Part II Statistical Mechanics

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Abstract

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

It is recommended that the summary briefly addresses:

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

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

The abstract should not contain references.

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

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Chapter 1

The Basics of Thermodynamics

1.1 Introduction

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

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

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

- **Thermodynamics** is primarily concerned with *the flow of energy*: (a) from macroscopic to microscopic length scales, and vice-versa, and (b) between one kind of microscopic degree of freedom and another. Thermodynamics is a macroscopic 'phenomenological' theory which involves no assumptions about the microscopic nature of matter or radiation. Indeed much of the theory of thermodynamics was developed before accurate microscopic pictures were developed.

- **Equilibrium statistical mechanics** is primarily concerned with the "storage" and balance between energy and entropy at the microscopic level, i.e. with the question of how energy is distributed among the many internal degrees of freedom of an object. Statistical mechanics involves a detailed microscopic theory and the use of probabilities to deduce macroscopic, observable characteristics.

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

1.1.1 Ideal Gas

1.1.1.1 Energy Storage

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

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

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

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

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

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

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

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

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

1.1.1.2 Energy Flow In and Out of an Ideal Gas

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

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

where we have used conservation of energy to state that the work done, $đW$, must be equal to the change in the internal energy of the gas.[1] The slash through the symbol đ

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

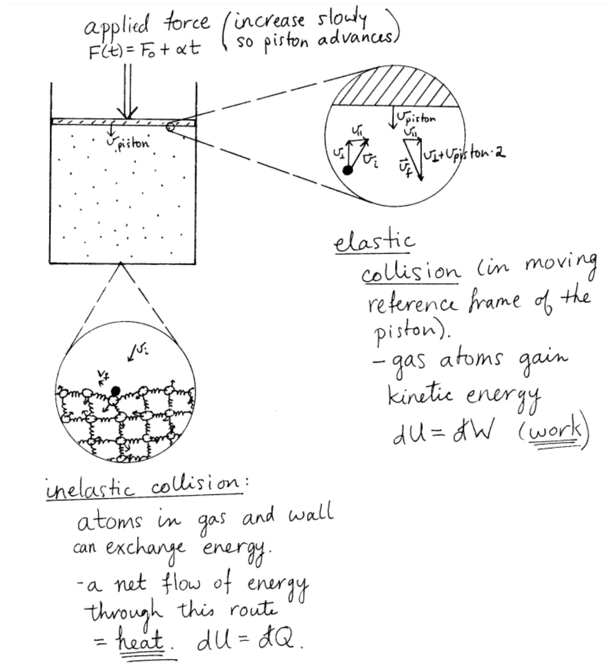

applied force (increase slowly so piston advances)
F(t) = F₀ + αt
v_piston
v_piston
v_∥
v_⊥
v_i
v_f
v_⊥+v_piston·2
elastic collision (in moving reference frame of the piston).
– gas atoms gain kinetic energy
dU = đW (work)
v_i
v_f
inelastic collision:
atoms in gas and wall can exchange energy.
-a net flow of energy through this route = heat. dU = đQ.

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

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

Microscopic ↔ Microscopic Energy Flow

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

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

$$\mathrm{d}U = đQ \quad (= T\,\mathrm{d}S \quad \text{if the heat flow is reversible}), \tag{1.6}$$

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

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

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

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

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

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

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

1.1.2 Van der Waals Gas and Other Systems

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

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

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

1.1.2.1 Energy Storage

Energy is stored in the van der Waals gas in the form of kinetic energy, as in the ideal gas, but also in the inter-molecular *potential energy*. When the molecules are far apart, in

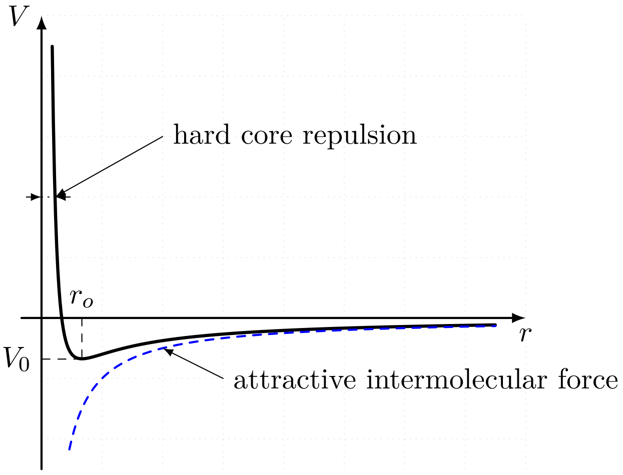


Fig. 1.2: The inter-molecular potential for a Van der Waals gas.

