begin{array}{c} N+r-1 \\ r \end{array}\right) b^r \qquad (4.171)
\end{aligned}$$

$$\begin{aligned}
Q_N(\beta) &= \sum_{r=0}^{\infty}\left(\begin{array}{c} N+r-1 \\ r \end{array}\right) e^{-N\beta\hbar w/2-\beta r\hbar w} \qquad (4.172) \\
&= \int dE\sum_{r}\left(\begin{array}{c} N+r-1 \\ r \end{array}\right)\delta\left[E-\left(\frac{N}{2}+r\right)\hbar w\right]e^{-\beta E} \qquad (4.173)
\end{aligned}$$

$$g(E) = \sum_r \left(\begin{array}{c} N+r-1 \\ r \end{array} \right) \delta \left[E - \left(\frac{N}{2} + r \right) \hbar w \right] . \tag{4.174}$$

Connection with microcanonical ensemble.
Question: How many ways are there to distribute energy E among N oscillators?
Answer: Each (distinguishable) oscillator can receive some of

$$R = \frac{E - N\hbar w/2}{\hbar w} \tag{4.175}$$

(indistinguishable) quanta. Thus there are

$$\left(\begin{array}{c} N+R-r \\ R \end{array} \right) \tag{4.176}$$

distinct combinations.
From this, we can find $S(E)$ and other thermodynamic quantities, if we use Eq. 4.175. We recover the same results as with the canonical ensemble approach. See Pathria for details.

4.10 Paramagnetism

Assume N particles with magnetic moments $\vec{\mu}$ and that the only degree of freedom is the orientation of $\vec{\mu}$. Energy

$$E = \sum_i E_i = -\sum_i \vec{\mu} \cdot B = -\mu B \sum_i \cos\theta_i \, . \tag{4.177}$$

Partition function

$$Q_1(\beta) = \sum_\theta e^{+\beta\mu B \cos\theta} \, , \tag{4.178}$$

$$Q_N(\beta) = [Q_1(\beta)]^N \, . \tag{4.179}$$

Mean magnetic moment $\langle \vec{M} \rangle$, magnitude is

$$\begin{aligned} M_z &= N \langle \mu \cos\theta \rangle && (4.180) \\ &= \frac{N \sum_\theta \mu \cos\theta e^{\beta\mu B \cos\theta}}{\sum_\theta e^{\beta\mu B \cos\theta}} && (4.181) \\ &= \frac{N}{\beta} \frac{\partial \ln Q_1}{\partial B} \, . && (4.182) \end{aligned}$$

4.10.1 Classical

Treatment (Langevin 1905)

$$\sum_{\theta} \to \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta = 2\pi \int_{-1}^{1} d(\cos\theta)\,. \tag{4.183}$$

$$Q_1(\beta) = 2\pi \int_{-1}^{1} d(\cos\theta) e^{\beta\mu B \cos\theta} = \frac{2\pi}{\beta\mu B}(e^{\beta\mu B} - e^{-\beta\mu B}) = \frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\,. \tag{4.184}$$

If $\langle\vec{\mu}\rangle$ is the mean magnetic moment, the magnitude is

$$\begin{aligned}
\bar{\mu}_z = \frac{M_z}{N} &= \frac{1}{\beta}\frac{\partial \ln Q}{\partial B} && (4.185)\\
&= -\frac{1}{\beta B} + \frac{\mu\beta}{\beta}\frac{\cosh\beta\mu B}{\sinh\beta\mu B} && (4.186)\\
&= \mu\left[\coth\beta\mu B - \frac{1}{\beta\mu B}\right] && (4.187)\\
&= \mu L(x), && (4.188)
\end{aligned}$$

where $x = \beta\mu B = \mu B/(kT)$ and L is Langevin function $L(x) = \coth x - 1/x$. Notice that x is an energy ratio.
Properties of Langevin

$\sim x/3$ for $x \ll 1$ and $L(x) \sim 1 - 1/(2x), x \gg 1$. For $L(x \to \infty) \to 1$ we have magnetic saturation (high magnetic field or low temperature).

Susceptibility

If $x = \beta\mu H \ll 1$ (high temperature or low magnetic field)

$$M_z \approx N\mu\frac{\beta\mu B}{3} = \frac{N\mu^2\beta}{3}B\,. \tag{4.189}$$

The magnetic susceptibility is defined as

$$\chi_T = \lim_{H\to 0}\left(\frac{\partial M_z}{\partial H}\right)_T . \tag{4.190}$$

In our case

$$\chi = \frac{\partial M_z}{\partial B} \approx \frac{N\mu^2}{3kT} = \frac{C}{T}\,, \tag{4.191}$$

where the righthand side is the Curie constant. Eq. 4.191 is the Curie law of paramagnetism.

4.10.2 Quantum Mechanical

$$\vec{\mu} = \left(g\frac{e}{2m}\right)\vec{l}, \tag{4.192}$$

where $g = e/2m$ is the gyromagnetic ratio. Lande g-factor $g \sim 1$ if $\vec{l}$ angular momentum only. g is 2 if $\vec{l}$ spin only.

$l^2 = J(J+1)\hbar^2, J = 0, 1, \ldots$ or $1/2, 3/2, \ldots$

l is quantised.

$\mu^2 = (g\mu_B)^2 J(J+1)$

Bohr magneton $\mu_B = (e/2m)\hbar \Rightarrow \mu_z = g\mu_B m$, where m is not the mass but $m = -J, -(J+1), ...(J-1), J$

Partition function

$$\begin{aligned}
Q_1(\beta) &= \sum_{m=-J}^{J} e^{\beta g\mu_B mB} = \sum_{m=-J}^{J} e^{mx/J} && (4.193)\\
&= e^{-x}\frac{[e^{(2J+1)x/J} - 1]}{e^{x/J} - 1} && (4.194)\\
&= \frac{e^{(2J+1)x/2J} - e^{-(2J+1)x/2J}}{e^{x/2J} - e^{-x/2J}} && (4.195)\\
&= \sinh\left(\frac{2J+1}{2J}x\right) \Big/ \sinh\left(\frac{x}{2J}\right)\,, && (4.196)
\end{aligned}$$

where $x = \beta g\mu_B JB$.

$$
\begin{aligned}
M_z = N\bar{\mu}_z &= \frac{N}{\beta}\frac{\partial \ln Q_1}{\partial B} && (4.197)\\
&= Ng\mu_B J\left[\left(1+\frac{1}{2J}\right)\coth\left(1+\frac{1}{2J}\right)x - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)\right]. && (4.198)
\end{aligned}
$$

The thing in square brackets is the Brillouin function $B_J(x)$ of order J.

Special cases:

a) $x \gg 1$ (low temperature or high field): $B_J(x) \to 1$.

b) $x \ll 1$ (high temperature or low field): $B_J(x) \to \frac{1}{3}\left(1+\frac{1}{J}\right)x$.

For $\beta g\mu_B JB \ll 1$,

$$
\bar{\mu}_z \approx g\mu_B J\frac{1}{3}\left(1+\frac{1}{J}\right)\frac{g\mu_B JB}{kT} \approx \frac{g^2\mu_B^2 J(J+1)}{3kT}B\,. \tag{4.199}
$$

Curie's law with

$$
C_J = \frac{Ng^2\mu_B^2 J(J+1)}{3k} = \frac{N\mu^2}{3k}\,. \tag{4.200}
$$

$J \to \infty$ gives the classical limit. Also $J \to 0$ limit.

4.11 Negative Temperatures

Normal systems $E_0 \le E < \infty$. $g(E)$ monotonically increasing.

$$
Q(\beta) = \int dE g(E) e^{-\beta E} \tag{4.201}
$$

is only defined for $\beta > 0$.

Special cases: $E_{\min} \le E \le E_{\max}$. $g(E)$ integrable. $Q(\beta)$ may be defined for $\beta > 0$ and $\beta < 0$.

Simple example.

Magnetic moments in a magnetic field, $s = 1/2$. Single particle energy: $E = \pm\varepsilon$, $\varepsilon = (1/2)q\mu_B B$, where q is just a number.

4.12 Problems

Chapter 5

Grand Canonical Ensemble

Consider systems which may exchange energy and particles. The macrostate is determined from (V, μ, T). The microstates s is determine by the energy E_s and number of particles N_s.

Question: What is the probability of finding system A in one state s of energy E_s with N_s particles.

Answer: Two approaches:

1. System in contact with a heat and particle reservoirs.

2. System as part of a canonical ensemble with $\mathcal{N}$ systems and constraints.

5.1 Equilibrium Between a System and a Particle-Energy Reservoir

$$
\begin{aligned}
N_r + N'_r = N^{(0)} &= \text{const}, && (5.1)\\
E_s + E'_s = E^{(0)} &= \text{const}. && (5.2)
\end{aligned}
$$

$$
\begin{aligned}
\frac{N_r}{N^{(0)}} = \left(1 - \frac{N'_r}{N^{(0)}}\right) &\ll 1, && (5.3)\\
\frac{E_s}{E^{(0)}} = \left(1 - \frac{E'_s}{E^{(0)}}\right) &\ll 1. && (5.4)
\end{aligned}
$$

$$
P_{r,s} \propto \Omega'(N'_r, E'_s) = \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) \tag{5.5}
$$

$$\begin{aligned}\ln\Omega'(N^{(0)}-N_r,E^{(0)}-E_s) &= \ln\Omega'(N^{(0)},E^{(0)})+\left(\frac{\partial\ln\Omega'}{\partial N'}\right)_{N'=N^{(0)}}(-N_r)\\ &\quad+\left(\frac{\partial\ln\Omega'}{\partial E'}\right)_{E'=E^{(0)}}(-E_s)+\ldots\\ &\approx \ln\Omega'(N^{(0)},E^{(0)})+\frac{\mu}{kT}N_r-\frac{1}{kT}E_s\,. \end{aligned}\tag{5.6}$$

$$P_{r,s}\propto\exp(-\alpha N_r-\beta E_s)\,,\tag{5.7}$$

where $\alpha=-\mu/(kT)$ and $\beta=1/(kT)$.

$$P_{r,s}=\frac{\exp(-\alpha N_r-\beta E_s)}{\sum_{r,s}\exp(-\alpha N_r-\beta E_s)}\,.\tag{5.8}$$

Now the ensemble point of view. $n_{r,s}$ is the number of systems that have number N_r of particles and amount E_s of energy.

$$\sum_{r,s}n_{r,s} = \mathcal{N}\,,\tag{5.9}$$

$$\sum_{r,s}n_{r,s}N_r = \mathcal{N}\overline{N}\,,\tag{5.10}$$

$$\sum_{r,s}n_{r,s}E_s = \mathcal{N}\overline{E}\,.\tag{5.11}$$

Maximise

$$W\{n_{r,s}\}=\frac{\mathcal{N}!}{\prod_{r,s}(n_{r,s}!)}\tag{5.12}$$

Most probable mode of distibution, $\{n^*_{r,s}\}$

$$\frac{n^*_{r,s}}{\mathcal{N}}=\frac{\exp(-\alpha N_r-\beta E_s)}{\sum_{r,s}\exp(-\alpha N_r-\beta E_s)}\,.\tag{5.13}$$

Expectation value (mean)

$$\langle n_{r,s}\rangle=\frac{\sum' n_{r,s}W\{n_{r,s}\}}{\sum' W\{n_{r,s}\}}\,.\tag{5.14}$$

$$\lim_{\mathcal{N}\to\infty}\frac{\langle n_{r,s}\rangle}{\mathcal{N}}\approx\frac{n^*_{r,s}}{\mathcal{N}}=\frac{\exp(-\alpha N_r-\beta E_s)}{\sum_{r,s}\exp(-\alpha N_r-\beta E_s)}\,.\tag{5.15}$$

where $n^*_{r,s}$ is the most probable value.

5.2 A System in the Grand Canonical Ensemble

If n_s is the number of systems, among the $\mathcal{N}$ in the ensemble that are in state s, The statistics are

$$\begin{aligned}
P_{r,s} &= \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}\,, && (5.16)\\
\bar{N} &= \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \alpha}\left(\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)\,, && (5.17)\\
\bar{E} &= \frac{\sum_{r,s} E_s e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = -\frac{\partial}{\partial \beta}\left(\ln \sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)\,, && (5.18)
\end{aligned}$$

where $\alpha = -\mu/(kT)$ and $\beta = 1/(kT)$.

5.3 Physical Significance

Typically the energy depends on the number of particles: $E_s = E_s(N_r)$. Thus the sum over E_s can be written as another sum over number of particles, and the sum in he denominator $P_{r,s}$ is a function of all the E_s.

Define the q-potential

$$q(\alpha, \beta, E_s) = \ln\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)\,. \tag{5.19}$$

From Eq. (5.17) and Eq. (5.18),

$$dq = -\bar{N}d\alpha - \bar{E}d\beta - \beta\frac{\sum_{r,s}\exp(-\alpha N_r - \beta E_s)dE_s}{\sum_{r,s}\exp(-\alpha N_r - \beta E_s)}\,. \tag{5.20}$$

In the third term, the denominator is $\sum_r(\langle n_{r,s}\rangle/\mathcal{N})dE_s$ and $\langle n_{r,s}\rangle/\mathcal{N} = P_{r,s}$. We write

$$d(q + \alpha\bar{N} + \beta\bar{E}) = \alpha d\bar{N} + \beta d\bar{E} - \beta\sum_{r,s} P_{r,s}dE_s\,. \tag{5.21}$$

Compare Eq. (5.21) with the first law of thermodynamics, $dQ = d\bar{E} + dW - \mu d\bar{N}$, we have the correspondence

$$d(q + \alpha\bar{N} + \beta\bar{E}) \leftrightarrow \beta dQ\,. \tag{5.22}$$

where

$$\frac{\alpha}{\beta} = -\mu \quad \text{and} \quad \beta = \frac{1}{kT} \Rightarrow \alpha = -\frac{\mu}{kT}. \tag{5.23}$$

and

$$\sum_{r,s} P_{r,s} dE_s = -dW \,. \tag{5.24}$$

From Eq.(5.22) and $dQ = TdS$,

$$d(q + \alpha \bar{N} + \beta \bar{E}) = \frac{dS}{k} \,. \tag{5.25}$$

Integrating,

$$\begin{aligned} q &= \frac{S}{k} - \alpha \bar{N} - \beta \bar{E} \\ &= \frac{S}{k} + \frac{\mu}{kT} \bar{N} - \frac{1}{kT} \bar{E} \\ &= \frac{ST - \bar{E} + \mu \bar{N}}{kT} \,. \end{aligned} \tag{5.26}$$

But $\mu \bar{N} = G = E - TS + PV$ (by definition of G and because E, μ, S, N are extensive). Therefore

$$q = \ln \left(\sum_{r,s} e^{-\alpha N_r - \beta E_s} \right) = \frac{PV}{kT} \,. \tag{5.27}$$

The lefthand side is statistics and the right-hand side is thermodynamics.

Define $z = e^{-\alpha}$ as the fugacity of the system.

$$q = \ln \left(\sum_{r,s} z^{N_r} e^{-\beta E_s} \right) = \ln \left(\sum_{N} z^{N} Q_N(V,T) \right) \,, \tag{5.28}$$

where $Q_0 = 1$. We write

$$q(z,V,T) = \ln \mathcal{Q}(z,V,T) \,, \tag{5.29}$$

with

$$\mathcal{Q}(z,V,T) = \sum_{r,s} z^{N_r} e^{-\beta E_s} = \sum_{N} z^{N} Q_N(V,T) \,. \tag{5.30}$$

Define $\mathcal{Q}(z,V,T)$ to be the grand partition function, where q is the q-potential.

5.3.1 Connections with Thermodynamics

The leading thermodynamic quantities are

$$P(z,V,T) = \frac{kT}{V} q = \frac{kT}{V} \ln \mathcal{Q}(z,V,T)\,, \tag{5.31}$$

$$N(z,V,T) = z \left.\frac{\partial q}{\partial z}\right|_{V,T} = kT \left(\frac{\partial q}{\partial \mu}\right)_{V,T}\,, \tag{5.32}$$

$$U(z,V,T) = -\left.\frac{\partial q}{\partial \beta}\right|_{z,V} = kT^2 \left(\frac{\partial q}{\partial T}\right)_{z,V}\,. \tag{5.33}$$

Equation of state: $P = P(N,V,T)$ (not z). Eliminate z between Eq. (5.31) and Eq. (5.32). Equation of internal energy: $U = U(N,V,T)$ (not z). Eliminate z between Eq. (5.32) and Eq. (5.33). Notice that from Eq. (5.30), $\mathcal{Q}$ can be calculated from Q_N. In practice, a direct calculation is often easier.

Recall $G = E - TS + PV = N\mu$. Helmholtz free energy

$$\begin{aligned} A &= E - TS && (5.34)\\ &= G - PV && (5.35)\\ &= N\mu - PV && (5.36)\\ &= NkT \ln z - kT \ln \mathcal{Q} && (5.37)\\ &= -kT \ln\left(\frac{\mathcal{Q}}{z^N}\right)\,. && (5.38) \end{aligned}$$

Recall $z = e^{-\alpha} = e^{\mu/(kT)}$. Compare with $A = -kT \ln Q(N,V,T)$ in the canonical ensemble.

Entropy

$$S = \frac{U - A}{T} = kT \left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk \ln z + kq\,, \tag{5.39}$$

where we made use of Eq. (5.38).

5.4 Examples

5.4.1 Ideal Gas

Consider point particles, possibly internal degrees of freedom, and that the particles are not localised. The partition function is

$$Q_1(V,T) = V f(T)\,, \tag{5.40}$$

$$Q_N(V,T) = \frac{[Vf(T)]^N}{N!}\,. \tag{5.41}$$

The grand partition function of the gas is

$$\mathcal{Q}(z,V,T) = \sum_N z^N Q_N = \sum_N \frac{[zVf(T)]^N}{N!} = e^{zVf(T)}\,, \tag{5.42}$$

where

$$q = zVf(T)\,. \tag{5.43}$$

$$P = \frac{kT}{V}\ln\mathcal{Q} = zkTf(T)\,, \tag{5.44}$$

$$N = z\frac{\partial}{\partial z}q = zVf(T)\,, \tag{5.45}$$

$$U = kT^2\frac{\partial q}{\partial T} = zVkT^2f'(T)\,, \tag{5.46}$$

$$A = -kT\ln\left(\frac{\mathcal{Q}}{z^N}\right) = NkT\ln z - zVkTf(T)\,, \tag{5.47}$$

$$\begin{aligned} S &= kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk\ln z + k\ln Q \\ &= zVkTf'(T) - Nk\ln z + zVkf(T) \\ &= -Nk\ln z + zVk[Tf'(T)+f(T)]\,. \end{aligned} \tag{5.48}$$

Eq. (5.44) and Eq. (5.45) → $PV = NkT$.
Eq. (5.45) and Eq. (5.46) → $U = NkT^2f'/f$. $\Rightarrow C_V = Nk\frac{[2Tf'f+T^2f''f-T^2(f')^2]}{f^2}$.
Special case: $f(T) = AT^n \Rightarrow C_V = nNk$.
Eq. (5.46) and Eq. (5.48) → $S = -Nk\ln\left(\frac{U}{kT^2Vf'}\right) + \frac{U}{T^2f'}(Tf'+f)$.
Eq. (5.46) and Eq. (5.47) → $A = \cdots$.

5.4.2 Localised Noninteracting Particles

Consider
$Q_1(V,T) = \phi(T)$, independent of volume.

$$Q_N = [Q_i(V,T)]^N = \phi^N(T) \tag{5.49}$$

is a function of temperature only.

The grand partition function is

$$\mathcal{Q}(z,V,T) = \sum_N z^N Q_N = \sum_N [z\phi(T)]^N = \frac{1}{1-z\phi}\,, \tag{5.50}$$

if $|z\phi| < 1$.

Thermodynamics:

$$P = \frac{kT}{V}\ln\mathcal{Q} = -\frac{kT}{V}\ln(1 - z\phi)\,, \tag{5.51}$$

$$N = z\frac{\partial}{\partial z}q = \frac{z\phi}{1 - z\phi}\,, \tag{5.52}$$

$$U = kT^2\frac{\partial q}{\partial T} = kT^2\frac{z\phi}{1 - z\phi}\,, \tag{5.53}$$

$$A = -kT\ln\left(\frac{\mathcal{Q}}{z^N}\right) = NkT\ln z + kT\ln(1 - z\phi)\,, \tag{5.54}$$

$$\begin{aligned} S &= kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk\ln z + k\ln Q & (5.55)\\ &= z\frac{kT\phi'}{1 - z\phi} - Nk\ln z + k\ln(1 - z\phi)\,. & (5.56)\end{aligned}$$

From Eq. (5.52) $z\phi = N/(1+N) \sim 1 - 1/N \Rightarrow 1 - z\phi \sim 1/N$.

From Eq. (5.52) and Eq. (5.53),

$$\frac{U}{N} = kT^2\frac{\phi'}{\phi}\,, \tag{5.57}$$

$$\frac{A}{N} = -kT\ln\phi + \mathcal{O}\left(\frac{\ln N}{N}\right) \tag{5.58}$$

$$\frac{S}{kT} = -kT\ln\phi + T\frac{\phi'}{\phi} + \mathcal{O}\left(\frac{\ln N}{N}\right)\,. \tag{5.59}$$

5.4.3 Solid-Vapour Equilibrium

The fugacities are equal at equilibrium $z_g = z_s$, and using Eq. (5.45)

$$\frac{N_g}{V_g f(T)} = \frac{1}{\phi(T)} \Rightarrow \frac{N_g}{V_g} = \frac{f(T)}{\phi(T)}\,. \tag{5.60}$$

For an ideal gas

$$P = \frac{N_g}{V_g}kT = kT\frac{f(T)}{\phi(T)}\,. \tag{5.61}$$

Assuming a monatomic ideal gas

$$f(T) = \frac{1}{h^3}(2\pi mkT)^{3/2}\,. \tag{5.62}$$

The Einstein model for the solid is localised oscillators with a single frequency:

$$\phi(T) = \left[2\sinh\frac{\hbar\omega}{2kT}\right]^{-3}. \tag{5.63}$$

If ε is the energy needed to extract an atom from the solid

$$\phi(T) = \left[2\sinh\frac{\hbar\omega}{2kT}\right]^{-3} e^{+\varepsilon/(kT)}, \tag{5.64}$$

$$\Rightarrow P = kT\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\left[2\sinh\frac{\hbar\omega}{2kT}\right]^{3} e^{-\varepsilon/(kT)}. \tag{5.65}$$

Notice that from Eq. (5.60),

$$\frac{N}{V} > \frac{f(T)}{\phi(T)} \tag{5.66}$$

The left-hand side is a density, and if $V_g \approx V$,

$$N > V\frac{f(T)}{\phi(T)} \tag{5.67}$$

is a necessary condition to have a solid phase.

Equivalently, T_c is determined from

$$\frac{f(T_c)}{\phi(T_c)} = \frac{N}{V}\,, \tag{5.68}$$

where T_c is the temperature at which sublimation starts. Require $T < T_c$.

5.5 Density and Energy Fluctuations

From

$$\bar{N} = \frac{\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)}\,, \tag{5.69}$$

we find

$$\left(\frac{\partial\bar{N}}{\partial\alpha}\right)_{\beta,E_s} = -\overline{N^2} + \overline{N}^2, \tag{5.70}$$

$$\Rightarrow \langle(\Delta N)^2\rangle = -\left(\frac{\partial\bar{N}}{\partial\alpha}\right)_{\beta,E_s} = -\left(\frac{\partial\bar{N}}{\partial\alpha}\right)_{T,V} = kT\left(\frac{\partial\bar{N}}{\partial\mu}\right)_{T,V}. \tag{5.71}$$

Use: $Nd\mu = VdP - SdT$

Proof: $dE = TdS - PdV + \mu dN$

Define $x = E - TS + PV - \mu N \Rightarrow dx = -SdT + VdP - Nd\mu$. But $x = 0$ from the fundamental equation of thermodynamics $E = TS - PV + \mu N \Rightarrow dx = 0$

For $dT = 0$, constant:

$$\begin{aligned} \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} &= \frac{\bar{N}}{V}\left(\frac{\partial \bar{N}}{\partial P}\right)_{T,V} && (5.72) \\ &= \frac{\bar{N}}{V}\left(\frac{\partial V/v}{\partial P}\right)_{T,V}, && (5.73) \end{aligned}$$

where $v = V/\bar{N}$ is the mean volume per particle.

$$\frac{\langle(\Delta N)^2\rangle}{\bar{N}^2} = -\frac{kT}{\bar{N}^2}\frac{\bar{N}}{v^2}\left(\frac{\partial v}{\partial P}\right)_T = +\frac{kT}{V}\kappa_T\,, \tag{5.74}$$

where κ_T is the iso-thermoal compresability

$$\kappa_T = \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\,. \tag{5.75}$$

$$\left[\frac{\langle(\Delta N)^2\rangle}{\bar{N}^2}\right]^{1/2} \propto \left(\frac{1}{Nv}\right)^{1/2} = \mathcal{O}(N^{-1/2})\,, \tag{5.76}$$

which is negliable unless κ_T is very large. κ_T is large close to phase transitions.

Similarly for the energy (read Pathria for details):

$$\frac{\langle(\Delta E)^2\rangle}{v^2} = \frac{\langle(\Delta E)^2\rangle}{v^2}(\text{canonical}) + \frac{1}{v^2}\left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2 \overline{\Delta N}^2. \tag{5.77}$$

The first term is always $\propto 1/N$. The second term may be large close to phase transition.

5.6 Density and Energy Fluctuations in the Grand Canonical Ensemble

For any member of the ensemble

$$\begin{aligned} 0 \leq N \leq \infty\,. && (5.78) \\ 0 \leq E \leq \infty\,. && (5.79) \end{aligned}$$

This is different from other ensembles. But thermodynamics the same. This implice the relative fluctuations in the quantities must be negligible.

Consider relative flucuations in particle density n and energy E.

$$\overline{N} = \frac{\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \tag{5.80}$$

$$\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_{\beta.E_s} = -\overline{N^2} + \overline{N}^2 \,. \tag{5.81}$$

Means squared fluctuation

$$\overline{(\Delta N)^2} \equiv \overline{N^2} - \overline{N}^2 = -\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_{T,V} = kT\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} \,. \tag{5.82}$$

Using $n \equiv N/V$ gives

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = \frac{\overline{(\Delta N)^2}}{\overline{N}^2} = \frac{kT}{\overline{N}^2}\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} \,. \tag{5.83}$$

Defining the $v \equiv V/\overline{N}$ mean volume per particle gives

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = \frac{kTv^2}{V^2}\left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} = -\frac{kT}{V}\left(\frac{\partial v}{\partial \mu}\right)_{T} \,. \tag{5.84}$$

In general $E = TS - PV + \mu N$. Let $x = E - TS + PV - \mu N = 0$. Then $0 = dx = dE - TdS - SdT + PdV + VdP - \mu dN - Nd\mu$.

The fundamentla law of thermodynamics $E(S,V,N) = TS - PV + \mu N$. $dE = TdS - PdV + \mu dN$. Therefore $-SdT + VdP - Nd\mu = 0$. This implices

$$d\mu = \frac{V}{N}dP - \frac{S}{N}dT = vdP - sdT \,. \tag{5.85}$$

For constant $T \Rightarrow d\mu = vdP$.

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = -\frac{kT}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{T} = \frac{kT}{V}\kappa_T \,, \tag{5.86}$$

where

$$\kappa_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{T} \,. \tag{5.87}$$

is the isothermal compressibility.

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} \propto \frac{1}{V} \propto \frac{1}{N} \,, \tag{5.88}$$

$$\left[\frac{\overline{(\Delta n)^2}}{\overline{n}^2}\right]^{1/2} \propto \frac{1}{\sqrt{N}} = \mathcal{O}(N^{-1/2}) \,, \tag{5.89}$$

which is negligible.

Now consider energy fluctuations.

$$\overline{(\Delta E)^2} \equiv \overline{E^2} - \overline{E}^2 = -\left(\frac{\partial \overline{E}}{\partial \beta}\right)_{z,V} = kT^2 \left(\frac{\partial U}{\partial T}\right)_{z,V} . \tag{5.90}$$

Use

$$\left(\frac{\partial U}{\partial T}\right)_{z,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{z,V} . \tag{5.91}$$

<u>I can not prove this.</u>

Now

$$\begin{aligned} N &= z\left(\frac{\partial q}{\partial z}\right)_{V,T} = z\left(\frac{\partial q}{\partial \alpha}\right)_{V,T}\left(\frac{\partial \alpha}{\partial z}\right)_{V,T} = -\left(\frac{\partial q}{\partial \alpha}\right)_{V,T} = -\left(\frac{\partial}{\partial \alpha}\ln \mathcal{Q}\right)_{V,T} && (5.92)\\ U &= -\left(\frac{\partial q}{\partial \beta}\right)_{z,V} = -\left(\frac{\partial}{\partial \beta}\ln \mathcal{Q}\right)_{\alpha,V} . && (5.93)\end{aligned}$$

$$\begin{aligned} \left(\frac{\partial N}{\partial \beta}\right)_{\alpha,V} &= -\left[\frac{\partial}{\partial \beta}\left(\frac{\partial}{\partial \alpha}\ln \mathcal{Q}\right)_{V,T}\right]_{\alpha,V} && (5.94)\\ \left(\frac{\partial U}{\partial \alpha}\right)_{\beta,V} &= -\left[\frac{\partial}{\partial \alpha}\left(\frac{\partial}{\partial \beta}\ln \mathcal{Q}\right)_{\alpha,V}\right]_{\beta,V} . && (5.95)\end{aligned}$$

Therefore

$$\begin{aligned} \left(\frac{\partial N}{\partial \beta}\right)_{\alpha,V} &= \left(\frac{\partial U}{\partial \alpha}\right)_{\beta,V} \\ -kT^2\left(\frac{\partial N}{\partial T}\right)_{\alpha,V} &= -kT\left(\frac{\partial U}{\partial \mu}\right)_{\beta,V} \\ \left(\frac{\partial N}{\partial T}\right)_{\alpha,V} &= \frac{1}{T}\left(\frac{\partial U}{\partial \mu}\right)_{\beta,V} . && (5.96)\end{aligned}$$

Therefore

$$
\begin{aligned}
\overline{(\Delta E)^2} &= kT^2\left[\left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V}\right] \\
&= kT^2\left(\frac{\partial U}{\partial T}\right)_{N,V} + \frac{kT^2}{T}\left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial U}{\partial \mu}\right)_{T,V} \\
&= kTC_V + kT\left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\left(\frac{\partial U}{\partial \mu}\right)_{T,V}\left(\frac{\partial U}{\partial N}\right)_{T,V} \\
&= kTC_V + kT\left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\left(\frac{\partial n}{\partial \mu}\right)_{T,V} \\
&= kTC_V + \left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\overline{(\Delta N)^2} \\
&= \langle(\Delta E)^2\rangle + \left[\left(\frac{\partial U}{\partial N}\right)_{T,V}\right]^2\overline{(\Delta N)^2}\,. \qquad (5.97)
\end{aligned}
$$

5.7 Problems

Chapter 6

Formulation of Quantum Statistics

So far we have considered classical and quantum mechanical formalisms in which the particles are distinguishable. We now consider the quantum mechanical case of indistinguishable particles. We rewrite the formalism in terms of quantum mechanics from the beginning. In the high temperature and low density extremes of the quantum mechanical formalism, we expect to recover the classical description.

6.1 Summary of Quantum Mechanics

Schrödinger equation is

$$H\psi = i\hbar\frac{\partial\psi}{\partial t}\,, \tag{6.1}$$

where ψ is the wave function and H is the Hamiltonian (Hermitian operator). We will always assume that the ψ's are normalised.

The eigenvalues and eigenvectors of H are given by

$$H\psi_i = E_i\psi_i\,. \tag{6.2}$$

Since H is Hermitian ($H = H^\dagger$), the E_i are real.

