MONASH University

School of Physics & Astronomy

PHS4200/PHS4021 Statistical Mechanics

Lecture 1: Introduction to Thermodynamics and Statistical Mechanics

1.1   Introduction

In this lecture we introduce the mathematical framework of classical thermodynamics and statistical mechanics. We begin with a brief overview of thermodynamics, which provides a phenomenological description of macroscopic systems, based on three basic laws; namely, the zeroth, first and second laws of thermodynamics[1]. We will only be concerned with systems in thermal equilibrium, for which there is a simple relationship between microscopic properties and macroscopic behaviour. A major focus of statistical mechanics is how the physical behaviour of a system comprised of many particles (typically of the order of Avogadro's number N_A = 6.022 × 10^{23}) can be understood in terms of an ensemble of "similarly prepared" systems. We will first consider classical statistical mechanics, where the state of a system of N particles at time t is specified by $3N$ canonical coordinates $\{q_i(t)\}$ (i = 1,2,...,$3N$) and $3N$ canonical momenta $\{p_i(t)\}$ (i = 1,2,...,$3N$). The dynamics of the system is described by the classical Hamiltonian, which is an energy functional of the canonical coordinates and momenta, i.e., H = $H(\{q_i\},\{p_i\})$. In the Hamiltonian formulation of classical mechanics, the equations of motion are given by:

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \quad and \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \quad (i = 1,2,3,...,3N). \tag{1.1}$$

The state of the system is then described by a point in a $6N$-dimensional space, called phase space or Γ-space. Statistical mechanics describes the equilibrium state of a system as an average over all states in phase space. We will return to discuss this important point in a later lecture, but first we turn our attention to the macroscopic laws of thermodynamics.

1.2   Laws of Thermodynamics

The laws of thermodynamics are based on empirical observations of the physical world (e.g., the phase transitions of water). Macroscopic thermodynamics seeks to describe the state of a system in terms of physical quantities (the state variables) and relate these variables using the equations of state and the laws of thermodynamics. The thermodynamics of a system is specified by thermodynamic potentials, which are functions of state variables; these potentials are considered to completely characterise the macrostate of the system and are sufficiently general that they can be used to understand a physical system independent of its specific details.   Each thermodynamic potential has associated with it a number of state variables, e.g., the internal energy U is considered to be a function of entropy S, volume V, particle number N, and so on, whence U = $U(S,V,N,...)$. There are a number of different thermodynamic potentials that provide

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[1] There is a third law of thermodynamics (also known as Nernst's law), which states that the entropy of a system at absolute zero is a universal constant. Without loss of generality this constant may be set to zero. A consequence of the third law is that absolute zero temperature cannot be reached via a finite number of quasi-static processes (i.e., those remaining arbitrarily close to equilibrium at all stages of the process), see e.g., https://en.wikipedia.org/wiki/Third_law_of_thermodynamics

an equivalent way of encoding information, each related to U via a Legendre transformation (see Appendix A); however, in these lectures we will mainly be concerned with the Helmholtz free energy $F = F(T,V,N)$, whose state variables are temperature T (or inverse temperature[2] $\beta = 1/k_B T$), volume V and particle number N.

1.2.1 The Zeroth Law

Two systems in thermal contact are said to be in thermal equilibrium if they have the same temperature. The zeroth law of thermodynamics defines temperature (but does not fix the temperature scale) by postulating a state quantity β (or equivalently the temperature $T = 1/k_B \beta$). If two systems are characterised by different values of β they will not remain in equilibrium when brought into contact. Likewise if two system are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other. The temperature of a system can be measured by bringing it into contact with a thermometer and measuring some thermometric parameter θ. The temperature will be the value of θ when the thermometer has come into thermal equilibrium with the system being measured. There are many suitable thermometric parameters, such as the electrical resistance of a conductor, the height of a column of mercury in a tube, etc.

Example 1.1: Show that the behaviour of an ideal gas can be used to define a suitable thermometric parameter θ.

Solution

Many gases exhibit the same behaviour when they are dilute. Consider a dilute gas contained within a glass bulb whose volume V is constant. The mean value of the pressure p of the gas plays the role of the thermometric parameter, since

$$\frac{p_0 V}{p_1 V} = \frac{p_0}{p_1} = \frac{\theta_0}{\theta_1} \quad or \quad \theta_1 = \left(\frac{p_1}{p_0}\right)\theta_0.$$

This constant volume gas thermometer can therefore be used to define temperature. Similarly a constant pressure gas thermometer can be constructed for which

$$\frac{p V_0}{p V_1} = \frac{V_0}{V_1} = \frac{\theta_0}{\theta_1} \quad or \quad \theta_1 = \left(\frac{V_1}{V_0}\right)\theta_0.$$

The equation of state for an ideal gas[3], relates the pressure p, volume V and temperature T of a dilute gas via

$$pV = nRT,$$

where n is the number of moles of gas and R is the ideal gas constant:

$$R = N_A k_B = 8.3144598 \; J \; mol^{-1} K^{-1}.$$

To describe real gases we can generalise the ideal gas law to a virial equation of the form:

$$pV = nRT + b(T)p + c(T)p^2 + \ldots ,$$

where the quantities $b(T)$, $c(T)$,... are known as the virial coefficients [1].

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[2] As from May 20th 2019 Boltzmann's constant has the precise value $k_B = 1.380649 \times 10^{-23} \; JK^{-1}$.

[3] In a later lecture we will derive the ideal gas law using the methods of statistical mechanics.

1.2.2 The First Law

The first law of thermodynamics is a statement of conservation of energy - it assigns an internal energy U to a macroscopic state. If the system is isolated and does not exchange heat or work with its surroundings, the internal energy is a constant; it is identical to the total energy defined in mechanics. However, if the system interacts, by exchanging heat or work (reversibly or irreversibly) with its surroundings, there is a change in the internal energy given by:

$$dU = dW + dQ, \tag{1.2}$$

where dW and dQ represent small changes in the work done by the system and the heat absorbed by the system, respectively. One must be careful in interpreting Eq. (1.2), since the changes are written as exact differentials. However, this may not be the case, and in general the work done by the system and the heat absorbed by the system depend on how the changes take place. To emphasise this, we should use the symbols $đW$ and $đQ$ to denote inexact differentials. On the other hand the change in internal energy dU is an exact (total) differential, which depends only on the initial and final state of the system, i.e., the state function U (thermodynamic potential) can be obtained by path integration along an arbitrary curve.

Example 1.2: Consider the compression of an ideal gas. Show that the work done on the system depends on the path taken between states.