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

1.1.3 Paramagnetic Salt in an Applied Magnetic Field

The work required to change the magnetic moment of a substance from $\mathbf{m}$ to $\mathbf{m} + \mathrm{d}\mathbf{m}$ in an applied external field $\mathbf{H}$ depends on the precise definition of the process involved (let's not confuse the extensive total magnetic moment $\mathbf{m}$ and the intensive local field of magnetisation $\mathbf{M}$). The conventional definition regards only the work needed to change the state of the substance, returning any external sources of field back to zero. For example, a paramagnetic substance with magnetic moment $\mathbf{m}(\mathbf{H})$ at some large distance from a permanent magnet will experience an attractive force proportional to $(\mathbf{m} \cdot \boldsymbol{\nabla})\mathbf{H}$. Letting the substance approach the magnet until it experiences a field $\mathbf{H}_1$, we can extract work, so that the work done on the substance is $W' = -\mu_0 \int_0^{H_1} \mathbf{m}(\mathbf{H})\, \mathrm{d}\mathbf{H}$. However, the magnet is still near the substance, so in order to calculate the work required to change the state of the substance alone, we need to pull the magnet away to the previous separation, while the magnetic moment of the substance is clamped at its final value $\mathbf{m}_1$ (this is problematic in practice, but does not violate the laws of physics, so possible in a thought experiment). Pulling the magnet away requires a larger work, to be done on the system, $W_1 = \mu_0 \int \mathbf{m}_1 \, \mathrm{d}\mathbf{H} = \mu_0 \mathbf{m}_1 \mathbf{H}_1$, giving a net work $W = \mu \int \mathbf{H}\, \mathrm{d}\mathbf{m}$. This argument produces the conventional expression for the work done on a magnetic substance, when its magnetisation is changed by first applying a field $\mathbf{H}$ and then removing the source of the field again:

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

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

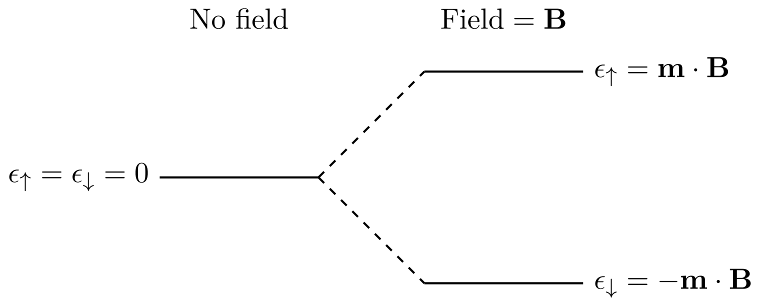

No field
Field = **B**
$\epsilon_\uparrow = \mathbf{m}\cdot\mathbf{B}$
$\epsilon_\uparrow = \epsilon_\downarrow = 0$
$\epsilon_\downarrow = -\mathbf{m}\cdot\mathbf{B}$

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

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

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

1.1.3.1 Energy Storage

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

1.1.3.2 Energy Flow In and Out of the System

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

– as explained in the preceding section – was $đW' = -\mu_0 \mathbf{m}\, \mathrm{d}\mathbf{H}$.. Setting $\mathrm{d}U = đQ + đW'$, we find that heat is extracted during this process:

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

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

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

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

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

1.1.4 Assembly of One-Dimensional Simple Harmonic Oscillators

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

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

1.1.4.1 Energy Storage

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

1.1.4.2 Energy Flow In and Out of the System

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

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

1.2 Thermodynamic Variables

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

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

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

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

Thermodynamic variables and potentials are special because they are *functions of state*, i.e., properties of a system which are completely determined by the contents and