Orthonormality gives

$$\int d^3x\psi_i^*\psi_j \equiv \langle\psi_i|\psi_j\rangle = \delta_{ij}\,. \tag{6.3}$$

For any square integrable Ψ the completeness relationship can be obtained:

$$\Psi = \sum_i a_i\psi_i\,, \tag{6.4}$$

with

$$a_i = \int d^3r\psi_i^*\Psi \equiv \langle\psi_i|\Psi\rangle\,. \tag{6.5}$$

$$\begin{aligned}\Psi(\vec{x}) &= \sum_i \int d^3x' \psi_i^*(\vec{x}')\Psi(\vec{x}')\psi_i(\vec{x}) \\ &= \int d^3x' \sum_i \psi_i^*(\vec{x}')\psi_i(\vec{x})\Psi(\vec{x}')\,, \qquad (6.6)\end{aligned}$$

which means

$$\sum_i \psi_i^*(\vec{x}')\psi_i(\vec{x}) = \delta(\vec{x}-\vec{x}')\,. \qquad (6.7)$$

Expectation value of operator G:

$$\begin{aligned}\frac{d}{dt}\langle\psi|G\psi\rangle &= \Big\langle\frac{\partial\psi}{\partial t}|G\psi\Big\rangle + \Big\langle\psi|\frac{\partial G}{\partial t}\psi\Big\rangle + \Big\langle\psi|G\frac{\partial\psi}{\partial t}\Big\rangle \\ &= \frac{i}{\hbar}\langle\psi|(HG-GH)\psi\rangle + \Big\langle\psi|\frac{\partial G}{\partial t}\psi\Big\rangle \\ &= \frac{i}{\hbar}\langle\psi|[H,G]\psi\rangle + \Big\langle\psi|\frac{\partial G}{\partial t}\psi\Big\rangle\,. \qquad (6.8)\end{aligned}$$

6.2 Preliminaries

Ensemble of $\mathcal{N}$ identical systems, $k = 1,\ldots,\mathcal{N}$. Each system is described by Hamiltonian H. System k at time t is described by wave function $\psi^k(\vec{r}_i,t)$. Time evolution of ψ^k is given by $i\hbar\dot{\psi}^k = H\psi^k$. Assume $\{\phi_n\}$ is a complete set of orthonormal bases functions.

$$\begin{aligned}\psi^k(t) &= \sum_n a_n^k(t)\phi_n\,, \qquad (6.9)\\ a_n^k(t) &= \langle\phi_n|\psi^k(t)\rangle \qquad (6.10)\end{aligned}$$

$$\begin{aligned}i\hbar\dot{a}_n^k &= \langle\phi_n|H\psi\rangle \\ &= \sum_m \langle\phi_n|Ha_m\phi_m\rangle \\ &= \sum_m \langle\phi_n|H\phi_m\rangle a_m\,. \qquad (6.11)\end{aligned}$$

For convenience define $H_{nm} \equiv \langle\phi_n|H\phi_m\rangle$.

Normalization

$$
\begin{aligned}
1 = \langle\psi^k|\psi^k\rangle &= \sum_{nm}\langle a_n^k\phi_n|a_m^k\phi_m\rangle \\
&= \sum_{nm} a_n^{k*}a_m^k\langle\phi_n|\phi_m\rangle \\
&= \sum_n |a_n^k|^2 \,. \qquad (6.12)
\end{aligned}
$$

$|a_n^k|^2$ probability finding system k in state ϕ_n.

Ensemble average of an expectation value is given by

$$
\bar{G} = \frac{1}{\mathcal{N}}\sum_k^{\mathcal{N}}\langle\psi^k|G\psi^k\rangle \,. \qquad (6.13)
$$

Using ϕ_n as a basis

$$
\begin{aligned}
\bar{G} &= \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\sum_{n,m} a_n^{k*}a_m^k\langle\phi_n|G\phi_m\rangle \\
&= \sum_{n,m}\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} a_n^{k*}(t)a_m^k(t)G_{nm} \\
&= \sum_{m,n}\rho_{mn}G_{nm} \\
&= \mathrm{Tr}(\hat{\rho}\hat{G}) \,. \qquad (6.14)
\end{aligned}
$$

This is independent of the choice of $\{\phi_n\}$ and

$$
\rho_{mn}(t) \equiv \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} a_m^k(t)a_n^{k*}(t) \,. \qquad (6.15)
$$

Properties of ρ.

$$
\mathrm{Tr}(\hat{\rho}) = \sum_n \rho_{nn} = 1 \,. \qquad (6.16)
$$

This also follows from taking $G = I$ in Eq. (6.14). The equation of motion for the density matrix is

$$\begin{aligned}
i\hbar\dot{\rho}_{mn} &= \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} i\hbar(\dot{a}_m^k a_n^{k*} + a_m^k \dot{a}_n^{k*}) \\
&= \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\sum_l (H_{ml}a_l^k a_n^{k*} - a_m^k H_{nl}^* a_l^{k*}) \\
&= (H_{ml}\rho_{ln} - \rho_{ml}H_{ln}) \\
&= \left[\hat{H}, \hat{\rho}\right] . \qquad (6.17)
\end{aligned}$$

If $\hat{\rho}$ is in the energy representation, $\rho_{mn} = 0$ for $m \neq n$. $\hat{\rho}$ is diagonal if $H\phi_n = E_n\phi_n$. In other representations, $\hat{\rho}$ is not diagonal.
Using Eq. (6.15),

$$\rho_{nm} = \rho_{mn}^* \Rightarrow \hat{\rho}^\dagger = \hat{\rho} \qquad (6.18)$$

i.e., $\hat{\rho}$ is Hermitian.

6.3 Statistics with Various Ensembles

6.3.1 Microcanonical Ensemble

The macrostate depends on (N, V, E), in which N and V are fixed for the system. The energy lies in the shell $E_0 - \Delta/2 \leq E \leq E_0 + \Delta/2$, where $\Delta \ll E_0$. The number of accessible microsates is $\Gamma(N, V, E_0, \Delta)$. All states have equal a priori probabilities. Assuming the energy representation $\{\phi_m\} = \{\phi^k\}$:

$$\rho_{mn} = \frac{\delta_{mn}}{\Gamma} , \qquad (6.19)$$

where ρ_{mn} is diagonal.

Pure State

When all systems are in the same state, up to a phase difference, $\Gamma = 1$. The quantum state is unique and ρ_{mn} has one diagonal element (unity). Also, $S = k\ln\Gamma = 0$. Then, $\psi_m^k = \psi_0 e^{i\phi_k}$, for some phase ϕ_k (not wave function).

$$\begin{aligned}
a_m &= \langle\phi_m|\psi^k\rangle = \langle\phi_m|\psi_0\rangle e^{i\phi_k} \\
&= a_m^0 e^{i\phi_k} \qquad (6.20)
\end{aligned}$$

$$\Rightarrow \rho_{mn} = \frac{1}{\mathcal{N}}\sum_k a_m^0 a_n^{*0} = a_m^0 a_n^{*0} . \qquad (6.21)$$

Then

$$\begin{aligned}\sum_l \rho_{ml}\rho_{ln} &= \sum_l a_m^0 a_l^{0*} a_l^0 a_n^* \\ &= a_m^0 a_n^{0*} \sum_l a_l^{0*} a_l^0 \end{aligned} \tag{6.22}$$

But $\sum_l a_l^{0*} a_l^0 = 1$. For all representations,

$$\hat{\rho}^2 = \hat{\rho} \tag{6.23}$$

for a pure state.

Mixed States

Now consider ρ_{mn} zero along the off diagonal elements and all diagonal elements are equal; $\rho_{mn} \propto \delta_{mn}$. In the energy representation

$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_k |a_m^k|^2 \delta_{mn} = P_m \delta_{mn} \,. \tag{6.24}$$

6.3.2 Canonical Ensemble

The macrostate depends on (N, V, T) and E may vary. Probability of having a state of energy E_s

$$P_s = \frac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \frac{e^{-\beta E_s}}{Q_N(\beta)} \,, \tag{6.25}$$

The density operator in this ensemble is

$$\begin{aligned}\hat{\rho} &= \sum_m |\phi_m\rangle \frac{e^{-\beta E_m}}{Q_N(\beta)} \langle \phi_m| \\ &= \frac{e^{-\beta \hat{H}}}{Q_N(\beta)} \\ &= \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})} \,. \end{aligned} \tag{6.26}$$

The expectation value of a physical quantity G, represented by the operator $\hat{G}$ is

$$\langle G \rangle_N = Tr(\hat{\rho}\hat{G}) = Tr(\hat{G}\hat{\rho}) = \frac{Tr(\hat{G} e^{-\beta \hat{H}})}{Tr(e^{-\beta \hat{H}})} \,, \tag{6.27}$$

where the subscript N reminds us that N is fixed. The cyclic property of the trace $\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$ has been used. The exponential of an operator is defined as $e^{-\beta \hat{H}} = \sum_{k=0}^{\infty} \frac{(-\beta \hat{H})^k}{k!}$.

6.3.3 Grand Canonical Ensemble

The macrostate depends on (V, T, μ). Since N varies, we introduce the number operator $\hat{n}$,

$$\hat{n} = \sum_s \hat{n}_s = \sum_s a_s^\dagger a_s \,. \tag{6.28}$$

$$\hat{n}\psi^k = N_k \psi^k \,. \tag{6.29}$$

Generalisation gives

$$\hat{\rho} = \frac{e^{-\beta\hat{H}-\alpha\hat{n}}}{\mathrm{Tr}(e^{-\beta\hat{H}-\alpha\hat{n}})} = \frac{e^{-\beta\hat{H}-\alpha\hat{n}}}{\mathcal{Q}(\mu, V, T)} \,. \tag{6.30}$$

The ensemble average $\langle G\rangle$ is

$$\begin{aligned}
\langle G\rangle &= \frac{\mathrm{Tr}[\hat{G}\exp(-\beta\hat{H}-\alpha\hat{n})]}{\mathcal{Q}} \\
&= \frac{\sum_m \sum_n G_{mn}[\exp(-\beta\hat{H}-\alpha\hat{n})]_{nm}}{\sum_m [\exp(-\beta\hat{H}-\alpha\hat{n})]_{mm}} \\
&= \frac{\sum_m G_{mm}\exp(-\beta E_m - \alpha N_m)}{\sum_m \exp(-\beta E_m - \alpha N_m)} \\
&= \frac{\sum_N z^N \langle G\rangle_N Q_N}{\sum_N z^N Q_N} \,,
\end{aligned} \tag{6.31}$$

where $\langle G_N\rangle$ represents the canonical average with N fixed.

6.4 Examples

6.4.1 Electron in a Magnetic Field

The intrinsic spin of a single electron is

$$\hat{S} = \frac{1}{2}\hbar\hat{\sigma} \,, \tag{6.32}$$

where the Pauli matrices are defined as

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{6.33}$$

The magnetic moment (for an electron) is

$$\hat{\mu} = g\frac{e}{2m}\hat{S} = 2\frac{e}{2m}\frac{\hbar}{2}\hat{\sigma} = \mu_B\hat{\sigma} \,. \tag{6.34}$$

The Hamiltonian for a magnetic field in the z-direction is

$$\hat{H} = -\hat{\mu} \cdot \vec{B} = -\mu_B B \hat{\sigma}_z \,, \tag{6.35}$$

The density matrix is

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})} = \frac{\begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix}}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} \,. \tag{6.36}$$

$$\langle \sigma_z \rangle = \mathrm{Tr}(\langle \hat{\sigma}_z \hat{\rho} \rangle) = \frac{e^{\beta \mu_B B} - e^{-\beta \mu_B B}}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} = \tanh(\beta \mu_B B) \,. \tag{6.37}$$

$$\langle \hat{\mu} \rangle = \mu_B \langle \hat{\sigma} \rangle = \mu_B \tanh(\beta \mu_B B) \,. \tag{6.38}$$

This agrees with earlier results.

6.4.2 Free Particle in a Box

Consider the volume as a cube with sides of length L. For a point particle of mass m and no internal degrees of freedom

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 \,. \tag{6.39}$$

For periodic boundary conditions

$$\phi_k(\vec{r}) = \frac{1}{L^{3/2}} e^{i \vec{k} \cdot \vec{r}} \tag{6.40}$$

and the wave vector is

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \,, \tag{6.41}$$

where n_i is an integer $0, \pm 1, \pm 2, \ldots$ The energies are

$$E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \,. \tag{6.42}$$

The density matrix is

$$\hat{\rho} = \sum_{m,n} |\phi_m\rangle \langle \phi_m | \hat{\rho} | \phi_n \rangle \langle \phi_n | \,. \tag{6.43}$$

Review of r-Representation $|\vec{r}_1\rangle$ is such that $\langle\phi|\vec{r}_1\rangle = \phi^*(\vec{r}_1)$. Formally, $|\vec{r}_1\rangle = \delta(\vec{r}-\vec{r}_1)$. Properties:

1)

$$\begin{aligned} \langle\vec{r}_2|\vec{r}_1\rangle &= \int d^3r\delta(\vec{r}-\vec{r}_2)\delta(\vec{r}-\vec{r}_1) \\ &= \delta(\vec{r}_2-\vec{r}_1)\,. \end{aligned} \tag{6.44}$$

2) Identity operator

$$\int d^3r|r\rangle\langle r| = 1\,. \tag{6.45}$$

For all ψ_1, ψ_2,

$$\begin{aligned} \langle\psi_1|\vec{r}\rangle\langle\vec{r}|\psi_2\rangle &= \int d^3r'\psi_1^*(\vec{r}\,')\psi_2(\vec{r})\delta(\vec{r}\,'-\vec{r}) \\ &= \psi_1^*(\vec{r})\psi_2(\vec{r})\,. \end{aligned} \tag{6.46}$$

$$\begin{aligned} \int d^3r\langle\psi_1|\vec{r}\rangle\langle\vec{r}|\psi_2\rangle &= \int d^3r\psi_1^*(\vec{r})\psi_2(\vec{r}) \\ &= \langle\psi_1|\psi_2\rangle\,. \end{aligned} \tag{6.47}$$

In the coordinate representation, $|\phi_m\rangle = e^{i\vec{k}\cdot\vec{r}}/L^{3/2}$ and

$$\begin{aligned} \rho_{\vec{r},\vec{r}\,'} &= \langle\vec{r}\,|\hat{\rho}|\vec{r}\,'\rangle \\ &= \sum_{k_1,k_2}\langle\vec{r}|\phi_{k_1}\rangle\langle\phi_{k_1}|\hat{\rho}|\phi_{k_2}\rangle\langle\phi_{k_2}|\vec{r}\,'\rangle \\ &= \sum_{k}\langle\vec{r}|\phi_{k}\rangle\langle\phi_{k}|\hat{\rho}|\phi_{k}\rangle\langle\phi_{k}|\vec{r}\,'\rangle\,, \end{aligned} \tag{6.48}$$

because ϕ_k are eigenvectors of ρ, with $\langle\vec{r}|\phi_k\rangle = \phi_k(\vec{r})$ and $\langle\phi_k|\vec{r}\,'\rangle = \phi_k^*(\vec{r}\,')$.

Recall

$$\hat{\rho} = \frac{\exp(-\beta\hat{H})}{\mathrm{Tr}\left[\exp(-\beta\hat{H})\right]} \tag{6.49}$$

and

$$\langle\vec{r}|e^{-\beta\hat{H}}|\vec{r}\,'\rangle = \frac{1}{L^3}\sum_{\vec{k}}\exp\left[-\frac{\beta\hbar^2k^2}{2m} + i\vec{k}\cdot(\vec{r}-\vec{r}\,')\right]\,. \tag{6.50}$$

Using $(\Delta k)^3 = (2\pi/L)^3$,

$$\begin{aligned}\langle\vec{r}|e^{-\beta H}|\vec{r}'\rangle &\approx \frac{1}{(2\pi)^3}\int d^3k \exp\left[-\frac{\beta\hbar^2k^2}{2m} + i\vec{k}\cdot(\vec{r}-\vec{r}')\right] \\ &= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}\exp\left(-\frac{m|\vec{r}-\vec{r}'|^2}{2\beta\hbar^2}\right). \qquad (6.51)\end{aligned}$$

$$\begin{aligned}\mathrm{Tr}\left(e^{-\beta\hat{H}}\right) &= \int d^3r\langle\vec{r}|e^{-\beta\hat{H}}|\vec{r}\rangle \\ &= V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \\ &= V\left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2} \\ &= Q_1(\beta)\,. \qquad (6.52)\end{aligned}$$

for a single particle in a box.

The density matrix in the coordinate representation is

$$\langle\vec{r}|\hat{\rho}|\vec{r}'\rangle = \frac{1}{V}\exp\left(-\frac{m|\vec{r}-\vec{r}'|^2}{2\beta\hbar^2}\right) \qquad (6.53)$$

which is a Gaussian with standard deviation $\hbar/\sqrt{mkT}$.

Notice that $\rho_{\vec{r},\vec{r}'}$ is probability density of finding the particle at $\vec{r}$. $\rho_{\vec{r},\vec{r}'}$ is symmetric in $\vec{r}$ and $\vec{r}'$. Diagonal element $(\vec{r} = \vec{r}')$ of the density matrix show that the probability density $(1/V)$ for a particle to be in the neighbourhood of $\vec{r}$ is independent of $\vec{r}$. This means all positions in the box are equally likely. The nondiagonal elements of the density matrix measure the pobability of spontanous transitions between positions coordinates $\vec{r}$ and $\vec{r}'$. This is the relative intensity of the wavepacket at a distance $|\vec{r}-\vec{r}'|$ from the centre of the packet. The spatial extent of the wavepacket means there is an uncertainty in locating the position of the particle. $\rho_{\vec{r},\vec{r}'}$ is related to uncertainty principle $\Delta p\Delta x \geq \hbar/2$, with $\Delta p \sim \sqrt{kTm}$. $\hbar/\sqrt{kTm}$ is the mean thermal wavelength.

Consider

$$\exp\left[-\frac{m}{2\beta\hbar^2}|\vec{r}-\vec{r}'|^2\right] = \exp\left[-\frac{\pi}{\lambda^2}|\vec{r}-\vec{r}'|^2\right] \qquad (6.54)$$

where

$$\lambda^2 = \frac{2\pi\beta\hbar^2}{m} = \frac{h^2}{2\pi mkT} \qquad (6.55)$$

$$\lambda = \frac{h}{\sqrt{2\pi mkT}} \qquad (6.56)$$

is the mean thermal wavelength of the particle. This is a pure quantum mechanical effect. The effect vanishes at high temperatures $\beta \to 0$ and the guassian becomes a delta function and we recover the classical result.

The function vanishes rapidly as distance r_{ij} is large compared to the mean thermal wavelength λ. The mean interparticle distance $(V/N)^{1/3}$ in the system is much larger than λ.

$$\left(\frac{V}{N}\right)^{1/3} \gg \lambda = \frac{h}{\sqrt{2\pi mkT}} \tag{6.57}$$

$$\begin{aligned} \frac{hn^{1/3}}{(2\pi mkT)^{1/2}} &\ll 1 & (6.58) \\ \frac{nh^3}{(2\pi mkT)^{3/2}} &\ll 1\,. & (6.59) \end{aligned}$$

The expectation value of the Hamiltonian is

$$\begin{aligned} \langle H \rangle &= \mathrm{Tr}\left(\hat{H}\hat{\rho}\right) = -\frac{\hbar^2}{2mV}\int d^3r \left[\nabla^2 \exp\left(-\frac{m|\vec{r}-\vec{r}'|^2}{2\beta\hbar^2}\right)\right]_{\vec{r}'=\vec{r}} \\ &= -\frac{\hbar^2}{2mV}\int d^3r \left(-\frac{3m}{\beta\hbar^2} + \frac{m^2}{\beta^2\hbar^4}|\vec{r}-\vec{r}'|^2\right) \exp\left(-\frac{m|\vec{r}-\vec{r}'|^2}{2\beta\hbar^2}\right)\Bigg|_{\vec{r}'=\vec{r}} \\ &= \frac{3}{2}kT\,, \end{aligned} \tag{6.60}$$

as expected. Alternatively

$$\langle H \rangle = -\frac{\partial}{\partial\beta} \ln \mathrm{Tr}(e^{-\beta\hat{H}})\,. \tag{6.61}$$

Notice that we assumed

$$\frac{\beta\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \ll 1 \Rightarrow \sum_k \sim \int d^3k\,. \tag{6.62}$$

Derive the corresponding expression for

$$\frac{\beta\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \gg 1\,. \tag{6.63}$$

6.5 Indistinguishable Particles

Assuming noninteracting particles, the Hamiltonian is

$$\hat{H}(q,p) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i) \tag{6.64}$$

where all $\hat{H}_i$ are of the same functional form. The single-particle Schrödinger equation is $\hat{H}_i(q_i,p_i)U(q_i) = \varepsilon_i U(q_i)$. The full Schrödinger equations is $\hat{H}\psi = E\psi$ with $E = \sum_i \varepsilon_i$, and the "Boltzmannian" wave function is

$$\psi = \prod_{i=1}^{N} U_{\vec{k}_i}(q_i)\,. \tag{6.65}$$

The distribution of particles among the possible one-particle eigenvalues is $\{n_i\}$, where n_i is number of particles in state i. The conditions are

$$N = \sum_i n_i\,, \tag{6.66}$$

$$E = \sum_i n_i \varepsilon_i\,, \tag{6.67}$$

$$\psi = \prod_{m=1}^{n_1} U_1(m) \prod_{m=n_1+1}^{n_1+n_2} U_2(m) \cdots\,, \tag{6.68}$$

where $U_i(m) = U_{\vec{k}_i}(q_m)$.

Classically, identical particles are distinguishable. Particles (1,2) in states (7,15) or (15,7) are two different states. Each mode of the distribution $\{n_i\}$ has

$$\frac{N!}{n_1! n_2! \ldots} \tag{6.69}$$

different (distinct) microstates

For idential particles in quantum mechanics, particles (1,2) in states (7,15) or (15,7) is only one state, or 0 if $\{n_i\}$ is disallowed. What is important is the number of particles in a state, not which particles are in the state.

The Boltzmanian wave function is inadequate because interchange of particles implies a different wave function. The solution is to form a linear superposition of all $N!$ permutations with the condition $|P\psi|^2 = |\psi|^2$ for all ψ. $P\psi = \psi$ for all P for bosons. $P\psi = \pm\psi$, where $P\psi = +\psi$ for even permutations and $-\psi$ for odd permutations (representing Fermi statistics). ψ is symmetric/antisymmetric in its arguments.

$$\psi_S(q) = \text{constant} \sum_p P\psi_{\text{Boltz}}(q) \tag{6.70}$$

$$\psi_A(q) = \text{constant} \sum_p S_P P\psi_{\text{Boltz}}(q) \tag{6.71}$$

with $S_P = \pm 1$ if P is even/odd. ψ_A can be written as a Slater determinatnt (for fermions)

$$\psi_A(q) = \text{constant} \begin{vmatrix} U_{k_1}(1) & U_{k_1}(2) & \cdots & U_{k_1}(N) \\ U_{k_2}(1) & U_{k_2}(2) & \cdots & U_{k_2}(N) \\ \vdots & & & \\ U_{k_N}(1) & U_{k_N}(2) & \cdots & U_{k_N}(N) \end{vmatrix} . \tag{6.72}$$

ψ_A obays Pauli's exclusion principle.

Summary: $\{n_i\}$ is 1 state for bosons/fermions if $\sum_i n_i^2 = N$, or 0 states for fermions if $\sum_i n_i^2 > N$.

$$W_{BE}\{n_i\} = 1; \quad n_i = 0, 1, 2, \ldots \tag{6.73}$$

$$W_{FD}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i^2 = N\,, \\ 0 & \text{if } \sum_i n_i^2 > N\,. \end{cases} \tag{6.74}$$

6.6 $\hat{\rho}$ and Q_N for a System of Free Particles

The density matrix in the canonical ensemble is

$$\langle \vec{r}_1, \ldots, \vec{r}_N | \hat{\rho} | \vec{r}'_1, \ldots, \vec{r}'_N \rangle = \frac{1}{Q_N(\beta)} \langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle\,, \tag{6.75}$$

where $1 \to \vec{r}_1, 2 \to \vec{r}_2, \ldots, N \to \vec{r}_N$.

The partition function is

$$Q_N(\beta) = \int d1 \ldots dN \langle 1, \ldots, N | e^{-\beta \hat{H}} | 1, \ldots, N \rangle\,. \tag{6.76}$$

Writing

$$e^{-\beta \hat{H}} = \sum_{\vec{k}}^{*} |\vec{k}\rangle e^{-\beta \hat{H}} \langle \vec{k}|\,, \tag{6.77}$$

where $|\vec{k}\rangle$ is eigenfunction of $\hat{H}$ with energy $E_{\vec{k}}$, and $*$ in the summation is over "distinct" $\vec{k}$ states. We have

$$\begin{aligned} \langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle &= \sum_{\vec{k}}^{*} \langle 1, \ldots, N | \vec{k} \rangle e^{-\beta E_{\vec{k}}} \langle \vec{k} | 1', \ldots, N' \rangle \\ &= \sum_{\vec{k}}^{*} e^{-\beta E_{\vec{k}}} \psi_{\vec{k}}(1, \ldots, N) \psi^{*}_{\vec{k}}(1', \ldots, N')\,, \end{aligned} \tag{6.78}$$

Because the particles are noninteracting

$$\begin{aligned}\psi_{\vec{k}} &= \frac{1}{\sqrt{N!}}\sum_p S_p P\{U_{\vec{k}_1}(1)\ldots U_{\vec{k}_N}(N)\} && (6.79)\\ &= \frac{1}{\sqrt{N!}}\sum_p S_p\{U_{\vec{k}_1}(P1)\ldots U_{\vec{k}_N}(PN)\} && (6.80)\\ &= \frac{1}{\sqrt{N!}}\sum_p S_p\{U_{P\vec{k}_1}(1)\ldots U_{P\vec{k}_N}(N)\}\,, && (6.81)\\ E_{\vec{k}} &= \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + \ldots + k_N^2) && (6.82)\end{aligned}$$

with

$$\begin{aligned}U_{\vec{k}} &= \frac{1}{V^{1/2}}e^{i\vec{k}\cdot\vec{r}} && (6.83)\\ \vec{k}_i &= \frac{2\pi}{L}\vec{n}_i && (6.84)\\ S_p &= (\pm 1)^{[P]}\,, && (6.85)\end{aligned}$$

where $[P]$ is the parity of the permutation. The upper sign $(+1)$ is for bosons and the lower sign $((-1^{[P]}))$ is for fermions. We therefore find

$$\begin{aligned}\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle &= \frac{1}{N!}\sum_{\vec{k}}^{*} e^{-\beta\hbar^2k^2/2m}\sum_p S_p U_{k_1}(P1)\ldots U_{k_N}(PN)\\ &\quad\times\sum_{\bar{p}} S_{\bar{p}}U^*_{k_1}(\bar{P}1')\ldots U^*_{k_N}(\bar{P}N')\,. && (6.86)\end{aligned}$$

Permutations among k_i change the wave function ψ at most by a sign and thus the quantity $\psi^*\psi$ does not change. We write

$$\sum_{\vec{k}}^{*} \sim \frac{1}{N!}\sum_{\vec{k}_1,\ldots,\vec{k}_N} \qquad (6.87)$$

where the last sum is unrestricted. All permutations make equal contributions to the sum because they differ from one another only in ordering of k_i.

$$\sum_p\sum_{\bar{p}} = N!\sum_p\,. \qquad (6.88)$$

$$\begin{aligned}\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle &= \frac{1}{N!}\sum_{\vec{k}_1,\ldots,\vec{k}_N} e^{-\beta\hbar^2k^2/2m}\\ &\quad\times\sum_p S_p U_{k_1}(P1)\ldots U_{k_N}(PN)U^*_{k_1}(1)\ldots U^*_{k_N}(N')\,. && (6.89)\end{aligned}$$

Using $U_{\vec{k}}(1) = 1/\sqrt{V} e^{i\vec{k}\cdot\vec{r}}$ and $\sum_{\vec{k}} \sim V/(2\pi)^3 \int d^3k$,

$$\begin{aligned} \langle 1, \ldots, N| e^{\beta \hat{H}} |1', \ldots, N'\rangle &\approx \frac{1}{N!(2\pi)^{3N}} \\ &\quad \times \int d^3k_N e^{-\beta\hbar^2 k_N^2/2m + i\vec{k}_N\cdot(PN-N')} \end{aligned} \tag{6.90}$$

But

$$\int d^3k e^{-\beta\hbar^2k^2/2m + i\vec{k}(\vec{r}-\vec{r}')} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} e^{-m(\vec{r}-\vec{r}')^2/2\beta\hbar^2} \tag{6.91}$$

and

$$\langle 1, \ldots, N| e^{-\beta \hat{H}} |1', \ldots, N'\rangle \approx \frac{1}{N!}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2} \sum_P S_P f(P1-1') \ldots f(PN-N') \tag{6.92}$$

where $f(\zeta) = e^{-m\zeta^2/2\beta\hbar^2}$.

In terms of the mean thermal wavelength

$$\langle 1, \ldots, N| e^{-\beta \hat{H}} |1', \ldots, N'\rangle \approx \frac{1}{N!\lambda^{3N}} \sum_P S_P f(P1-1') \ldots f(PN-N') \tag{6.93}$$

with $f(\vec{r}) = e^{-\pi r^2/\lambda^2}$.

The partition function is

$$\begin{aligned} Q_N(V,T) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right] &= \int d1 \ldots dN \langle 1, \ldots, N| e^{-\beta \hat{H}} |1, \ldots, N\rangle \\ &\approx \frac{1}{N!}\frac{1}{\lambda^{3N}} \int d1 \ldots dN \sum_P S_P f(P1-1) \ldots f(PN-N) \end{aligned} \tag{6.94}$$

The difference between coordinates are permutations of the same coordinate. Hence

$$\sum_P S_P f(P1-1) \ldots f(PN-N) = 1 \pm \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} \pm \cdots, \tag{6.95}$$

where $f_{ij} = f(\vec{r}_i - \vec{r}_j)$ and unity comes from $f_{ii} = f(\vec{r}_i - \vec{r}_i) = f(0) = 1$. The first term is no purmutatons and the second term is one pair of permutations, etc. If the interparticle distance is much larger than the thermal wavelength ($n\lambda^3 \ll 1$), the second term is small, and the third term is smaller.

To lowest order

$$Q_N(V,T) = \frac{1}{N!}\frac{1}{\lambda^{3N}}V^N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N . \tag{6.96}$$

Notice that the Gibbs factor is obtained automatically. In the classical limit (diagonal element of $\hat{\rho}$)

$$\hat{\rho} \approx \frac{1}{N!\lambda^{3N}}\frac{N!\lambda^{3N}}{V^N} = \left(\frac{1}{V}\right)^N . \tag{6.97}$$

This is the same results as seen previously for an ideal gas, and for a single particle in a box is $1/V$.

To first order,

$$\begin{aligned} Q_N(V,T) &= \frac{1}{N!\lambda^{3N}}\int d1\ldots dN\left[1 \pm \frac{N(N-1)}{2}f_{12}f_{21}\right] \\ &= \frac{1}{N!}\left[\left(\frac{V}{\lambda^3}\right)^N \pm \frac{N(N-1)V^{N-2}}{2\lambda^{3N}}\int d^3r_1 d^3r_2 e^{-2\pi r_{12}^2/\lambda^2}\right] \\ &\approx \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\left[1 \pm \frac{N^2}{2V^2}V\int d^3r e^{-2\pi r^2/\lambda^2}\right] \\ &= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\left[1 \pm \frac{1}{4\sqrt{2}}Nn\lambda^3\right] , \end{aligned} \tag{6.98}$$

where $n \equiv N/V$ is the particle density. Higher order terms cause spatial correlations between particles. The correlations are not due to interactions but rather the result of quantum mechanical symmetrisation of the wave function.

Consider the $N = 2$ case. Define the reduced density matrix

$$\langle 1,2|\hat{\rho}_2|1,2\rangle = \int d3\ldots dN\langle 1,2,\ldots,N|\hat{\rho}|1,\ldots,N\rangle . \tag{6.99}$$

From Eq. (6.93),

$$\begin{aligned} \int d3\ldots dN\langle 1,\ldots,N|e^{-\beta\hat{H}}|1,\ldots,N\rangle &\approx \frac{1}{N!}\frac{1}{\lambda^{3N}}\int d3\ldots dN[1 \pm f_{12}f_{21} \\ &\quad + \sum_{j>2}(f_{1j}f_{j1} + f_{2j}f_{j2}) + \sum_{2<i<j} f_{ij}f_{ji}] \\ &\approx \frac{1}{N!}\frac{V^{N-2}}{\lambda^{3N}}(1 \pm e^{-2\pi r_{12}^2/\lambda^2}) \end{aligned} \tag{6.100}$$

From $\hat{\rho} = e^{-\beta\hat{H}}/\mathrm{Tr}[e^{-\beta\hat{H}}]$ and Eq. (6.98),

$$\langle 1,2|\hat{\rho}_2|1,2\rangle \approx \frac{1}{V^2}(1 \pm e^{-2\pi r_{12}^2/\lambda^2}) . \tag{6.101}$$

Classically the exponential term vanishes. In the extreme quantum mechanical case for $r \to 0 \Rightarrow \langle 1,2|\hat{\rho}_2|1,2\rangle \approx (1 \pm 1)/V^2$. $\to 2/V^2$ for bosons (positive spatial correlations). $\to 0$ for fermions (negative spatial correlations).

6.7 Problems

Chapter 7

Simple Gases

7.1 Microcanonical Ensemble

Read Pathria

7.2 Other Ensembles

We will calculate Q_N and $\mathcal{Q}(z,V,T)$ for different statistics: Bose, Fermi, and Maxwell-Boltzmann. In the canonical ensemble, the partition function is

$$Q_N(V,T) = \sum_s e^{-\beta E_s}\,. \tag{7.1}$$

For noninteracting particles, $E_s = \sum_i n_i \varepsilon_i$. We characterise the system by $\{n\}$, where n_i is the number of particles in state i. The number of particles is constraint by $\sum_i n_i = N$. We can write

$$Q_N(V,T) = \sideset{}{'}\sum_{\{n\}} g\{n\} e^{-\beta \sum_s n_s \varepsilon_s}\,, \tag{7.2}$$

where $g\{n\}$ is the statistical weight for a given statistics and the prime represents the sum over all states that satisfy the number of particles constraint, $\sum_i n_i = N$.