Solution

The work performed on an ideal gas when it is compressed at constant temperature between state A with volume V_A and state B with volume V_B is:

$$W_{A \to B} = - \int_{V_A}^{V_B} p \, dV = -nRT \int_{V_A}^{V_B} \frac{dV}{V} = nRT \ln \left(\frac{V_A}{V_B} \right).$$

The negative sign arises because positive work is done on the gas when it is compressed (i.e., the change in volume $dV < 0$). If we now go from state A to state B via an intermediate state C, so that the temperature is no longer constant during the process, then from Fig. 1.1 the work done on the gas is:

$$W_{A \to C \to B} = -p_A(V_B - V_A) = nRT \left(\frac{V_A - V_B}{V_A} \right).$$

Again since $V_A > V_B$ the work done on the gas is positive. Further, it is also evident that:

$$W_{A \to B} > W_{A \to C \to B}.$$

Hence the work done by an ideal gas depends on the path taken in going from A to B. For this reason dW is not an exact differential and there is no state function representing work in thermodynamics. The processes represented in the above scenarios are only well defined if they take place slowly, so the system is considered to be in thermal equilibrium at each stage. These type of processes are referred to as quasi-static and are reversible. If no heat flows into or out of the system the process is known as adiabatic, which occurs for thermally isolated systems. The isothermal process $A \to B$ (at constant temperature) is not adiabatic and since $T_A = T_B$, we have $U(A) = U(B)$. In this case $dU = 0$ and $dQ = - dW$.
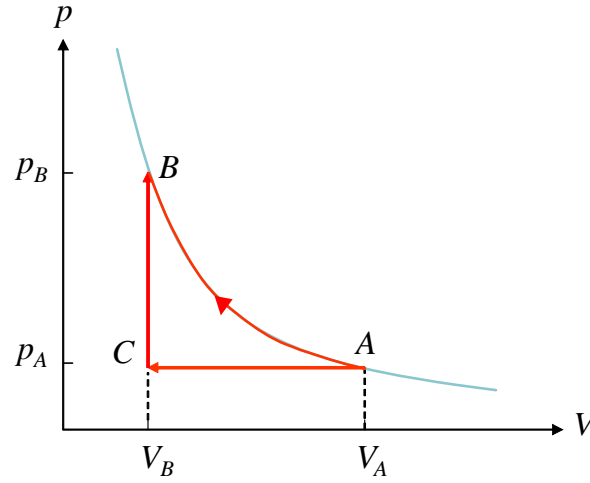
Figure 1.1: *The work done on an ideal gas depends on the path in p-V space.*

1.2.3 The Second Law

The second law of thermodynamics defines a state variable, called the entropy S, which provides a fundamental connection between thermodynamics and statistical mechanics. In this context entropy S is a measure of the disorder of a system and is related via Boltzmann's postulate to the number of possible microscopic configurations Ω of the system, i.e., $S \propto \ln\Omega$. In classical thermodynamics the entropy of a system is such that a thermally isolated system going from one macrostate to another will lead to an increase in entropy, i.e.,

$$\Delta S \geq 0. \tag{1.3}$$

The entropy can be defined for a system that is not isolated and undergoes a quasi-static process in which it absorbs an amount of heat dQ:

$$dS = \frac{dQ}{T}, \tag{1.4}$$

where T is the absolute temperature. The definition (1.4) is only valid for quasi-static processes. However, the entropy is a state function and we can calculate the change in entropy in an arbitrary process between two equilibrium states A and B as follows:

$$\Delta S = S(B) - S(A) = \int_A^B \frac{dQ}{T}. \tag{1.5}$$

A consequence of the second law is that it is not possible to build a machine whose sole effect is to extract heat from a thermal bath[4] and convert it directly into work - there are no perpetual motion machines! Consider a Carnot process (also known as a Carnot engine) in which a substance (e.g., an ideal gas) is carried through the reversible process shown in the *p-V* diagram in Fig. 1.2 (a). The path AB is an isotherm at temperature T_2 during which the system absorbs an amount of heat Q_{AB}. Likewise the path CD is an isotherm at temperature $T_1 < T_2$, during which the system gives up heat Q_{CD}. Paths BC and DA are adiabatic processes. The Carnot process can also be represented schematically as shown in Fig. 1.2 (b). The work done in one cycle is determined from the first law of thermodynamics:

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[4] A thermal bath, also know as a heat bath or heat reservoir, is a much larger system, with which our sub-system interacts. A process involving the absorption or rejection of heat from the sub-system will not change the temperature of the thermal bath.

$$\Delta U = \Delta W + \Delta Q \quad \Rightarrow \quad W = Q_{AB} - Q_{CD}, \tag{1.6}$$

where we have used the fact that $\Delta U = 0$ for a closed path. The efficiency of the Carnot process is defined as:

$$\eta_C = \frac{W}{Q_{AB}} = \frac{Q_{AB} - Q_{CD}}{Q_{AB}} = 1 - \frac{Q_{CD}}{Q_{AB}}. \tag{1.7}$$

If $W > 0$, then $Q_{AB} > 0$ and $Q_{CD} > 0$. If $W < 0$, then $Q_{AB} < 0$ and $Q_{CD} < 0$, and the heat engine operates in reverse, i.e., it becomes a refrigerator, removing heat from a thermal bath at a lower temperature and rejecting it to the thermal bath at a higher temperature. Real heat engines will have an efficiency less that η_C.
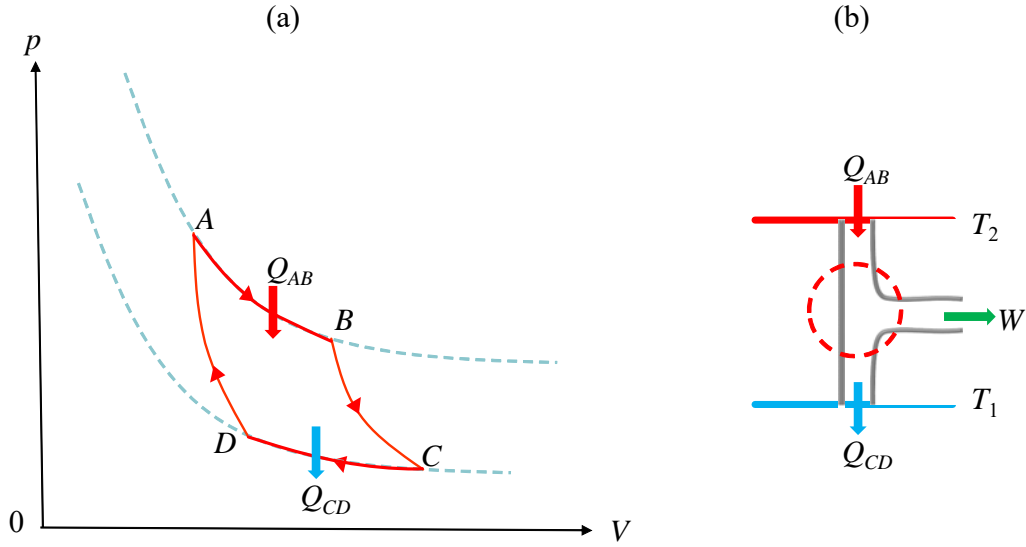

Figure 1.2: (a) *The Carnot process is described by the two isothermal and two adiabatic paths in p-V space.* (b) *Schematic representation of a Carnot engine.*

The second law is used to define the absolute temperature scale. Consider a Carnot engine operating between two thermal reservoirs with absolute temperatures T_1 and $T_2 > T_1$. We can show that Eq. (1.7) can be re-written as:

$$\eta_C = 1 - \frac{T_1}{T_2}. \tag{1.8}$$

Since $0 \le \eta_C \le 1$, the absolute temperature of any thermal bath is always greater than zero. The definition of absolute temperature[5] does not depend on the properties of a specific material; further, as defined by the second law, the absolute temperature scale is identical to the that determined using the thermometric properties of an ideal gas (see Sec. 1.2.1).