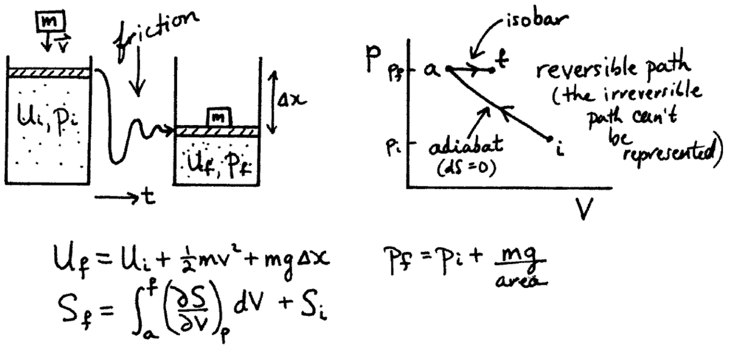

m
$\vec{v}$
friction
U_i, p_i
m
Δx
U_f, p_f
→t
isobar
p
p_f
a
f
reversible path
(the irreversible path can't be represented)
p_i
adiabat
($dS = 0$)
i
V
$U_f = U_i + \frac{1}{2}mv^2 + mg\Delta x$
$S_f = \int_a^f \left(\frac{\partial S}{\partial V}\right)_p dV + S_i$
$p_f = p_i + \frac{mg}{\text{area}}$

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

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

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

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

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

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

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

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

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

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

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

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

1.3.1 The Equation of State of a Van der Waals Gas

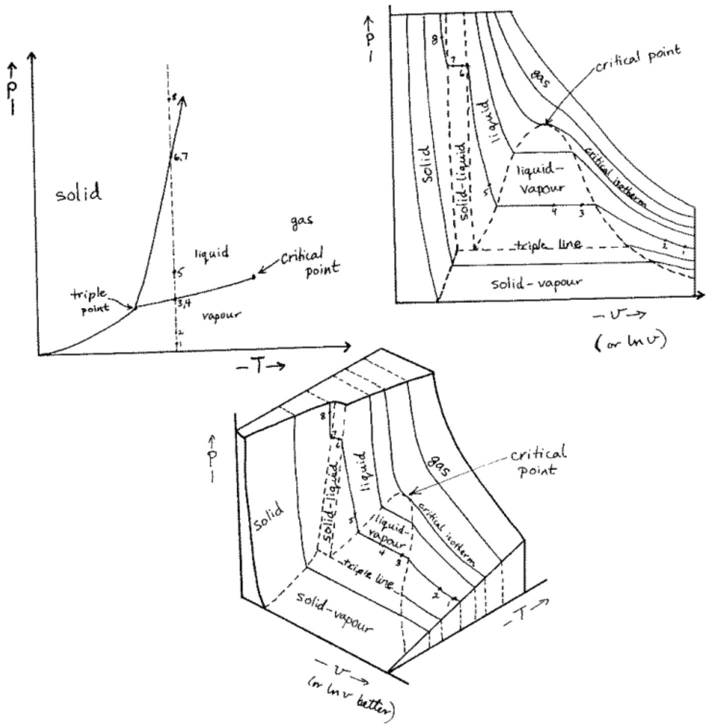
The van der Waals equation (Eq. (1.9)) is an example of an equation of state. Isotherms on its $p-V-T$ surface, projected into the $p-V$ plane, are shown in Fig. 1.7.