The statistical weight factors are

$g\{n\} = 1$ for Bose-Einstein,

$g\{n\} = 1$ for Fermi-Dirac if $n = 0, 1$, else $g\{n\} = 0$,

$g\{n\} = N! \prod_s (1/n_s!)$ for Maxwell-Boltzmann (classical case).

7.2.1 Maxwell-Boltzmann Case

$$\begin{aligned}
Q_N(V,T) &= \frac{1}{N!}\sum_{\{n\}}{}' N!\left(\prod_s \frac{1}{n_s!}\right)\prod_r \left(e^{-\beta\varepsilon_r}\right)^{n_r} \\
&= \frac{1}{N!}\sum_{\{n\}}{}' \frac{N!}{\prod_s n_s!}\prod_r \left(e^{-\beta\varepsilon_r}\right)^{n_r} \\
&= \frac{1}{N!}\left(\sum_s e^{-\beta\varepsilon_s}\right)^N \\
&= \frac{1}{N!}[Q_1(\beta,V)]^N\,, \qquad (7.3)
\end{aligned}$$

where the multi-nomial theorem was used in the second to last step.

Recall

$$Q_1 = \frac{V}{\lambda^3} \quad \Rightarrow \quad Q_N = \frac{V^N}{N!\lambda^{3N}} \qquad (7.4)$$

as seen before

The grand partition function of the system is

$$\mathcal{Q} = \sum_N z^N Q_N = \sum_N z^N \frac{V^N}{N!\lambda^{3N}} = \sum_N \frac{(zV/\lambda^3)^N}{N!} = e^{zV/\lambda^3}\,, \qquad (7.5)$$

as seen before.

7.2.2 Bose-Einstein and Fermi-Dirac Statistics

Bose-Einstein or Fermi-Dirac give different possible distributions $\{n\}$. In this case, $\mathcal{Q}$ is easier to calculate:

$$\begin{aligned}
\mathcal{Q}(z,V,T) &= \sum_N z^N \left[\sum_{\{n\}}{}' e^{-\beta\sum_i n_i\varepsilon_i}\right] \\
&= \sum_N \left[\sum_{\{n\}}{}' \prod_i \left(z e^{-\beta\varepsilon_i}\right)^{n_i}\right]\,. \qquad (7.6)
\end{aligned}$$

Sum over n_i with constraint of fixed N and sum over all possible N is the same as a single sum over all n_i independent of one another.

$$
\begin{aligned}
\mathcal{Q}(z,V,T) &= \sum_{n_0,n_1,\ldots}\left[\prod_i \left(ze^{-\beta\varepsilon_i}\right)^{n_i}\right] \\
&= \prod_i \left[\sum_{n_0,n_1,\ldots} \left(ze^{-\beta\varepsilon_i}\right)^{n_i}\right] \\
&= \left[\sum_{n_0}\left(ze^{-\beta\varepsilon_0}\right)^{n_0}\right]\left[\sum_{n_1}\left(ze^{-\beta\varepsilon_1}\right)^{n_1}\right]\cdots .
\end{aligned}
\tag{7.7}
$$

Consider one factor. For Bose-Einstein,

$$
\sum_{n_0}(ze^{-\beta\varepsilon_0})^{n_0} = \sum_{n_0=0}^{\infty}(ze^{-\beta\varepsilon_0})^{n_0} = \frac{1}{1-ze^{-\beta\varepsilon_0}} \quad \Rightarrow \quad \mathcal{Q} = \prod_i \left(\frac{1}{1-ze^{-\beta\varepsilon_i}}\right) . \tag{7.8}
$$

where $ze^{-\beta\varepsilon} < 1$ must be satisfied for the series to converge.
For Fermi-Dirac

$$
\sum_{n_0}(ze^{-\beta\varepsilon_0})^{n_0} = \sum_{n_0=0}^{1}(ze^{-\beta\varepsilon_0})^{n_0} = 1+ze^{-\beta\varepsilon_0} \quad \Rightarrow \quad \mathcal{Q} = \prod_i \left(1+ze^{-\beta\varepsilon_i}\right) . \tag{7.9}
$$

Now consider the q-potential for all three cases.

$$
q(z,V,T) = \ln\mathcal{Q} = \mp\sum_s \ln(1\mp ze^{-\beta\varepsilon_s}) \quad \text{Bose-Einstein or Fermi-Dirac} \tag{7.10}
$$

$$
q(z,V,T) = \ln\mathcal{Q} = z\frac{V}{\lambda^3} = zQ_1 = z\sum_s e^{-\beta\varepsilon_s} \quad \text{Maxwell-Boltzmann.} \tag{7.11}
$$

A generalised expression is

$$
q(z,V,T) = \frac{PV}{kT} = \frac{1}{a}\sum_s \ln(1+aze^{-\beta\varepsilon_s}) , \tag{7.12}
$$

where $a=-1$ for Bose-Einstein, $a=+1$ for Fermi-Dirac, and $a=0^+$ Maxwell-Boltzmann (cf. $\lim_{x\to 0^+}\ln(1+x)\to x$).

It follows that

$$
\bar{N} = z\left.\frac{\partial q}{\partial z}\right|_{V,T} = \sum_s \frac{ze^{-\beta\varepsilon_s}}{1+aze^{-\beta\varepsilon_s}} = \sum_s \frac{1}{z^{-1}e^{\beta\varepsilon_s}+a} , \tag{7.13}
$$

$$
\bar{E} = -\left.\frac{\partial q}{\partial\beta}\right|_{z,V} = \sum_s \frac{z\varepsilon_s e^{-\beta\varepsilon_s}}{1+aze^{-\beta\varepsilon_s}} = \sum_s \frac{\varepsilon_s}{z^{-1}e^{\beta\varepsilon_s}+a} . \tag{7.14}
$$

From Eq. (7.7)

$$\mathcal{Q} = \sum_{n_0 \cdots} z^{n_0 + n_1 \cdots} e^{-\beta(n_0 \varepsilon_o + n_1 \varepsilon_1 \ldots)} \, , \tag{7.15}$$

the mean occupation number of a single particle state with energy ε_r is

$$\begin{aligned}
\langle n_r \rangle &= \frac{1}{\mathcal{Q}} \left[-\frac{1}{\beta} \left(\frac{\partial \mathcal{Q}}{\partial \varepsilon_r} \right)_{z,T,\varepsilon_i, i \neq r} \right] \\
&= -\frac{1}{\beta} \frac{\partial q}{\partial \varepsilon_r} \bigg|_{z,T,\epsilon_i, i \neq r} \\
&= \frac{z e^{-\beta \varepsilon_r}}{1 + a z e^{-\beta \varepsilon_r}} \\
&= \frac{1}{z^{-1} e^{\beta \varepsilon_r} + a} \\
&= \frac{1}{e^{(\varepsilon_r - \mu)/(kT)} + a} \, .
\end{aligned} \tag{7.16}$$

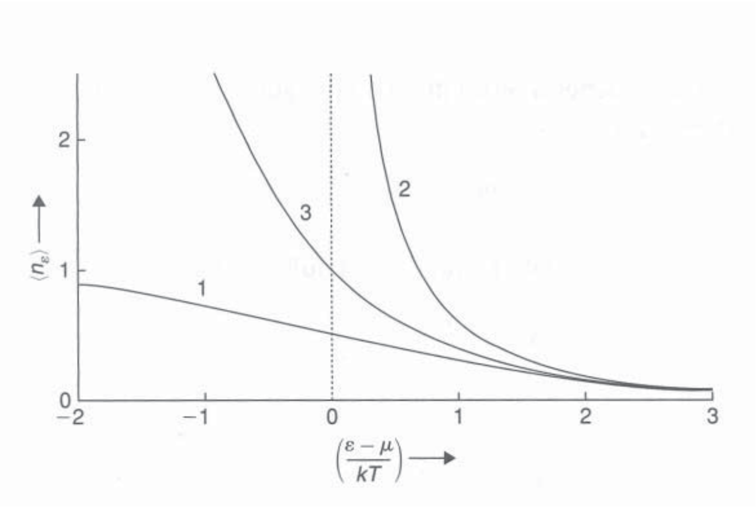


Figure 7.1: Mean occupation number $\langle n_\varepsilon \rangle$ of a single-particle energy state ε in a system of noninteracting particles: curve 1 is for fermions, curve 2 is for bosons, and curve 3 for the Maxwell-Boltzmann particles.

Classically $T \to \infty$ (or for the case $\varepsilon_r = \mu$ with finite T) so $\langle n_r \rangle \to 1/(1+a)$, giving

$$\langle n_r \rangle \to \begin{cases} 1/2 & \text{for Fermi-Dirac,} \\ \infty & \text{for Bose-Einstein, and} \\ 1 & \text{for Maxwell-Boltzmann.} \end{cases} \tag{7.17}$$

For $T \to 0$ and $\varepsilon_r > \mu$, we have $\langle n_r \rangle \to \exp[-(\varepsilon_r - \mu)/(kT)]$, and $\langle n_r \rangle \to 0$ for all statistics. For $T \to 0$ and $\varepsilon_r < \mu$, the Bose-Einstein case is not allowed since $\langle n_r \rangle \geq 0$ requires $\exp[(\varepsilon_r - \mu)/(kT)] - 1 > 0 \Rightarrow (\varepsilon_r - \mu)/kT > 0 \Rightarrow \varepsilon_r > \mu$.

Else, $\langle n_r \rangle \to 1/a$, giving

$$\langle n_r \rangle \to \begin{cases} 1 & \text{for Fermi-Dirac and} \\ \infty & \text{for Maxwell-Boltzmann.} \end{cases} \tag{7.18}$$

7.3 Statistics of Occupation Numbers

Consider $P_r(n)$ the probability of having n particles in states r. From Eq. (7.6),

$$\mathcal{Q} = \sum_N \sum_{\{n\}}{}' \prod_i \left(z e^{-\beta \varepsilon_i} \right)^{n_i} , \tag{7.19}$$

we infer that

$$p_r(n) \propto \left(z e^{-\beta \varepsilon_r} \right)^n . \tag{7.20}$$

The normalisation depends on the type of statistics. For Bose-Einstein statistics,

$$p_r(n) = (z e^{-\beta \varepsilon_r})^n (1 - z e^{-\beta \varepsilon_r}) . \tag{7.21}$$

But we found

$$\langle n_r \rangle = \frac{z e^{-\beta \varepsilon_r}}{1 - z e^{-\beta \varepsilon_r}} \tag{7.22}$$

$$\Rightarrow z e^{-\beta \varepsilon_r} = \frac{\langle n_r \rangle}{1 + \langle n_r \rangle} \tag{7.23}$$

$$\Rightarrow p_r(n) = \left[\frac{\langle n_r \rangle}{\langle n_r \rangle + 1} \right]^n \frac{1}{\langle n_r \rangle + 1} = \frac{\langle n_r \rangle^n}{[\langle n_r \rangle + 1]^{n+1}} . \tag{7.24}$$

For Fermi-Dirac statistics,

$$p_r(n) = \frac{(z e^{-\beta \varepsilon_r})^n}{(1 + z e^{-\beta \varepsilon_r})} . \tag{7.25}$$

We found

$$\langle n_r \rangle = \frac{z e^{-\beta \varepsilon_r}}{1 + z e^{-\beta \varepsilon_r}} \tag{7.26}$$

$$\Rightarrow z e^{-\beta \varepsilon_r} = \frac{\langle n_r \rangle}{1 - \langle n_r \rangle} \tag{7.27}$$

$$\Rightarrow p_r(n) = \left[\frac{\langle n_r\rangle}{1-\langle n_r\rangle}\right]^n (1-\langle n_r\rangle); \quad n = 0 \text{ or } 1\,, \tag{7.28}$$

which is $p_r(0) = 1 - \langle n_r\rangle$ for $n = 0$ and $p_r(1) = \langle n_r\rangle$ for $n = 1$.

For Maxwell-Boltzmann statistics,

$$p_r(n) = \frac{(ze^{-\beta\varepsilon_r})^n}{n!} e^{-ze^{-\beta\varepsilon_r}}\,, \tag{7.29}$$

where the exponential of the exponential is the normalization factor. This comes from

$$Q_N(V,T) = \frac{1}{N!}\sum_{\{n\}} \frac{N!}{\prod_i n_i!} \prod (e^{-\beta\varepsilon_i})^{n_i}\,. \tag{7.30}$$

Since

$$\langle n_r\rangle = ze^{-\beta\varepsilon_r} \tag{7.31}$$

$$\Rightarrow p_r(n) = \frac{\langle n_r\rangle^n}{n!} e^{-\langle n_r\rangle}\,. \tag{7.32}$$

Notice that this is a Poisson distribution.

7.4 Problems

Chapter 8

Ideal Bose Systems

We will now study systems in which quantum statistics, due to indistinguishability of particles, is important. We will continue to still neglect interactions among the particles. The conditions of high temperature and low density will no longer apply. The criterion

$$\frac{nh^3}{(2\pi mkT)^{3/2}} = n\lambda^3 \ll 1\,. \tag{8.1}$$

will no longer be satisfied. It should be noted that the expression is also not satisfied for very low-mass particles.

The quantity $n\lambda^3$ is an appropriate parameter in which to study the various properties of the system. For $n\lambda^3 \to 0$, the system goes over to its classical counterpart. For small but finite $n\lambda^3$, we can expand in a power series about this parameter. The system will no longer be classical, and the first signs of quantum mechanical behaviour will become evident. When $n\lambda^3 \to 1$, the system shows a very different behaviour from the classical one, and quantum effects are important.

In the quantum regime, it is important to distinguish if the particles of the system obey Bose-Einstein or Fermi-Dirac statistics.

8.1 Thermodynamic Behaviour of an Ideal Bose Gas

For an ideal Bose gas

$$\frac{PV}{kT} = \ln \mathcal{Q} = -\sum_s \ln(1 - ze^{-\beta\varepsilon_s})\,, \tag{8.2}$$

where $z = \exp[\mu/(kT)]$ and $z\exp(-\beta\varepsilon) < 1$ always. In the continum limit,

$$\sum_s \to \frac{V}{(2\pi)^3}\int d^3k = \frac{V}{(2\pi)^3}4\pi\int k^2 dk\,, \tag{8.3}$$

where the last equality assumes spherical symmetry. Since non-relativistically

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar}\,, \tag{8.4}$$

the differentials are

$$d\varepsilon = \frac{\hbar^2}{m} k dk \Rightarrow k^2 dk = \frac{m}{\hbar^2}\frac{\sqrt{2m}}{\hbar}\sqrt{\varepsilon} d\varepsilon\,. \tag{8.5}$$

Equation (8.3) becomes

$$\sum_s \to \frac{V}{(2\pi)^3} 4\pi \frac{\sqrt{2} m^{3/2}}{\hbar^3} \int_0^\infty d\varepsilon \sqrt{\varepsilon} = V 2\pi \frac{(2m)^{3/2}}{h^3} \int_0^\infty d\varepsilon \sqrt{\varepsilon}\,. \tag{8.6}$$

And Eq. (8.2) becomes

$$\frac{P}{kT} = -\frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \ln(1 - z e^{-\beta\varepsilon})\,. \tag{8.7}$$

But the ground state ($\varepsilon = 0$) is not accounted for because of $\sqrt{\varepsilon}$ from energy density. Removing the ground-state ($s = 0$) contributon from the sum give

$$\frac{P}{kT} = -\frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \ln(1 - z e^{-\beta\varepsilon}) - \frac{1}{V}\ln(1 - z)\,. \tag{8.8}$$

Notice that the integral at $\varepsilon \to 0$ gives no contribution.

Also for an ideal Bose gas,

$$N = \sum_s \langle n_s \rangle = \sum_s \frac{1}{z^{-1} e^{\beta\varepsilon_s} - 1}\,, \tag{8.9}$$

and similarly

$$\frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty \frac{d\varepsilon \sqrt{\varepsilon}}{z^{-1} e^{\beta\varepsilon} - 1} + \frac{1}{V}\frac{z}{1 - z}\,. \tag{8.10}$$

Lets examine the significance of the ground-state terms. For Bose-Einstein statistics, $\varepsilon > \mu$. If the ground-state energy vanishes, $\mu < 0$. Thus z is bound between $0 < z < 1$.

1. If $z \to 0$, the ground-sate contribution is negligible in both Eq. (8.8) and Eq. (8.10).
2. If $z \to 1^-$, in Eq. (8.10) N_0/V becomes very large. This is known as Bose-Einstein condensation.
3. If $z \ll 1$ but not $z \to 0$, classical limit.
4. For non-extreme z, Eq. (8.10) gives $N_0 = z/(1 - z) \Rightarrow z = N_0/(N_0 + 1)$. Substituting this value of z into Eq. (8.8) gives the ground state pressure $P_0 = (kT/V)\ln(N_0 + 1)$. For $N_0 = 0$, $P_0 = 0$. For $N_0 \gg 1$, $P_0 \to (kT/V)\ln N \sim (1/N)\ln N$, which is negligible for large N. Therefore the ground-state pressure is negligible for all z.

Can not take $T \to 0$ and $T \to \infty$ limits and call them quantum mechanical and classical limits because must also consider high and low density limits, i.e. classically $T_C \to 0$ so no room for quantum mechanical regime.

Let $x = \beta\varepsilon = \varepsilon/(kT)$, to obtain

$$\frac{P - P_0}{kT} = -2\pi \frac{(2mkT)^{3/2}}{h^3} \int_0^\infty dx x^{1/2} \ln(1 - ze^{-x}) = \frac{1}{\lambda^3} g_{5/2}(z) \tag{8.11}$$

and

$$\frac{N - N_0}{V} = 2\pi \frac{(2mkT)^{3/2}}{h^3} \int_0^\infty \frac{dx x^{1/2}}{z^{-1}e^x - 1} = \frac{1}{\lambda^3} g_{3/2}(z)\,, \tag{8.12}$$

where

$$g_\nu(z) \equiv \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{dx x^{\nu-1}}{z^{-1}e^x - 1} \tag{8.13}$$

are Bose-Einstein functions. Notice that

$$g_\nu(z) = \sum_{k=1}^\infty \frac{z^k}{k^\nu}\,. \tag{8.14}$$

Eq (8.11). and Eq. (8.12) can be used to eliminate z to obtain the equation of state.

8.1.1 Internal Energy

The internal energy is

$$\begin{aligned} U &= -\left(\frac{\partial}{\partial \beta} \ln \mathcal{Q}\right)_{z,V} = kT^2 \frac{\partial}{\partial T}\left(\frac{PV}{kT}\right)_{z,V} = kT^2 V g_{5/2}(z) \frac{\partial}{\partial T}(\lambda^{-3}) \\ &= \frac{3}{2} kT^2 V \frac{g_{5/2}}{\lambda^3} \frac{1}{T} = \frac{3}{2} kTV \frac{P}{kT} = \frac{3}{2} PV\,. \end{aligned} \tag{8.15}$$

This result is universal and contains no quantum corrections.

8.1.2 Viral Expansion

We now use Eq. (8.11) and Eq. (8.12) to eliminate z and derive the equation of state. Assume z small, neglecting N_0, and solve for z as function of $1/v \equiv N/V$. Using Eq. (8.12) and Eq. (8.14) gives

$$\begin{aligned}
\frac{\lambda^3}{v} &= g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \ldots \\
z &= \frac{\lambda^3}{v} - \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \ldots \\
&= \frac{\lambda^3}{v} - \frac{(\lambda^3/v - z^2/2^{3/2} - z^3/3^{3/2} - \ldots)^2}{2^{3/2}} - \frac{(\lambda^3/v - z^2/2^{3/2} - z^3/3^{3/2} - \ldots)^3}{3^{3/2}} - \ldots \\
&\approx \frac{\lambda^3}{v} - \left(\frac{\lambda^3}{v}\right)^2 \frac{1}{2^{3/2}} - \ldots \qquad (8.16)
\end{aligned}$$

Substituting into Eq. (8.11) gives

$$\begin{aligned}
\frac{P}{kT} &= \frac{g_{5/2}(z)}{\lambda^3} = \frac{1}{\lambda^3}\left[z + \frac{z^2}{2^{5/2}} + \ldots\right] \\
&= \frac{1}{\lambda^3}\left[\frac{\lambda^3}{v} + \left(\frac{1}{2^{5/2}} - \frac{1}{2^{3/2}}\right)\left(\frac{\lambda^3}{v}\right)^2 + \ldots\right] \qquad (8.17) \\
\frac{PV}{NkT} &= \left[1 - 0.1767767\frac{\lambda^3}{v} + \ldots\right] \\
&= \sum_{l=1}^{\infty} a_l \left(\frac{\lambda^3}{v}\right)^{l-1}, \qquad (8.18)
\end{aligned}$$

where a_l are viral coefficients. The classical limit $(T \to \infty, \lambda \to 0)$ or $v \to \infty$ gives $P = nkT$.

For the specific heat, assuming $(\lambda^3/v) \ll 1$, gives

$$\frac{C_V}{Nk} = \frac{1}{Nk}\left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{3}{2}\frac{\partial}{\partial T}\left(\frac{PV}{Nk}\right) = \frac{3}{2}\sum_{l=1}^{\infty}\frac{5-3l}{2}a_l\left(\frac{\lambda^3}{v}\right)^{l-1}. \qquad (8.19)$$

The classical limit $(T \to \infty, \lambda \to 0)$ or $v \to \infty$ gives $C_V = 3Nk/2$.

8.1.3 Characteristic Temperature

As T decreases the viral expansion can not be approximated and we need to determine z exactly. Define $N_e = N - N_0$ as the number of particles in the excited state. From Eq. (8.12), the number of particles in excited states is

$$N_e = \frac{V}{\lambda^3} g_{3/2}(z). \qquad (8.20)$$

We are just considering the N_e term. We are not neglecting the N_0 term.

Equation (8.20) has an upper bound. For $z < 1$, $g_{3/2}|_{\max} = g_{3/2}(1) = \sum_{k=1}^{\infty} 1/k^{3/2} \equiv \zeta(3/2) \approx 2.612$, where ζ is the Riemann zeta function. Thus

$$N_e < N_e^{\max} \equiv \frac{V}{\lambda^3}\zeta(3/2)\,. \tag{8.21}$$

If $N > N_e^{\max}$, a fraction of the particles must condensate into the ground state. This is known as Bose-Einstein condensation. It has a purely quantum mechanical origin. The number in the ground state is

$$N_0 = N - N_e = N - V\frac{\zeta(3/2)}{\lambda^3} = N - V\frac{(2\pi mkT)^{3/2}}{h^3}\zeta(3/2)\,. \tag{8.22}$$

We can express the onset of Bose-Einstein condensation in terms of a characteristic temperature when $N_e = N_e^{\max}$

$$T_c = \frac{h^2}{2\pi mk}\left[\frac{N}{V\zeta(3/2)}\right]^{2/3} = \frac{h^2}{2\pi mk}\left(\frac{n}{\zeta(3/2)}\right)^{2/3}\,. \tag{8.23}$$

We now consider N_0 and N_e as a function of T.

For $T < T_c$, we have $N = N_e + N_0$, which is given by

$$\frac{N}{V} = \frac{g_{3/2}(z)}{\lambda^3} + \frac{1}{V}\frac{z}{1-z}\,. \tag{8.24}$$

If $N_0 \gg 1$, $z = N_0/(N_0+1) \approx 1^-$, and

$$\begin{aligned}
\frac{N_0}{N} &\approx 1 - \frac{g_{3/2}(1)}{\lambda^3}\frac{V}{N} \\
&\approx 1 - \frac{\zeta(3/2)}{\lambda^3}\frac{V}{N} \\
&= 1 - \frac{V\zeta(3/2)}{N}\frac{(2\pi mkT)^{3/2}}{h^3} \\
&= 1 - \left(\frac{T}{T_c}\right)^{3/2}\,.
\end{aligned} \tag{8.25}$$

This is plotted in Fig. 8.1 as curve 2 (N_0/N).

For $T \to T_c$ from below,

$$\frac{N_0}{N} \approx \frac{3}{2}\frac{T_c - T}{T_c}\,, \tag{8.26}$$

which give the slope near $T \approx T_c$.

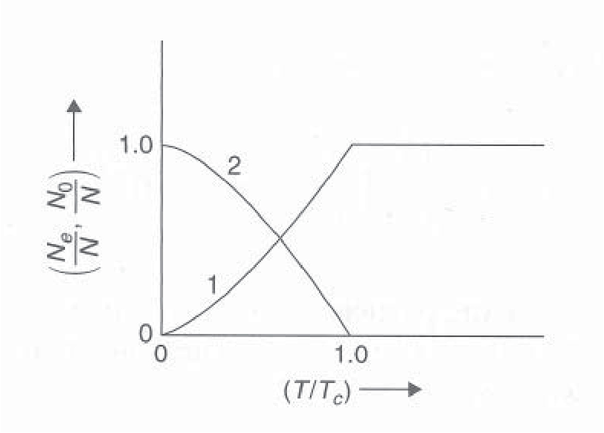


Figure 8.1: Fractions of the normal phase (1) and the condensed phase (2) in an ideal Bose gas as a function of the temperature parameter T/T_c.

For $T > T_c$, $N_0 \ll N \approx N_e$ (all in excited state). See Fig. 8.1 as curve 1 (N_e/N).

$$N \approx \frac{V}{\lambda^3} g_{3/2}(z) \quad \Rightarrow \quad g_{3/2}(z) = \frac{\lambda^3}{v}\,. \tag{8.27}$$

If $\lambda^3/v \ll 1$, $g_{3/2}(z) \approx z \Rightarrow z \approx \lambda^3/v$. Then

$$\begin{aligned} N_0 &= \frac{z}{1-z} = \frac{\lambda^3/v}{1-\lambda^3/v} && (8.28)\\ &\approx \frac{\lambda^3}{v}\left(1+\frac{\lambda^3}{v}\right) && (8.29)\\ &\approx \frac{\lambda^3}{v} \propto T^{-3/2} && (8.30)\end{aligned}$$

To summarise

For $T > T_c$, $N_0 \ll N$ and essentially all particles are in the excited states $N \approx N_e$ (single phase).

For $T < T_c$, $N_0 \gg 1$ there is a significant fraction of particles are in the ground state (two phases).

8.1.4 (P, T) Diagram

Next, we examine the (P, T) diagram for v fixed. From before

$$\frac{P}{kT} \approx \frac{g_{5/2}(z)}{\lambda^3} \,. \tag{8.31}$$

For $T < T_c, z \approx 1$.

$$P(T) \approx \frac{kT}{\lambda^3}\zeta(5/2) \propto T^{5/2} \,, \tag{8.32}$$

independent of v. The gas has an infinite compressibility since $\partial P/\partial V = 0$.

At $T = T_c$,

$$P(T_c) = \left(\frac{2\pi m}{h^2}\right)^{3/2} (kT_c)^{5/2} \, \zeta(5/2) \,. \tag{8.33}$$

From

$$T < T_c = \frac{h^2}{2\pi mk}\left(\frac{N}{V\zeta(3/2)}\right)^{2/3} \,, \tag{8.34}$$

$$\Rightarrow P(T_c) = \frac{\zeta(5/2)}{\zeta(3/2)}\left(\frac{N}{V}kT_c\right) \approx 0.5134 \left(\frac{N}{V}kT_c\right) \,. \tag{8.35}$$

This shows that the pressure is about 1/2 the classical value at $T = T_c$. All exerted by excited phase since the ground state has no pressure.

For $T > T_c$, $N_0 \approx 0$

$$P(T) = \frac{N}{V}kT\frac{g_{5/2}(z)}{g_{3/2}(z)} \propto T \,. \tag{8.36}$$

Recall $U = 3PV/2$. Thus $PV/(NkT_c) = 2U/(3NkT_c)$, and the same diagram can be used.

Now consider the specific heat (slope in U versus T curve). C_V starts at 0 for $T \to 0$, C_V has a cusp at $T = T_c$. C_V approaches constant (classical value) as $T \to \infty$.

For $T < T_c$,

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \frac{3}{2}Vk\zeta(5/2)\frac{d}{dT}\left(\frac{T}{\lambda^3}\right) \,, \tag{8.37}$$

$$\frac{C_V}{Nk} = \frac{3}{2}\frac{V}{N}\zeta(5/2)\left(\frac{1}{\lambda^3} + \frac{3}{2}\frac{1}{\lambda^3}\right) = \frac{15}{4}\zeta(5/2)\frac{v}{\lambda^3} \propto T^{3/2} \,. \tag{8.38}$$

For $T = T_c$,

$$\left.\lambda^3\right|_{T=T_c} = v\zeta(3/2) \,. \tag{8.39}$$

Therefore

$$\frac{C_V}{Nk} = \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)} \approx 1.935 \,, \tag{8.40}$$

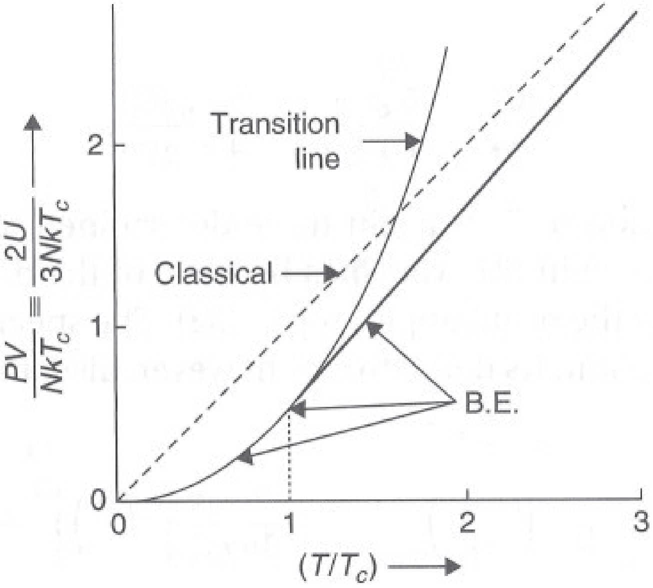


Figure 8.2: Pressure and internal energy of an ideal Bose gas as a function of the temperature parameter T/T_c.

which is higher than the classical value of 1.5.

For $T > T_c$,

$$C_V = \frac{3}{2}V\frac{\partial}{\partial T}\left[\frac{N}{V}kT\frac{g_{5/2}(z)}{g_{3/2}(z)}\right]_V \Rightarrow \frac{C_V}{Nk} = \frac{3}{2}\frac{\partial}{\partial T}\left[\frac{Tg_{5/2}(z)}{g_{3/2}(z)}\right]. \tag{8.41}$$

Now

$$z\frac{\partial}{\partial z}g_{3/2}(z) = g_{1/2}(z) \quad \text{and also} \quad g_{3/2}(z) = \frac{\lambda^3}{v} \propto T^{-3/2} \tag{8.42}$$

$$\Rightarrow \left(\frac{\partial}{\partial T}g_{3/2}(z)\right)_V = \left(\frac{\partial}{\partial T}\frac{\lambda^3}{v}\right)_V = -\frac{3}{2}\frac{\lambda^3}{Tv} = -\frac{3}{2}\frac{g_{3/2}(z)}{T}. \tag{8.43}$$

Therefore

$$\left[\frac{\partial}{\partial T}g_{3/2}(z)\right]_V = \left[\frac{\partial}{\partial z}g_{3/2}(z)\right]_V\left(\frac{\partial z}{\partial T}\right)_V \Rightarrow \left(\frac{\partial z}{\partial T}\right)_V = \left(\frac{\partial g_{3/2}(z)}{\partial T}\right)\Big/\left(\frac{\partial g_{3/2}(z)}{\partial z}\right), \tag{8.44}$$

$$\left(\frac{\partial z}{\partial T}\right)_V = -\frac{3}{2}\frac{g_{3/2}(z)}{T}\frac{z}{g_{1/2}(z)} \Rightarrow \frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_V = -\frac{3}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}. \tag{8.45}$$

Therefore

$$\begin{aligned}
\frac{C_V}{Nk} &= \frac{3}{2}\left[\frac{g_{5/2}(z)}{g_{3/2}(z)} + T\frac{g_{3/2}(z)}{g_{3/2}(z)}\left(\frac{-3}{2T}\right)\frac{g_{3/2}(z)}{g_{1/2}(z)} - T\frac{g_{5/2}(z)}{g_{3/2}^2(z)}g_{1/2}(z)\left(\frac{-3}{2T}\right)\frac{g_{3/2}(z)}{g_{1/2}(z)}\right] \\
&= \frac{3}{2}\left[\left(1+\frac{3}{2}\right)\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right] \\
&= \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}\,. \qquad (8.46)
\end{aligned}$$

$g_{1/2}(z)$ diverges as $z \to 1$ and thus

$$\lim_{z\to 1}\frac{C_V}{Nk} = \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}\,, \qquad (8.47)$$

Hence, C_V is continuous.

For $z \to 0$,

$$\left(\frac{C_V}{Nk}\right)_{z\to 0} = \frac{15}{4} - \frac{9}{4} = \frac{3}{2}\,, \qquad (8.48)$$

which is the classical result.