Exercise 1.1: *Show that Eq. (1.8) follows from Eq. (1.7).*

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[5] The absolute temperature scale, which defines the SI unit of kelvin (K), utilises the triple point of water. Accordingly $0\ K = -273.15\ °C$, see e.g.,
https://en.wikipedia.org/wiki/Thermodynamic_temperature

However, from May 20th 2019 the thermodynamic temperature is defined by taking the fixed numerical value of Boltzmann's constant to be $k_B = 1.380649 \times 10^{-23}\ JK^{-1}$.

The entropy of a system is an extensive[6] quantity, one of a number of such quantities upon which the internal energy depends, i.e., $U = U(S,V,N,...)$. The differential dU is:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N,...} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N,...} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V,...} dN + ...$$ (1.9)

$$= TdS - pdV + \mu dN + ... ,$$

where we have defined the corresponding intensive parameters from the derivatives of the internal energy, i.e.,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N,...} , \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N,...} , \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V,...} \quad etc.$$ (1.10)

where T, p and μ denote the temperature, pressure and chemical potential, respectively.

Example 1.3: Calculate the entropy of an ideal gas as a function of T and V. You may assume the number of particles is fixed.

Solution

From Eq. (1.9) we have for a reversible process:

$$dU = TdS - pdV \quad (dN = 0).$$

The relevant equations for an ideal gas are:

$$pV = nRT = Nk_BT \quad and \quad U = \frac{3}{2}Nk_BT,$$

where N is the number of particles in the gas. The expression for U follows from the equipartition theorem, which assigns an energy $\frac{1}{2}k_BT$ for each degree of freedom. Solving for dS:

$$dS = \frac{dU}{T} + \frac{pdV}{T} = \frac{3}{2}Nk_B\frac{dT}{T} + Nk_B\frac{dV}{V}.$$

Upon integrating from an initial state (T_i,V_i,S_i) to a final state (T_f,V_f,S_f) we obtain:

$$S_f(T_f,V_f) - S_i(T_i,V_i) = \int_{S_i}^{S_f} dS = \frac{3}{2}Nk_B\int_{T_i}^{T_f}\frac{dT}{T} + Nk_B\int_{V_i}^{V_f}\frac{dV}{V}$$

$$= \frac{3}{2}Nk_B\ln\left(\frac{T_f}{T_i}\right) + Nk_B\ln\left(\frac{V_f}{V_i}\right)$$

$$= Nk_B\left[\ln\left(\frac{T_f}{T_i}\right)^{3/2} + \ln\left(\frac{V_f}{V_i}\right)\right].$$

As one would expect, the entropy of an ideal gas increases with temperature and volume. It is also expected to increase with particle number; however, in this example we have fixed N. For an isolated system the equilibrium state is one having maximum entropy.

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[6] An extensive parameter is an additive state quantity proportional to the amount of matter in the system, e.g., entropy S, volume V, the number of particles N, etc. By way of comparison, an intensive parameter is not additive and does not depend on the amount of matter in the system, e.g., temperature T, pressure p, chemical potential μ, etc.

As Example 1.2 shows, the entropy of an ideal gas is only defined up to an arbitrary additive constant. The second law does not uniquely determine the entropy of a system. The third law of thermodynamics (see Footnote 1) is invoked to remedy this situation; it states that the entropy per particle of two large systems in equilibrium will approach the same value as $T \to 0^+$. At absolute zero the entropy is a universal constant, which may be taken to be zero, i.e., as $T \to 0^+$, $S \to 0$.

1.3   Thermodynamic Potentials

In addition to the internal energy, thermodynamics exploits a number of different thermodynamic potentials (also known as state functions). The bewildering array of thermodynamic variables and state functions can be a source of confusion. However, the basic idea behind this "zoo" of thermodynamic potentials is very simple. Consider the internal energy, $U = U(S,V)$ defined in terms of the two state variables S and V. These are the "natural" variables of U. However, in many situations it is easier to control the intensive variable T, than the extensive variable S. Similarly one may want to know the pressure p of a system rather than its volume V. In these (and other situations) we seek a new state function (thermodynamic potential), which is expressed in terms of T and V, or S and p, etc. There is a straightforward way of achieving this using a Legendre transformation (see Appendix A). The essential idea is that any convex function of a set of variables can be expressed in an equivalent way by eliminating one or more variables in favour of the derivative(s) of the function with respective to the relevant variable(s). For example, starting with the internal energy $U = U(S,V)$, we can perform a Legendre transformation to a new thermodynamic potential $F = F(T,V)$ by replacing S with T, defined in Eq. (1.10):

$$U(S,V) \to F(T,V) = U(S,V) - TS \quad where \quad T = \left(\frac{\partial U}{\partial S} \right)_V. \tag{1.11}$$

The new thermodynamic potential is known as the Helmholtz free energy and it will be pivotal to our treatment of statistical mechanics. The total differential of F is:

$$dF = dU - d(TS) = TdS - pdV - TdS - SdT = -SdT - pdV. \tag{1.12}$$

Hence we see that the Helmholtz free energy is a function of T and V. We can also extend the list of variables upon which U depends. For example, including the term μN [see Eq. (1.9)] we have:

$$dF = dU - d(TS) = TdS - pdV + \mu dN - TdS - SdT = -SdT - pdV + \mu dN. \tag{1.13}$$

In this case F depends on T, V and N, and we have:

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V} \right)_{T,N.} \quad and \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}. \tag{1.14}$$

There are other commonly used thermodynamic potentials, also related to the internal energy by a Legendre transformation. Table 1.1 lists the most frequently used potentials in classical thermodynamics. We conclude this overview of classical thermodynamics with a discussion of the Maxwell relations. These relations follows from the fact that the thermodynamic potentials are exact differentials. For example, consider a function $f = f(R)$ of three state variables $R = (X,Y,Z)$ whose differential is:

$$df = \left(\frac{\partial f}{\partial X} \right)_{Y,Z} dX + \left(\frac{\partial f}{\partial Y} \right)_{X,Z} dY + \left(\frac{\partial f}{\partial Z} \right)_{X,Y} dZ = \nabla f \cdot dR. \tag{1.15}$$

The differential df is exact if and only if

$$\oint_C df = \oint_C \nabla f \cdot d\mathbf{R} = \oint_C \mathbf{F} \cdot d\mathbf{R} = 0 \qquad (\mathbf{F} = \nabla f), \tag{1.16}$$

where C is a closed curve in state space. It follows from Stokes' theorem that the condition for exactness reduces to:

$$\nabla \times \mathbf{F} = 0 \quad \Rightarrow \quad \frac{\partial F_Z}{\partial Y} = \frac{\partial F_Y}{\partial Z}, \qquad \frac{\partial F_X}{\partial Z} = \frac{\partial F_Z}{\partial X} \quad and \quad \frac{\partial F_Y}{\partial X} = \frac{\partial F_X}{\partial Y}. \tag{1.17}$$

Exercise 1.2: *Use Stokes' theorem to establish Eq.* (1.17).

We can now apply Eq. (1.17) to establish the Maxwell relations for U. From Eqs. (1.9) and (1.10) we have the following correspondences:

$$U(S,V,N) \;\leftrightarrow\; f(X,Y,Z) \quad and \quad (F_X,F_Y,F_Z) \;\leftrightarrow\; (T,-p,\mu), \tag{1.18}$$

from which the Maxwell relations follow, i.e.,

$$\left(\frac{\partial \mu}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial N}\right)_{S,V}, \qquad \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad and \quad \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}. \tag{1.19}$$

The Maxwell relations reflect the fact that the variables in the thermodynamic potentials are not completely independent.