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

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

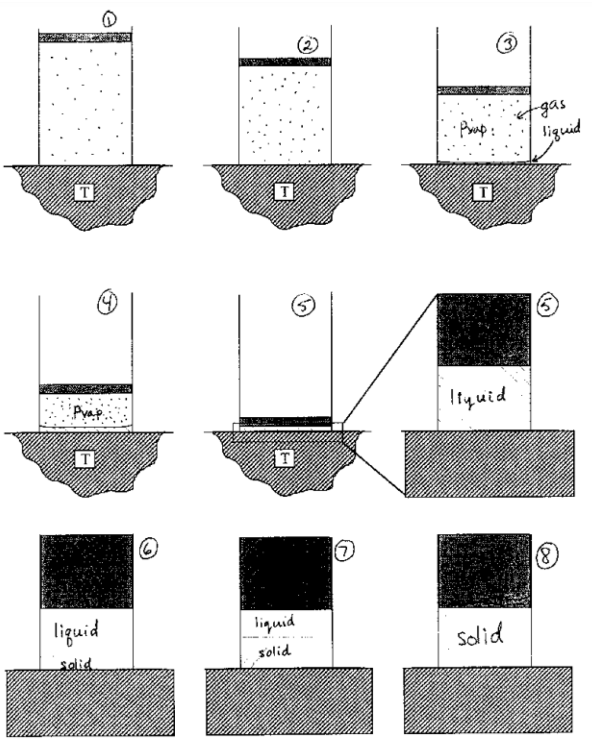
---

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



p
solid
liquid
gas
critical point
triple point
vapour
T
8
6,7
5
3,4
2
1
solid
solid-liquid
liquid
gas
critical point
liquid-vapour
critical isotherm
triple line
solid-vapour
V
(or ln V)
T
V
(or ln V better)

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



①
②
③
④
⑤
⑤
⑥
⑦
⑧
T
gas
liquid
Pvap
liquid
solid
liquid
solid
solid

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

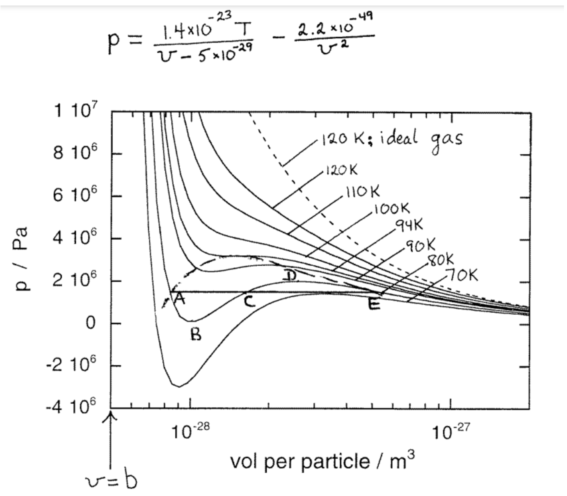


Fig. 1.7: Isotherms of the van der Waals equation of state.

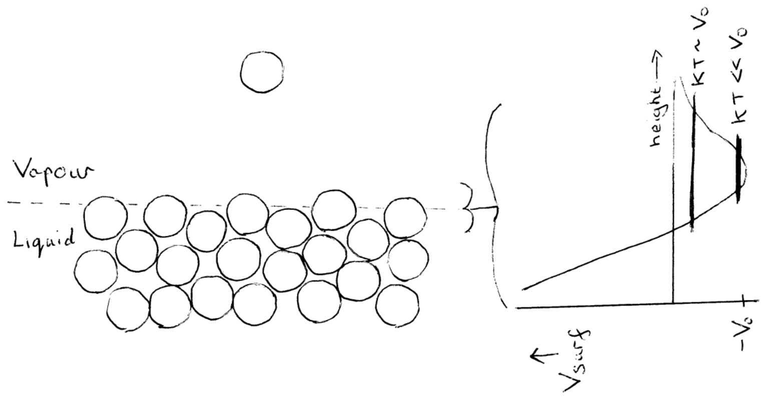

Vapour
Liquid
height →
kT ~ V0
kT << V0
−V0
← Vsurf

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

1.4 The Laws of Thermodynamics

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

- **1^{st} Law** The First Law states that energy is conserved when heat is taken into account. This applies to the flow of energy from macroscopic to microscopic length scales and between microscopic length scales.

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

The crowning glory of thermodynamics is that these statements (which are essentially all equivalent) imply that we can assign a value of a measurable quantity known as entropy to every equilibrium state of every system. Although it only holds on average, significant violations of it are incredibly unlikely. The Second Law of Thermodynamics is one of the most sacrosanct of all physical laws. This contrasts with Maxwell's equations (to which there are quantum corrections), Schrödinger's equation (relativistic corrections), and Newton's law of gravitation (general relativistic corrections).