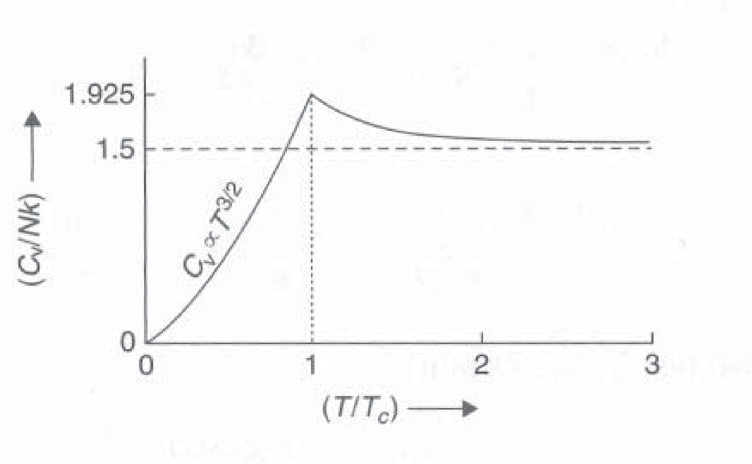


Figure 8.3: Specific heat of an ideal Bose gas as a function of the temperature parameter T/T_c.

8.1.5 Isotherms

Now consider the isotherms of an ideal Bose gas, i.e. P versus v for constant T. Define a characteristic volume at which Bose-Einstein condensation sets in. From

$$N = V\frac{\zeta(3/2)}{\lambda^3} \quad \Rightarrow \quad v_c = \frac{\lambda^3}{\zeta(3/2)}, \quad v_c \propto T^{-3/2}. \tag{8.49}$$

For $v \ll v_c$,

$$P_0 = \frac{kT}{\lambda^3}\zeta(5/2), \tag{8.50}$$

independent of v.

The transition line is evaluated by eliminating T:

$$v_c^{5/3} = \frac{h^5}{(2\pi mT)^{5/2}}\frac{1}{\zeta^{5/3}(3/2)} \quad \text{and} \quad P_0 = \frac{(2\pi mT)^{3/2}}{h^3}kT\zeta(5/2)\,, \tag{8.51}$$

$$P_0 v_c^{5/3} = \frac{h^2}{2\pi m}\frac{\zeta(5/2)}{\zeta^{5/3}(3/2)} = \text{constant}. \tag{8.52}$$

We now solve for the adiabats, for $v > v_c$. Consider the entropy using $U - TS + PV = N\mu$;

$$\begin{aligned} \frac{S}{Nk} &= \frac{U + PV}{NkT} - \frac{\mu}{kT} \\ &= \frac{3PV/2 + PV}{NkT} - \ln z \\ &= \frac{5}{2}\frac{PV}{NkT} - \ln z\,. \end{aligned} \tag{8.53}$$

For $T \le T_c$, $P = kT\zeta(5/2)/\lambda^3$ and $z \approx 1$, gives

$$\frac{S}{Nk} = \frac{5}{2}\frac{V}{N}\frac{\zeta(5/2)}{\lambda^3} = \frac{5}{2}\frac{v}{\lambda^3}\zeta(5/2)\,. \tag{8.54}$$

For $T > T_c$, $P = nkTg_{5/2}(z)/g_{3/2}(z)$, gives

$$\frac{S}{Nk} = \frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z\,. \tag{8.55}$$

For a reversible adibatic process, S and N constant. Thus z and v/λ^3 are constant. Since $\lambda^3 \propto T^{-3/2}$, therefore

$$vT^{3/2} = \text{constant} \tag{8.56}$$

or $v^{5/3}T^{5/2} = \text{constant}$. Also $P = kT\zeta(5/2)/\lambda^3 \Rightarrow P/T^{5/2} = \text{constant}$. Therefore

$$Pv^{5/3} = \text{constant}\,. \tag{8.57}$$

This is an equation for an adiabat of the ideal Bose gas (it holds for all T).

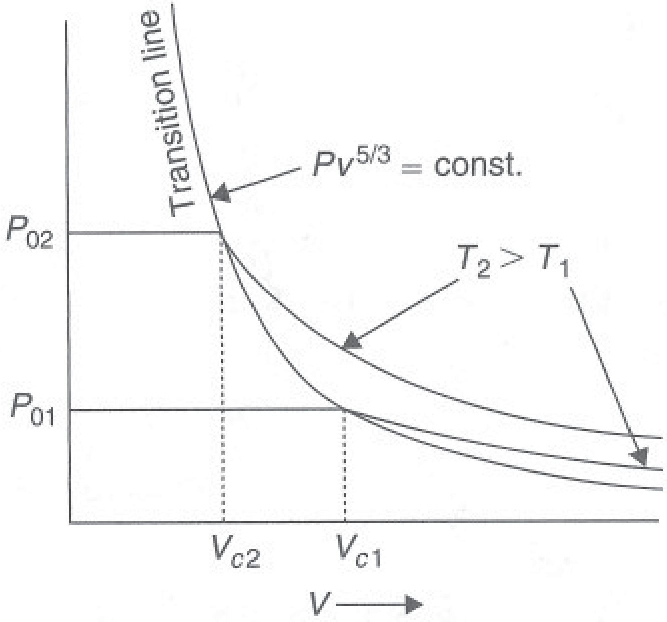


Figure 8.4: Isotherms of an ideal Bose gas.

8.1.6 Ratio of Heat Capacities and Entropy per Particle

The ratio of heat capacities, without proof, is

$$\gamma \equiv \frac{C_P}{C_V} = 1 + \frac{4}{9}\frac{C_V}{Nk}\frac{g_{1/2}(z)}{g_{3/2}(z)} = \frac{5}{3}\frac{g_{5/2}(z)g_{1/2}(z)}{[g_{3/2}(z)]^2}\,. \tag{8.58}$$

For $T \gg T_c, \gamma \to 5/3$, which is the classical result. Else $\gamma > 5/3$. As $T \to T_c, \gamma \to \infty$.

For $T < T_c$,

$$S = N_e \frac{5}{2} k \frac{\zeta(5/2)}{\zeta(3/2)} \propto N_e\,, \tag{8.59}$$

where

$$N_e = \frac{V}{\lambda^3}\zeta(3/2)\,. \tag{8.60}$$

Thus each particle contributes

$$\frac{5}{2} k \frac{\zeta(5/2)}{\zeta(3/2)} \tag{8.61}$$

to the entropy. But, the N_0 particles in the condensed phase do not contribute at all to the entropy.

8.2 Blackbody Radiation

Two idential but conceptually different approaches.

8.2.1 Planck

Here we treat the problem as an assembly of harmonic oscillators with quantized energies. The oscillators are distinguishable from one another since they have different values of ω_s.

From Eq (3.8.20) Parthia (canonical ensemble),

$$U = N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] \tag{8.62}$$

for a system of harmonic oscillators.
Ignoring the zero-point energy (not important for thermodynamics)

$$\frac{U}{N} = \langle\varepsilon_s\rangle = \frac{\hbar\omega_s}{e^{\beta\hbar\omega_s}-1}\,. \tag{8.63}$$

We approximate the spectrum by a continuum. Using $\omega = kc$ and realizing there are two transverse modes,

$$\sum_s \to \frac{2\times V}{(2\pi)^3}\int d^3k = \frac{2V}{(2\pi)^3}4\pi\int_0^\infty dk k^2 = \frac{V}{\pi^2c^3}\int_0^\infty d\omega\omega^2\,, \tag{8.64}$$

where the number of normal modes per unit volume is

$$\frac{\omega^2 d\omega}{\pi^2c^2}\,. \tag{8.65}$$

The energy density $u(\omega)\Delta\omega$ is the energy per unit volume in the frequency range $(\omega, \omega+\Delta\omega)$:

$$u(\omega) = \frac{U(\omega)}{V} = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,, \tag{8.66}$$

which is Planck's formula for the distribution of energy over the blackbody spectrum.

8.2.2 Bose-Einstein

Here we treat the system as a gas of idential and indistinguishable quanta, or a gas of photons. The energies of the photons correspond to the frequencies of the radiation mode. We examine the statistics of the energy levels themselves, not the photons.

The mean occupation number is

$$\langle n_s\rangle = \frac{1}{z^{-1}e^{\beta\hbar\omega}-1}\,. \tag{8.67}$$

For photons, N is not conserved and hence $z = 1$ (see later – no Lagrange multiplier α).

Hence

$$\langle\varepsilon_s\rangle = \hbar\omega_s\langle n_s\rangle = \frac{\hbar\omega_s}{e^{\beta\hbar\omega}-1}\,, \tag{8.68}$$

which is the same as Planck's results. The phase-space factor is also idential to Planck's. Thus

$$u(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,. \tag{8.69}$$

The total energy density is

$$\frac{U}{V} = \int_0^\infty d\omega u(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{1}{(\beta\hbar)^4}\int_0^\infty \frac{dx x^3}{e^x-1} = \frac{\pi^2 k^4}{15\hbar^3 c^3}T^4\,, \tag{8.70}$$

where $x=\beta\hbar\omega$ has been used and the integral is $\pi^4/15$.

Leakage of photons from a small hole (see Sec. 6.4 in Pathria's book) gives the power per unit area

$$\frac{dP}{da} = \frac{U}{V}\frac{c}{4} = \sigma T^4 \tag{8.71}$$

with

$$\sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} = 5.670\times 10^{-8}\ \mathrm{Wm^{-2}K^{-4}}\,, \tag{8.72}$$

which is the Stefan-Boltzmann law.

We now derive the thermodynamics. Consider the grand partition function of a photon gas, with $z=1$,

$$\ln\mathcal{Q} = -\sum_\varepsilon \ln(1-e^{-\beta\varepsilon})\,. \tag{8.73}$$

In the continuum limit

$$\begin{aligned}\sum_\varepsilon &\to 2\times\frac{V}{(2\pi)^3}d^3k \\ &= \frac{2V}{(2\pi)^3}4\pi k^2 dk \\ &= \frac{2V}{(2\pi)^3}4\pi\frac{\omega^2 d\omega}{c^3} \\ &= \frac{2V}{(2\pi)^3}\frac{4\pi}{c^3}\frac{\varepsilon^2 d\varepsilon}{\hbar^3} \\ &= \frac{8\pi V}{h^3c^3}\varepsilon^2 d\varepsilon\,. \end{aligned} \tag{8.74}$$

We obtain

$$\begin{aligned}
\ln \mathcal{Q} &= -\frac{8\pi V}{h^3c^3}\int_0^\infty d\varepsilon\varepsilon^2 \ln(1-e^{-\beta\varepsilon}) \\
&= -\frac{8\pi V}{h^3c^3}\left[\frac{\varepsilon^3}{3}\ln(1-e^{-\beta\varepsilon})\bigg|_0^\infty - \frac{\beta}{3}\int_0^\infty d\varepsilon\frac{\varepsilon^3}{e^{\beta\varepsilon}-1}\right] . \qquad (8.75)
\end{aligned}$$

The first integral vanishes and the second integral is $\pi^4/(15\beta^4)$. Therefore

$$\ln \mathcal{Q} = \frac{PV}{kT} = \frac{8\pi^5 V}{45h^3c^3}\frac{(kT)^4}{kT} , \qquad (8.76)$$

$$\Rightarrow PV = \frac{1}{3}U . \qquad (8.77)$$

Notice that this can also be obtained from kinetic consideration, with $u(\varepsilon)$ the energy density and $p(\varepsilon) = [u(\varepsilon)/4\pi c]\hat{\Omega}$ the momentum density/solid angle. $P(\varepsilon)$ is two times the flux of momentum/unit area. We have

$$\begin{aligned}
P(\varepsilon) &= 2\times\int d\Omega\hat{n}\cdot\vec{p}(c\hat{\Omega}\cdot\hat{n}) \\
&= 4\pi\int_0^1 d\mu\frac{u(\varepsilon)}{4\pi c}\mu\times c\mu, \quad (\mu=\cos\theta) \\
&= \frac{u(\varepsilon)}{3} . \qquad (8.78)
\end{aligned}$$

The Helmholtz free energy is

$$A = E - TS = (TS - PV + \mu N) - TS = -PV , \qquad (8.79)$$

since $\mu = 0$.

$$\Rightarrow A = -\frac{1}{3}U . \qquad (8.80)$$

The entropy is

$$S = \frac{U-A}{T} = \frac{4}{3}\frac{U}{T} \propto VT^3 . \qquad (8.81)$$

The specific heat is

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = 3S = \frac{4U}{T} . \qquad (8.82)$$

Notice that we do not use $T(\partial S/\partial T)_{V,N}$. Why? Similarly,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{4U}{T}\,. \tag{8.83}$$

For a reversible adiabatic process $S \propto VT^3$ is constant. But $P \propto T^4 \Rightarrow PV^{4/3}$ is constant, which is an adiabat.

The average number of photons is

$$\begin{aligned}\overline{N} &= \int d\omega \frac{U(\omega)}{\hbar\omega} \\ &= \frac{V}{\pi^2 c^3}\int_0^\infty d\omega \frac{\omega^2}{e^{\beta\hbar\omega}-1} \\ &= \frac{V}{\pi^2 c^3}\frac{(kT)^3}{\hbar^3}\int_0^\infty dx \frac{x^2}{e^x-1} \\ &= V\frac{2\zeta(3)(kT)^3}{\pi^2 c^3 \hbar^3}\,, \end{aligned} \tag{8.84}$$

where the integral is $\Gamma(3)g_3(1) = 2\zeta(3)$.

Now consider density fluctuations. From the section on the grand canonical ensemble (Sec. 4.5 in Pathria),

$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{kT}{V}\kappa_T\,, \tag{8.85}$$

with $\kappa_T = (1/V)(\partial V/\partial P)_T$, which approaches ∞ for photons. This is because $P \propto T^4$ is independent of V, and $\partial P/\partial V|_T = 0 \Rightarrow \partial V/\partial P|_T \to \infty$. Remember that this came from

$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{kT}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}\,, \tag{8.86}$$

where $n = N/V$. But this does not apply here because $\mu = 0$ for photons.

Alternatively, we can compute $\overline{\Delta N^2}$ from the statistics.

$$P_\omega(n) = \frac{(\langle n_\omega\rangle)^n}{[\langle n_\omega\rangle + 1]^{n+1}}\,, \tag{8.87}$$

with

$$\langle n_\omega\rangle = \frac{1}{e^{\beta\hbar\omega}-1}\,. \tag{8.88}$$

For a given mode (and polarisation)

$$\begin{aligned}
\bar{n} &= \sum_{n=0}^{\infty} n P_\omega(n) \\
&= \sum_{n=0}^{\infty} n \frac{1}{x+1}\left(\frac{x}{x+1}\right)^n, \quad x = \langle n_\omega \rangle \\
&= \frac{1}{x+1}\sum_{n=0}^{\infty} n\alpha^n, \quad \alpha = \frac{x}{x+1} \\
&= \frac{1}{x+1}\alpha\frac{\partial}{\partial\alpha}\sum_{n=0}^{\infty}\alpha^n \\
&= \frac{1}{x+1}\alpha\frac{\partial}{\partial\alpha}\frac{1}{1-\alpha} \\
&= x = \langle n_\omega \rangle , \qquad (8.89)
\end{aligned}$$

as expected. Similarly,

$$\overline{n^2} = \frac{1}{x+1}\left(\alpha\frac{\partial}{\partial\alpha}\right)^2 \sum_{n=0}^{\infty}\alpha^n \qquad (8.90)$$

$$= \langle n_\omega \rangle (2\langle n_\omega \rangle + 1) . \qquad (8.91)$$

Therefore

$$\frac{\overline{(\Delta n_\omega)^2}}{\bar{n}_\omega^2} = \frac{\langle n_\omega \rangle + 1}{\langle n_\omega \rangle} . \qquad (8.92)$$

8.3 Photon Statistics in Canonical Ensemble

Photon statistics should not be treated in the grand canonical formalism because the number of photons is not conserved. In the canonical ensemble formalism, the partition function is

$$\begin{aligned}
Q &= \sum_{n_0, n_1, \cdots} \left(e^{-\beta\varepsilon_0}\right)^{n_0}\left(e^{-\beta\varepsilon_1}\right)^{n_1}\cdots \\
&= \prod_{i=0}^{\infty}\left(\frac{1}{1-e^{-\beta\varepsilon_i}}\right) . \qquad (8.93)
\end{aligned}$$

The Helmholtz free energy is

$$\begin{aligned}
A &= -kT\ln Q \\
&= kT\sum_{i=0}^{\infty}\ln(1-e^{-\beta\varepsilon_i}) . \qquad (8.94)
\end{aligned}$$

Since $A = U - TS$, where $U = TS - PV \Rightarrow A = -PV$,

$$PV = -kT \sum_{i=0}^{\infty} \ln(1 - e^{-\beta \varepsilon_i}) \,. \tag{8.95}$$

This agrees with

$$q = \frac{PV}{kT} = -\sum_{i=0}^{\infty} \ln(1 - z e^{-\beta \varepsilon_i}) \tag{8.96}$$

obtained in the grand canonical formalism by setting $z = 1$.

8.4 Problems

Chapter 9

Ideal Fermi Systems

In this case z is unrestricted: $0 \leq z < \infty$. The Pauli exclusion principle applies, and there is no Bose-Einstein condensate.

9.1 Thermodynamic Behaviour of an Ideal Fermi Gas

For an ideal Fermi gas

$$\ln \mathcal{Q} = \frac{PV}{kT} = \sum_s \ln(1 + ze^{-\beta\varepsilon_s}) \tag{9.1}$$

and

$$N = \sum_s \langle n_s \rangle = z \left(\frac{\partial}{\partial z} \ln \mathcal{Q} \right)_{V,\beta} = \sum_s \frac{1}{z^{-1} e^{\beta\varepsilon_s} + 1} \,. \tag{9.2}$$

Replace the summation by an integration

$$\sum_s \to gV \frac{2\pi(2m)^{3/2}}{h^3} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \,, \tag{9.3}$$

where g is a statistical weight due to internal structure, like spin. The rest is the same as the Bose-Einstein case.

$$\frac{PV}{kT} = gV 2\pi \frac{(2m)^{3/2}}{h^3} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \ln(1 + ze^{-\beta\varepsilon}) \,, \tag{9.4}$$

$$\frac{P}{kT} = \frac{g}{\lambda^3} f_{5/2}(z) \,. \tag{9.5}$$

Similarly

$$\frac{N}{V} = g 2\pi \frac{(2m)^{3/2}}{h^3} \int_0^\infty \frac{d\varepsilon \sqrt{\varepsilon}}{z^{-1} e^{\beta\varepsilon} + 1} = \frac{g}{\lambda^3} f_{3/2}(z) \,, \tag{9.6}$$

with

$$\lambda^3 = \frac{h^3}{(2\pi mkT)^{3/2}} \tag{9.7}$$

the mean thermal wavelength of the particles and

$$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x + 1} = z - \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} - \frac{z^4}{4^\nu} \cdots . \tag{9.8}$$

is the Fermi-Dirac function. The equation of state can be obtained by eliminating z in Eq. (9.5) and Eq. (9.6).

Now consider the derived quantities.

$$\begin{aligned} U &= -\left(\frac{\partial}{\partial\beta}\ln\mathcal{Q}\right)_{V,z} \\ &= kT^2\left(\frac{\partial}{\partial T}\frac{PV}{kT}\right)_{V,z} \\ &= kT^2\frac{\partial}{\partial T}\left[V\frac{g}{\lambda^3}f_{5/2}(z)\right]_{V,z} \\ &= kT^2 V\frac{g}{\lambda^3}f_{5/2}(z)\frac{3}{2}\frac{1}{T} \\ &= \frac{3}{2}PV\,. \end{aligned} \tag{9.9}$$

which again is a universal result.

Differentiating Eq. (9.6) and using making use of

$$\frac{\partial f_\nu}{\partial z} = \frac{1}{z}f_{\nu-1} \tag{9.10}$$

gives

$$\left(\frac{\partial}{\partial T}\frac{N}{V}\right)_{N,V} = \left(\frac{\partial}{\partial T}\frac{gf_{3/2}(z)}{\lambda^3}\right)_{N,V} = 0 \tag{9.11}$$

$$\Rightarrow \frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_{N,V} = -\frac{3}{2T}\frac{f_{3/2}(z)}{f_{1/2}(z)} \tag{9.12}$$

The specific heat is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left[\frac{\partial}{\partial T}\left(\frac{3}{2}NkT\frac{f_{5/2}(z)}{f_{3/2}(z)}\right)\right]_{N,V} . \tag{9.13}$$

$$\Rightarrow \frac{C_V}{Nk} = \frac{15}{4}\frac{f_{5/2}}{f_{3/2}} - \frac{9}{4}\frac{f_{3/2}}{f_{1/2}}\,. \tag{9.14}$$

The Helmholtz free energy is

$$\begin{aligned} A &= N\mu - PV \\ &= NkT\ln z - \left[\frac{kTg}{\lambda^3}f_{5/2}(z)\right]\left[\frac{N\lambda^3}{g}\frac{1}{f_{3/2}(z)}\right] \\ &= NkT\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right]\,. \end{aligned} \tag{9.15}$$

The entropy is given by

$$U - ST + PV = N\mu \tag{9.16}$$

$$\begin{aligned} \Rightarrow S &= \frac{U-A}{T} \\ &= \frac{3}{2}\frac{PV}{T} - Nk\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \\ &= Nk\left[\frac{5}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z\right]\,. \end{aligned} \tag{9.17}$$

Properties for Fermi gas in terms of n, T, means we need $z = z(n,T)$. If the density of the gas is very low and/or its temperature is very high, then

$$n = \frac{g}{\lambda^3}f_{3/2}(z) \Rightarrow f_{3/2}(z) = \frac{nh^3}{g(2\pi mkT)^{3/2}} \ll 1\,. \tag{9.18}$$

Since $f_\nu(z) = z - z^2/2^\nu + z^3/3^\nu - \ldots$ and $f_{3/2}(z) \ll 1$, $f_\nu(z) \approx z$ because $z \ll 1$.

Therefore

$$\frac{P}{kT} = \frac{g}{\lambda^3}f_{5/2}(z) \approx \frac{g}{\lambda^3}z \quad \text{and} \quad n \approx \frac{g}{\lambda^3}z\,. \tag{9.19}$$

$$\frac{P}{kT} \approx n \Rightarrow P \approx \frac{NkT}{V}\,. \tag{9.20}$$

$$U = \frac{3}{2}PV \approx \frac{3}{2}NkT\,. \tag{9.21}$$

$$\frac{C_V}{Nk} = \frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} \approx \frac{15}{4} - \frac{9}{4} = \frac{3}{2} \Rightarrow C_V \approx \frac{3}{2}Nk\,. \tag{9.22}$$

$$A = NkT\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \approx NkT\left[\ln\left(\frac{n\lambda^3}{g}\right) - 1\right]\,. \tag{9.23}$$

$$S = Nk\left[\frac{5}{2}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z\right] = Nk\left[\frac{5}{2} - \ln\left(\frac{n\lambda^3}{g}\right)\right]\,. \tag{9.24}$$

For $z < 1$, but not $z \ll 1$, we can use a series approximation. Proceed as with Bose-Einstein statistics, the viral expansion is

$$\frac{PV}{NkT} = \sum_{l=1}^{\infty} (-1)^{l-1} a_l \left(\frac{\lambda^3}{gv}\right)^{l-1}, \tag{9.25}$$

where a_l is the same as for the Bose-Einstein case. Similarly for other thermodynamic quantities.

Consider the low temperature limit.

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1}e^{\beta\varepsilon}+1} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1} \approx H(\mu-\varepsilon)\,, \tag{9.26}$$

where H is the Heavyside step function, which is 1 for $\varepsilon < \mu$ (all states filled), 0 for $\varepsilon > \mu$ (all states empty). Let $\epsilon_F = \mu_0$ be the Fermi energy, which is the chemical potential at $T = 0$. Using this, we can approximate the integral for the number density (recall $x = \beta\varepsilon$):

$$\begin{aligned} \frac{N}{V} &= \frac{g}{\lambda^3}\frac{1}{\Gamma(3/2)}\int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^x+1} \\ &= \frac{g}{\lambda^3}\frac{1}{\Gamma(3/2)}\frac{1}{(kT)^{3/2}}\int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-\mu)/kT}+1} \\ &= g\frac{(2\pi mkT)^{3/2}}{h^3}\frac{2}{\sqrt{\pi}}\frac{1}{(kT)^{3/2}}\int_0^{\varepsilon_F} d\varepsilon\sqrt{\varepsilon} \\ &= \frac{4\pi}{3}g\frac{(2m)^{3/2}}{h^3}\varepsilon_F^{3/2} = \frac{4\pi}{3}\frac{g}{h^3}p_F^3\,. \end{aligned} \tag{9.27}$$

$$\Rightarrow \varepsilon_F \equiv \left(\frac{3N/V}{4\pi g}\right)^{2/3}\frac{h^2}{2m} \tag{9.28}$$

is the Fermi energy (low T limit).

For the energy (low T limit),

$$\begin{aligned} U &= \frac{3}{2}PV = \frac{3}{2}VkT\frac{g}{\lambda^3}f_{5/2}(z) \\ &= \frac{3}{2}V\frac{g}{h^3}(2\pi m)^{3/2}\frac{1}{\Gamma(5/2)}\int_0^\infty d\varepsilon\frac{\varepsilon^{3/2}}{e^{(\varepsilon-\mu)/kT}+1} \\ &= \frac{3}{2}V\frac{g}{h^3}(2\pi m)^{3/2}\frac{4}{3\sqrt{\pi}}\int_0^{\varepsilon_F} d\varepsilon\varepsilon^{3/2} \\ &= \frac{3}{5}V\frac{4\pi}{3}g\frac{(2m)^{3/2}}{h^3}\varepsilon_F^{5/2}. \end{aligned} \tag{9.29}$$

The energy per particle is

$$\frac{U}{N} = \frac{3}{5}\varepsilon_F\,. \tag{9.30}$$

9.2 Pauli Paramagnetism

Consider the equilibrium state of a gas of noninteracting fermions in the presence of an external magnetic field $\vec{B}$. The main problem is to determine the net magnetic moment $\vec{M}$ acquired by the gas as a function of $\vec{B}$ and T, and then calculate the susceptibility $\chi(T)$.

In general, the magnetic behaviour of a Fermi gas is determined jointly by the intrinsic magnetic moment of the particles (Pauli paramagnetism) and the quantization of their orbits (Landau diamagnetism). If the spin-orbit interaction is negligible, the resultant behaviour is obtained by a simple addition of the two effects.

Assuming spin-1/2 particles, for particles with spin up

$$\varepsilon_+ = \frac{p_+^2}{2m} - \mu B \,. \tag{9.31}$$

For particles with spin down

$$\varepsilon_- = \frac{p_-^2}{2m} + \mu B \,. \tag{9.32}$$

At $T = 0$, the energy is minimum. All levels are filled from 0 to ε_F. The kinetic energy varies between 0 and $\varepsilon_F \mp \mu B$. The maximum momentum is $p_\pm = \sqrt{2m(\varepsilon_F \pm \mu B)}$. In equilibrium,

$$\frac{p_+^2}{2m} - \mu B = \frac{p_-^2}{2m} + \mu B \,, \tag{9.33}$$

$$p_+ = p_- \left[1 + \frac{4m\mu B}{p_-^2}\right]^{1/2} , \tag{9.34}$$

$$p_- = p_+ \left[1 - \frac{4m\mu B}{p_+^2}\right]^{1/2} . \tag{9.35}$$

Now, consider the numbers N_+ and N_- of electrons with $\vec{\mu}$ up and down, respectively:

$$N_\pm = V\frac{4\pi}{3h^3}p_\pm^3 \,. \tag{9.36}$$

The total number of particles per unit volume is

$$\begin{aligned} n = \frac{N_+ + N_-}{V} &= \frac{4\pi}{3h^3}(p_+^3 + p_-^3) \\ &= \frac{4\pi}{3h^3}\left[p_-^3\left(1 + \frac{4m\mu B}{p_-^2}\right)^{3/2} + p_-^3\right] \\ &\approx \frac{4\pi}{3h^3}2p_-^3\left(1 + \frac{3m\mu B}{p_-^2}\right) \\ &\approx \frac{8\pi}{3h^3}p_-^3\left(1 + \frac{3\mu B}{2\varepsilon_F}\right) , \end{aligned} \tag{9.37}$$

where a weak field approximation has been made. Similarly,

$$n \approx \frac{8\pi}{3h^3} p_+^3 \left(1 - \frac{3}{2}\frac{\mu B}{\varepsilon_F}\right) . \tag{9.38}$$

Inverting gives

$$p_\pm^3 \approx \frac{3h^3}{8\pi} n \left(1 \pm \frac{3}{2}\frac{\mu B}{\varepsilon_F}\right) . \tag{9.39}$$

The magnetisation (week field approximation) is then given by

$$\begin{aligned} M = \frac{N_+ - N_-}{V}\mu &= \frac{4\pi}{3h^3}(p_+^3 - p_-^3)\mu \\ &\approx \frac{4\pi}{3h^3}\left(\frac{3h^3}{8\pi}n\right)\left(3\frac{\mu B}{\varepsilon_F}\mu\right) \\ &\approx \frac{3\mu^2 B}{2\varepsilon_F} n \, . \end{aligned} \tag{9.40}$$

Using

$$n = \frac{8\pi}{3h^3}(2m\varepsilon_F)^{3/2}, \tag{9.41}$$

we can also write

$$M \approx \frac{4\pi\mu^2(2m)^{3/2}\varepsilon_F^{1/2}}{h^3} B \, . \tag{9.42}$$

In the weak-field approximation

$$\chi_{T\to 0} = \lim_{B\to 0}\left(\frac{M}{B}\right) \to \frac{4\pi\mu^2(2m)^{3/2}\varepsilon_F^{1/2}}{h^3} = \frac{3}{2}\frac{n\mu^2}{\varepsilon_F} \, . \tag{9.43}$$

Previously we obtained the classical, or high-temperature, results

$$\chi_{T\to\infty} = \frac{n\mu^2}{kT} \, . \tag{9.44}$$

Thus

$$\frac{\chi_{T\to 0}}{\chi_{T\to\infty}} = \mathcal{O}\left(\frac{kT}{\varepsilon_F}\right) . \tag{9.45}$$

9.3 Problems

Chapter 10

Thermodynamics of the Early Universe

The Big Bang is the hypothesis that the universe began abruptly 13.75 ± 0.11 billion years ago (accurate to 0.8%). Thermodynamics and statistical mechanics play a role in our understanding of the sequence of transitions that the universe went through shortly after the Big Bang. These transitions left signatures that can be exploited to learn about the earliest moments of the universe.

10.1 Observational Evidence of the Big Bang

There are three main observations that support the Big Bang.

10.1.1 Expanding Universe

Nearly every galaxy in the universe is moving away from every other galaxy and the recessional velocities are almost linearly dependent on the distance between the galaxies. This is expressed by the Hubble-Fridmann relation:

$$v = \frac{da}{dt} = Ha = \sqrt{\frac{8\pi G u}{3c^2}}\, a\,, \tag{10.1}$$

where a is the distance between any two points in space that grows with time as the universe expands, v is the recessional velocity, G is the universal constant of gravitation, and u is the energy density of the universe. The Hubble parameter H is the characteristic expansion rate and is of the order of the inverse age of the universe. The particular form of Eq. (10.1) assumes that the energy density u is equal to the critical value so that space-time is flat, which appears to be the case. This means the universe is balanced between expanding forever and recollapsing due to gravity. The measured value of the Hubble parameter is $H_0 = 74.2 \pm 3.6$ $\mathrm{km\,s^{-1}\,Mpc^{-1}}$ (accurate to 5%).

10.1.2 Microwave Background

A nearly uniform and isotropically distribution of microwave radiation is coming from deep space with a blackbody average temperature of $T_{\text{CMB}} = 2.725 \pm 0.002$ K. This cosmic microwave background (CMB) is identified as the remnant blackbody radiation from the era following the Big Bang.

The CMB represents the photons that were in thermal equilibrium with the high temperature plasma that existed from the very first moments of the universe until it cooled down to approximately 3 000 K about 380 000 years after the Big Bang. As the temperature fell below 3 000 K, the electrons and protons in the plasma combined for the first time into neutral hydrogen atoms, a period known as the era of recombination. After this era of the last scattering of photons from free electrons, the quantum structure of the atoms prevented them from absorbing radiation except at their narrow spectral frequencies, so the universe became transparent and the blackbody radiation quickly fell out of equilibrium with the neutral atoms. As the universe continued to expand, the wavelengths of the blackbody radiation grew linearly with the expansion scale of the universe a. The photon number density fell as a^{-3} and the energy density as a^{-4}, so the Planck distribution was preserved with a blackbody temperature that scales as $T(t)a(t) = \text{constant}$.

Measurements of the Hubble parameter, the temperature and temperature fluctuations of the CMB allow a determination of the current total energy density of the universe and its composition. The current energy density of the universe is

$$u = \frac{3c^2H_0^2}{8\pi G} = 8.36 \times 10^{-10}\ \mathrm{J\,m^{-3}}\,. \tag{10.2}$$

It is comprised of 72.8% dark energy, 22.7% dark matter, and 4.56% baryonic matter (protons and neutrons). This gives a baryon number density $n_B = 0.26\ \mathrm{m}^{-3}$. The number density of photons in a blackbody enclosure as a function of temperature is

$$n_\gamma(T) = \frac{2\zeta(3)}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3 . \tag{10.3}$$

At the current temperature of 2.725 K, this gives a CMB photon number density of $n_\gamma = 4.10 \times 10^8\ \mathrm{m}^{-3}$, so the current baryon to photon ratio is

$$\eta = \frac{n_B}{n_\gamma} \approx 6 \times 10^{-10}\,. \tag{10.4}$$

The ratio η has remained constant as the universe has expanded since both these quantities scale as $a^{-3}(t)$. The numerical value of η plays a very important role in the thermal evolution of the early universe.