Exercise 1.3: *Establish the Maxwell relations for the Helmholtz free energy* $\mathbf{F} = F(T,V,N)$.

Table 1.1: *Commonly used thermodynamic potentials with the corresponding Legendre transformations.*

Thermodynamic Potential	State Variables	Legendre Transformation
Internal energy U	(S, V, N)	-
Helmholtz free energy F	(T, V, N)	$U - TS$
Enthalpy H	(S, p, N)	$U + pV$
Gibbs free energy G	(T, p, N)	$U - TS + pV$
Grand potential Φ	(T, V, μ)	$U - TS - \mu N$

1.4 Statistical Mechanics

Having discussed the laws of thermodynamics we now turn our attention to statistical mechanics, whose objective is to relate the equilibrium properties of a system to the behaviour of its constituents, which typically involves a very large number of particles ($\sim 10^{23}$). In later lectures we will establish the full machinery of classical and quantum statistical mechanics. However, it is useful to begin by highlighting the connection between macroscopic quantities (e.g., entropy) and the microscopic properties of a system.

The state of a system of N particles is described by a point in a $6N$-dimensional phase space (i.e., Γ-space). A microstate is therefore described by a set of coordinates in phase space:

$$(\mathbf{q},\mathbf{p}) \equiv (\{q_i\},\{p_i\}) = (q_1,q_2, \cdots ,q_{3N}; p_1,p_2, \cdots ,p_{3N}) \tag{1.20}$$

We denote the number of microstates accessible to the system by Ω. A fundamental postulate of statistical physics is that, in equilibrium, a system has equal a priori probability of being found in any one of the accessible microstates. The number of microstates Ω compatible with a given macrostate is a quantity similar to the entropy of the system. If we consider two independent systems, then the total number of microstates for the combined system is:

$$\Omega_T = \Omega_1 \Omega_2. \tag{1.21}$$

Since the entropy is an extensive (additive) quantity, the total entropy of the combined system is simply:

$$S_T = S_1 + S_2. \tag{1.22}$$

If we assume that the entropy is a function of the number of microstates Ω, then the obvious functional relationship that satisfies Eqs. (1.21) and (1.22) is:

$$S \propto \ln\Omega, \tag{1.23}$$

which establishes the fundamental relationship between thermodynamics and statistical mechanics. Later we will show that the constant of proportionality is none other than Boltzmann's constant, whence $S = k_B \ln\Omega$. The following simple example illustrates these ideas.

Example 1.4: Evaluate Ω and S for a system of N independent indistinguishable particles, each of which can be in two discrete states, having energy E_1 and E_2.

Solution

Consider n_1 particles in state 1 and n_2 particles in state 2, with $n_1 + n_2 = N$. The number of ways of assigning N particles so that n_1 of them are in state 1 and n_2 are in state 2 is given by the usual combinatoric formula[7], i.e.,

$$\frac{N!}{n_1! n_2!} = \frac{N!}{n_1!(N-n_1)!}.$$

The total number of accessible microstates is then:

$$\Omega(N) = \sum_{n_1 = 0}^{N} \frac{N!}{n_1!(N-n_1)!},$$

with the following constraints: $n_1 + n_2 = N$ and $n_1 E_1 + n_2 E_2 = E$. Let's ignore the second constraint[8], whence we can evaluate the sum exactly. To do so we exploit the binomial expansion, which is written as:

$$(a + b)^N = \sum_{n_1 = 0}^{N} \frac{N!}{n_1!(N-n_1)!} a^{n_1} b^{N-n_1}.$$

Upon setting $a = b = 1$, we obtain $\Omega(N) = 2^N$.

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[7] This is just the number of different combinations of N indistinguishable particles, n_1 of which are in state 1 and n_2 are in state 2, i.e.,

$$^N C_{n_1} \equiv \binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!} = \frac{N!}{n_1! n_2!} \qquad (n_1 + n_2 = N),$$

where the factor $n_1! n_2!$ in the denominator accounts for the irrelevant permutations of the indistinguishable particles.

[8] In a later lecture we will treat the problem of constraints using the method of Lagrange multipliers.

We could have anticipated this result, since each particle can be in one of two states. The corresponding entropy is:

$$S = k_B \ln \Omega(N) = k_B N \ln 2.$$

Example 1.5: Use Stirling's approximation (see Appendix B) to evaluate $\Omega(N)$ in Example 1.4.

Solution

Start with the expression for the number of microstates $\Omega(N)$, i.e.,

$$\Omega(N) = \sum_{n_1 = 0}^{N} \frac{N!}{n_1!(N-n_1)!} = \sum_{n_1 = 0}^{N} t(n_1),$$

We will evaluate $\Omega(N)$ for large N by retaining the largest term in the sum. Consider the term:

$$t(n_1) = \frac{N!}{n_1!(N-n_1)!},$$

We want to maximise this term for large N by exploiting Stirling's approximation (see Appendix B):

$$N! \approx \sqrt{2\pi N}\, e^{-N} N^N \qquad (N \gg 1).$$

It is more convenient to deal with $\ln N!$ which is a more slowly varying function, in which case Stirling's approximation has the form:

$$\ln N! \approx \frac{1}{2}\ln 2\pi N - N + N\ln N = N\ln N - N + O(\ln N) \qquad (N \gg 1).$$

Using this approximation we have:

$$\ln t(n_1) \approx N\ln N - N - n_1\ln n_1 + n_1 - (N-n_1)\ln(N-n_1) + N - n_1$$
$$= N\ln N - n_1\ln n_1 - (N-n_1)\ln(N-n_1).$$

The maximum is found from:

$$\left(\frac{d\ln t(n_1)}{dn_1} \right)_{n_1 = n_1^*} = 0 \quad \Rightarrow \quad -\ln n_1 - 1 + \ln(N-n_1) + 1 = 0.$$

Hence we have:

$$\ln\left(\frac{N-n_1}{n_1} \right) = 0 \quad or \quad n_1 = n_1^* = \frac{1}{2}N.$$

Thus the most probable distribution has $n_1^* = N/2,$ and the largest term in $\ln\Omega(N)$ is:

$$\ln t(n_1^*) = N\ln N - n_1^*\ln n_1^* - (N-n_1^*)\ln(N-n_1^*).$$
$$= N\ln N - \frac{N}{2}\ln\left(\frac{N}{2}\right) - \left(\frac{N}{2}\right)\ln\left(\frac{N}{2}\right).$$
$$= N\ln N - N\ln\left(\frac{N}{2}\right)$$
$$= N\ln 2.$$

The entropy $S = k_B N \ln 2$ therefore agrees with the previous calculation, which is surprising, since it means that the largest term in the sum gives the exact result as the full summation! To see how this comes about consider the bounds on $\Omega(N)$, i.e.,

$$t(n_1^*) \leq \Omega(N) \leq N t(n_1^*) \quad and \quad \ln t(n_1^*) \leq \ln\Omega(N) \leq \ln[N t(n_1^*)].$$

Hence we have:

$$N\ln 2 \le \ln\Omega(N) \le N\ln 2 + \ln N.$$

However, since N is large, the term $\ln N$ is negligible (i.e., $\ln N \ll N$).