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

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

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

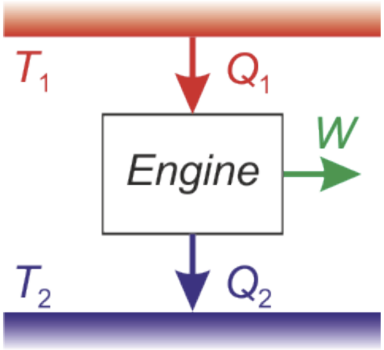


Fig. 1.9: Schematic representation of a heat engine operating between a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2.

1.5 Entropy

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

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

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

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

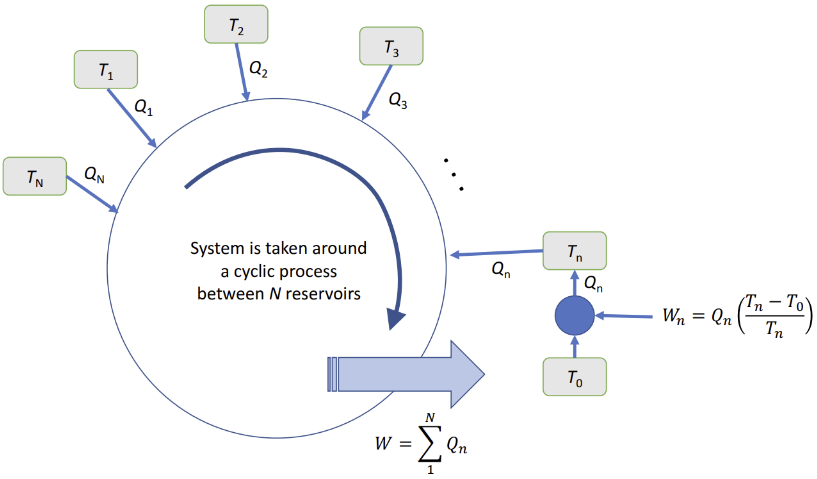

T_1
T_2
T_3
T_N
Q_1
Q_2
Q_3
Q_N
System is taken around a cyclic process between N reservoirs
Q_n
T_n
Q_n
$W_n = Q_n\left(\frac{T_n - T_0}{T_n}\right)$
T_0
$W = \sum_1^N Q_n$

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

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

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

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

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

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

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

$$\oint đQ/T \leq 0, \tag{1.18}$$

and hence

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

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

Fig. 1.12: A Carnot cycle and an irreversible cycle.

but the latter gives the entropy change; therefore:

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

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

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

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

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

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

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

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

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

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

$$\mathrm{d}U = \text{đ}Q + \text{đ}W, \tag{1.23}$$

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

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

$$đQ = T\,\mathrm{d}S\,, \tag{1.25}$$

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

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

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

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

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

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

1.6 The Gibbs-Duhem Equation

Although there are a number of ways in which changes between equilibrium states can be expressed mathematically, that based on Eq. (1.27) has a very special place. It expresses changes in the energy, which is itself an extensive quantity, in terms of changes in the other extensive quantities. We know that the energy is a homogeneous first order function of the extensive variables, or in plain English, if we simultaneously double the volume, number of particles and entropy of a system, while holding the temperature, pressure and chemical potential constant, then its energy also doubles. Therefore, generalising to an increase by a factor of λ we can write $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$, so that