10.1.3 Relative Abundances of Light Elements

The relative abundances of the light elements ^{1}H, ^{2}H, ^{3}He, ^{4}He, ^{7}Li and so on created during the first few minutes of the universe are sensitive functions of the baryon-to-photon ratio η.

10.2 Evolution of the Temperature of the Universe

As the universe expanded and cooled, the cooling rate was proportional to the Hubble parameter, that is, of the order of the inverse of the age of the universe at that point in its expansion. This led to a sequence of important events when different particles and interactions fell out of equilibrium with the gas of the background photons. The neutrinos and neutron-proton conversion reactions fell out of equilibrium at $t \approx 1$ s. Nuclear reactions that formed light nuclei fell out of equilibrium at $t \approx 3$ min. Neutral atoms fell out of equilibrium at $t \approx 380\,000$ yr. All these degrees of freedom froze out when the reaction rates that had kept them in equilibrium with the blackbody photons fell far below the cooling rate of the expanding universe. Each components that fell out of equilibrium left behind a marker of the properties of the universe characteristic of that era. It is these markers that provide evidence of the properties and behaviour of the universe during its earliest moments.

From the first moments of the universe up until the recombination era 380 000 years later, the cosmic plasma was in thermal equilibrium with the blackbody radiation through Thomson scattering. Due to the high density of charged particles, the photon scattering mean free time was much shorter than the time scale for temperature changes of the universe as it expanded and cooled, which kept the plasma in thermal equilibrium with the photons. For the first few hundred thousand years of its expansion, the energy density of the universe was dominated by photons and other relativistic particles. This is because the energy density of the blackbody radiation scales as a^{-4}, whereas the energy density of non-relativistic matter scales as a^{-3}.

At early times, radiation dominated the energy density, so $T \sim t^{-1/2}$. At later times ($t > 10^{13}$ s) nonrelativistic matter dominated the energy density, so $T \sim t^{-2/3}$. In the current dark energy dominated stage, the universe is beginning to expand exponentially with times, so the photon temperature is beginning to fall exponentially. Temperature of the blackbody photons as a function of the age of the universe is shown in Table 10.1

Table 10.1: Temperature versus age of the universe.

Time (s)	Temperature (K)	Event
0.01	1×10^{11}	strong interaction not dominate
0.1	3×10^{10}	
1.0	1×10^{10}	weak interactions out of equilibrium
12.7	3×10^{9}	
168	1×10^{9}	light nuclei out of equilibrium
1980	3×10^{8}	electrons and positrons out of equlibrium
1.78×10^{4}	10^{8}	
1.20×10^{13}	3000	photons out of equilibrium
4.34×10^{17}	2.725	today

During the first one-hundredth of a second, the universe expanded and cooled from its singular beginning to a temperature of about 10^{11} K. The physics from this time onward was controlled by the weak and electromagnetic interactions. The strong interactions could be ignored since the baryon to photon ratio was so small and the temperature was too low to create additional hadrons. We will follow the thermodynamic behaviour of the universe from $t = 0.01$ s when the temperature was 10^{11} K to $t = 380\,000$ yr when the temperature fell below $3\,000$ K. At that point neutral atoms formed, photon scattering ended, and the universe became transparent to radiation. After recombination and last scattering there were no new sources of radiation in the universe since the baryonic matter consisted entirely of neutral atoms. This state of affairs lasted until atoms were first reionised by the gravitational clumping that formed the first stars and galaxies 100 to 200 million years after the Big Bang. This reionization epoch ended the so-called cosmic dark ages.

10.3 Relativistic Electrons, Positrons, and Neutrinos

During the earliest moments of the universe, the temperature was high enough to create several kinds of relativistic particles and antiparticles. If $kT \gg mc^2$, then particle-antiparticle pairs each with mass m can be created from photon-photon interactions. At these temperatures, almost all the particles that are created will have an energy-momentum (dispersion) relation described by the relativistic limit, namely $\varepsilon_k \approx \hbar ck$, where $\hbar k$ is the magnitude of the momentum. This relation applies to photons, neutrinos, antineutrinos, electrons and positrons. The threshold for electron-positron pair formation is $m_e c^2/k = 5.9 \times 10^9$ K. The relativistic dispersion relation gives essentially the same density of states for all species of relativistic particles:

$$a(\varepsilon) = \frac{g_s}{(2\pi)^3} \int \delta(\varepsilon - \varepsilon_k) d\vec{k} = \frac{4\pi g_s}{(2\pi)^3} \int_0^\infty k^2 \delta(\varepsilon - \hbar ck) dk = \frac{g_s \varepsilon^2}{2\pi^2 (\hbar c)^3}\,, \tag{10.5}$$

where g_s is the spin degeneracy. Photons have a spin degeneracy $g_s = 2$ (left and right circular polarisation). The other species are all spin-1/2 fermions. Electrons and positrons have spin degeneracy $g_s = 2$, while neutrinos and antineutrions have spin degeneracy $g_s = 1$ since all neutrinos have left-handed helicity.

During this era, because of the charge neutrality of the universe and the small size of the baryon to photon ratio η, the number density of the electrons and positrons were nearly equal, so their chemical potentials were both rather small. Assuming that the net lepton number of the universe is also small, the same applies to the neturinos and antineutrinos. We have shown that the chemical potential for photons is exactly zero. The pressure, number density, energy density, and entropy density of a relativistic gas of fermions (+) or bosons (−) with zero chemical potential are given by

$$\begin{aligned}
P(T) &= \pm kT \int a(\varepsilon)\ln(1 \pm e^{-\beta\varepsilon})d\varepsilon = \frac{g_s (kT)^4}{2\pi^2(\hbar c)^3}\int_0^\infty x^2 \ln(1\pm e^{-x})dx\,, && (10.6)\\
n(T) &= \int a(\varepsilon)\frac{1}{e^{\beta\varepsilon}\pm 1}d\varepsilon = \frac{g_s}{2\pi^2}\left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty \frac{x^2}{e^x \pm 1}dx\,, && (10.7)\\
u(T) &= \int a(\varepsilon)\frac{\varepsilon}{e^{\beta\varepsilon}\pm 1}d\varepsilon = \frac{g_s (kT)^4}{2\pi^2(\hbar c)^3}\int_0^\infty \frac{x^3}{e^x \pm 1}dx\,, && (10.8)\\
s(T) &= \left(\frac{\partial P}{\partial T}\right)_\mu = \frac{2g_s k}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty x^2 \ln(1\pm e^{-x})dx\,. && (10.9)
\end{aligned}$$

Using the values of the Bose integrals, we arrive at the following expressions for the blackbody photons:

$$\begin{aligned}
P_\gamma(T) &= \frac{\pi^2}{45}\frac{(kT)^4}{(\hbar c)^3}\,, && (10.10)\\
n_\gamma(T) &= \frac{2\zeta(3)}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3\,, && (10.11)\\
u_\gamma(T) &= \frac{\pi^2}{15}\frac{(kT)^4}{(\hbar c)^3}\,, && (10.12)\\
s_\gamma(T) &= \frac{4\pi^2 k}{45}\left(\frac{kT}{\hbar c}\right)^3\,. && (10.13)
\end{aligned}$$

All relativistic species with $\mu = 0$ have the same power law temperature dependences for the pressure, energy density, and entropy density, as the photons, while the Fermi and Bose integrals are the same except for a constant prefactor:

$$\int_0^\infty \frac{x^{n-1}}{e^x+1}dx = \left(1-\frac{1}{2^{n-1}}\right)\int_0^\infty \frac{x^{n-1}}{e^x-1}dx\,. \qquad (10.14)$$

The contributions to the pressure, energy density, and entropy density result from counting the spin degeneracies, the number of particles and antiparticles, and accounting for the different Fermi/Bose factors (1 for bosons, 7/8 for fermions). The photons, three generations of neutrinos (electron, muon, and tau neutrinos and their antiparticles), and the electrons and positrons contribute to the total pressure, number density, energy density, and entropy density in the proportions shown in Table 10.2. The counting is done relative to the contribution per spin state of the photons. The contributions to the number density are the same except that the Fermi/Bose factor is now 3/4.

The totals then are

Table 10.2: Relativistic contributions to pressure, energy density, and entropy density.

Particle	Fermi/Bose Factor	Spin Degeneracy	Number of Species	$2P_{\text{total}}/P_\gamma$
γ	1	2	1	2
ν_e, ν_μ, ν_τ	7/8	1	3	21/8
$\bar{\nu}_e, \bar{\nu}_\mu, \bar{\nu}_\tau$	7/8	1	3	21/8
e^-	7/8	2	1	7/4
e^+	7/8	2	1	7/4

$$P_{\text{total}}(T) = \left(2+\frac{21}{4}+\frac{7}{2}\right)\frac{P_\gamma(T)}{2} = \frac{43}{8}P_\gamma(T)\,, \tag{10.15}$$

$$u_{\text{total}}(T) = \left(2+\frac{21}{4}+\frac{7}{2}\right)\frac{u_\gamma(T)}{2} = \frac{43}{8}u_\gamma(T)\,, \tag{10.16}$$

$$s_{\text{total}}(T) = \left(2+\frac{21}{4}+\frac{7}{2}\right)\frac{s_\gamma(T)}{2} = \frac{43}{8}s_\gamma(T)\,, \tag{10.17}$$

$$n_{\text{total}}(T) = \left(2+\frac{9}{2}+3\right)\frac{n_\gamma(T)}{2} = \frac{19}{4}n_\gamma(T)\,. \tag{10.18}$$

The density of the universe was high enough in this era, so the weak and electromagnetic interaction rates kept all these species in thermal equilibrium with one other. Therefore, as the universe expanded adiabatically, the entropy in a comoving volume of linear size a remained constant as the volume expanded from some initial value a_0^3 to a final volume a_1^3: $s_{\text{total}}(T_0)a_0^3 = s_{\text{total}}(T_1)a_1^3$. Since the entropy density is proportional to T^3, the temperature and length scale at time t are related by $T(t)a(t) = \text{constant}$. This temperature scaling relation and Eq. (10.1) leads to the temperature of the universe as a function of the age of the universe t during this era as

$$T(t) = \sqrt{\frac{0.992\ \text{s}}{t}} \times 10^{10}\ \text{K}\,. \tag{10.19}$$

10.4 Neutron Fraction

During the first second of the universe, when $T > 10^{10}$ K, and before protons and neutrons combined into nuclei, the weak interaction kept the free neutrons and protons in thermal beta-equilibrium with each other and with the protons, neutrinos, electrons and positrons through the processes

$$
\begin{aligned}
n+\nu_e &\rightleftharpoons p+e^-+\gamma\,, &(10.20)\\
n+e^+ &\rightleftharpoons p+\nu+\gamma\,, &(10.21)\\
n &\rightleftharpoons p+e^-+\nu+\gamma\,. &(10.22)
\end{aligned}
$$

We can treat this as a chemical equilibrium process. Since the chemical potential of the photons, electrons, positrons, neutrinos, and antineutrinos are all zero, the neutron and proton chemical potential must be equal at equilibrium:

$$\mu_n = \mu_p\,. \tag{10.23}$$

At these temperatures ($\approx 10^{11}$ K) and densities ($\approx 10^{32}$ m^{-3}), the protons and neutrons can be treated as classical nonrelativistic ideal gas. We use

$$\mu_A = \left(\frac{\partial A}{\partial N_A}\right)_{T,V} = \varepsilon_A + kT\ln(n_A\lambda_A^3) - kT\ln j_A(T)\,, \tag{10.24}$$

for the chemical potential of species A, where $j_A(T)$ is the partition function for the internal degrees of freedom of the species A and where $\lambda = h/\sqrt{2\pi mkT}$ is the thermal deBroglie wavelength. The spin-1/2 proton and neutron chemical potentials are

$$
\begin{aligned}
\mu_p &= m_pc^2 + kT\ln\left(n_p\lambda_p^3\right) - kT\ln 2\,, &(10.25)\\
\mu_n &= m_nc^2 + kT\ln\left(n_n\lambda_n^3\right) - kT\ln 2\,, &(10.26)
\end{aligned}
$$

The mass of the neutron is greater than the mass of the proton by $m_nc^2 - m_pc^2 = \Delta\varepsilon = 1.293$ MeV. Ignoring the small mass difference in the thermal deBroglie wavelength gives

$$n_n = n_p e^{-\beta\Delta\varepsilon}\,. \tag{10.27}$$

The baryon number density is the sum of the neutron and proton number densities

$$n_B = n_n + n_p\,, \tag{10.28}$$

so the equilibrium neutron fraction is given by

$$q = \frac{n_n}{n_B} = \frac{1}{e^{\beta\Delta\varepsilon}+1}\,. \tag{10.29}$$

The mass difference gives a crossover temperature $T_{np} = \Delta\varepsilon \approx 1.50\times 10^{10}$ K, so the neutron fractions drops from 46% when $T = 10^{11}$ K to 16% when $T = 9\times 10^9$ K at $t_1 \approx 1$ s. As the temperature fell below 10^{10} K ($kT = 0.86$ MeV), the weak interaction rate began to fall far below the cooling rate of the universe, so the baryons quickly fell out of equilibrium with the neutrinos. From that time onward the neutrons began to beta-decay with their natural radioactive decay lifetime of $\tau_n = 886$ s, so the neutron fraction fell exponentially:

$$q \approx 0.16 \exp\left(\frac{-(t-t_1)}{\tau_n}\right) \quad \text{for } t > t_1 = 1\ \text{s}\,. \tag{10.30}$$

By the time of nucleosynthesis, about 3.7 min later, the neutron fraction had dropped to $q \approx 0.12$. At that point, the remaining neutrons bound with protons to form deuterons and other light nuclei.

10.5 Annihilation of the Positrons and Electrons

About one second after the Big Bang, the temperature approached the crossover temperature T_e for creating-positron pairs:

$$kT_e = m_e c^2 = 0.511\ \text{MeV}\,, \tag{10.31}$$

where $T_e = 5.93 \times 10^9$ K. As the temperature fell below T_e, the rate of creating e^+e^- pairs began to fall below the rate at which pairs annihilate. The full relativistic dispersion relation for electrons is

$$\varepsilon_k = \sqrt{(\hbar ck)^2 + (m_e c^2)^2}\,, \tag{10.32}$$

which give the density of states

$$a_e(\varepsilon) = \frac{8\pi}{(2\pi)^3}\int_0^\infty k^2 \delta(\varepsilon - \varepsilon_k)dk = \frac{\varepsilon\sqrt{\varepsilon^2 - (m_e c^2)^2}}{\pi^2(\hbar c)^3} \quad \text{for } \varepsilon \geq m_c e^2\,. \tag{10.33}$$

Since the electrons and positrons were in equilibrium with the blackbody photons via the reaction $e^+ + e^- \rightleftharpoons \gamma + \gamma$, the equilibrium equation implied that the chemical potential of the species were related by

$$\mu_- + \mu_+ = 2\mu_\gamma = 0\,. \tag{10.34}$$

The ratio of the number density of electrons to photons was

$$\frac{n_-}{n_\gamma} = \frac{1}{2\zeta(3)}\int_{\beta m_e c^2}^\infty \frac{x\sqrt{x^2 - (\beta m_e c^2)^2}}{e^x e^{-\beta\mu_-} + 1}dx\,, \tag{10.35}$$

while the positron density ratio was

$$\frac{n_+}{n_\gamma} = \frac{1}{2\zeta(3)}\int_{\beta m_e c^2}^\infty \frac{x\sqrt{x^2 - (\beta m_e c^2)^2}}{e^x e^{\beta\mu_-} + 1}dx\,. \tag{10.36}$$

The electron and positron densities became unbalanced as the universe cooled.

Eventually all the positrons got annihilated leaving behind the electrons that currently remain. Charge neutrality of the universe required the difference between the number density of electrons and the number density of positrons to be equal to the number density of protons, $(1-q)n_B$, hence

$$\frac{n_- - n_+}{n_\gamma} = \frac{\sinh(\beta\mu_-)}{2\zeta(3)} \int_{\beta m_e c^2}^{\infty} \frac{x\sqrt{x^2 - (\beta m_e c^2)^2}}{\cosh(x) + \cosh(\beta\mu_-)} dx = (1-q)\eta \,. \tag{10.37}$$

We can use Eq. (10.37) to determine the electron chemical potential as a function of temperature numerically and then use that value to determine the electron and positron densities.

Initially, the electron and positron densities both decreased proportional to $\exp(-\beta m_e c^2)$ as the temperature fell below the electron-positron pair threshold, but they remained nearly equal to each other until $T \approx m_e c^2/k \ln[1/(1-q)\eta] \approx 3 \times 10^8$ K. At that temperature, the electron density began to level off at the proton density while the positron density continued to fall.

Using the baryon to photon ratio $\eta = 6 \times 10^{-10}$, we infer that during the first second of the universe that for every 1.7 billion positrons there must have been on extra electron. It is these few extra electrons that will combine with nuclei during the recombination era composing of all the atoms now present in the universe. All baryonic matter currently in the universe is the result of this initial asymmetry between matter and antimatter.

10.6 Neutrino Temperature

For temperatures above $T = 10^{10}$ K, the rates for the weak interaction reactions kept the neutrinos in beta-equilibrium with the electrons, positrons, and photons. Starting at time $t \approx 1$ s, when $T = 10^{10}$ K, the weak interaction rates began to fall far below the expansion rate of the universe so the neutrinos quickly fell out of equilibrium. Following the decoupling, the neutrinos expanded freely so the neutrino temperature scaled with the expansion length scale.

The system of electrons, positrons, and photons remained in thermal equilibrium with each other and expanded adiabatically during the electron-positron annihilation era from temperature $T_0 = 10^{10}$ K when the annihilations began, until temperature $T_1 = 3 \times 10^8$ K when nearly all the positrons had been annihilated. Since this was an adiabatic expansion, we can determine the temperature evolution using entropy conservation. Consider a comoving cubic volume that expanded from an initial linear size a_0 to a final size a_1 during the same time period. The total entropy in the comoving volume at temperature T_0 was due to the photons, electrons, and positrons

$$S(T_0) = \frac{11}{4} s_\gamma(T_0) a_0^3 \,, \tag{10.38}$$

while the entropy at temperature T_1 was due solely to the photons since, by then, nearly all of the electrons and positrons had been annihilated:

$$S(T_1) = s_\gamma(T_1) a_1^3 \,. \tag{10.39}$$

Entropy conservation during the adiabatic expansion relates the initial and final temperatures as

$$\left(\frac{11}{4}\right)^{1/3} T_0 a_0 = T_1 a_1 \,. \tag{10.40}$$

In essence, the entropy of the annihilating electrons and positrons was transferred to the photons. Since the neutrino and photon temperatures were equal before the electron-positron annihilation and the neutrinos expanded freely during the annihilation, the neutrino temperature decreased more than the photon temperature during the annihilation era:

$$T_{\nu 1} = \left(\frac{4}{11}\right)^{1/3} T_1 \,. \tag{10.41}$$

After the e^+e^- annihilation, both the neutrino and the photon temperatures evolved accordingly so the current temperature of the relic Big Bang neutrinos should be

$$T_\nu = \left(\frac{4}{11}\right)^{1/3} T_{\rm CMB} \approx 1.945 \text{ K} \,. \tag{10.42}$$

10.7 Primordial Nucleosynthesis

Light nuclei other than hydrogen first formed between 3 and 4 minutes after the Big Bang when the temperature had cooled to about 10^9 K. Prior to that time, the high-temperature blackbody radiation rapidly photodissociated any deuterium nuclei that happened to form. The first step for the formation of light nuclei from the protons and neutrons is the formation of deuterium because all of the rates for forming nuclei at these densities are dominated by two-body collisions. Once deuterons formed, most of these nuclei would have been quickly converted to helium and other more stable light nuclei in a series of two-body collisions with the remaining protons, neutrons, and with each other. The proton/neutron mixture at this time was about $q = 12\%$ neutrons and $1 - q = 88\%$ protons. By $t \approx 3$ min the temperature had fallen to $T \approx 10^9$ K so protons and neutrons could begin to bind themselves into deuterons via the process

$$p + n \rightleftharpoons d + \gamma \,. \tag{10.43}$$

The chemical equilibrium relation for this reaction is

$$\mu_p + \mu_n = \mu_d \,, \tag{10.44}$$

since the chemical potential of the blackbody photons is zero. At these temperatures and densities the protons, neutrons, and deuterons can be treated as classical ideal gases. The proton and neutron are spin-1/2 particles so they have two spin states each while the deuteron is spin-1 and has three spin states:

$$\begin{aligned}\mu_p &= m_pc^2 + kT\ln(n_p\lambda_p^3) - kT\ln 2\,, &(10.45)\\ \mu_n &= m_nc^2 + kT\ln(n_n\lambda_n^3) - kT\ln 2\,, &(10.46)\\ \mu_d &= m_dc^2 + kT\ln(n_d\lambda_d^3) - kT\ln 3\,. &(10.47)\end{aligned}$$

The binding energy of the deuteron is $\varepsilon_b = m_pc^2 + m_nc^2 - m_dc^2 = 2.20$ MeV. Since the deuteron is approximately twice as massive as protons or neutrons, the deuteron number density is given by

$$n_d = \frac{3}{4}n_pn_n\frac{\lambda_p^3\lambda_n^3}{\lambda_d^3}e^{\beta\varepsilon_b} \approx \frac{3}{\sqrt{2}}n_pn_n\lambda_p^3e^{\beta\varepsilon_b}\,. \tag{10.48}$$

The total number density of baryons is determined by the baryon to photon ratio η: $n_B = \eta n_\gamma = n_p + n_n + 2n_d$. The neutron number density is $qn_B = n_n + n_d$, so the deuteron fraction is given by

$$f_d = \frac{n_d}{n_B} = (1-q-f_d)(q-f_d)s\,, \tag{10.49}$$

where the parameter s is

$$s = \frac{12\zeta(3)}{\sqrt{\pi}}\left(\frac{kT}{m_pc^2}\right)^{3/2}\eta e^{\beta\varepsilon_b}\,. \tag{10.50}$$

The solution is

$$f_d = \frac{1+s-\sqrt{(1+s)^2-4s^2q(1-q)}}{2s}\,. \tag{10.51}$$

For high temperatures, s is small and $f_d \approx q(1-q)s$, while for low temperatures, s is large and $f_d \approx q$, that is, all the neutrons are bound into deuterons. The small values of the baryon to photon ratio η and ε_b/m_pc^2 delayed the nucleosynthesis until the temperature had fallen to

$$kT_n \approx \frac{\varepsilon_b}{\ln\left[\frac{1}{\eta}\left(\frac{m_pc^2}{\varepsilon_b}\right)^{3/2}\right]}\,, \tag{10.52}$$

providing the time for the neutron fraction to have decayed to $q = 0.12$.

The simple equilibrium calculation presented here assumes that no further reactions take place. Including the fast nonequilibrium two-body reactions, namely

$$\begin{aligned} d + d &\rightarrow {}^3\mathrm{H} + p + \gamma\,, &(10.53)\\ d + d &\rightarrow {}^3\mathrm{He} + n + \gamma\,, &(10.54)\\ d + {}^3\mathrm{H} &\rightarrow {}^4\mathrm{He} + n + \gamma\,, &(10.55)\\ d + {}^3\mathrm{He} &\rightarrow {}^4\mathrm{He} + p + \gamma\,, &(10.56)\end{aligned}$$

results in almost all of the deuterons being cooked into the very stable isotope ^{4}He and small amounts of other light nuclei. Since each ^{4}He nucleus is composed of two protons and two neutrons, this gives a helium mass fraction of $2q = 24\%$ and proton mass fraction of $1 - 2q = 76\%$. The complete calculation involves nonequilibrium effects modelled with rate equations for each of the nuclear interactions, including those for heavier isotopes, but that only changes the predicted concentration for ^{4}He slightly. The largest theoretical uncertainty is, remarkably, the uncertainty in the radioactive decay time of the neutron.

10.8 Recombination

After the nucleosynthesis took place in the first few minutes, the universe continued to cool, with the nuclei and electrons remaining as an ordinary plasma in thermal equilibrium with the photons. It took several hundred thousand years for the temperature to drop below the atomic ionisation energies of a few electron volts needed for nuclei to capture electrons and form atoms. Hydrogen was the last neutral species to form since it has the smallest ionisation energy of a Rydberg, 1 Ry = 13.6 eV. At first glance, one would think that atoms form when the temperature falls below $\mathrm{Ry}/k = 158\,000$ K but the huge number of photons per proton delayed recombination until $T \approx 3\,000$ K. Once all the electrons and protons formed into neutral hydrogen atoms, the universe became transparent due to the last scattering of radiation from free electrons. These CMB blackbody photons were suddenly free to propagate and hence have been travelling unscattered since that time.

The recombination reaction (that is, the inverse of the hydrogen photoionization reaction) is

$$p + e \rightleftharpoons H + \gamma \tag{10.57}$$

so the chemical equilibrium relation gives

$$\mu_p + \mu_e = \mu_H \tag{10.58}$$

since the chemical potential of the blackbody photons is zero. At the temperatures and densities prevailing during this era (a few thousand degrees Kelvin and only about 10^9 atoms per cubic meter), the electrons, protons, and hydrogen atoms can all be treated as classical ideal gases:

$$\begin{aligned}
\mu_p &= m_p c^2 + kT\ln(n_p\lambda_p^3) - kT\ln 2\,, && (10.59)\\
\mu_e &= m_e c^2 + kT\ln(n_e\lambda_e^3) - kT\ln 2\,, && (10.60)\\
\mu_H &= m_H c^2 + kT\ln(n_H\lambda_H^3) - kT\ln 4\,. && (10.61)
\end{aligned}$$

The binding energy of hydrogen is $m_p c^2 + m_e c^2 - m_H c^2 = 1$ Ry. The equilibrium condition and the ideal gas chemical potential then give a simple relation between the number densities of the three species:

$$n_H = n_p n_e \lambda_e^3 e^{\beta\,\mathrm{Ry}}\,. \tag{10.62}$$

The number density of free electrons and protons are the same due to charge neutrality:

$$n_e = n_p\,. \tag{10.63}$$

The protons remaining after nucleosynthesis are either free or combined into hydrogen atoms, so

$$n_p + n_H = (1-2q)n_B = (1-2q)\eta n_\gamma\,. \tag{10.64}$$

Putting the equations together gives the Saha equation for the neutral hydrogen fraction:

$$f_H = \frac{n_H}{n_p + n_H} = (1-f_H)^2 s\,, \tag{10.65}$$

where the parameter s is

$$s = 4\zeta(3)\sqrt{\frac{2}{\pi}}(1-2q)\eta\left(\frac{kT}{m_e c^2}\right)^{3/2} e^{\beta\,\mathrm{Ry}}\,. \tag{10.66}$$

The solution is

$$f_H = \frac{1+2s-\sqrt{1+4s}}{2s}\,. \tag{10.67}$$

At temperatures above the recombination temperature, s is small so f_H is small, making the plasma fully ionised. At low temperatures s is large so f_H approaches unity, leaving just neutral atoms. The small values of the baryon to photon ratio η and $\mathrm{Ry}/m_e c^2$ make the onset of recombination at temperature

$$kT_r \approx \frac{Ry}{\ln\left[\frac{1}{\eta}\left(\frac{m_e c^2}{Ry}\right)^{3/2}\right]}\,, \tag{10.68}$$

which delays the last scattering until $T \approx 2\,000$ K.

10.9 Epilogue

The formation of neutral atoms about 380 000 years after the Big Bang effectively ended the scattering of photons from free charges. The universe became transparent and entered the dark ages before the first star formation. The CMB photons were no longer in equilibrium but maintained their Planck distribution as the universe expanded. Small density fluctuations that were present in the electron-proton plasma just before recombination were imprinted on the CMB as temperature fluctuations. These small mass density fluctuations led to gravitational clumping that resulted in the formation of the first stars and galaxies 100 to

200 million years after the Big Bang. The large fraction of nonbaryonic cold dark matter was crucial in this process. Early stars that exploded as supernovae spewed their heavy elements (carbon, oxygen, silicon, iron, gold, uranium, etc.) into the cosmos. Our own solar system formed from a gas and dust cloud that included heavy elements that had been created in an earlier supernova event.

Chapter 11

Black Hole Thermodynamics

11.1 Review of Black Holes

Schwarzschild metric can be written as ($c = 1$)

$$ds^2 - \left(1 - \frac{2GM}{r}\right) dt^2 + \left(1 - \frac{2GM}{r}\right)^{-1} dr^2 + r^2 d\Omega^2 \,. \tag{11.1}$$

$ds^2 = 0$ radial null curves gives

$$\frac{dt}{dr} = \pm \left(1 - \frac{2GM}{r}\right)^{-1} \,, \tag{11.2}$$

where

$$\begin{array}{lll} r \to \infty, & \frac{dt}{dr} = \pm 1 & \text{flat space time,} \\ r \to 2GM, & \frac{dt}{dr} = \pm \infty & \text{light cones close up.} \end{array} \tag{11.3}$$

Hawking emission is governed by the occupation number

$$\langle n_\omega \rangle = \frac{\Gamma(\omega)}{e^{2\pi(\omega-\mu)/\kappa} \pm 1} \,. \tag{11.4}$$

The Hawking temperature is give by

$$T_H = \frac{\kappa}{2\pi} \,, \tag{11.5}$$

where κ is the surface gravity.

The chemical potential μ characterises the tendency of the black hole to shed its conserved quantum numbers. The first law of black hole thermodynamics (see later) leads to

$$\langle n_\omega \rangle = \frac{\Gamma(\omega)}{e^{(\omega - m\Omega - q\phi)/T_H} + s} \,, \tag{11.6}$$

where $s = -1$ for bosons, $s = +1$ for fermions, and Ω is the angular velocity of the horizon and m is the z-component of the spin of the emitted radiation.

11.2 Thermodynamics of Black Holes

Let us consider an isolated black holed placed in empty space. The black hole emits radiation and thus loses its mass. To calculate the flux L of the radiated energy, we can treat the black hole as a spherical body with the surface area

$$A = 4\pi r_g^2 = 16\pi M^2 \tag{11.7}$$

in Planck units ($\hbar = c = k = G = 1$), where the gravitational radius is

$$r_g = \frac{2GM}{c^2} \, . \tag{11.8}$$

The surface temperature is

$$T_{\mathrm{H}} = \frac{1}{8\pi M} \, . \tag{11.9}$$

Using the Stefan-Boltzmann law

$$\frac{dP}{da} = \sigma T^4 \tag{11.10}$$

we obtain

$$\frac{dE}{dt} \equiv L = \Gamma\gamma\sigma T_{\mathrm{H}}^4 A = \Gamma\gamma \frac{\pi^2}{60} \frac{1}{(8\pi M)^4} 16\pi M^2 = \frac{\Gamma\gamma}{15360\pi M^2} \, , \tag{11.11}$$

where Γ is the coefficient correcting for the greybody factors, γ is the total number of the "massless" degrees of freedom, and $\sigma = \pi^2/60$ is the Stefan-Boltzmann constant in Planck units. Then the mass of the black hole decreases with time according to

$$\frac{dM}{dt} = -L = -\frac{\Gamma\gamma}{15360\pi M^2} \, . \tag{11.12}$$

The solution of this equation with the initial condition $M|_{t=0} = M_0$ is

$$M(t) = M_0 \left(1 - \frac{t}{t_L}\right)^{1/3} \quad \text{and} \quad t_L = 5120\pi \frac{M_0^3}{\Gamma\gamma} \, . \tag{11.13}$$

Thus an isolated black hole has a finite lifetime $t_L \sim M_0^3$. During this time the black hole evaporates, and its temperature becomes very high at the last stages of evaporation, increasing inverse proportion to its mass.

Questions

Estimate the lifetimes of black holes with masses $M_1 = M(\text{sun}) = 2 \times 10^{30}$ kg, $M_2 = 10^{15}$ g, $M_3 = 10^{-5}$ g.

Solutions

The loss of energy due to Hawking radiation can be written as

$$\frac{dM}{dt} = -\frac{1}{BM^2}\,, \tag{11.14}$$

where B is a constant. Then the lifetime of a black hole of initial mass M_0 is

$$t_L = \frac{BM_0^3}{3}\,. \tag{11.15}$$

In SI units, this formula becomes

$$t_L = \frac{G^2}{\hbar c^4}\frac{BM_0^3}{3}\,. \tag{11.16}$$

The dimensionless coefficient B depends on γ, the number of available degrees of freedom in quantum fields. The order of magnitude of B is estimated as

$$B = \frac{15360\pi}{\gamma} = \frac{4.8\times 10^4}{118} \sim 10^4\,. \tag{11.17}$$

Units of B

$$\frac{G^2}{\hbar c^4} = \frac{(6.6742\times 10^{-11})^2}{1.054\times 10^{-34}\times(3\times 10^8)^4} = 5.22\times 10^{-21} \tag{11.18}$$

We find $t_L \sim 10^{74}$ s for $M = M(\text{sun})$; $t_L \sim 10^{19}$ s for $M = 10^{15}$ g; $t_L \sim 10^{-41}$ s for $M = 10^{-5}$ g. For comparison, the age of the universe is of order $\sim 10^{10}$ years or $\sim 3\times 10^{17}$ s; the Planck time is $t_{\rm Pl} \approx 5.4\times 10^{-44}$ s.