1.4.1 Entropy Encoding

An interesting application of the concept of entropy is in lossless data compression. For an "alphabet" comprising N symbols $\{\alpha_i\}$ ($i = 1,2,...,N$), each with probability $\{p_i\}$ ($i = 1,2,...,N$), the Shannon entropy of the source is defined as:

$$H_S(\{p_i\}) = -\sum_{i=1}^{N} p_i \log_2 p_i, \tag{1.24}$$

where a base 2 logarithm is used. Here H_S represents the average number of bits per symbol from the source. According to the Shannon source coding theorem[9] no lossless data compression scheme can improve on the entropy (1.24). There is a vast literature on data compression schemes based on entropy encoding[10].

Exercise 1.4: *Using an 8 bit ASCII code requires* $21 \times 8 = 168$ *bits to encode the letters (including the space) in the source text* "statistical mechanics". *Calculate the Shannon entropy of this source text. There are many different codes that can be used to represent information. A popular data compression technique is Huffman encoding (see e.g.,* https://en.wikipedia.org/wiki/Huffman_coding). *Show that the number of bits per symbol required using Huffman encoding is* 3.2602, *which demonstrates a compression of* 40.8% *compared to ASCII encoding.*

1.4.2 A Random Walk in One Dimension

It is instructive to conclude our introduction to statistical mechanics by analysing a random walk, which is used as a model of Brownian motion, as well as many other processes, including fluctuations in stock market prices. The continuum limit of a random walk is the diffusion equation. In mathematical finance this diffusion equation is known as the Black-Scholes equation, and is used to model options (or more generally financial derivatives).

Figure 1.3 shows a random walk of 1,000 steps in two dimensions (generated using Mathematica); however, here we consider a simpler one-dimensional random walk, in which at each step the "walker" can either turn left (L) or right (R). After a total of N steps, each of step length a, the walker will have made n_L steps to the left, and n_R steps to the right; consequently the walker will have moved a distance:

$$d = a(n_L - n_R) = as \qquad (n_L + n_R = N). \tag{1.25}$$

---

[9] A pdf of Shannon's 1948 paper which provides the foundations for modern information theory can be accessed at:
    http://jim-stone.staff.shef.ac.uk/BookInfoTheory/shannons_book_1948.pdf

[10] A starting point to access the literature on entropy coding and data compression may be found at:

    https://en.wikipedia.org/wiki/Entropy_(information_theory)
    http://www.data-compression.info/Algorithms/EC/

Figure 1.3: *A random walk of* 1000 *steps in two dimensions.*

We assume the steps are independent - the walker has no "memory", so the process is Markovian (i.e., future steps are dictated only by the present location of the walker). At each step we also assume there is equal probability that the walker steps left or right ($p_L = p_R = \frac{1}{2}$). The number of ways the walker can take N steps of which n_L are to the left and n_R to the right is given by:

$$\mathbb{N}(n_L) = \frac{N!}{n_L! n_R!} = \frac{N!}{n_L!(N-n_L)!}. \tag{1.26}$$

You should immediately recognise this as the same formula that we met in Examples 1.4 and 1.5, and hence we expect the analysis for large N to be similar! The probability that the walker makes n_L steps to the left out of a total of N steps is:

$$P(n_L) = \mathbb{N}(n_L) p_L^{n_L} p_R^{n_R} = \frac{N!}{n_L!(N-n_L)!}\left(\frac{1}{2}\right)^{n_L}\left(\frac{1}{2}\right)^{n_R} = \frac{N!}{n_L!(N-n_L)!}\left(\frac{1}{2}\right)^{N}. \tag{1.27}$$

From Eq. (1.25) we have:

$$n_L = \frac{1}{2}(N + s) \quad and \quad n_R = \frac{1}{2}(N - s). \tag{1.28}$$

The probability (1.27), which is just the binomial probability, can now be written in terms of the variable $s = n_L - n_R$, i.e.,

$$P(s) = \frac{N!}{[\frac{1}{2}(N+s)]![\frac{1}{2}(N-s)]!}\left(\frac{1}{2}\right)^{N}. \tag{1.29}$$

It is more convenient to work with $\ln P(s)$, which is a more slowly varying function of s than $P(s)$, whence we have:

$$\ln P(s) = \ln N! - \ln[\frac{1}{2}(N+s)]! - \ln[\frac{1}{2}(N-s)]! + \ln\left(\frac{1}{2}\right)^{N}. \tag{1.30}$$

For large values of N we once again exploit Stirling's approximation (see Appendix B), i.e.,

$$\ln N! \approx \frac{1}{2}\ln 2\pi N - N + N\ln N = N\ln N - N + O(\ln N) \quad (N \gg 1). \tag{1.31}$$

Applying this approximation to Eq. (1.30) we obtain:

$$\ln P(s) \approx (N \ln N - N) - \left[\frac{1}{2}(N+s)\ln\tfrac{1}{2}(N+s) - \tfrac{1}{2}(N+s)\right]$$
$$- \left[\frac{1}{2}(N-s)\ln\tfrac{1}{2}(N-s) - \tfrac{1}{2}(N-s)\right] - N\ln 2. \tag{1.32}$$

Expanding and simplifying gives:

$$ln P(s) \approx N\ln\left(\frac{N}{2}\right) - \frac{N}{2}\left(1 + \frac{s}{N}\right)\ln\left[\frac{N}{2}\left(1 + \frac{s}{N}\right)\right] - \frac{N}{2}\left(1 - \frac{s}{N}\right)\ln\left[\frac{N}{2}\left(1 - \frac{s}{N}\right)\right]$$
$$= -\frac{N}{2}\ln\left(1 + \frac{s}{N}\right) - \frac{s}{2}\ln\left(1 + \frac{s}{N}\right) - \frac{N}{2}\ln\left(1 - \frac{s}{N}\right) + \frac{s}{2}\ln\left(1 - \frac{s}{N}\right). \tag{1.33}$$

For large N the probability is sharply peaked around $s \approx 0$, so that $s/N \ll 1$, which allows us to use the approximation $\ln(1 + x) = x - \tfrac{1}{2}x^2 + O(x^3)$, for which Eq. (1.33) becomes:

$$ln P(s) \approx -\frac{N}{2}\left(\frac{s}{N}\right) - \frac{N}{2}\left(-\frac{1}{2}\frac{s^2}{N^2}\right) - \frac{s}{2}\left(\frac{s}{N}\right) - \frac{s}{2}\left(-\frac{1}{2}\frac{s^2}{N^2}\right)$$
$$- \frac{N}{2}\left(-\frac{s}{N}\right) - \frac{N}{2}\left(-\frac{1}{2}\frac{s^2}{N^2}\right) + \frac{s}{2}\left(-\frac{s}{N}\right) - \frac{s}{2}\left(-\frac{1}{2}\frac{s^2}{N^2}\right) + \ldots. \tag{1.34}$$

Simplifying and only retaining terms $O(s^2/N)$, we arrive at the result:

$$ln P(s) \approx -\frac{s^2}{2N} \qquad or \qquad P(s) \approx e^{-s^2/2N}. \tag{1.35}$$

We can utilise a one-dimensional continuous variable, $d \rightarrow x = as$, whence Eq. (1.35) becomes:

$$P(x) = e^{-x^2/2Na^2}. \tag{1.36}$$

Equation (1.36) is just the unnormalised Gaussian probability distribution. This result could have been anticipated from the central limit theorem. Imposing the usual normalisation condition:

$$\int_{-\infty}^{+\infty} P(x)dx = 1 \qquad \Rightarrow \qquad P(x) = \frac{1}{a\sqrt{2\pi N}}e^{-x^2/2Na^2}, \tag{1.37}$$

where we have used the standard Gaussian[11] integral:

$$\int_{-\infty}^{+\infty} e^{-\tfrac{1}{2}\alpha x^2}dx = \sqrt{\frac{2\pi}{\alpha}}. \tag{1.38}$$

Equation (1.37) is a Gaussian centred on $x = 0$ with a standard deviation $\sigma_x = \sqrt{N}a$.