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

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

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

But we know from Eq. (1.27) that

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

hence it must be true that

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

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

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

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

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

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

CHAPTER **2**

Thermodynamic Equilibrium

2.1 Internal Equilibrium of Closed Systems

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

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

2.1.1 Maximum Entropy Principle

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

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

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

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

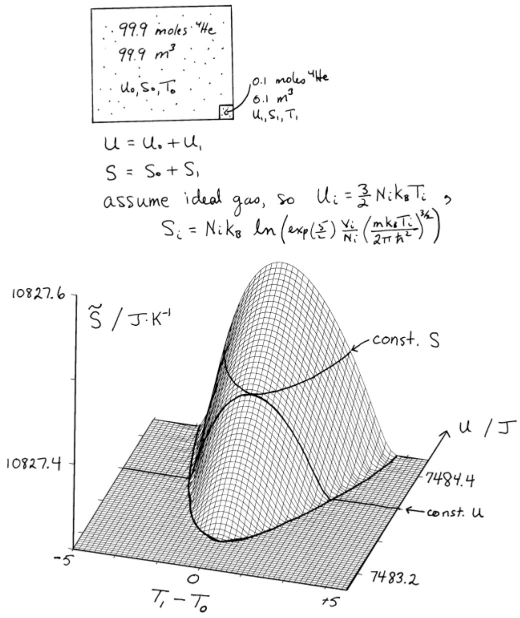


Fig. 2.1: A small section of the $(S - U - (T_1 - T_0))$ surface for a volume of ideal gas partitioned by an adiathermal wall. We imagine that we can transfer energy across the partition (using external heat engines for example) and then we calculate the total entropy, using the SackurTetrode expression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

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

   The entropy statement of the Second Law of thermodynamics gives

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

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

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

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

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

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

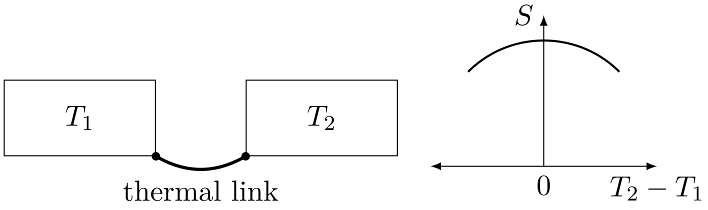


Fig. 2.2: Two systems connected by a thermal link. The heat flows from the hotter to the colder body and at equilibrium $T_1 = T_2$.

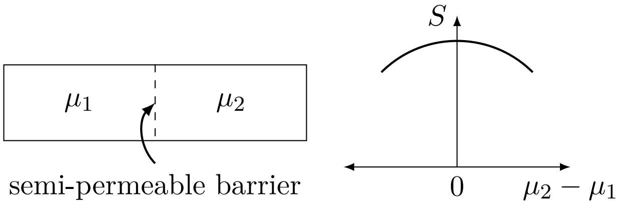


Fig. 2.3: A container is divided into two parts by a membrane which is permeable to salt but not to water. On the left of the semi-permeable membrane the water contains some salt, and on the right is pure water. The entropy is maximised when $\mu_1 = \mu_2$, i.e., the salt concentrations are equal.

2.2 Thermodynamic Equilibrium in Open Systems

2.2.1 The Availability

For thermally isolated systems, as we have seen, thermodynamic equilibrium can be defined as the state of maximum entropy for a given total energy, or we can define it as the state of minimum energy for a given total entropy. However, for a system in contact with a reservoir – and most thermodynamic systems are in thermal and/or mechanical contact with the rest of the universe – it turns out that there is a very useful alternative to maximising the total entropy of the system *and* the reservoir with respect to the state of the system: there is a property of the *system*, called the *availability*, which is minimised when the entropy of the *universe* (system + reservoir) is maximised with respect to the state of the system.

To see this, consider a system (denoted by quantities without subscripts) and reservoir (labelled ”R”), which can exchange energy in the form of heat and/or work, and particles. The Entropy Statement of the Second Law is

$$\begin{aligned} \mathrm{d}S_{\mathrm{tot}} &= \mathrm{d}S + \mathrm{d}S_R \geq 0 \\ &= \mathrm{d}S + \frac{\mathrm{d}U_R + p_R\,\mathrm{d}V_R - \mu_R\,\mathrm{d}N_R}{T_R} && (2.5) \\ &= \frac{T_R\,\mathrm{d}S - \mathrm{d}U - p_R\,\mathrm{d}V + \mu_R\,\mathrm{d}N}{T_R}, && (2.6) \end{aligned}$$