Aside

Planck time

$$\sqrt{\frac{G\hbar}{c^5}} = \left[\frac{6.6742^{-11}\times 1.054\times 10^{-34}}{(3\times 10^8)^5}\right]^{1/2} = 5.4\times 10^{-44}\ \text{s}\,. \tag{11.19}$$

Planck length

$$\sqrt{\frac{G\hbar}{c^3}} = \left[\frac{6.6742^{-11}\times 1.054\times 10^{-34}}{(3\times 10^8)^3}\right]^{1/2} = 1.6\times 10^{-35}\ \text{m} \approx 10^{-33}\ \text{cm}\,. \tag{11.20}$$

Continuing, $T_H = 1/(8\pi M)$ and $k = 1.380\times 10^{-23}$ JK^{-1} give

$$\begin{aligned} kT = \frac{\hbar c^3}{8\pi GM} &= \frac{1.054\times 10^{-34}\times(3\times 10^8)^3}{8\pi\times 6.6742\times 10^{-11}}\frac{\text{kg m}^2\ \text{s}^{-1}\ \text{m}^3\ \text{s}^{-3}}{\text{m}^3\ \text{kg}^{-1}\ \text{s}^{-2}}\frac{1}{M} \\ &= \frac{1.70}{M}\ \text{kg}^2\ \text{m}^2\ \text{s}^{-2} = \frac{1.70}{M}\ \text{kg J} \end{aligned} \tag{11.21}$$

$$T = \frac{1.70}{1.380\times 10^{-23}}\frac{1}{M}\ \text{kg K} = \frac{1.23\times 10^{23}}{M}\ \text{kg K} \tag{11.22}$$

$$M = 2\times 10^{30}\ \text{g} \quad\Rightarrow\quad T = 6.2\times 10^{-8}\ \text{K} \tag{11.23}$$

$$M = 10^{15}\ \text{g} \quad\Rightarrow\quad T = 1.23\times 10^{11}\ \text{K} \tag{11.24}$$

$$M = 10^{-5}\ \text{g} \quad\Rightarrow\quad T = 1.23\times 10^{31}\ \text{K} \tag{11.25}$$

The Hawking temperature is extremely small for astrophysical black holes with masses of order the solar mass and bigger. Therefore the Hawking effect could be observed only if astronomers discover a black hole near the end of its life, with a very high surface temperature. The lifetimes of astrophysically plausible black holes are much larger than the age of the universe which is of order 10^{10} years. To evaporate within this time, a black hole must be lighter than $\sim 10^{15}$ g. Such black hole could not have been formed as a result of stellar collapse and must be primordial, i.e. created at very early times when the universe was extremely dense and hot. There is currently no direct observational evidence for the existence of such primordial black holes.

It is almost certain that the final stage of the black hole evaporation cannot be described using classical general relativity. When the mass of the back hole reaches 10^{-5} g, its size is of the order the Planck scale (10^{-33} cm), and so one expects that nonperturbative quantum gravity effects must become dominant. It is possible that these effects stabilize a “remnant”, and a microscopic black hole with mass 10^{-5} g does not radiate, similar to electrons in atoms that do not radiate on the lowest orbit.

11.3 Laws of black hole thermodynamics

Prior to the discovery of black hole radiation, Bekenstein conjectured that black holes must have a nonvanishing intrinsic entropy. Consider some matter with nonzero entropy. Consider a black hole which always has zero entropy. If the black hole absorbs matter, the total entropy of the system including the black hole would decrease. This would violate the second law of thermodynamics. Bekenstein concluded that the second law of thermodynamics can be preserved only if one attributes to a black hole an intrinsic entropy S_{BH} proportional to its surface area A. The coefficient of proportionality could not be fixed until the concept of Hawking radiation.

The temperature and surface area of a black hole are

$$T_{\text{H}} = \frac{1}{8\pi M} \quad \text{and} \quad A = 16\pi M^2\,. \tag{11.26}$$

Differentiation give

$$dM = \frac{1}{8\pi M} d\left(\frac{A}{4}\right) = T_{\text{H}} d\left(\frac{A}{4}\right)\,. \tag{11.27}$$

For a black hole at rest, $dM = dE$, and from the first law of thermodynamics $dE = TdS$, we write

$$S_{\rm BH} = \frac{1}{4}A = 4\pi M^2 \,. \tag{11.28}$$

The first law of black hole thermodynamics becomes

$$dM = T_{\rm H} dS_{\rm BH} \,. \tag{11.29}$$

The entropy of a typical astrophysical plausible black hole is extremely large. This large entropy implies a large number of possible microstates hidden behind the horizon of the black hole. The origin of these microstates can in principle be related to the number of possible matter configurations from which a black hole of a given mass can be formed.

A static black hole without charge is completely characterized by its mass M. The first law of black hole thermodynamics can be generalized also for the case of rotating and charged black holes. For no work done

$$\begin{aligned} \delta E &= T\delta S + \sum \mu dN \,, & (11.30) \\ \delta M &= \frac{\kappa}{8\pi}\delta A + [\Omega \delta J + \phi] & \\ &= T_H \frac{\delta A}{4} + \Omega\delta J + \phi \delta Q \,. & (11.31) \end{aligned}$$

Taking into account the entropy of the black holes, the generalized second law of thermodynamics states that the total entropy of all the black holes and of ordinary matter never decreases,

$$\delta S_{\rm total} = \delta S_{\rm matter} + \delta S_{\rm BH} \geq 0 \,. \tag{11.32}$$

In classical general relativity it has been established that the combined area of all black hole horizons cannot decrease. This statement applies not only to adiabatic processes but also to strongly out-of-equilibrium situations, such as a collision of black holes with the resulting merger.

Ordinary thermodynamical systems can be in stable equilibrium with an infinite heat reservoir. However, this is not true for black holes because they have a negative heat capacity $C_{\rm BH}$. In other words, black holes become colder when they absorb energy. Taking into account that $E(T) = M = (8\pi T)^{-1}$, we obtain

$$C_{\rm BH} = \frac{\partial E}{\partial T} = -\frac{1}{8\pi T^2} < 0 \,. \tag{11.33}$$

A black hole surrounded by an infinite thermal bath with the temperature $T < T_{\rm BH}$ would emit radiation and become even hotter. The process of evaporation is not halted in an infinite thermal reservoir whose temperature T remains constant. Similarly, a black hole placed inside an infinite reservoir with a higher temperature $T > T_{\rm BH}$ will be absorbing radiation and becoming colder. In either case, no stable equilibrium is possible. A stable equilibrium can be achieved only if the black hole is placed in a reservoir with a finite energy. In this case, the radiation emitted by the black hole changes the temperature of the reservoir.

Under which conditions can a black hole be stabilized with respect to absorption or emission of radiation?

Questions

1. Find the range of heat capacities C_r of a heat reservoir for which a black hole of mass M is in a stable equilibrium with the reservoir.

2. Assume that the reservoir is a completely reflecting cavity of volume V filled with thermal radiation (massless fields). The energy of the radiation is $E_r = \sigma\gamma V T^4$, where the constant γ characterizes the number of degrees of freedom in the radiation fields. Determine the largest volume V for which a black hole of mass M can remain in a stable equilibrium with the surrounding radiation. Hint: A stable equilibrium is the state with the largest total entropy.

Solutions

1. Here we consider the black hole as a thermodynamical system with a peculiar equation of state. The results are essentially independent of the details of the Hawking radiation, of the kinds of particles emitted by the black hole, and of the nature of the reservoir.

   Solution 1: elementary considerations of equilibrium.

   The equilibrium of a black hole with a reservoir is stable if any small heat exchange causes a reverse exchange. It is intuitively clear that in the equilibrium state the temperature of the black hole T_{BH} and of the reservoir T_r must be equal. Suppose that initially $T_r = T_{\mathrm{BH}}$ and the black hole absorbs an infinitesimal quantity of heat, $\delta Q > 0$, from the reservoir. Then the mass M of the black hole will increase by $\delta M = \delta Q$ and the temperature will change according to

   $$\delta T_r = -\frac{1}{C_r}\delta Q \quad \text{and} \quad \delta T_{\mathrm{BH}} = \delta \frac{1}{8\pi M} = -\frac{dQ}{8\pi M^2} + O(\delta Q^2) \,. \tag{11.34}$$

   This creates a temperature difference

   $$T_{\mathrm{BH}} - T_r = \left(\frac{1}{C_r} - \frac{1}{8\pi M^2}\right)\delta Q + O(\delta Q^2) \,. \tag{11.35}$$

   If $0 < C_r < 8\pi M^2$, then $T_{\mathrm{BH}} > T_r$ and the black hole will subsequently tend to give heat to the reservoir, restoring the balance. However, for $C_r > 8\pi M^2$ the created temperature difference is negative, $T_{\mathrm{BH}} - T_r < 0$, and the situation is further destabilized since the black hole will tend to absorb even more heat.

   Similarly, if $\delta Q < 0$ (heat initially lost by the black hole), the resulting temperature difference will stabilize the system when $C_r < 8\pi M^2$. Therefore a black hole of mass M

can be in a stable equilibrium with the reservoir at $T_{\mathrm{BH}} = T_r$ only if the heat capacity C_r of the reservoir is positive and not too large, $0 < C_r < 8\pi M^2$.

Solution 2: maximizing the entropy

This is a more formal thermodynamical consideration. If a black hole is placed inside a closed reservoir, the total energy of the system is constant and the stable equilibrium is the state of maximum entropy. Let $C_r(T_r)$ be the heat capacity of the reservoir as a function of the reservoir temperature T_r. We shall determine the energy E_r and the entropy S_r of the reservoir which maximize the entropy.

If the reservoir absorbs an infinitesimal quantity of heat δQ, the first law of thermodynamics yields

$$\delta Q = dE_r = C_r(T_r) dT_r = T_r dS_r \,. \tag{11.36}$$

Therefore

$$E_r(T_r) = \int_0^{T_r} C_r(T) dT \quad \text{and} \quad S_r(T_r) = \int_0^{T_r} \frac{C_r(T)}{T} dT \,. \tag{11.37}$$

The entropy of the black hole with mass M is

$$S_{\mathrm{BH}} = 4\pi M^2 = \frac{1}{16\pi T_H^2} \tag{11.38}$$

and the energy of the black hole is equal to its mass,

$$E_{\mathrm{BH}} = M = \frac{1}{8\pi T_{\mathrm{BH}}} \,. \tag{11.39}$$

This indicates a negative heat capacity,

$$C_{\mathrm{BH}}(T) = \frac{dE_{\mathrm{BH}}}{dT} = -\frac{1}{8\pi T^2} \,. \tag{11.40}$$

Now we have the following thermodynamical situation: two systems with temperature T_1 and T_2 and heat capacities $C_1(T_1)$ and $C_2(T_2)$ are in thermal contact and the combined energy is constant, $E_1(T_1) + E_2(T_2) = \text{const}$. We need to find the state which maximizes the combined entropy $S = S_1(T_1) + S_2(T_2)$. This problem is solved by standard variational methods. The energy constraint

$$\frac{dE_1}{dT_1} + \frac{dE_2}{dT_2}\frac{dT_2}{dT_1} = 0 \tag{11.41}$$

gives T_2 as a function of T_1 such that

$$\frac{dT_2(T_1)}{dT_1} = -\frac{C_1(T_1)}{C_2(T_2)}\,. \tag{11.42}$$

The extremum condition $dS/dT_1 = 0$ gives

$$\frac{dS}{dT_1} = \frac{C_1(T_1)}{T_1} + \frac{C_2(T_2)}{T_2}\frac{dT_2}{dT_1} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) C_1(T_1) = 0\,. \tag{11.43}$$

Therefore $T_1 = T_2$ is a necessary condition for the equilibrium. The equilibrium is stable if $d^2S/dT_1^2 < 0$, which yields the condition

$$\left.\frac{d^2S}{dT_1^2}\right|_{T_1=T_2} = \frac{d}{dT_1}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) C_1(T_1) = -\frac{C_1}{C_2}\frac{C_1 + C_2}{T_1^2} < 0\,. \tag{11.44}$$

Hence, the stability condition is $C_1 C_2^{-1}(C_1 + C_2) > 0$. Usually heat capacities are positive and the thermal equilibrium is stable. However, in our case $C_1 = C_{\mathrm{BH}} < 0$. Therefore the equilibrium is stable if and only if $0 < C_2 = C_r < |C_{\mathrm{BH}}|$, in other words

$$0 < C_r < \frac{1}{8\pi T_{\mathrm{BH}}^2} = 8\pi M^2\,. \tag{11.45}$$

We find that the equilibrium is stable only if the reservoir has certain finite heat capacity. A combination of a black hole and a sufficiently large reservoir is unstable.

2. The heat capacity of a radiation-filled cavity of volume V is

$$C_r(T_r) = 4\sigma V T_r^3\,. \tag{11.46}$$

In equilibrium, we have $T_r = T_{\mathrm{BH}} = T$. The stability condition yields

$$C_r = 4\sigma V T^3 < \frac{1}{8\pi T^2} \Rightarrow V < V_{\max} = \frac{1}{32\pi\sigma T^5}\,. \tag{11.47}$$

A black hole cannot be in a stable equilibrium with a reservoir of volume V larger than $V_{\max}$.

Chapter 12

Interacting Systems: Cluster Expansions

Assume a classical gas with Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} U_{ij} \,, \tag{12.1}$$

where $U_{ij} = U(|\vec{r}_i - \vec{r}_j|) = U(r_{ij})$ is a two-body central potential.

The partition function is

$$\begin{aligned} Q_N &= \frac{1}{N!h^{3N}} \int d^{3N}r d^{3N}p \exp\left(-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i<j} U_{ij}\right) \\ &= \frac{1}{N!\lambda^{3N}} \int d^{3N}r \exp\left(-\beta \sum_{i<j} U_{ij}\right) \\ &= \frac{1}{N!\lambda^{3N}} Z_N(V,T) \,, \end{aligned} \tag{12.2}$$

where $\lambda = h/(2\pi mkT)^{1/2}$ is the mean thermal wavelength and $Z_N(V,T)$ is refereed to as a configuration integral:

$$Z_N(V,T) = \int d^{3N}r \prod_{i<j} e^{-\beta U_{ij}} \,. \tag{12.3}$$

Notice for noninteracting particles $Z_N(V,T) = V^N$ and $Q_N = V^N/(N!\lambda^{3N})$ as before.

Consider the case for interacting particles when $e^{-\beta U_{ij}} \approx 1$ except when r_{ij} is small. Define

$$f_{ij} = e^{-\beta U_{ij}} - 1 \approx 0 \tag{12.4}$$

almost everywhere except near $f_{ij} \approx 0$. We can write

$$\prod_{i<j} e^{-\beta U_{ij}} \equiv \prod_{i<j}(1+f_{ij}) = 1+\sum_{i<j} f_{ij} + \sum_{i<j,i\le k<l,l\ne j \text{ if } k=i} f_{ij}f_{kl} + \sum_{i<j,i\le k<l,l\ne j \text{ if } i=k,i\le m<n\ldots} f_{ij}f_{kl}f_{mn} + \cdots\,, \tag{12.5}$$

$$Z_N(V,T) = \int d^3r_1\ldots d^3r_N \left(1+\sum_{i<j} f_{ij} + \sum_{i<j,i\le k<l,l\ne j \text{ if } k=i} f_{ij}f_{kl} + \sum_{i<j,i\le k<l,l\ne j \text{ if } i=k,i\le m<n\ldots} f_{ij}f_{kl}f_{mn} + \cdots\right). \tag{12.6}$$

Can represent terms in Eq. (12.6) by an N-particle graph. Take $N = 6$ as an example and consider two terms

$$\int d^3r_1\ldots d^3r_6 f_{34}f_{45}f_{46} = \int d^3r_1 \int d^3r_2 \int d^3r_3 d^3r_4 d^3r_5 d^3r_6 f_{34}f_{45}f_{46} \tag{12.7}$$

and

$$\int d^3r_1\ldots d^3r_6 f_{12}f_{34}f_{36} = \int d^3r_5 \int d^3r_1 d^3r_2 f_{12} \int d^3r_3 d^3r_4 d^3r_6 f_{34}f_{36}\,. \tag{12.8}$$

Factorisation of terms is the equivalent to decomposition of graphs into clusters. Eq. (12.7) has two clusters of one particle and one cluster of four particles. Eq. (12.8) has one cluster of one particle, one cluster of two particles, and one cluster of three particles.

An N-particle graph is the collection of members of circles with lines linking some, or all, of them.

l-cluster graph in which each member is connected at least indirectly to every other. Notice that l clusters cannot be decomposed. l particles are many distinct l-clusters (except for $l = 1, 2$).

We define the cluster integral

$$b_l(V,T) \equiv \frac{1}{l!\lambda^{3(l-1)}V} \times (\text{sum of all possible } l\text{-clusters})\,. \tag{12.9}$$

A few example are:

$$b_1 = \frac{1}{V}[1] = \frac{1}{V}\int d^3r_1 = 1\,. \tag{12.10}$$

$$\begin{aligned} b_2 &= \frac{1}{2\lambda^3 V}[1-2] = \frac{1}{2\lambda^3 V}\int d^3r_1 d^3r_2 f_{12} \\ &= \frac{2\pi}{\lambda^3}\int drr^2\left(e^{-U(r)/kT}-1\right) . \end{aligned} \tag{12.11}$$

$$\begin{aligned} b_3 &= \frac{1}{6\lambda^6 V}\{[]+[]+[]+[]\} \\ &= \frac{1}{6\lambda^6 V}\int d^3r_1 d^3r_2 d^3r_3 \left[f_{12}f_{13}+f_{12}f_{23}+f_{13}f_{12}+f_{12}f_{13}f_{23}\right] \\ &= \frac{1}{6\lambda^6 V}\left[3V\int d^3r_{12}d^3r_{13}f_{12}f_{13}+V\int d^3r_{12}d^3r_{13}f_{12}f_{13}f_{23}\right] \\ &= \frac{1}{6\lambda^6}\left[3(2\lambda^3 b_2)^2+\int d^3r_{12}d^3r_{13}f_{12}f_{13}f_{23}\right] \\ &= 2b_2^2+\frac{1}{6\lambda^6}\int d^3r_{12}d^3r_{13}f_{12}f_{13}f_{23} . \end{aligned} \tag{12.12}$$

Notice that b_l is independent of V (assuming short-range forces) and is dimensionless.

We now calculate $Z_N(V,T)$, which is the sum of all possible distinct N-particle graphs. For each graph, distribution of l-particle clusters $\{m\}$. m_1 is the number of 1-particle clusters, m_l is the number of l-particle clusters

$\{m\}$ satisfies the condition

$$\sum_{l=1}^{N} l m_l = N . \tag{12.13}$$

Notice that a given distribution $\{m\}$ has many distinct graphs. Let $S\{m\}$ be the sum of all distinct graphs for a given distribution $\{m\}$. For example consider $N=5$:

$$S\{0,1,1,0,0\} = [][] \tag{12.14}$$

We can write

$$Z_N(V,T) = \sum_{\{m\}}^{\prime} S\{m\} . \tag{12.15}$$

Now consider some combinatorics. The number of ways to distribute N particles in $\{m\}$ and form distinct clusters

$$\frac{N!}{(1!)^{m_1}(2!)^{m_2}\cdots} = \frac{N!}{\prod_l (l!)^{m_l}} . \tag{12.16}$$

Exchange of all particles in a cluster with all those from another cluster must not be counted as giving a distinct graph. The correction factor is

$$\prod_l \frac{1}{(m_l)!}\,. \tag{12.17}$$

If the number of particles l in an l-cluster determined the cluster uniquely, then we would have

$$Z_N(V,T) = \sum_{\{m\}}^{\prime} N! \prod_l \frac{1}{(l!)^{m_l}(m_l)!} \times (\text{value of } l\text{-cluster})^{m_l}. \tag{12.18}$$

In reality, $l > 2$ determines many distinct clusters.

$$Z_N(V,T) = \sum_{\{m\}}^{\prime} N! \prod_l \frac{(\text{sum of all possible } l\text{-clusters})^{m_l}}{(l!)^{m_l} m_l!}\,. \tag{12.19}$$

Notice that this last step is not trivial. Consider examples to understand.

Recall

$$b_l = \frac{1}{l!\lambda^{3(l-1)}V} \times (\text{sum of all possible } l\text{-clusters}). \tag{12.20}$$

$$\begin{aligned} Z_N(V,T) &= \sum_{\{m\}}^{\prime} N! \prod_l \frac{(l!\lambda^{3(l-1)}Vb_l)^{m_l}}{(l!)^{m_l} m_l!} \\ &= N!\lambda^{3N} \sum_{\{m\}}^{\prime} \prod_l \left(\frac{b_l V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!}\,, \end{aligned} \tag{12.21}$$

where use is made of $\prod_l \left(\lambda^{3l}\right)_l^m = \lambda^{3\sum_l l m_l} = \lambda^{3N}$.

From

$$\begin{aligned} Q_N(V,T) &= \frac{1}{N!\lambda^{3N}} Z_N(V,T) \\ &= \sum_{\{m\}}^{\prime} \prod_l \left(\frac{b_l V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!}\,. \end{aligned} \tag{12.22}$$

Notice the constraint $\sum_l l m_l = N$ complicates the summation in Eq. (12.22).

Consider the grand partition function

$$\begin{aligned}
\mathcal{Q}(z,V,T) &= \sum_{N=0}^{\infty} z^N Q_N(V,T) \\
&= \sum_{N=0}^{\infty} \sum_{\{m\}}' \prod_{l=1}^{N} \left(\frac{b_l z^l V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!} \\
&= \sum_{m_1 m_2 \ldots} \prod_{l=1}^{\infty} \left(\frac{b_l z^l V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!} \\
&= \prod_{l=1}^{\infty} \sum_{m_l}^{\infty} \left(\frac{b_l z^l V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!} \\
&= \prod_{l} \exp\left(\frac{b_l z^l V}{\lambda^3}\right) \\
&= \exp\left(\sum_l b_l z^l \frac{V}{\lambda^3}\right) , \qquad (12.23)
\end{aligned}$$

$$\Rightarrow \frac{1}{V}\ln\mathcal{Q} = \frac{1}{\lambda^3}\sum_l b_l z^l \, . \qquad (12.24)$$

Take the thermodynamic limits

$$\frac{P}{kT} \equiv \lim_{V\to\infty}\left(\frac{1}{V}\ln\mathcal{Q}\right) \to \frac{1}{\lambda^3}\sum_l b_l z^l, \qquad (12.25)$$

$$\frac{N}{V} = \lim_{V\to\infty}\left(\frac{z}{V}\frac{\partial\ln\mathcal{Q}}{\partial z}\right)_{V,\beta} = \frac{1}{\lambda^3}\sum_l l b_l z^l. \qquad (12.26)$$

Eq. (12.25) and Eq. (12.26) are the cluster expansion of Mayer-Ursell. Use Eq. (12.26) to solve for z in terms of λ^3/v, where $v = V/N$, and substitute this in Eq. (12.25) to get the equation of state.

Other quantities can be calculated as follows.

$$U = -\beta\left.\frac{\partial q}{\partial\beta}\right|_{z,V} = kT^2\left.\frac{\partial}{\partial T}\right|_{z,V} q = kT\sum_{l=1}^{\infty} T\frac{\partial}{\partial T}\left(\frac{b_l}{\lambda^3}\right)_{z,V} V z^l. \qquad (12.27)$$

$$\begin{aligned}
H &= U + PV \\
&= kT\sum_l\left[T\frac{\partial}{\partial T}\left(\frac{b_l}{\lambda^3}\right)_{z,V} z^l V + \frac{b_l z^l V}{\lambda^3}\right] , \qquad (12.28)
\end{aligned}$$

$$\mu = kT\ln z \, , \qquad (12.29)$$

$$G = \mu N = (kT \ln z) \left(\frac{V}{\lambda^3} \sum_l l b_0 z^l \right) \,, \tag{12.30}$$

$$S = \frac{H - G}{T} \,. \tag{12.31}$$

12.1 Virial Expansion of the Equation of State

Equation of state as a virial expansion:

$$\frac{Pv}{kT} = \sum_{l=1}^{\infty} a_l(T) \left(\frac{\lambda^3}{v} \right)^{l-1} \,. \tag{12.32}$$

From Eq. (12.26)

$$\begin{aligned}
b_1 z &= \frac{\lambda^3}{v} - 2b_2 z^2 - 3b_3 z^3 - \ldots \\
&= \frac{\lambda^3}{v} - 2b_2 \left(\frac{\lambda^3}{v} - 2b_2 z^2 \ldots \right)^2 - 3b_3 \left(\frac{\lambda^3}{v} \ldots \right)^3 \\
&= \frac{\lambda^3}{v} - 2b_2 \left(\frac{\lambda^3}{v} - 2b_2 \left(\frac{\lambda^3}{v} \right)^2 \ldots \right)^2 - 3b_3 \left(\frac{\lambda^3}{v} \right)^3 \ldots \\
&= \frac{\lambda^3}{v} \left(1 - 2b_2 \frac{\lambda^3}{v} + (8b_2^2 - 3b_3) \left(\frac{\lambda^3}{v} \right)^2 \ldots \right] \,.
\end{aligned} \tag{12.33}$$

Substituting in Eq. (12.25) and using $b_1 = 1$ gives

$$\begin{aligned}
\frac{Pv}{kT} &= \left[1 - 2b_2 \frac{\lambda^3}{v} + (8b_2^2 - 3b_3) \left(\frac{\lambda^3}{v} \right)^2 \ldots \right] + b_2 \frac{\lambda^3}{v} \left[1 - 2b_2 \frac{\lambda^3}{v} \right]^2 + b_3 \left(\frac{\lambda 3}{v} \right)^2 \\
&= 1 - b_2 \frac{\lambda^3}{v} + (4b_2^2 - 2b_3) \left(\frac{\lambda^3}{v} \right)^2 \,.
\end{aligned} \tag{12.34}$$

Therefore $a_1 = 1$,

$$a_2 = -b_2 = -\frac{1}{2\lambda^3} \int d^3 r_{12} f_{12} \,, \tag{12.35}$$

$$a_3 = 4b_2^2 - 2b_3 = -\frac{1}{3\lambda^6} \int d^3 r_{12} d^3 r_{13} f_{12} f_{13} f_{23} \,. \tag{12.36}$$

More generally,

$$a_l = -\frac{l-1}{l}\beta_{l-1}, \quad l \geq 2\,, \tag{12.37}$$

where β_{l-1} is the irreducible cluster integral.

$$\beta_{l-1} = \frac{1}{(l-1)!\lambda^{3(l-1)}V} \times (\text{sum of all irreducible } l\text{-clusters}). \tag{12.38}$$

An irreducible cluster is an l-particle graph that is multiply connected. That is, there are at least two independent non-intersecting paths connecting each pair of circles.

12.2 Lennard-Jones Potential

Semi-empirical potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\,. \tag{12.39}$$

Approximate $U(r) = \infty$ for $r < r_0$ and $U(r) = -U_0(r_0/r)^6$ for $r \geq r_0$, with $r_0 = 2^{1/6}\sigma$ the position of the minimum. $U(r_0) = -\varepsilon = -U_0$ is the minimum potential of the potential.

The lowest-order nontrivial virial coefficient is

$$\begin{aligned}
a_2 = -b_2 &= -\frac{1}{2\lambda^3}\int d^3r_{12}\left(e^{-\beta U_{12}} - 1\right) \\
&= \frac{2\pi}{\lambda^3}\int drr^2\left(1 - e^{-\beta U_{12}}\right) \\
&= \frac{2\pi}{\lambda^3}\left[\int_0^{r_0} drr^2 + \int_{r_0}^{\infty} drr^2\left(1 - e^{-\beta U_{12}}\right)\right] \\
&\approx \frac{2\pi}{\lambda^3}\left[\frac{r_0^3}{3} - \int_{r_0}^{\infty} drr^2\frac{U_0}{kT}\left(\frac{r_0}{r}\right)^6\right] \\
&\approx \frac{2\pi r_0^3}{3\lambda^3}\left[1 - \frac{U_0}{kT}\right]\,.
\end{aligned} \tag{12.40}$$

From Eq. (12.39)

$$\frac{PV}{kT} \approx 1 + \frac{2\pi r_0^3}{32^3}\left(1 - \frac{U_0}{kT}\right)\frac{\lambda^3}{v}\,, \tag{12.41}$$

$$P \approx \frac{kT}{v}\left[1 + \frac{B_2(T)}{v}\right]\,, \tag{12.42}$$

with

$$\frac{B_2(T)}{v} = \frac{2\pi r_0^3}{3v}\left(1 - \frac{U_0}{kT}\right) \ll 1\,. \tag{12.43}$$

Alternatively,

$$\begin{aligned}
\frac{1}{kT}\left(Pv + \frac{2\pi r_0^3}{3}\frac{U_0}{v}\right) &\approx 1 - \frac{2\pi r_0^3}{3v} && (12.44)\\
\left(P + \frac{2\pi r_0^3}{3}\frac{U_0}{v^2}\right)\left(1 + \frac{2\pi r_0^3}{3v}\right) v &\approx kT \\
\left(P + \frac{\bar{a}}{v}\right)(v - b) &\approx kT && (12.45)
\end{aligned}$$

Notice that this is the van der Waals equation of state

$$v - b = \frac{V}{N} - \frac{2\pi r_0^3}{3} = \left(V - N\frac{2\pi}{3}r_0^3\right)\frac{1}{N}\,. \tag{12.46}$$

For hard spheres, $r_0 = 2a$, where a is the sphere radius. $N2\pi r_0^3/3 = 16\pi a^2 N/3 = 4\times$ volume occupied by the spheres. Also, $U_0 = 0 \Rightarrow \bar{a} = 0$.

12.3 Problems

Chapter 13

Phase Transitions: criticality, Universality, Scaling

Consider the Van der Waals equation of state

$$P = \frac{kT}{v-b} - \frac{a}{v^2}\,, \tag{13.1}$$

where $v = V/N$ is the molar volume.

For certain temperatures, there exits conditions for which $(\partial P/\partial v)_T > 0$. This signifies a instability or phase transition and must be corrected with a maxwell construction.

$v_l(T)$ is the molar volume in the liquid state, while $v_g(T)$ is the bolar volume in the gasious state. Co-existence curves are locus of $v_l(T)$, $v_g(T)$ and P as prescribed by the Maxwll conditions. The critical point is the point where $v_l(T) = v_g(T)$. The critical temperature occurs when $T = T_c$. Notice that at the critical point

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0\,. \tag{13.2}$$

This is a point of inflection.

From the equation of state, we find that at the critical points

$$v_c = 3b \quad T_c, = \frac{8a}{27bk}, \quad P_c = \frac{a}{27b^2} \tag{13.3}$$

Consider the dimensionless parameter. We only have two adjustable paramters. Let us construct a quantity that is independent of both and thus universal. Try $v_c^\alpha (kT_c)^\beta P_c^\delta \Rightarrow b^{\alpha-\beta-2\delta} a^{\beta+\delta} \Rightarrow \beta - \delta$ and $\alpha - \beta - 2\delta = 0$, or $\alpha = \delta$. Therefore there is only one independent universal experesson corresponding to $\beta = 1, \alpha = \delta = -1$.

$$\kappa = \frac{kT_v}{P_c v_c} = \frac{8}{3} \tag{13.4}$$

Experimentally, $\kappa \sim 3.67 - 3.9$ fro many substances. This is different from 2.67, but nvertheless is approximately universal.