Exercise 1.5: *Plot the binomial probability (1.29) for large values of N and show that it is peaked at* $s = 0$.

Exercise 1.6: *Calculate the extremum of* $\ln P(s)$ *defined by Eq. (1.32) and show that the maximum occurs at* $s = 0$.

---

[11] A discussion of the real-valued Gaussian integral can be found at:
https://en.wikipedia.org/wiki/Gaussian_integral

To see how the diffusion (heat) equation arises from a random walk we endow the probability distribution with an explicit time dependence, so that $N \to t = N\tau,$ where τ is the discrete time step; in fact we will consider t as a continuous time variable, just as we considered $x = as,$ to be a continuous spatial variable. In this case the probability becomes a function of both space and time, i.e., $P = P(x,t)$. The probability of the walker starting from $x \pm \Delta x$ at time t, and moving to x at the next time step $t + \Delta t$ is:

$$P(x,t+\Delta t) = \frac{1}{2}P(x-\Delta x,t) + \frac{1}{2}P(x+\Delta x,t). \tag{1.39}$$

where we have assumed equal probabilities for steps to the left and to the right. Taylor expanding Eq. (1.39) gives:

$$P(x,t) + \frac{\partial P(x,t)}{\partial t}\Delta t = \frac{1}{2}\left[P(x,t) - \left(\frac{\partial P(x,t)}{\partial x}\right)\Delta x + \frac{1}{2}\left(\frac{\partial^2 P(x,t)}{\partial x^2}\right)(\Delta x)^2 + ...\right]$$

$$+ \frac{1}{2}\left[P(x,t) + \left(\frac{\partial P(x,t)}{\partial x}\right)\Delta x + \frac{1}{2}\left(\frac{\partial^2 P(x,t)}{\partial x^2}\right)(\Delta x)^2 + ...\right] \tag{1.40}$$

$$= P(x,t) + \frac{1}{2}\left(\frac{\partial^2 P(x,t)}{\partial x^2}\right)(\Delta x)^2 + O(\Delta x^3).$$

Upon simplifying and neglecting terms $O(\Delta x^3),$ we obtain the one-dimensional diffusion equation for the probability density function, i.e.,

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}, \tag{1.41}$$

where the diffusion constant D is given by:

$$D = \frac{(\Delta x)^2}{2\Delta t}. \tag{1.42}$$

The diffusion equation governs random walks in higher dimensions; for example in three dimensions Eq. (1.41) becomes:

$$\frac{\partial P(\boldsymbol{r},t)}{\partial t} = D\nabla^2 P(\boldsymbol{r},t). \tag{1.43}$$

Equation (1.43) can be solved using standard techniques from the theory of partial differential equations (PDEs); however, we will not pursue these techniques here[12].

Exercise 1.7: *Show that the following function is a solution to the one-dimensional diffusion equation (1.41):*

$$P(x,t) = \frac{1}{\sqrt{2\pi Dt}}e^{-x^2/2Dt} \quad [c.f. \ Eq. \ (1.37)].$$

---

[12] See e.g., https://en.wikipedia.org/wiki/Heat_equation

Appendix A: The Legendre Transformation

The Legendre transformation provides two completely equivalent ways of describing a physical system using functions of two (or more) related conjugate variables. The transformation exploits the convexity (or concavity) of a function, thereby allowing that function to be specified in the conventional manner, by giving the value of the function for each of its independent variables, or alternatively, by reconstructing the function from the "y-intercept" of each tangent line to the function. In other words we can either encode information using the function $f(x)$ or its slope $s = f'(x)$. In thermodynamics it is often easier to measure quantities related to the derivative of $f(x)$ than it is to measure x itself.

Consider a convex function $y = f(x)$, of one variable x, i.e., a function with $d^2f(x)/dx^2 = f''(x) > 0$. Since the tangent $f'(x)$ is monotonic and single-valued it is invertible; consequently it is possible to find another function $g = g(s)$ of the new conjugate variable $s = f'(x)$, which is equivalent to the function $f(x)$. Convexity ensures that we can calculate $g(s)$ from the function $f(x)$ and visa versa. The total differential of $f(x)$ is given by:

$$df(x) = \frac{df(x)}{dx}dx = s(x)dx \quad with \quad s(x) = f'(x). \tag{A1.1}$$

The Legendre transformation of $f(x)$ is defined as:

$$g(s) = sx - f(x), \tag{A1.2}$$

where $g(s)$ is the value of the intersection of the tangent to $f(x)$, at the point $(x, f(x))$, with the y-axis. To make these ideas concrete, refer to Fig. A.1, which shows the geometric interpretation of the Legendre transformation. If we know the vertical position (y-intercept) of each tangent line to $f(x)$, then the function can be reconstructed as the envelope of all the tangents. The purpose of the Legendre transformation is to find a function $g(s)$ of the new variable $s = f'(x)$, which is equivalent to the function $f(x)$. At x_0 the function assumes the value $f(x_0)$ and the tangent line to $f(x)$, passing through the point $(x_0, f(x_0))$, has the form:

$$t(x) = s_0 x - g(s_0) \quad with \quad s_0 = f'(x_0) = \left(\frac{df(x)}{dx} \right)_{x=x_0}. \tag{A1.3}$$

where $g(s_0)$ is the intersection of the tangent line with the y-axis. It is evident that:

$$f(x_0) = t(x_0) = s_0 x_0 - g(s_0) \quad or \quad g(s_0) = s_0 x_0 - f(x_0). \tag{A1.4}$$

For an arbitrary point x the Legendre transformation is defined as:

$$g(s) = sx - f(x) \quad with \quad s = f'(x) = \frac{df(x)}{dx}. \tag{A1.5}$$

A unique Legendre transformation is only possible if $s = f'(x)$ represents a bijective mapping, so that there exists an inverse, such that:

$$x = f'^{-1}(s), \tag{A1.6}$$

Using Eq. (A1.6) allows $g(s)$ to be explicitly written in terms of s, i.e.,

$$g(s) = f'^{-1}(s)s - f(f'^{-1}(s)). \tag{A1.7}$$

If $f'(x)$ is not strictly monotonic, there may be several values of x corresponding to s and the Legendre transformation will no longer be unique.
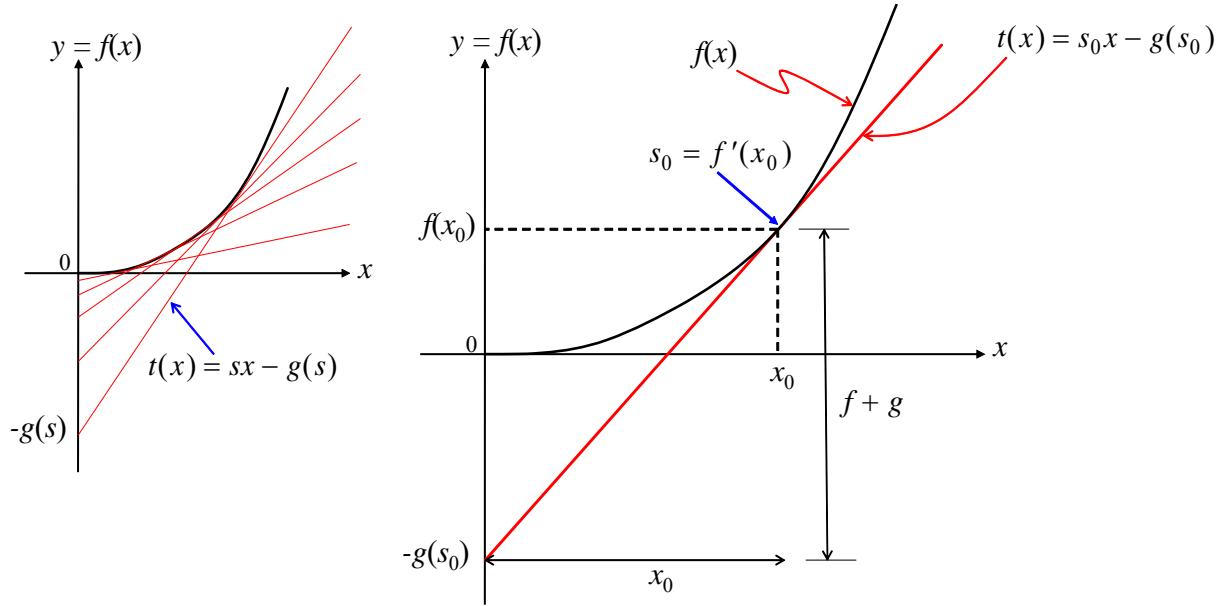
Figure A.1: *Geometric interpretation of the Legendre transformation.*

Example A1.1: Calculate the Legendre transformation of $f(x) = \alpha x^2$.

Solution

$$y = f(x) = \alpha x^2, \qquad s(x) = f'(x) = 2\alpha x.$$

Note that $f(x) = \alpha x^2$ $(\alpha > 0)$ is a convex function, since $f''(x) > 0$. The Legendre transformation is given by Eq. (A1.5), i.e.,

$$g(s) = sx - f(x) = sx - \alpha x^2.$$

The inverse function of $f'(x)$ is:

$$x = f^{-1}(s) = \frac{1}{2\alpha}s.$$

Using Eq. (A1.7) allows us to write the Legendre transformation explicitly in terms of s:

$$g(s) = f^{-1}(s)s - f(f^{-1}(s)) = \left(\frac{1}{2\alpha}s\right)s - \alpha\left(\frac{1}{2\alpha}s\right)^2 = \frac{1}{4\alpha}s^2.$$

You should check that this result is consistent with $g(s) = sx - f(x)$. Also note that the curvatures in f and g (i.e., 2α and $(2\alpha)^{-1}$) are inverses of each other.

The generalisation of the Legendre transformation to functions of many variables is straightforward. For example, consider a function of two variables x and y. The total differential is given by:

$$df = \left(\frac{\partial f(x,y)}{\partial x}\right)_y dx + \left(\frac{\partial f(x,y)}{\partial y}\right)_x dy = s(x,y)dx + t(x,y)dy, \qquad \text{(A1.8)}$$

where

$$s(x,y) = \left(\frac{\partial f(x,y)}{\partial x}\right)_y \quad and \quad t(x,y) \left(\frac{\partial f(x,y)}{\partial y}\right)_x. \qquad \text{(A1.9)}$$

We can use a Legendre transformation to replace one or more of the variables x and y. For example, if we replace both x and y by s and t, the appropriate Legendre transformation is:

$$g(s,t) = sx + ty - f(x,y). \qquad \text{(A1.10)}$$

The total differential is then:

$$dg(s,t) = sdx + xds + tdy + ydt - df(x,y) = xds + ydt,$$ (A1.11)

where we have used Eq. (A1.8) for $df(x,y)$. The procedure with more that two variables proceeds in the same manner. For completeness let us consider a function of N variables $\boldsymbol{X} = (x_1, x_2, ..., x_N)$. The total differential is given by:

$$
df = \sum_{i=1}^{N} \left(\frac{\partial f(x_1, x_2, ..., x_N)}{\partial x_i} \right)_{x_{j \neq i}} dx_i = \nabla f \cdot d\boldsymbol{X}
$$

$$
= \sum_{i=1}^{N} s_i(x_1, x_2, ..., x_N) dx_i
$$ (A1.12)

where

$$
s_i(x_1, x_2, ..., x_N) = \left(\frac{\partial f(x_1, x_2, ..., x_N)}{\partial x_i} \right)_{x_{j \neq i}}.
$$ (A1.13)

We can now choose to replace a subset of variables $\{x_k\} \in \{x_1, x_2, ..., x_N\}$ with $\{s_k\}$. The Legendre transformation is given by:

$$
g(s_1, s_2, ..., s_M, x_{M+1}, ..., x_N) = \sum_{k=1}^{M} s_k x_k - f(x_1, x_2, ..., x_N)
$$ (A1.14)

Using Eq. (A1.12) allows the total differential to be expressed as:

$$
dg(s_1, s_2, ..., s_M, x_{M+1}, ..., x_N) = \sum_{k=1}^{M} (s_k dx_k + x_k ds_k) - df(x_1, x_2, ..., x_N)
$$

$$
= \sum_{k=1}^{M} (s_k dx_k + x_k ds_k) - \sum_{k=1}^{N} s_k dx_k
$$ (A1.15)

$$
= \sum_{k=1}^{M} x_k ds_k - \sum_{k=M+1}^{N} s_k dx_k.
$$

Example A1.2: Show that the Lagrangian and Hamiltonian are Legendre transforms of each other.

Solution

In classical mechanics the state of a system of N particles at time t is specified by $3N$ generalised coordinates $\{q_i(t)\}$ ($i = 1, 2, ..., 3N$). The Lagrangian describing N non-relativistic particles is given by:

$$
L(\{q_i\}, \{\dot{q}_i\}) = \sum_{i=1}^{3N} \frac{1}{2} m \dot{q}_i^2(t) - V(q_1, q_2, ..., q_{3N}),
$$

where the potential is a function of the generalised coordinates $\{q_i(t)\}$. We can replace the generalised velocities $\{\dot{q}_i(t)\}$ with the conjugate variables $\{p_i(t)\}$. The corresponding Legendre transformation is given by Eq. (A1.14):

$$
H(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} p_i \dot{q}_i - L(\{q_i\}, \{\dot{q}_i\}) \quad with \quad p_i = \frac{\partial L}{\partial \dot{q}_i} = m \dot{q}_i.
$$

Here $\{p_i\}$ denotes the generalised conjugate (canonical) momenta. For a free non-relativistic particle, or for a potential that does not contain velocity-dependent terms, the momentum is the usual kinematical momentum "mv"; however, in general the canonical momentum is not mv.