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

The present situation is rather special, because it involves exchange of all possible quantities with the reservoir: there are many cases (discussed in more detail below, when thermodynamic potentials are introduced), in which the contact with the reservoir is only partial. For instance, the reservoir may receive volume from the system, but not particles. In such a case, $\mathrm{d}V_R = -\,\mathrm{d}V$, still, but $\mathrm{d}N_R = 0$. You could rederive what follows below for such special cases, and this would lead to the definitions of the various potentials, or you can take the general route (now following) and then formally – as a shortcut – set certain terms to 0. For instance, the effect of having no particle exchange, $\mathrm{d}N_R = 0$, on the reservoir entropy in Eq. (2.5) above can be achieved in Eq. (2.6) by simply setting $\mu_R = 0$.

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

$$\boxed{\begin{aligned} \mathrm{d}A &= \mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N \\ &= (T - T_R)\,\mathrm{d}S - (p - p_R)\,\mathrm{d}V + (\mu - \mu_R)\,\mathrm{d}N \end{aligned}} \tag{2.7}$$

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

$$A = U - T_R S + p_R V - \mu_R N. \tag{2.8}$$

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

$$\mathrm{d}A \leq 0. \tag{2.9}$$

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

Because the availability is directly related to the overall entropy, Boltzmann's expression for entropy: $S_{\text{Boltz}} = k_B \ln \Omega$, where Ω is the statistical weight or degeneracy, can be used to motivated an important aspect of this analysis, namely the relationship for the *probability* for the system (in contact with the reservoir) to have a certain set of values for its variable, e.g. X:

$$P(X) \propto e^{-\frac{A(X)}{k_B T}}. \tag{2.10}$$

2.2.2 Availability = Useful Work

The availability function in Eq. (2.8) has some subtleties: its natural variables are S, V, N (because these are the natural variables of U), as well as T_R, p_R, μ_R. So, in general, the system can be at temperature $T = (\partial A/\partial S)_{V,N} \neq T_R$, pressure $p = -(\partial A/\partial V)_{S,N} \neq p_R$ and chemical potential $\mu = (\partial A/\partial N)_{S,V} \neq \mu_R$. It would then not be in equilibrium with the reservoir. How much work could be extracted by bringing the system in contact with the reservoir? It turns out that the availability, which is also called *exergy*, directly gives the maximum useful work possible during a process that brings the system into equilibrium with a reservoir. This can be shown by revisiting the derivation of Eq. (2.8) and allowing for $\mathrm{d}U_R$ not to be $= -\mathrm{d}U$, but rather putting $\mathrm{d}U_R + \mathrm{d}U = -\mathrm{d}W_{\text{extr}}$, the amount of work extracted in the process. Alternatively, we can go directly for $-\mathrm{d}W_{\text{extr}} = \mathrm{d}U + \mathrm{d}U_R$ and replace U by $A + T_R S - p_R V + \mu_R N$:

$$\begin{aligned} -\mathrm{d}W_{\text{extr}} &= \mathrm{d}U + \mathrm{d}U_R = \mathrm{d}(A + T_R S - p_R V + \mu_R N) + T_R\,\mathrm{d}S_R - p_R \underbrace{\mathrm{d}V_R}_{=-\mathrm{d}V} + \mu_R \underbrace{\mathrm{d}N_R}_{=-\mathrm{d}N} \\ &= \mathrm{d}A + T_R \underbrace{\mathrm{d}(S + S_R)}_{\geq 0}\,. \end{aligned} \tag{2.11}$$

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

$$\Delta W_{\text{extr}} = -\Delta A. \tag{2.12}$$

2.2.3 Legendre Transformations

The natural variables of A as in Eq. (2.8) are S, V, N (because these are the natural variables of U), as well as T_R, p_R, μ_R. In equilibrium, the condition $\mathrm{d}A = 0$ for all variations of S, V, N then produces $(\partial A/\partial S)_{V,N} = (\partial U/\partial S)_{V,N} - T_R = T - T_R = 0 \implies T = T_R$, and likewise $p = p_R$ and $\mu = \mu_R$. Moreover, the requirement that the gradient of U w.r.t. S is equal to the fixed reservoir temperature T_R, is only fulfilled for one value of the entropy $S = S_{\text{eq}}$, the entropy in equilibrium. Likewise for V and N. So when the system is in equilibrium with the reservoir, the system variables S, V, N assume values S_{eq}, V_{eq}, N_{eq}, which are dictated by the reservoir temperature, pressure and chemical potential. As a consequence, the availability *in equilibrium* has as its natural values T_R, p_R, μ_R, which are equal to T, p, μ in equilibrium.