Now try to write the equation of state in a universal form. Let $v = v_r v_c, P = P_r P_c, T = T_r T_c$, where v_r, P_r, T_r are dimensionless reduced variables. Then, the van der Waals equation of state becomes

$$\left(P_r + \frac{3}{v_r^2}\right)(3V_R - 1) = 8T_r \tag{13.5}$$

Deifferent systems with idential relative parameters are in corresponding states.
Near criticality $P_r = 1 + \pi, v_r = 1 + \psi, T_r = 1 + \tau$.
$\Rightarrow \pi(2 + 7\psi + 8\psi^2 + 3\psi^3_+ 3\psi^3 = 8\tau(1 + 2\psi + \psi^2)$
Close to the critical point, along the isotherm ($\tau = 0$): $\pi \sim -3/2\psi^3$.
ψ versus τ:
Equation of state: $3\psi^3 + 8(\pi - \tau)\psi^2 + (7\pi - 16\tau)\psi + 2(\pi - 4\tau) = -3\pi\psi^3 \approx 0$
If $\psi = 0$, we see that we must have $\pi = 4\tau$.
$\Rightarrow \psi \approx \pm 2\sqrt{-\tau}$, for $\tau \to 0^-$.
Isthermal Compressibility

$$\left(\frac{\partial\psi}{\partial\pi}\right)_\tau \tag{13.6}$$

From (5)

$$2 + 7\pi\left(\frac{\partial\psi}{\partial\pi}\right)_\tau + 8\psi^2\left(\frac{\partial\psi}{\partial\pi}\right)_\tau = 8\tau \times 2\left(\frac{\partial\psi}{\partial\pi}\right)_\tau + 16\tau\psi\left(\frac{\partial\psi}{\partial\pi}\right)_\tau + \text{small order terms} \tag{13.7}$$

$$\Rightarrow -\left(\frac{\partial\psi}{\partial\pi}\right)_\tau = \frac{2}{7\pi + 9\psi^2 - 16\tau} \tag{13.8}$$

Use $\pi \sim 4\tau$:

$$\Rightarrow -\left(\frac{\partial\psi}{\partial\pi}\right)_\tau \to \begin{cases} \frac{1}{6\tau} & \text{for } \tau \to 0^+ \text{ along } \psi = 0 \text{ (isochore)} \\ \frac{1}{12\tau} & \text{for } \tau \to 0^- \text{ along } \psi^2 = -4\tau \text{ (co-existence curve)} \end{cases} \tag{13.9}$$

Specific heat

$$C_V \approx \begin{cases} C_{\text{Videal}} + \frac{9}{2}Nk\left(1 + \frac{28}{24}\tau\right) & \tau \leq 0 \\ C_{\text{Videal}} & \tau > 0 \end{cases} \tag{13.10}$$

13.1 Dynamic Model for Phase Transitions

How: regular lattice and nearest neighbour interactions.

Very simple but applicable to: farromagnetism, phase separation in binary solutions, gas-liquid, liquid-liquid transitions, order-disorder in binary alloys.

This implies long range order cooperative phenomena.

Consider Faromagnetism $s = 1/2$, $s_z = \pm 1/2 \to \mu_z = \pm\mu_B$.

$$B_{dipole} = \frac{\mu}{4\pi}\frac{3(\vec{m}\cdot\hat{r})\hat{r} - \vec{m}}{r^3} \tag{13.11}$$

Interaction energy;
electrostatic (fixed)

$$K_{ij} = \frac{\rho^2}{4\pi\epsilon_0 r_{ij}} \tag{13.12}$$

magnetic

$$J_{ij} = -\frac{\mu_0\mu_B^2}{4\pi}\frac{3\hat{n}_1\cdot\hat{r}_{12}\hat{n}_2\cdot\hat{r}_{12} - \hat{n}_1\cdot\hat{n}_2}{r_{12}^3} \tag{13.13}$$

Take $E = -J\sigma_i\sigma_j$ with $s_i = \pm 1/2 = z$-component of spin, and $\sigma_i = \pm 1$.
For N particles in an external field $\vec{B} = B\hat{z}$.

$$H = -\frac{J}{2}\sum_{ij}\sigma_i\sigma_j - \mu B\sum_i \sigma_i \tag{13.14}$$

Partition function

$$Q_N(B,T) = \sum_{\{\sigma\}}\exp\left(\beta\frac{J}{2}\sigma_{ij}\sigma_i\sigma_j + \beta\mu B\sum_i\sigma_i\right) \tag{13.15}$$

Derived quantities

$$A = -kT\ln Q \tag{13.16}$$

$$U = -\left(\frac{\partial \ln Q}{\partial\beta}\right)_{N,B} = -T^2\left(\frac{\partial}{\partial T}\frac{A}{T}\right)_{N,B} \tag{13.17}$$

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{B,N} = -T\left(\frac{\partial^2 A}{\partial T^2}\right) \tag{13.18}$$

$$\vec{\mu} = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial B}\right)_{\beta} = -\left(\frac{\partial A}{\partial\beta}\right)_T \tag{13.19}$$

Definitions
N_+ number of particles with spin up.
N_- number of particles with spin down.
N_{++} number of up-up nearest neighbours
N_{--} number of down-down nearest neighbours
N_{+-} number of up-down nearest neighbours
Relations: $N_+ + N_- = N$
Neglecting “and” effects $qN_+ = 2N_{++} + N_{+-}$ and $qN_- = 2N_{--} + N_{+-}$ and

Q is the coordination number of the lattice and is equal to the number of nearest neighbours.

Example. If $N_+ = 5, N_- = 3, N_{++} = 3, N_{--} = 1, N_{+-} = 4$, means $q = 2$.

We have five variables $(N_+, N_-, N_{++}, N_{+-}, N_{--})$ and three equations. Which means we have two independent variables, say N_+, N_{++}:

$$\begin{aligned} N_- &= N_- N_+ && (13.20)\\ N_{+-} &= qN_+ - 2N_{++} && (13.21)\\ N_{--} &= \frac{q}{2}N - qN_+ + N_{++} && (13.22) \end{aligned}$$

That is, N_+ is asymmetric and N_{++} is is an order or correlation.

Hamiltonian

$$\begin{aligned} H &= -J(N_{++} + N_{--} - N_{+-}) - \mu B(N_+ - N_-) && (13.23)\\ &= -J\left(\frac{q}{2}N - 2qN_+ + 4N_{++}\right) - \mu B(2N_+ - N) && (13.24) \end{aligned}$$

Define $g_N(N_+, N_{++})$ as the number of distinct N_+, N_{++} configurations.

The partition function is

$$\begin{aligned} Q_N(B,T) &= \sum_{N_+,N_{++}}{}' g_N(N_+, N_{++}) e^{-\beta H_N(N_+,N_-)} && (13.25)\\ &= \exp\left(\beta\left(\frac{qJ}{2} - \mu N\right) B\right) \sum_{N_+=0}^{N} e^{-2\beta(qJ-\mu B)N_+} \sum_{N_{++}}{}' g_N(N_+, N_{++}) e^{4\beta J N_{++}} && (13.26) \end{aligned}$$

13.2 Lattice Gas, Binary Alloy

(+,-) Feromagnetism, (a,b) latice gas, (1,2) binary aloy

a,b: occupied, vacant sites

1,2: species occupying a site

There is a formal correspondence between the three (read Pathria for details).

13.3 Ising Model Zeroth Approximation

Order parameter

$$L = \frac{N_+ - N_-}{N} = 2\frac{N_+}{N} - 1\,, \tag{13.27}$$

where $-1 \le L \le 1$.
Also,

$$N_+ = \frac{N}{2}(1+L) \quad \text{and} \quad N_- = \frac{N}{2}(1-L) \tag{13.28}$$

Let $M = \mu(N_+ - N_-) = N\mu L$.
Mean Field Approximation

$$H = -J\sum_{i<j}\sigma_i\sigma_j - \mu B\sum_i \sigma_i \approx -\sum_i\left(\frac{Jq\bar{\sigma}}{2}\sigma_i + \mu B\sigma_i\right) \tag{13.29}$$

with $M = N\mu\bar{\sigma} = N\mu\bar{L}$, we see that $\bar{\sigma} = \bar{L}$.

$$H \approx -\sum_i\left(J\frac{q}{2}\bar{L} + \mu B\right)\sigma_i \approx -\left(J\frac{q}{2}\bar{L} - \mu B\right)NL \tag{13.30}$$

$$U = \bar{H} \approx -J\frac{q}{2}N\bar{L}^2 - \mu BN\bar{L} \tag{13.31}$$

For a given $\bar{\sigma}$, consider the energies for the up and down states, for a single particle

$$\varepsilon_i = -(Jq\bar{\sigma}\sigma_i + \mu B\sigma_i) = -\mu(Jq\frac{\bar{\sigma}}{\mu} + B)\sigma_i \tag{13.32}$$

Where $B' = Jq\bar{\sigma}/\mu$. That is, for $N \gg 1, \bar{\sigma}$ is nearly independent of σ_i.

$$P_+ = \frac{e^{\mu(B'+B)/kT}}{e^{\mu(B'+B)/kT} + e^{-\mu(B'+B)/kT}} \tag{13.33}$$

$$P_- = \frac{e^{-\mu(B'+B)/kT}}{e^{\mu(B'+B)/kT} + e^{-\mu(B'+B)/kT}} \tag{13.34}$$

$$\frac{P_-}{P_+} = \frac{N_-}{N_+} = e^{-2\mu(B'+B)/kT} = \frac{1-\bar{L}}{1+\bar{L}} \tag{13.35}$$

$$\frac{1-\bar{L}}{1+\bar{L}} = \exp\left[-2(Jq\bar{L} + \mu B)/kT\right] \tag{13.36}$$

$$\Rightarrow \bar{L} = \tanh\left(\frac{Jq\bar{L} + \mu B}{kT}\right) \tag{13.37}$$

Spontaneous Magnetization ($B \to 0$)

$$\bar{L}_0 = \tanh\left(\frac{Jq\bar{L}_0}{kT}\right) \tag{13.38}$$

Non-trivial solution when

$$\frac{d}{d\bar{L}_0}\tanh\left(\frac{JqL_0}{kT}\right)_{L_0=0} > 1 \tag{13.39}$$

$$\Rightarrow \frac{Jq}{kT} > 1 \tag{13.40}$$

Curie temperature: $T_c = Jq/k$.
Near Criticality $T \sim T_c$: $L \approx 0$.

$$\tanh x \approx x - \frac{x^3}{3} \tag{13.41}$$

$$L \approx \frac{Jq}{kT}L - \frac{1}{3}\left(\frac{Jq}{kT}\right)^3 L^3 \tag{13.42}$$

$$\frac{1}{3}\left(\frac{T_c}{T}\right)^3 L^3 = \left(\frac{T_c}{T} - 1\right) L \tag{13.43}$$

$$\Rightarrow L \approx \sqrt{3\left(\frac{T}{T_c}\right)^2\left(1 - \frac{T}{T_c}\right)} \approx \sqrt{3\left(1 - \frac{T}{T_c}\right)} \tag{13.44}$$

$$U_0 = -\frac{1}{2}qJN\bar{L}_0^2 \tag{13.45}$$

$$C_{0B} = \left(\frac{\partial U_0}{\partial T}\right)_B = -qJN\bar{L}_0\frac{\partial \bar{L}_0}{\partial T} \tag{13.46}$$

But from $\bar{L}_0 = \tanh(T_c\bar{L}_0/T)$

$$\left(\frac{\partial \bar{L}_0}{\partial T}\right)_B = -\frac{1}{T_c}\frac{\bar{L}_0}{\frac{(T/T_c)^2}{1-\bar{L}_0} - \frac{T}{T_c}} \tag{13.47}$$

Using $T_c = Jq/k$

$$C_0 = \frac{Nk\bar{L}_0^2}{\frac{(T/T_c)^2}{1-\bar{L}_0^2} - \frac{T}{T_c}} \tag{13.48}$$

From 49, for $T < T_c$, let $T = T_c(1-\tau)$.

$$C_0 \to \frac{Nk3\tau}{\frac{(1-\tau)^2}{1-3\tau} - (1-\tau)} \to \frac{3}{2}Nk \tag{13.49}$$

Notice that for $T > T_c$, $U_0 = 0$, $C_0 = 0$.
Entropy

$$S_0 = \int_0^T \frac{C_0}{T'}dT' = -qJN\int_0^T \frac{\bar{L}_0}{T}\frac{d\bar{L}_0}{dT'}dT' \tag{13.50}$$

But $\bar{L}_0/T = \tanh^{-1}(\bar{L}_0)/T_c$

$$\begin{aligned} S_0 &= -qJ\frac{Nk}{qJ}\int_1^{\bar{L}_0} dL(\tanh^{-1} L) && (13.51)\\ &= Nk\int_{\bar{L}_0}^{1} dL\frac{1}{2}\ln\left(\frac{1+L}{1-L}\right) && (13.52)\\ S_0(L_0) &= Nk\left[\ln 2 - \frac{1}{2}\ln(1-L_0)^2 - \frac{\bar{L}_0}{2}\ln\left(\frac{1+\bar{L}_0}{1-\bar{L}_0}\right)\right] && (13.53)\end{aligned}$$

$S_0(0) = nk\ln 2$ as expected.
For $T \ll T_c$

$$\bar{L}_0 = \tanh\left(\frac{T_c}{T}\bar{L}_0\right) \approx 1 - 2e^{-2T_c\bar{L}_0/T} \approx 1 - 2e^{-2T_c/T} \qquad (13.54)$$

$$U_0 = -\frac{1}{2}NqJ\bar{L}_0^2 \approx -\frac{1}{2}NqJ\left(1 - 4e^{-2T_c/T}\right) \qquad (13.55)$$

$$C_0 = \frac{\partial U_0}{\partial T} \approx 4NqJ\frac{T_c}{T^2}e^{-2T_c/T} \approx 4Nk\left(\frac{T_c}{T}\right)^2 e^{-2T_c/T} \qquad (13.56)$$

Magnetic Susceptibility

$$\bar{M} = N\mu\bar{L} = N\mu\tanh\left(\frac{Jq\bar{L}+\mu B}{kT}\right) \qquad (13.57)$$

$$\chi = \left(\frac{\partial\bar{M}}{\partial B}\right)_T = N\mu\left(\frac{\partial\bar{L}}{\partial B}\right)_T \qquad (13.58)$$

$$\frac{\partial\bar{L}}{\partial B} = \left(\frac{Jq}{kT}\frac{\partial\bar{L}}{\partial B} + \frac{\mu}{kT}\right)\operatorname{sech}^2() = \frac{\mu}{kT}\frac{1-\tanh^2()}{1 - T_c/T\tanh^2()} \qquad (13.59)$$

Therefore

$$\chi = \frac{N\mu^2}{k}\frac{1-\bar{L}^2}{T - T_c(1-\bar{L}^2)} \qquad (13.60)$$

For $\bar{L} \ll 1$, $T \gg \mu B/k$ and $T > T_c$.

$$\chi(T) \approx \frac{n\mu^2}{k}\frac{1}{T-T_c} \qquad (13.61)$$

This is the Curie-Weiss law.
If $T < T_c$, $T \gg \mu B/k$:
From $\bar{L}^2 \sim 3(1 - T/T_c)$

$$\chi(T) \approx \frac{N\mu^2}{2k(T_c - T)} \tag{13.62}$$

Recall the curie law:

$$\chi(T) \approx \begin{cases} \frac{N\mu^2}{3kT}(\text{classical}) \\ \frac{N\mu^2}{kT}(\text{Q.M. j=1/2}) \end{cases} \tag{13.63}$$

$T = T_c$, $kT_c \gg \mu B$.

$$\bar{L} = \tanh\left(\frac{T_c}{T}\bar{L} + \frac{\mu B}{kT}\right) \tag{13.64}$$

$$\approx \bar{L} + \frac{\mu B}{kT} - \frac{1}{3}\left(\bar{L} + \frac{\mu B}{kT}\right)^3 \tag{13.65}$$

$$\Rightarrow \bar{L} \approx \left(3\frac{\mu B}{kT_c}\right)^{1/3} \tag{13.66}$$

Universality

There are similarities between this system and phase transitions for the van der Walls equation of state near critical.

Example $L \approx \sqrt{3(1 - T/T_c)}$ and $\psi \approx \pm 2\sqrt{\tau}$.

$$\left(\frac{\partial \mu}{\partial B}\right)_T \approx \begin{cases} \frac{N\mu^2}{k(T-T_c)} & T \to T_c^+ \\ \frac{N\mu^2}{3k(T-T_c)} & T \to T_c^- \end{cases} \tag{13.67}$$

$$-\left(\frac{\partial \psi}{\partial \pi}\right)_T \approx \begin{cases} \frac{1}{6}\tau & T \to 0^+ \\ \frac{1}{12}\tau & T \to 0^- \end{cases} \tag{13.68}$$

Random Mixing Approximation

Initial approach for this type of problems. States are uncorrelated. This is equivalent to the mean field approximation (zeroth order).

Proof: From (31)

$$U = -\frac{JNq}{2} + 2Jq\bar{N}_+ - 4J\bar{N}_{++} - \mu B(2\bar{N}_+ - N) \tag{13.69}$$

where $\bar{N}_+ = N(1 + \bar{L})/2$.

From (4):

$$U = -\frac{J}{2}Nq\bar{L}^2 - \mu BN\bar{L} \tag{13.70}$$

$$\begin{aligned} \frac{\bar{N}_{++}}{N} &= \frac{q}{8}(1+\bar{L})^2 && (13.71) \\ \frac{\bar{N}_{++}}{Nq/2} &= \left(\frac{N_+}{N}\right)^2 && (13.72) \end{aligned}$$

$$\begin{aligned} \bar{N}_{+-} &= qN\left(\frac{1+\bar{L}}{2}\right)\left(\frac{1-\bar{L}}{2}\right) && (13.73) \\ N_{--} &= \frac{1}{2}qN\left(\frac{1-L}{2}\right)^2 && (13.74) \end{aligned}$$

First Order Approximation

Bethe approximation. Random mixing → "Quasi-chemical approximation". Read Pathra for details

13.4 Critical Exponents

Close to the critical point. Many systems have similar behaviour. Physical quantities follow power laws. → critical exponents.

Definitions:

Order parameter m: as $T \to T_c^+$: $m \to 0$, For $T < T_c$: $m \neq 0$.

Ordering field h: as $h \to 0$, $m \to m_0$, a limiting value, with $m_0 = 0$ for $T > T_c$.

Examples

1) magnetic system: $m = L$ and $h = \mu B/kT_c$

2) gas-liquid transition: $m = P - P_c$, (or $|P - P_c|$) and $h = P - P_c$.

Critical Exponents

β: $T \to T_c^-$: $m \to (T_c - T)^\beta$ $(h \to 0)$ on coexistence curve.

γ, γ':

$$\chi_0 \equiv \left(\frac{\partial m}{\partial h}\right)_T \sim \begin{cases} (T-T_c)^{-\gamma} & T > T_c \\ (T_c - T)^{-\gamma} & T < T_c \end{cases} \tag{13.75}$$

δ: $h \to 0^-$: $m \sim h^{1/\delta}$ $(T = T_c)$

α, α':

$$C_h \sim \begin{cases} (T-T_c)^{-\alpha} & T > T_c \\ (T_c - T)^{-\alpha} & T < T_c \end{cases} \tag{13.76}$$

Notice that van der Waals gas-liquid transition and mean field systems have the same exponents:

$\beta = 1/2, \gamma = \gamma' = 1, \delta = 3, \alpha = \alpha' = 0.$

Q & A:

1) Are exponents independent from on another?

No. Only two are truly independent.

2) What determines them?

- The dimension d of the system and not so much the geometry of the lattice.
- Number of components n
- Range of interaction.

Read Pathira for the dependence on d and n. For $d > 4$, exponents become independent of $d \to$ mean field values.

13.5 Thermodynamic Inequalities

Rushbrooke: $\alpha' + 2\beta + \gamma' \leq 2$ exactly. Griffiths: $\alpha' + \beta(\delta + 1) \leq 2$ exactly.

Based on plausible assumptions $\gamma' \geq \beta(\delta - 1)$ $\gamma \geq (2 + \alpha)(\delta - 1)/(\delta + 1)$.

Proof: Consider

$$C_P = C_V + TV \frac{[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P]^2}{[-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T]} \tag{13.77}$$

$$\Rightarrow C_P \geq \frac{[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P]^2}{[-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T]} \tag{13.78}$$

For $T \to T_c^-$:

$$()(T_c - T)^{-\alpha'} \geq \frac{()(T_c - T)^{2(\beta-1)}}{()(T_c - T)^{-\gamma'}} \tag{13.79}$$

$$\Rightarrow (T_c - T)^{2-(\alpha' - 2\beta - \gamma')} \geq \text{some constant} \tag{13.80}$$

$$\Rightarrow 2 - (\alpha' - 2\beta - \gamma') \leq 0 \tag{13.81}$$

Read Pathria for more on inequalities.

13.6 Landau's Phenomenological Theory

(Ehrenfest versus modern clasification)

1st order phase transition: -Associated with latent heat (modern) 1st order derivative of A is discontinuous (Ehrenfest) ex. solid-liquid ρ is discontinuous.

2nd order phase transition: - no latent heat (Modern) - 2nd order derivatives of A are discontinuous (Ehrenfest) ex. paro-feriomagnetism: $\chi - \partial M/\partial B$ is discontinuous.

$$\psi_0 \equiv \frac{A_0}{NkT_c} = q(t) + r(t)m_0^2 + s(t)m_0^4 \tag{13.82}$$

Notice that the subscript 0 indicates $h = 0$. Even powers in m imply a symmetry.

$t = (T - T_c)/T_c$, $|t| \ll 1$.
Close to critical, expand q, r, s in powers of t.

$$q(t) = \sum_{k=0}^{\infty} q_k t^k \quad \text{and} \quad r(t) = \sum_{k=0}^{\infty} r_k t^k \quad \text{and} \quad s(t) = \sum_{k=0}^{\infty} s_k t^k \tag{13.83}$$

Equilibrium: minimize ψ_0 with respect to m_0.

$$r(t)m_0 + 2s(t)m_0^3 = 0 \tag{13.84}$$

$$\Rightarrow m_0 = \begin{cases} 0 & \text{only solution for} \quad t > 0 \\ \pm\sqrt{-r(t)/2s(t)} & \qquad \text{when} \qquad\quad t < 0 \end{cases} \tag{13.85}$$

Sensible results:

$$m_0 \approx \pm \left[-\frac{r_0}{2s_0} \left[1 + \left(\frac{r_1}{r_0} - \frac{s_1}{s_0} \right) t \right] \right]^{1/2} \tag{13.86}$$

But we need m_0 when $t \to 0 \Rightarrow r_0 = 0$.

$$\Rightarrow m_0 \approx \pm \sqrt{-\frac{r_1 t}{2s_0}} \tag{13.87}$$

Must be real for $t < 0$, $\Rightarrow r_1 > 0, s_0 > 0$, $\Rightarrow \beta = 1/2$.

$$\psi_0(t, m_0) \approx q_0 + r_1 t m_0^2 + s_0 m_0^4 \tag{13.88}$$

Effect of ordering field h: assume $h > 0$.

$$\psi_h(t, m) \approx -hm + q(t) + r(t)m^2 + s(t)m^4 \tag{13.89}$$

Minimize with respect to m:

$$-h + 2rm + 4sm^3 = 0 \tag{13.90}$$

Susceptibility:

$$\chi = \left(\frac{\partial h}{\partial m} \right)_t^{-1} = \frac{1}{2r(t) + 12s(t)m^2} \tag{13.91}$$

a) $t \to 0^+$, $m = 0$:

$$\chi \approx \frac{1}{2r_1 t} \tag{13.92}$$

b) $t \to 0^-$, $m \approx \sqrt{r_1|t|/(2s_0)}$:

$$\chi \approx \frac{1}{4r_1|t|} \tag{13.93}$$

$\Rightarrow \gamma = \gamma' = 1$

$t = 0$, from (65): $m \approx (h/(4s_0))^{1/3}$, $\Rightarrow \delta = 3$.
Specific Heats

$$\begin{aligned} C_B &= T\left(\frac{\partial S}{\partial T}\right)_B = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_B = -TNkT_c\left(\frac{\partial^2 \psi}{\partial T^2}\right)_B = -\frac{NkTT_c}{T_c^2}\left(\frac{\partial^2 \psi}{\partial t^2}\right)_h \quad (13.94) \\ &\approx Nk\left(\frac{\partial^2 \psi}{\partial t^2}\right)_h \quad (13.95) \end{aligned}$$

Define $C_{h,m} = C_{B,\mu}/(Nk)$.
a) $t \to 0^+$, $m = 0$

$$c_h = c_m = -\left(\frac{\partial^2 \psi}{\partial t^2}\right)_h \approx -(2q_2 + 6q_3 t + \ldots) \quad (13.96)$$

b) $t \to 0^-$, $m^2 \approx -r_1 t/(2s_0)$

$$\begin{aligned} c_m &\approx -[(2q_2 + 6q_3 t + \ldots) + (2r_2 + \ldots)m^2 + \ldots] \quad (13.97) \\ &\approx -[2q_2 + (6q_3 - r_1 r_2/s_0)t + \ldots] \quad (13.98) \\ &\to -2q_2 \text{ as } t \to 0^- \quad (13.99) \end{aligned}$$

But

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_B \quad \text{and} \quad C_\mu = T\left(\frac{\partial S}{\partial T}\right)_\mu \quad (13.100)$$

Consider $S = S(T, \mu)$ and $\mu = \mu(T, B)$.

$$\begin{aligned} \delta S &= \left(\frac{\partial S}{\partial T}\right)_\mu \delta T + \left(\frac{\partial S}{\partial \mu}\right)_T \delta\mu \quad (13.101) \\ &= \frac{C_\mu}{T}\delta T + \left(\frac{\partial S}{\partial \mu}\right)_T \left[\left(\frac{\partial \mu}{\partial T}\right)_B \delta T + \left(\frac{\partial \mu}{\partial T}\right)_T \delta B\right] \quad (13.102) \end{aligned}$$

$$\Rightarrow C_B = T\left(\frac{\partial S}{\partial T}\right)_B = T\frac{C_\mu}{T} + T\left(\frac{\partial S}{\partial \mu}\right)_T \left(\frac{\partial \mu}{\partial T}\right)_B \quad (13.103)$$

$$C_\mu - C_B = -T\left(\frac{\partial S}{\partial \mu}\right)_T \left(\frac{\partial \mu}{\partial T}\right)_B \quad (13.104)$$

But $dE = TdS + Bd\mu$ and $dA - -SdT + Bd\mu$.

$$\left(\frac{\partial S}{\partial \mu}\right)_T = -\left(\frac{\partial B}{\partial T}\right)_\mu = \frac{(\partial \mu/\partial T)_B}{(\partial \mu/\partial B)_T} \quad (13.105)$$

$$\Rightarrow C_B = C_\mu = T\frac{[(\partial\mu/\partial T)_B]^2}{(\partial\mu/\partial B)_T} \tag{13.106}$$

with $T = T_c(1+t)$, $B = (kT_c/\mu)h$, $M = N\mu m$

$$\Rightarrow C_h = C_m = \frac{[(\partial m/\partial t)_h]^2}{(\partial m/\partial h)_T} \tag{13.107}$$

Recall

$$\chi = \left(\frac{\partial m}{\partial h}\right)_t \approx \frac{1}{4r_i|t|}, \quad t \to 0^- \tag{13.108}$$

$$m \approx \sqrt{\frac{r_1}{2s_0}|t|} \Rightarrow \left(\frac{\partial m}{\partial t}\right)_h \approx \frac{1}{2\sqrt{|t|}}\sqrt{\frac{r_1}{2s_0}} \tag{13.109}$$

$$\Rightarrow c_h - c_m \to \frac{r_1^2}{2s_0} \text{ as } t \to 0^- \tag{13.110}$$

c_m is continuous at $t = 0$

$$c_h|_{0^-}^{0^+} = -\frac{r_1^2}{2s_0} \tag{13.111}$$

and $\alpha = \alpha' = 0$

13.7 Scaling Hypothesis

Equation of state in Landau's model, close to critical.

Eq. (65) $h \approx 2r_1tm + 4s_0m^3$.

For $t \to 0^-$, recall $m \approx \pm\sqrt{f_1|t|/(2s_0)}$ rewrite 79 as

$$h \approx \frac{r_1^{3/2}}{s_0^{1/2}}|t|^{3/2}\left[2sgn(t)\frac{s_0^{1/2}m}{r_1^{1/2}|t|^{1/2}} + 4\left(\frac{s_0^{1/2}m}{r_1^{1/2}|t|^{1/2}}\right)^3\right] \tag{13.112}$$

$$\Rightarrow m = \frac{r_1^{1/2}|t|^{1/2}}{s_0^{1/2}} \propto f\left(\frac{s_0^{1/2}h}{r_1^{3/2}t^{3/2}}\right) \tag{13.113}$$

where f is a universal function for a given class of systems.

Similarly for $\psi \approx -hm + r_1tm^2 + s_0m^4$.

$$\psi \approx \frac{r_1^2}{s_0}t^2\left[-\frac{s_0^{1/2}}{r_1^{3/2}}\frac{h}{|t|^{3/2}}\frac{s_0^{1/2}m}{r_1^{1/2}|t|^{1/2}} + sgn(t)\left(\frac{s_0^{1/2}m}{r_1^{1/2}|t|^{1/2}}\right)^2 + \left(\frac{s_0^{1/2}m}{r_1^{1/2}|t|^{1/2}}\right)^4\right] \tag{13.114}$$

From (80):

$$\psi \approx \frac{r_1^2 t^2}{s_0} \times g\left(\frac{s_0^{1/2} h}{r_1^{3/2}|t|^{3/2}}\right) \tag{13.115}$$

Notice that the initial equation of state: 3 variables k, m, t. Scaled equation of state: only two variables $m/|t|^{3/2}$, $h/|t|^{3/2}$.

Notice: From (81)

$$m = -\left.\frac{\partial\psi}{\partial h}\right|_{t\to 0} \tag{13.116}$$

which is consistent with (82), (80).

Extension

$$\psi \approx F t^{2-\alpha} f\left(\frac{Gh}{|t|^{\triangle}}\right) \tag{13.117}$$

Notice: F, G: non universal parameters (depend on system)
f: universal function
$\alpha, \triangle$: universal exponents
$f = f_+$ for $t > 0$ or f_- for $t < 0$
Eq. 13.117 constitutes the "scaling hypothesis".

All critical exponents will be determined by α and $\triangle$.

In principle, we should consider $\alpha, \triangle$ for $t > 0$ and $\alpha', \triangle'$ for $t < 0$. Let us assume $\alpha = \alpha'$ and $\triangle = \triangle'$.

Connection with Critical Exponents

From 64.1:

$$m = -\frac{\partial\psi}{\partial h} = -F|t|^{2-\alpha}(f')\frac{G}{|t|^{\triangle}} = -FGt^{2-\alpha-\triangle}f' \tag{13.118}$$

$$\chi = \left(\frac{\partial m}{\partial h}\right)_t = -FG^2|t|^{2-\alpha-2\triangle}f''\left(\frac{Gh}{|t|^{\triangle}}\right) \tag{13.119}$$

Recall that: as $h \to 0$, $m \propto |t|^{\beta}$. As $|t| \to 0$, $h \to 0$: $\chi \to t^{-\gamma}$.

$$\beta = 2 - \alpha - \triangle \tag{13.120}$$
$$\gamma = 2\triangle + \alpha - 2 \tag{13.121}$$
$$2\beta + \gamma = 2 - \alpha \tag{13.122}$$
$$\alpha + 2\beta + \gamma = 2 \tag{13.123}$$

Consider

$$m = -FG|t|^{2-\alpha-\triangle} f'\left(\frac{Gh}{|t|^{\triangle}}\right) \tag{13.124}$$

$$\Rightarrow t = G^{1/\triangle} h^{1/\triangle} \phi\left(\frac{m}{|t|^{2-\alpha-\triangle}}\right) \tag{13.125}$$

Substitute in (84) to get

$$m \propto h^{(2-\alpha-\triangle)/\triangle} \phi\left(\frac{m}{|t|^{2-\alpha-\triangle}}\right) \propto h^{1/\delta} \tag{13.126}$$

$$\Rightarrow \delta \frac{\triangle}{2-\alpha-\triangle} \tag{13.127}$$

From (88):

$$\delta = \frac{2-\alpha-\beta}{\beta} = \frac{\beta+\gamma}{\beta} \tag{13.128}$$

From (90) $\Rightarrow \beta(\delta - 1) = \gamma$.
But from (*): $\beta(\delta + 1) = 2 - \alpha$

$$\Rightarrow \gamma = \frac{2-\alpha}{\delta+1}(\delta - 1) \tag{13.129}$$

Specific heat:

$$c_h|_{h=0} = -\left(\frac{\partial^2 \psi}{\partial t^2}\right) \propto |t|^{-\alpha} \tag{13.130}$$

α appearing in (83) is the critical exponent associated with c_h.

Chapter 14

Fluctuations

14.1 Spatial Correlations in a Fluid

A N-particle configuration distribution function $F_N(1,\dots,N)$ with $1 \leftrightarrow \vec{r}_1$. Normalization: $\int d1\dots dNF_N = 1$

Reduced distribution functions:

$$F_m(1,\dots,m) = \frac{N!}{(N-m)!}\int d(m+1)\cdots dNF_N \tag{14.1}$$

Special cases:

$$\begin{aligned} F_1(1) &= N\int d2\dots dNF_N & (14.2)\\ &= \int d2\cdots dNF_N + \int d1d3\cdots dNF_N + \cdots + \int d1\cdots d(N-1)F_N & (14.3)\end{aligned}$$

Equals the probability density of finding a particular particle time N. Equals particle density at position 1.

In a homogeneous system, $F_1 = N/V = n$.

Similarly,

$$F_2(1,2) = \sum_{i\neq j}\int \prod_{k\neq i, k\neq j} dkF_N \tag{14.4}$$

From the normalization of F_N

$$\int d1d2F(1,2) - N(N-1) \sim N^2 \tag{14.5}$$

For a homogeneous system without correlations between particles, $F(1,2) = n^2$

Define: $F_2(1,2) = n^2 g(\vec{r}_{12,})$.

In the absence of correlations, $g(\vec{r}) = 1$.

$g(\vec{r})$ is the probability density of finding a pair of particles $\vec{r}$ apart.