It is evident that the Hamiltonian is related to the Lagrangian via a Legendre transformation, since:

$$H(\{q_i\},\{p_i\}) = \sum_{i=1}^{3N} \dot{q}_i p_i - L(\{q_i\},\{\dot{q}_i\})$$

$$= \sum_{i=1}^{3N} q_i(m\dot{q}_i) - \sum_{i=1}^{3N}\left(\frac{1}{2}m\dot{q}_i^2 - V(q_1,q_2,...,q_{3N})\right)$$

$$= \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_1,q_2,...,q_{3N}).$$

We now see the origin of the "trivial" sign change in the Hamiltonian compared to the Lagrangian. Since the potential is only a function of $\{q_i\}$, it plays a passive role in the Legendre transformation, and hence must have the opposite sign in order to satisfy the following relationship (see Fig. A1):

$$f(x) + g(s) = sx \quad \Leftrightarrow \quad L(\{q_i\},\{\dot{q}_i\} + H(\{q_i\},\{p_i\}) = \sum_{i=1}^{3N} p_i\dot{q}_i.$$

Thus the sign change in the potential is a direct consequence of changing from the generalised velocity variables $\{\dot{q}_i\}$ to the canonically conjugate momentum variables $\{p_i\}$.

Appendix B: Stirling's Approximation

The Stirling approximation[13] for $n!$ exploits the asymptotic formula for the gamma function for large values of n. The Euler integral form of the gamma function $\Gamma(z)$ is defined for all complex numbers (except the non positive integers) as:

$$\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt \qquad (\Re e[z] > 0). \qquad (B1.1)$$

Integrating by parts leads to the following recursive property of the gamma function:

$$\Gamma(z) = (z-1)\Gamma(z-1). \qquad (B1.2)$$

It is evident that the gamma function is a continuous version of the factorial function. For $z \in Z^+$, Eqs. (B1.1) and (B1.2) define the factorial function as:

$$n! = \Gamma(n+1) = \int_0^\infty t^n e^{-t}dt. \qquad (B1.3)$$

Note that t^n is a rapidly increasing function of t, whereas e^{-t} is a rapidly decreasing function of t; hence the product $t^n e^{-t}$ is a peaked function with a maximum at some value $t = t_0$. For large n we can use the method of steepest descent to evaluate the asymptotic form of Eq. (B1.3). This method exploits the fact that only values of t close to $t = t_0$ contribute to any significant extent to the integral (B1.3). We begin by re-writing Eq. (B1.3) as:

$$n! = \int_0^\infty e^{n\ln t}e^{-t}dt = \int_0^\infty e^{n\ln t - t}dt = \int_0^\infty e^{F(t)}dt \quad where \quad F(t) = n\ln t - t. \qquad (B1.4)$$

---

[13] An elementary derivation of Stirling's approximation proceeds by noting that:

$$n! = n(n-1) \ldots 3.2.1 = \prod_{m=1}^{n} m \quad and \quad \ln n! = \sum_{m=1}^{n} \ln m \rightarrow \int_1^n \ln x\, dx = [x\ln x - x]_1^n \approx n\ln n - n.$$

We now expand $F(t)$ in a Taylor series about $t = t_0$, i.e.,

$$F(t) = F(t_0) + F'(t_0)(t-t_0) + \frac{1}{2!}F''(t_0)(t-t_0)^2 + \frac{1}{3!}F'''(t_0)(t-t_0)^3 + \ldots \qquad \text{(B1.5)}$$

The extremum is determined from:

$$F'(t) = \frac{n}{t} - 1 = 0 \quad \Rightarrow \quad t_0 = n. \qquad \text{(B1.6)}$$

Equation (B1.5) can now be expressed as:

$$F(t) = F(t_0) + \frac{1}{2!}F''(t_0)(t-t_0)^2 + O(t^3) \approx n\ln n - n - \frac{1}{2n}(t - n)^2. \qquad \text{(B1.7)}$$

Changing the variable to $t \to \xi = t-n$, allows the factorial function (B1.4) to be re-written as:

$$n! \approx \int_0^\infty e^{F(t)}dt = \int_{-n}^\infty e^{n\ln n - n - \xi^2/2n}d\xi = e^{n\ln n - n}\int_{-n}^\infty e^{-\xi^2/2n}d\xi. \qquad \text{(B1.8)}$$

Now since we are interested in large n, we can let $n \to \infty$, whence we can evaluate the Gaussian integral in Eq. (B1.8) to obtain:

$$n! \approx e^{n\ln n - n}\int_{-\infty}^\infty e^{-\xi^2/2n}d\xi = \sqrt{2\pi n}\, e^{-n}n^n \qquad (n \gg 1). \qquad \text{(B1.9)}$$

Equation (B1.9) is the Stirling formula, which is also commonly written as:

$$\ln n! \approx n\ln n - n + \frac{1}{2}\ln(2\pi n) \qquad (n \gg 1). \qquad \text{(B1.10)}$$

The accuracy of the Stirling approximation can be improved if we consider higher order terms in the Taylor expansion (B1.5). To fourth order we can write:

$$F(t) = n\ln n - n - \frac{1}{2n}(t - n)^2 + \frac{1}{3n^2}(t - n)^3 - \frac{1}{4n^3}(t - n)^4 \ldots \qquad \text{(B1.11)}$$

Changing the variable to $t \to \xi = t-n$, and letting $n \to \infty$, the integral (B1.8) becomes:

$$n! \approx \int_0^\infty e^{F(t)}dt = e^{n\ln n - n}\int_{-\infty}^\infty e^{-\xi^2/2n}e^{\xi^3/3n^2 - \xi^4/4n^3 + \ldots}d\xi. \qquad \text{(B1.12)}$$

We cannot evaluate this integral, as it is no longer contains a Gaussian function; however, since we know that the term $e^{-\xi^2/2n}$ dominates, we can expand the remaining terms to obtain:

$$n! \approx e^{n\ln n - n}\int_{-\infty}^\infty e^{-\xi^2/2n}\left[1 + \left(\frac{1}{3}\frac{\xi^3}{n^2} - \frac{1}{4}\frac{\xi^4}{n^3}\right) + \frac{1}{2}\left(\frac{1}{9}\frac{\xi^6}{n^4} - \frac{1}{6}\frac{\xi^7}{n^5} + \frac{1}{16}\frac{\xi^8}{n^6}\right)\right]d\xi. \qquad \text{(B1.13)}$$

The integrals can be evaluated using the following result:

$$\int_0^\infty e^{-\alpha\xi^2}\xi^m d\xi = \frac{1}{2}\Gamma\left(\frac{m+1}{2}\right)\alpha^{-(m+1)/2} \qquad (m = 0,1,2,\ldots) \qquad \text{(B1.14)}$$

Note that we only need to evaluate the integral (B1.13) for even powers of ξ, since the integral vanishes for odd powers due to the antisymmetry of the integrand. Using Eq. (B1.14) we now evaluate Eq. (B1.13) up to terms involving ξ^6, i.e.,

$$n! \approx e^{n\ln n - n}\left[\sqrt{2\pi n} - \frac{3}{16}\frac{1}{n^3}(2n)^{5/2} + \frac{15}{144}\frac{1}{n^4}(2n)^{7/2} + \ldots\right]$$
$$= \sqrt{2\pi n}\, e^{n\ln n - n}\left[1 - \frac{3}{4n} + \frac{5}{6n} + \ldots\right]. \qquad \text{(B.1.15)}$$

Hence Stirling's formula to next leading order is:

$$n! \approx \sqrt{2\pi n} e^{-n} n^n \left[1 + \frac{1}{12n} + O\left(\frac{1}{n^2} \right) \right].$$

(B1.16)

Exercise B1.1: *Carry out the steps leading to Eq.* (B1.16).

Exercise B1.2: *Determine the coefficient of the term* $O(1/n^2)$ *in Eq.* (B1.16).

References

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