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

$$\mathrm{d}g = f'\,\mathrm{d}x - y\,\mathrm{d}x - x\,\mathrm{d}y\,. \tag{2.13}$$

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

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

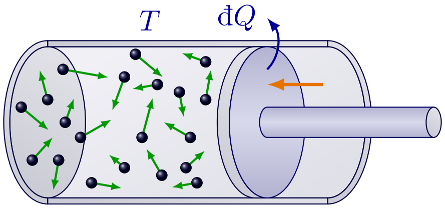


Fig. 2.4: Reversible compression of a monatomic ideal gas connected to a reservoir at constant temperature. Fixed temperature T implies constant internal energy U (Molecules in an ideal gas are assumed to have zero interaction with each other and so have only kinetic energy directly determined by T),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

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

$$\mathrm{d}F = \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} - T_R\right] \mathrm{d}S - S\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,, \tag{2.14}$$

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

$$\mathrm{d}F_{\text{eq}} = -S_{\text{eq}}\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,. \tag{2.15}$$

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

$$\mathrm{d}A_{\text{eq}} = -S_{\text{eq}}\,\mathrm{d}T_R + V_{\text{eq}}\,\mathrm{d}p_R - N_{\text{eq}}\,\mathrm{d}\mu_R \tag{2.16}$$

and $T = T_R$, $p = p_R$ and $\mu = \mu_R$ as the natural variables. Actually, the availability of a system in equilibrium with a reservoir is always simply zero! This follows from the realisation, mentioned above (Subsection 2.2.2), that the availability gives the extractable work on attaining equilibrium: if the system is already in equilibrium, then the availability must have reached zero. It also follows from Eq. (1.32), $U - TS + pV - \mu N = 0$.

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

2.3 Overview of the Thermodynamic Potentials

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

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

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

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

$$\mathrm{d}U = 0 \qquad \Longrightarrow \qquad \text{đ}Q = -\text{đ}W. \tag{2.17}$$

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

$$\begin{aligned}\text{đ}W &= \mathrm{d}U - T\,\mathrm{d}S \\ &= \mathrm{d}(U - TS)_T \quad \text{if } T \text{ is constant} \\ &\equiv (\mathrm{d}F)_T \end{aligned} \tag{2.18}$$

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

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

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

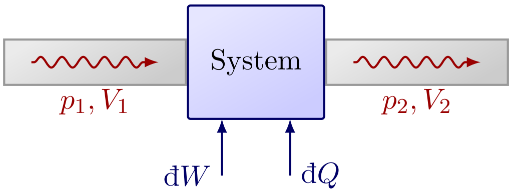


Fig. 2.5: A schematic flow process.

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

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

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

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

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

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

$$\begin{aligned}(\mathrm{d}A)_{p,S,N} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{p,S,N} \\ &= \mathrm{d}(U + pV)_{p,S,N} \quad (\text{used } \ \mathrm{d}S = 0, \mathrm{d}N = 0, p = p_R) \\ &\equiv \mathrm{d}(H)_{p,S,N}\,, \qquad (2.19)\end{aligned}$$

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

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

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

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

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

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

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

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

Chapter 3

The Basics of Statistical Mechanics

Chapter 4

Classical Ideal Gas

Chapter 5

The Grand Canonical Ensemble

CHAPTER **6**

Ideal Fermi Gas

CHAPTER 7

Ideal Bose Gases

Chapter 8

Non-ideal Gases and Liquids

Chapter 9

Phase Equilibria and Transitions

Chapter 10

Fluctuations in Equilibrium

CHAPTER 11

Elements of Stochastic Physics

APPENDIX A

Appendix