Define $\nu(\vec{r}) = g(\vec{r}) - 1$. Notice that $\nu(\vec{r}) \neq 0$ only when pairs of particles are correlated. Assumption: correlation length is way less than the size of the system.

Consider $\overline{(\Delta N)^2}$ in a given volume V_A. Define $\mu(\vec{r}) = 1$ if $\vec{r}$ in V_A, 0 otherwise.

$$\begin{aligned}
\bar{N}_A &= \sum_i \int d1 \cdots dN F_N \mu(\vec{r}_1) && (14.6)\\
&= N \int d1 \cdots dN F_N \mu(\vec{r}_1) && (14.7)\\
&= \int d1 F_1(1) \mu(\vec{r}_1) && (14.8)\\
&= \int_{V_A} d1 F_1 && (14.9)\\
&= nV_A && (14.10)
\end{aligned}$$

Similarly,

$$\begin{aligned}
N_A^2 &= \sum_i \mu(\vec{r}_i) \sum_j \mu(\vec{r}_j) && (14.11)\\
&= \sum_{i \neq j} \mu(\vec{r}_i)\mu(\vec{r}_j) + \sum_i \mu(\vec{r}_i) && (14.12)
\end{aligned}$$

$$\begin{aligned}
\overline{N_A^2} &= \int d1 \cdots dN \left[\sum_{i \neq j} \mu(\vec{r}_i)\mu(\vec{r}_j) + \sum_i \mu(\vec{r}_i) \right] F_N && (14.13)\\
&= \int_{V_A} d1 \int_{V_A} d2 F_2(1,2) + \int_{V_A} d1 F_1(1) && (14.14)\\
&= \int_{V_A} d1 \int_{V_A} d2 m^2 [\nu(\vec{r}_{12}) + 1] + \bar{N}_A && (14.15)
\end{aligned}$$

Changing integration variables $\vec{r}_1, \vec{r}_2 \to \vec{r}_1, \vec{r}_{12}$ and making use of the short correlation length assumption

$$\begin{aligned}
\overline{N_A^2} = m^2 \int d1 \int d^3 r_{12} [\nu(\vec{r}_{12}) + 1] + \bar{N}_A && (14.16)\\
= \frac{\bar{N}_A^2}{V_A^2} V_A [\int d^3 r \nu(\vec{r}) + V_A] + \bar{N}_A && (14.17)
\end{aligned}$$

Therefore

$$\begin{aligned}\frac{\overline{(\Delta N_A)^2}}{N_A} &= \frac{\overline{N_A^2} = \bar{N}_A^2}{N_A} & (14.18)\\ &= \frac{\bar{N}_A}{V_A}\int d^3r\nu(\vec{r}) + \bar{N}_A + 1 - \bar{N}_A & (14.19)\\ &= 1 + m\int d^3r\nu(\vec{r}) & (14.20)\end{aligned}$$

From 14.1.20 in Pathria:

$$(\Delta N)^2 = kT\kappa_T\frac{N^2}{V} \tag{14.21}$$

$$\int d^3r\nu(\vec{r}) = \frac{1}{n}[nkT\kappa_T - 1] \tag{14.22}$$

For an ideal gas: $V = NkT/P$,

$$-\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = \kappa_T = \frac{1}{P} = \frac{1}{nkT} \tag{14.23}$$

in that case

$$\int d^3r\nu(\vec{r}) = 0 \tag{14.24}$$

14.2 Einstein-Smolukowski Theory of Brownian Motion

Random walk in 1D: - Particles make random steps with equal probability to the right or to the left. - After n steps, the probability of having m steps to the right is

$$P(m) = \frac{n!}{m!(n-m)!}\left(\frac{1}{2}\right)^m\left(\frac{1}{2}\right)^{n-m} \tag{14.25}$$

Net displacement corresponding to m steps to the right:

$$\begin{aligned} x_m &= m\triangle - (n-m)\triangle & (14.26)\\ &= (2m-n)\triangle & (14.27)\end{aligned}$$

where $\triangle$ is the length of a single step.

$$
\begin{aligned}
\bar{x}_m &= \sum_{m=0}^{n} P(m)x_m &(14.28)\\
&= \sum_{m=0}^{n} \frac{n!}{m!(n-m)!}\left(\frac{1}{2}\right)^m\left(\frac{1}{2}\right)^{n-m}(2m-n)\triangle &(14.29)
\end{aligned}
$$

We use $\sum_{m=0}^{n} P(m) = 1$,

$$
\sum_{m=0}^{n} \frac{n!}{m!(n-m)!}\left(\frac{1}{2}\right)^m\left(\frac{1}{2}\right)^{n-m} m = \bar{m} = p\frac{\partial}{\partial p}\sum_m \frac{n!}{m!(m-n)!}p^m q^{n-m}\Bigg|_{p=q=1/2} \tag{14.30}
$$

$$
\bar{m} = p\frac{\partial}{\partial p}(p+q)^n\Bigg|_{p=q=1/2} = np|_{p=1/2} = \frac{n}{2} \tag{14.31}
$$

which gives $\bar{x}_m = 0$.

$$
\overline{x_m^2} = \triangle^2 \sum_{m=0}^{n} \frac{n!}{m!(n-m)!}p^m q^{n-m}(4m^2 - 4nm + n^2)\Bigg|_{n=1/2, m=1/2} \tag{14.32}
$$

We have expressions for $\sum_m P(m)$ and $\sum_m P(m)m$

We need $\sum_m P(m)m^2$ This is obtained as for $\sum_m P(m)m$

$$
\overline{m^2} = p\frac{\partial}{\partial p}\left[p\frac{\partial}{\partial p}(p+q)^n\right]\Bigg|_{p=q=1/2} = \frac{n(n+1)}{4} \tag{14.33}
$$

$$
\overline{x_m^2} = \triangle^2[n(n+1) - 2n^2 + n^2] = n\triangle^2 \tag{14.34}
$$

If a step is made every τ^* time intervals, then $n = t/\tau^*$

$$
\overline{x_m^2} = \sigma^2 = \frac{\triangle^2}{\tau^*}\tau \tag{14.35}
$$

14.2.1 Connection with Diffusion

Consider a 1D diffusion equation:

$$
\frac{\partial \rho}{\partial t} + \frac{\partial \Gamma}{\partial x} = 0 \tag{14.36}
$$

where Γ is the flux of ρ.

Fick's model: $\Gamma = -D\partial\rho/\partial x$, where D is diffusion coefficient (Fick's law of diffusion).

$$
\frac{\partial \rho}{\partial t} - D\frac{\partial^2 \rho}{\partial x^2} = 0 \tag{14.37}
$$

Solution for an initially localised (delta-function) distribution at $t = 0$:

$$\rho = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{14.38}$$

where $\sigma^2 = 2Dt$.

Comparing with (17), we get

$$D = \frac{1}{2}\frac{\triangle^2}{\tau^*} \tag{14.39}$$

Alternative derivation:

At x, the net particle flux to the right is (1/2 number of particles at $i-1 = 1/2$ number of particles at $i)/\tau^*$. Or

$$\Gamma(x) = \frac{N_{i-1} - N_i}{2\tau^*} \tag{14.40}$$

If ρ_i is the particle density, then $N_i = \rho_i \triangle$ and $N_{i-1} = \rho_{i-1}\triangle$.

$$\Gamma(x) = -\frac{\rho_i - \rho_{i-1}}{2\tau^*}\triangle = -\frac{\triangle^2}{2\tau^*}\frac{\rho_i - \rho_{i-1}}{\triangle} \approx -\frac{\triangle^2}{2\tau^*}\frac{\partial \rho}{\partial x} \tag{14.41}$$

14.3 Langerin's Theory

$$M\frac{d\vec{v}}{dt} = \mathcal{F} == \frac{v}{B} + F(t) \tag{14.42}$$

where $-v/B$ is an average friction and $F(t)$ is random. We assume $\bar{F} = 0$. For a charged particle in an electric field at steady state: $-\bar{v}/B + qE = 0, \Rightarrow \bar{v} = qBE - \mu E$, where $\mu = qB$ is the mobility.

Average of (23):

$$\mu\frac{d\langle\vec{v}\rangle}{dt} = -\frac{\langle\vec{v}\rangle}{B} \tag{14.43}$$

$$\langle\vec{v}\rangle = \vec{v}_0 e^{-t/\tau} \tag{14.44}$$

with $\tau = \mu B$.

Consider the equation for the velocity:

$$\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{A}(t) \tag{14.45}$$

where $\langle\vec{A}\rangle = 0$.

Take the dot product with $\vec{r}$.

$$\begin{aligned}\vec{r}\cdot\vec{v} &= \vec{r}\cdot\frac{d\vec{r}}{dt}=\frac{1}{2}\frac{dr^2}{dt} &(14.46)\\ \vec{r}\cdot\frac{d\vec{v}}{dt} &= \vec{r}\cdot\frac{d^2\vec{r}}{dt^2}=\frac{1}{2}\frac{d^2r^2}{dt^2}-v^2 &(14.47)\end{aligned}$$

Average and use $\langle\vec{r}\cdot\vec{A}\rangle=0$

$$\frac{d^2\langle r^2\rangle}{dt^2}+\frac{1}{\tau}\frac{d\langle r^2\rangle}{dt}=2\langle v^2\rangle \tag{14.48}$$

At thermal equilibrium $\langle v^2\rangle=3kT/\mu$

$$\frac{d^2\langle r^2\rangle}{dt^2}+\frac{1}{\tau}\frac{d\langle r^2\rangle}{dt}=6\frac{kT}{\mu} \tag{14.49}$$

Homogeneous solutions $h_1=1$ and $h_2=e^{-\tau/t}$
Particular solution $h_1u_1+h_2u_2$
with $h_1u_1'+h_2u_2'=0$
Substitute (35) in (32) and make use of (36)

$$\begin{pmatrix} h_1 & h_2\\ h_1' & h_2'\end{pmatrix}\begin{pmatrix} u_1'\\ u_2'\end{pmatrix}=\begin{pmatrix} 0\\ 6\frac{kT}{\mu}\end{pmatrix} \tag{14.50}$$

Solve for initial conditions $d\langle r^2\rangle/dt=0$ and $\langle r^2\rangle|_{t=0}=0$

$$\langle r^2\rangle=\frac{6kT\tau^2}{\mu}\left[\frac{t}{\tau}-(1-e^{-t/\tau})\right] \tag{14.51}$$

For

$$\begin{aligned} t\ll\tau:\langle r^2\rangle &\propto t^2 &(14.52)\\ t\gg\tau:\langle r^2\rangle &\approx \frac{6kT\tau}{M}t &(14.53)\end{aligned}$$

Compare with (20) in 1D: $\sigma^2=2Dt$.
In 1D:

$$\langle v^2\rangle=\frac{kT}{M}\Rightarrow\langle r^2\rangle=\frac{2kT\tau}{M}t \tag{14.54}$$

$$D=\frac{kT\tau}{\mu}=kTB=\frac{kT\mu}{q} \tag{14.55}$$

This is the Einstein relation, or Nernstrelation.
Consider $\langle v^2\rangle$:

$$\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} = \vec{A}(t) \tag{14.56}$$

$$\begin{aligned}
\frac{d}{dt}(ve^{t/\tau}) &= A(t)e^{t/\tau} && (14.57)\\
v(t) &= v_0 e^{-t/\tau} + \int_0^t dt' A(t') e^{-(t-t')/\tau} && (14.58)\\
v^2(t) &= v_0^2 e^-2t/\tau + 2v_0 e^{-t/\tau} \int_0^t dt' A(t') e^{-(t-t')/\tau} + \int_0^t dt' \int_0^t dt'' A(t')A(t'') e^{-(2t-t'-t'')} && (14.59)
\end{aligned}$$

We take the average of each term. Make use of $\langle A(t') \rangle = 0$ and $\langle A(t')A(t'') \rangle \equiv K(t,t')$
Properties of K:

1. In a stationary ensemble: $K(t',t'') = K(t'+T, t''+T) \Rightarrow K = K(t''-t') = K(s)$
2. $K(0) = \langle A^2 \rangle > 0$
3. $\forall s, K(s) \leq K(0)$ Proof:

$$\langle [A(t') \pm A(t'')]^2 \rangle = 2K(0) \pm 2K(t''-t') \geq 0 \Rightarrow |K(s)| \leq K(0) \tag{14.60}$$

4. $K(s) = K(-s)$ Proof:

$$\begin{aligned}
K(s) &= \langle A(t)A(t+s) \rangle && (14.61)\\
&= \langle A(t-s)A(t) \rangle \text{ from a stationary ensemble} && (14.62)\\
&= \langle A(t)A(t-s) \rangle \text{ from commutatinarity} && (14.63)\\
&= K(-s) && (14.64)
\end{aligned}$$

5. Assume $K(s) \to 0$ as $s \to \infty$, i.e., there is a finite coherence time.

Consider the last term in (44):

$$e^{-2t} \int_0^t dt' \int_0^t dt'' e^{(t'+r'')\tau} K(t''-t') = X \tag{14.65}$$

Change variables of integration:

$$T = \frac{t'+t''}{2} \quad \text{and} \quad S = t''-t' \tag{14.66}$$

$$X = \int_0^{t/2} dT e^{2T/\tau} \int_{-2T}^{2T} dS K(S) + \int_{t/2}^{t} dT e^{2T/\tau} \int_{2(t-T)}^{-2(t-T)} dS K(S) \tag{14.67}$$

Assume a short coherence time compared to t:

$$X \approx \int_0^t dT e^{2T/\tau} \int_{-\infty}^{\infty} dS K(S) \approx \frac{\tau}{2} C(e^{2t/\tau} - 1) \tag{14.68}$$

From (44)

$$\langle v^2 \rangle = v_0^2 e^{-2t/\tau} + \frac{C\tau}{2}(1 - e^{-2t/\tau}) \tag{14.69}$$

and

$$\lim_{t\to\infty} \langle v^2 \rangle = \frac{C\tau}{2} = \frac{3kT}{\mu} \tag{14.70}$$

from equipartition

$$C = \int_{-\infty}^{\infty} ds K(s) = 6\frac{kT}{M\tau} = 6\frac{kT}{BM^2} \tag{14.71}$$

or

$$\frac{1}{B} = \frac{M^2}{6kT} \int_{-\infty}^{\infty} ds K(s) \tag{14.72}$$

This is the fluctuation - dissipation theorem.

14.4 Kakker - Plank Equation

Consider the 1-particle distribution function f_1. Assume $W(\vec{x}, \vec{v}, \vec{w}, t)$ is the rate at which particles at $\vec{x}, \vec{v}, t$ change their velocity by $\vec{w}$, that is, the rate at which $\vec{v} \to \vec{v} + \vec{w}$. The evolution of f_1 is then given by

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f = \int d^3w \, \{-f(\vec{x}, \vec{v}, t)W(\vec{x}, \vec{v}, \vec{w}, t) + f(\vec{x}, \vec{v} - \vec{w}, t)W(\vec{x}, \vec{v} - \vec{w}, \vec{w}, t)\} \tag{14.73}$$

Assume: $W \approx 0$ unless $|\vec{w}|$ is small

$$\begin{aligned} \frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f &= \int d^2w \, \{-fW \qquad (14.74) \\ &+ \left(f - \vec{w} \cdot \partial_v f + \frac{1}{2}\vec{w}\vec{w} : \partial_v \partial_v f\right)\left(W - \vec{w} \cdot \partial_v W + \frac{1}{2}\vec{w}\vec{w} : \partial_v \partial_v W\right)\} \qquad (14.75) \end{aligned}$$

Keeping terms of order 2 or below:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + \partial_v(\vec{\mu}_1 f) - \frac{1}{2}\partial_v \partial_v : (\vec{\mu}_2 f) = 0 \tag{14.76}$$

where

$$\vec{\mu}_1 = \int d^3 w W \vec{w} \tag{14.77}$$

$$\vec{\mu}_2 = \int d^3 w W \vec{w}\vec{w} \tag{14.78}$$

$$\tag{14.79}$$

14.5 Onsager Relations

Consider a system described in terms of state variables x_i. At equilibrium, $x_i = \bar{x}_i$ are such that S is maximum. If x_i deviate slightly from $\bar{x}_i$, we expect "currents" $\dot{x}_i$ that will tend to restore equilibrium. For small deviations

$$\dot{x}_i = \gamma_{i,j} X_j \tag{14.80}$$

where X_j is the restoring "forces".

Consider S near equilibrium

$$S(x_i) \approx S(\bar{x}_i) + (x_i - \bar{x}_i)\frac{\partial S}{\partial x_i} + \frac{1}{2}(x_i - \bar{x}_i)(x_j - \bar{x}_j) \left.\frac{\partial^2 S}{\partial x_i \partial x_j}\right|_{\bar{x}_i} \tag{14.81}$$

where the first derivative vanishes at equilibrium.

$$\Delta S \equiv S(x_i) - S(\bar{x}_i) \approx -\frac{1}{2}\beta_{ij}(x_i - \bar{x}_i)(x_j - \bar{x}_j) \tag{14.82}$$

Driving forces:

$$X_i = \frac{\partial S}{\partial x_i} = -\beta_{ij}(x_j - \bar{x}_j) \tag{14.83}$$

Notice that

$$\beta_{ij} = -\left.\frac{\partial^2 S}{\partial x_i \partial x_j}\right|_{\bar{x}_i} = \beta_{ji} \tag{14.84}$$

Time scale: In $\dot{x}_i = \gamma_{ij} X_j$ the time derivative is considered on a macroscopic time, much larger than fluctuation times at a microscopic scale. On that time scale approach to equilibrium is irreversible.

At the microscopic level, there can be very short time scale variations. ON that scale, physics is time reversible.

Consider $\langle x_i(0) x_j(s) \rangle$ ensemble averaged over, with $s \ll$ macroscopic time scale. Time reversibility $\Rightarrow \langle x_i(0) x_j(s) \rangle = \langle x_i(0) x_j(-s) \rangle$.

Stationarity $\langle x_i(0) x_j(s) \rangle = \langle x_i(-s) x_j(0) \rangle \Rightarrow \langle x_i(0) x_j(s) \rangle = \langle x_i(s) x_j(0) \rangle$

Let τ^* be the characteristic microscopic collision time. $\tau \gg \tau^*$ but small macroscopically.

From (7.1)

$$\frac{\langle x_i(0)x_j(\tau)\rangle - \langle x_i(0)x_j(0)\rangle}{\tau} = \frac{\langle x_i(\tau)x_j(0)\rangle - \langle x_i(0)x_j(0)\rangle}{\tau} \tag{14.85}$$

or $\langle x_i(0)\dot{x}_j(0)\rangle = \langle \dot{x}_i(0)x_j(0)\rangle$

From (6) $\langle x_i(0)\gamma_{ij}X_k(0)\rangle = \langle \gamma_{ik}X_k(0)x_j(0)\rangle$
where

$$\langle x_iX_j\rangle = \frac{\int dx_1\dots dx_N x_ix_je^{S/k}}{\int dx_1\dots dx_N e^{S/k}} = \frac{\int dx_1\dots dx_N x_ix_je^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/(2k)}}{\int dx_1\dots dx_N e^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/(2k)}} \tag{14.86}$$

Similarly for

$$\langle x_i\rangle = \frac{\int dx_1\dots dx_N x_ie^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/(2k)}}{\int dx_1\dots dx_N e^{-\beta_{ij}(x_i-\bar{x}_i)(x_j-\bar{x}_j)/(2k)}} = \bar{x}_i \tag{14.87}$$

From (12)

$$\frac{\partial \bar{x}_k}{\partial \bar{x}_l} = \frac{1}{k}\langle x_k\beta_{ml}(x_m-\bar{x}_m)\rangle = -\frac{1}{k}\langle x_kX_l\rangle\delta_{kl} \Rightarrow \langle x_jX_l\rangle = -k\delta_{kl} \tag{14.88}$$

Thus, (9) becomes

$$\gamma_{jk}\delta_{ki} = \gamma_{ik}\delta_{jk} \tag{14.89}$$

or $\gamma_{ij} = \gamma_{ji}$.
This constitutes the Onsager reciprocity relations.

Part I

Appendices

Appendix A

Method of Steepest Descent

Example: approximate $n!$ for large n.

$$\begin{aligned} n! &= \int_0^\infty dx s^n e^{-x} && \text{(A.1)} \\ &= \int_0^\infty dx e^{-x+n\ln x} && \text{(A.2)} \end{aligned}$$

The integral has a maximum at $x_0 = n$.
Let us expand the exponent around the maximum

$$\begin{aligned} -x + n\ln x &\approx -x_0 + n\ln x_0 + \frac{(x-x_0)^2}{2}\,\frac{d^2}{dx^2}(-x+n\ln x)\bigg|_{x_0} && \text{(A.3)} \\ &= -x_0 + n\ln x_0 - \frac{(x-x_0)^2}{2x_0} && \text{(A.4)} \end{aligned}$$

Substitute into Eq. A.2 to get

$$\begin{aligned} n! &\approx \int_{x_0-a}^{x_0+a} dx e^{-x_0+n\ln x_0-n(x-x_0)^2/(2x_0^2)} + \int_{-\infty}^{x_0-a} dx e^{-x+n\ln x} + \int_{x_0+a}^{\infty} dx e^{-x+n\ln x} && \text{(A.5)} \\ &\approx x_0^n e^{-x_0} \int_{-\infty}^{\infty} dx e^{-n(x-x_0)^2/(2x_0^2)} + \int_{-\infty}^{x_0-a} dx e^{-x+n\ln x} + \int_{x_0+a}^{\infty} dx e^{-x+n\ln x} && \text{(A.6)} \end{aligned}$$

where the second two integrals are negligible.

Remember

$$\int_0^\infty dx x^p e^{ax^2} = \frac{1}{2}\Gamma\left(\frac{p+1}{2}\right)\frac{1}{a^{(p+1)/2}} \tag{A.7}$$

and

$$\Gamma(x) = (x-1)\Gamma(x-1) = (x-1)! \quad \text{and} \quad \Gamma(1/2) = \sqrt{\pi} \tag{A.8}$$

with $x_0 = n$

$$\begin{aligned} n! &\approx n^n e^{-n} \Gamma(1/2) \sqrt{2n} && \text{(A.9)} \\ &= \sqrt{2\pi} n^{n+1/2} e^{-n} && \text{(A.10)} \end{aligned}$$

Appendix B

Ising Model

$$H = -\sum_{i=1}^{N} B\mu_B \sigma_{zi} - \sum_{i<j} 2J_{ij}\vec{\sigma_i}\cdot\vec{\sigma_j} \tag{B.1}$$

Heisenberg model

$$\sum_{i<j} 2J_{ij}\vec{\sigma_i}\cdot\vec{\sigma_j} \approx 2J \sum_{\text{nearest neighbours}} \vec{\sigma_i}\cdot\vec{\sigma_j} \tag{B.2}$$

Ising model

$$\sum_{i<j} 2J_{ij}\vec{\sigma_i}\cdot\vec{\sigma_j} \approx J \sum_{\text{nearest neighbours}} \vec{s_i}\cdot\vec{s_j} \tag{B.3}$$

Define J as a coupling constant. More general, J_{ij} can be calculated from

$$\vec{B}_i j = \frac{\mu_0}{4\pi}\frac{3(\vec{m}\cdot\hat{r})\hat{r} - \vec{m}}{r^3} \tag{B.4}$$

$$J_{ij} = -\frac{\mu_0\mu_B^2}{4\pi}\frac{3(\hat{n}_i\cdot\hat{r}_{ij})(\hat{n}_j\cdot\hat{r}_{ij}) - \hat{n}_i\cdot\hat{n}_j}{r_{12}^3} \tag{B.5}$$

Ising model:

1D: no phase transitions, can be solved analytically

2D: phase transition is possible, analytic solution exists

3D: phase transition, no analytic solution

B.0.1 Example

1D system with periodic boundary conditions.

Consider the interaction energy only.

$$Q = \sum_{s_1 \ldots s_N} e^{\beta J(s_1 s_2 + s_2 s_3 + \ldots + s_N s_1)} \tag{B.6}$$

$$= \sum_{b_1 \ldots b_N}^{\prime} e^{\beta J(b_1 + \ldots + b_N)} \tag{B.7}$$

with $b_i = s_i s_{i+1}$ and $b_N = s_N s_1$

Constraint $\prod_i b_i = \prod_i s_i^2 = 1$.

For $N \to \infty$, consider all b_i as independent (i.e., remove the constraint).

$$Q \approx \sum_{b_1 \ldots b_N} e^{\beta J(b_1 + \ldots + b_N)} = (2\cosh \beta J)^N \tag{B.8}$$

Notice that there can be no phase transition in a 1D system.

Ground state: Consider all spins up (periodic boundary conditions) $E = -NJ\mu B$. Consider a magnetised state $N/2$ spin up in a row and $N/2$ spin down in a row.

$$E = -(\frac{N}{2} - 1)J\mu B - (\frac{N}{2} - 1)J\mu B + 2J\mu B = -(N-4)J\mu B \tag{B.9}$$

Excitation energy $\sim 4J\mu B$. Order is broken for $T \sim 4J\mu B/(Nk) \to 0$ in thermodynamic limit

In 2D, excitation $\propto N^{1/2}$. This is sufficient to stabilise an ordered state.

B.0.2 Solution

Onsager 1940 in 2D Ising model, $B = 0$.

$$Q = [2\cosh \beta J e^I]^N , \tag{B.10}$$

where

$$I = \frac{1}{2\pi} \int_0^{\pi} dQ \ln \frac{1}{2}[1 + (1 - \kappa^2 \sin^2 \phi)^{1/2}] \tag{B.11}$$

where

$$\kappa = \frac{2\sinh 2\beta J}{\cosh^2 2\beta J} \tag{B.12}$$

$A = -kT \ln Q$ is non analytic.

Spontaneous magnetisation for $T < T_c = 2.269J/k$.

Solution of

$$\sinh\left(\frac{2J}{kT_c}\right) = 1 \tag{B.13}$$

$$C_V = \frac{8k}{\pi}(\beta j)^2 \ln\frac{1}{|T-T_c|} \tag{B.14}$$

$M/N \sim (T_c - T)^\beta$, $T < T_c$, $\beta = 1/8$.
In 3D: no analytic solution has been found, but numerical solutions are possible.

B.1 Renormalisation Group Theory

Consider a 1D system for simplicity

$$Q = \sum_{s_1\ldots s_N} e^{\kappa(s_1s_2+s_2s_3+\ldots+s_Ns_1)} \tag{B.15}$$

where $\kappa = \beta J$.

Rewrite this as

$$\begin{aligned} Q(\kappa, N) &= \sum_{s_1\ldots s_N} e^{\kappa(s_1s_2+s_2s_3)}e^{\kappa(s_3s_4+s_4s_5)}\ldots && \text{(B.16)} \\ &= \sum_{s_1s_3\ldots}[e^{\kappa(s_1+s_3)}+e^{-\kappa(s_1+s_3)}][e^{\kappa(s_3+s_5)}+e^{-\kappa(s_3+s_5)}]\ldots && \text{(B.17)} \end{aligned}$$

Look for a transformation that makes (2) "look" like (1). If we have

$$e^{\kappa(s_1+s_3)} + e^{-\kappa(s_1+s_3)} = f(\kappa)e^{\kappa' s_1 s_2} \tag{B.18}$$

then

$$Q(\kappa, N) = \sum_{s_1s_3\ldots} f(\kappa)e^{\kappa' s_1s_3}f(\kappa)e^{\kappa' s_3s_5}\ldots = f(\kappa)^{N/2}Q(\kappa', N/2) \tag{B.19}$$

We start with N degrees of freedom. We now have $N/2$. The same transformation (if it exists) can be applied further to reduce the number of degrees of freedom.

Consider (3) for the various possibilities of s_1, s_3:

$$\begin{aligned} s_1 &= s_3 = \pm 1 && \text{(B.20)} \\ s_1 &= -s_3 = \pm 1 && \text{(B.21)} \end{aligned}$$

$$\begin{aligned} e^{2\kappa} + e^{-2\kappa} &= f(\kappa)e^{\kappa'} && \text{(B.22)} \\ 2 &= f(\kappa)e^{-\kappa'} && \text{(B.23)} \end{aligned}$$

$$e^{2\kappa'} = \frac{e^{2\kappa} + e^{-2\kappa}}{2} \tag{B.24}$$

where $\kappa'(1/2)\ln(\cosh 2\kappa)$
and

$$\begin{aligned} f^2(\kappa) &= 2(e^{2\kappa} + e^{-2\kappa}) && \text{(B.25)} \\ f(\kappa) &= 2\sqrt{\cosh 2\kappa} && \text{(B.26)} \end{aligned}$$

Let $\ln Q = Ng(\kappa)$. The left side is an extensive quantity and the right side is an intensive quantity.

From (3.1):

$$\ln Q = \frac{N}{2} \ln f(\kappa) + Q(\kappa', N/2) \tag{B.27}$$

$$\begin{aligned} g(\kappa) &= \frac{1}{2} \ln f(\kappa) + \frac{1}{2} g(\kappa') && \text{(B.28)} \\ g(\kappa') &= 2g(\kappa) - \ln(2\sqrt{\cosh 2\kappa}) && \text{(B.29)} \end{aligned}$$

Define: 6, 7, 10 are the “renomalisation group equations”.

Notice that from 6, $\kappa' < \kappa$.

Explanation: Transformation. - larger distances between “particles” - weaker coupling

Inverse transformation

$$\begin{aligned} \kappa &= \frac{1}{2} \cosh^{-1}(e^{2\kappa'}) && \text{(B.30)} \\ g(\kappa) &= \frac{1}{2} g(\kappa') + \frac{1}{2} \ln 2 + \frac{\kappa'}{2} && \text{(B.31)} \end{aligned}$$

Solution method: - start with $\kappa \ll 1 \rightarrow$ interactions are negligible - apply (11), (12) until κ is close to the value of interest.

Example: $\kappa = 0.01$, $Q(\kappa, N) \approx 2^N \Rightarrow g(0.01) \approx \ln 2$.

1st iteration: $\kappa = 0.10034, g = 0.698147$

2nd iteration: $\kappa = 0.327447, g = 0.745814$

5th iteration: $\kappa = 1.316710, g = 1.386078$

Appendix C

Lagrangian of a Point Particle in an Electromagnetic Field

Assuming $v \ll c \Rightarrow$, the equation of motion is

$$m\frac{dv_i}{dt} + q\left[\partial_i\phi + \frac{\partial A_i}{\partial t} - \vec{v}\times(\nabla\times\vec{A})|_i\right] = 0\,. \tag{C.1}$$

Write

$$\begin{aligned}
\vec{v}\times(\nabla\times\vec{A})|_i &= \varepsilon^{ijk}v_j\varepsilon^{klm}\partial_l A_m && \text{(C.2)}\\
&= (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})v_j\partial_l A_m && \text{(C.3)}\\
&= v_j\partial_i A_j - v_j\partial_j A_i && \text{(C.4)}
\end{aligned}$$

Eq. C.1 becomes

$$\begin{aligned}
m\frac{\partial v_i}{\partial t} + q\left[\partial_i\phi + \frac{\partial A_i}{\partial t} - \partial_i(\vec{v}\cdot\vec{A}) + \vec{v}\cdot\nabla A_i\right] &= 0 && \text{(C.5)}\\
\frac{\partial}{\partial t}(mv_i) + q\left[\frac{\partial A_i}{\partial t} + \vec{v}\cdot\nabla A_i\right] + q\left[\partial_i\phi + -\partial_i(\vec{v}\cdot\vec{A})\right] &= 0 && \text{(C.6)}\\
\frac{\partial}{\partial t}(mv_i + qA_i) + \partial_i(q\phi - q\vec{v}\cdot\vec{A}) &= 0 && \text{(C.7)}\\
& && \text{(C.8)}
\end{aligned}$$

Or

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v_i}\right) - \frac{\partial L}{\partial q_i} = 0 \tag{C.9}$$

with

$$L = \frac{mv^2}{2} + q\vec{v} \cdot \vec{A} - q\phi \,. \tag{C.10}$$

The canonical momenta as defined by

$$p_i = \frac{\partial L}{\partial v_i} = mv_i + qA_i \,. \tag{C.11}$$

The Hamiltonian is obtained from

$$\begin{aligned} H &= \sum_i p_i v_i - L & \text{(C.12)} \\ &= mv^2 + \vec{v} \cdot \vec{A} - \frac{mv^2}{2} - q\vec{v} \cdot \vec{A} + q\phi & \text{(C.13)} \\ &= \frac{mv^2}{2} + q\phi \,. & \text{(C.14)} \end{aligned}$$

But H must be written in terms of $\vec{r}$ and $\vec{p}$, where $\vec{r}$ is the position vector. Writing

$$\frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{|\vec{p} - q\vec{A}|^2}{2m} \tag{C.15}$$

we find

$$H = \frac{|\vec{p} - q\vec{A}|^2}{2m} + q\phi \,. \tag{C.16}$$

Appendix D

Useful Formula

The multinomial expansion is

$$(x_1 + x_2 + \ldots + x_m)^n = \frac{n!}{\sum_{k_1+k_2+\ldots k_m} k_1!k_1!\cdots k_n!} \prod_{1\leq t\leq n} x_t^{k_t} \,. \tag{D.1}$$