Notes for Thermal Physics course, CMI, Autumn 2019
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These lecture notes are very sketchy and are no substitute for books, attendance and taking notes at lectures. More information will be given on the course web site `http://www.cmi.ac.in/~govind/teaching/thermo-o19`. Please let me know (via govind@cmi.ac.in) of any comments or corrections. Help from Sonakshi Sachdev in preparing these notes is gratefully acknowledged.

Contents

1 Thermodynamic systems and states

• Thermodynamics arose in part from the needs of steam engine builders; the need to understand the possibility and limits of conversion of mechanical/electrical/chemical energy into heat and vice versa; the attempts to optimize efficiencies of heat engines and refrigerators etc. An important role was played by the study of the behavior of gases and of the heats released/absorbed in chemical reactions. Another motivation came from the remarkable phenomena discovered in phase transitions such as the boiling or freezing of water.

• Before discussing the state of a thermodynamic system, let us recall the concept of the dynamical state of a mechanical system. The state of a mechanical system of point particles is specified by giving the positions and momenta of all the particles at an instant of time.

• The state variables of a thermodynamic system depend on the sort of system it is. Some examples of thermodynamic systems include gases and liquids (fluids), solids, magnets, chemical solutions, electrolytes, blackbody radiation, stars, black holes etc. These systems typically contain a very large number of microscopic constituents and it would be impractical to follow their individual motions. What is more, in most cases, the thermodynamic understanding has preceded a detailed understanding of the nature of microscopic degrees of freedom. Thus, thermodynamics deals with 'macroscopic' properties of these systems without reference to positions and momenta of constituents. As opposed to the dynamical state of a gas of N molecules, which would be specified by N positions and momenta, the thermodynamic state is defined by just a handful of state variables (a number independent of N).

• Perhaps the simplest thermodynamic system is a homogeneous gas (or fluid) composed of a single chemical substance (e.g. oxygen or water) at rest (no flow). Volume, constant pressure and density are obvious mechanical properties associated with the uniform fluid. In addition to mechanical properties, thermodynamics deals with the temperature of the gas, which may be measured with, say, a mercury thermometer[1]. For the present we use the same thermometer for all temperature measurements to make them comparable.

• Thus, thermodynamics postulates the existence of **temperature as a thermal property of a system**. It is a parameter of state being defined by the instantaneous state of the system independent of its history.

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[1] Operationally, we have a column of mercury of height h at some reference temperature (say freezing point of water at atmospheric pressure). We say that the water freezes at temperature h. When heated, the mercury expands and the temperature is defined simply to be the height of the column.

• It is observed that a fluid when left to itself ('isolated') for some time settles into a state of thermal equilibrium, characterized by a common temperature everywhere. Thus the **zeroth law of thermodynamics** postulates that parts of a system (or different systems) are in thermal equilibrium if they have the same temperature. Furthermore, if system A is in thermal equilibrium with system B and B is in equilibrium with C then A is in equilibrium with C: all three have a common temperature. A consequence of this transitivity is that it allows us to conclude that a bar of iron and a bucket of water are in thermal equilibrium even without bringing them into contact, provided we check that each is separately in equilibrium with a third system, which plays the role of a thermometer.

1.1 Thermodynamic state of a gas and a paramagnet

• **Thermodynamic state of a homogeneous fluid.** For the purposes of thermodynamics, a uniform fluid has one mechanical degree of freedom, its volume. It is found that thermodynamic properties (like energy) are largely independent of the shape of the region occupied by the fluid as long as its volume is large (compared to molecular dimensions) and surface area not too large compared to that of a sphere of the same volume. This is not true for microscopic volumes nor for regions with very large surface area like the small intestine - we will exclude such regions from this discussion.

• Just as momentum is conjugate to the position of a particle in mechanics, we will see that pressure is the variable conjugate to volume[2]. The thermodynamic state of a fixed mass of homogeneous fluid is fixed once the volume V, the (uniform) pressure p and temperature t have been specified. Thus, the thermodynamic state space is three dimensional. However, not all triples (V, p, t) represent equilibrium states. Equilibrium states have the special property of remaining unchanged in time under fixed external conditions. For instance, a flowing gas is not in equilibrium (at the very least, one would need to specify the velocity and pressure at different locations in the gas to determine its state). Equilibrium states lie on a 2D surface (called the equilibrium manifold) determined by a relation $f(V, p, t) = 0$ called the equation of state. The equation of state allows us to express one of the state variables, say $p(V, t)$, as a function of the other two. We will see that for many dilute gases at sufficiently high temperatures and low pressures (ideal gases) the equation of state is approximately $pV = nRT$ where the proportionality constant nR is the product of the number of moles of gas (amount of substance) and the universal gas constant and T is the so-called gas thermometer temperature (to be introduced later).

• Following James Watt, the state of such a gas can conveniently be represented by a point in the V-p plane (indicator diagram) with abscissa V along the horizontal axis and ordinate p along the vertical axis. An isotherm is a curve along which temperature is constant. A PT-diagram is sometimes convenient especially when studying phase transitions, say between liquid and vapour.

• The first derivatives of p, V, T with respect to each other are used to define three material

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[2] Hydrostatic pressure at a point A is introduced as follows: Consider a small fictitious membrane (flat surface) passing through A in a gas/fluid. It is found that the fluid on one side of the membrane exerts a force normal to the membrane and towards the other side. This normal force per unit area is the hydrostatic pressure. The same value of pressure is obtained by considering the normal force per unit area due to the fluid on the other side. Moreover, the value of pressure at a point is independent of the orientation of the membrane through the point: it is a positive scalar quantity.

properties which describe the response of one due to a change in another keeping the third fixed. Thus we have the coefficients of thermal expansion, thermal tension[3] and isothermal compressibility

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V, \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \tag{1}$$

For instance, compressibility κ_T measures the fractional change in volume of a gas due to an increase in pressure. The minus sign is because gases are compressed upon the application of pressure. The reciprocal of compressibility is called the bulk modulus. There are three more such coefficients that we could define, involving $\frac{\partial T}{\partial V}$, $\frac{\partial T}{\partial p}$ and $\frac{\partial p}{\partial V}$. However, we will see that on the equilibrium surface, there are four relations among these six coefficients so that only two can be independent. Let us also note that the coefficients α, β and κ are in general not constant and vary from place to place on the equilibrium manifold.

- The fact that p, V and T satisfy the equation of state leads to the relations

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T, \quad \left(\frac{\partial T}{\partial p}\right)_V = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial T}{\partial V}\right)_p \tag{2}$$

as well as the remarkable relation among the three coefficients α, β and κ_T.

$$p\,\beta\,\kappa_T = \alpha. \tag{3}$$

This is obtained by replacing x, y, z by p, V, T in the identities we now derive.

- In general, if x, y, z satisfy a functional relation $f(x,y,z) = 0$ that allows us to locally express each as a function of the other two $z = z(x,y)$, $y = y(z,x)$ and $x = x(y,z)$, then we have the 'triple product' identity[4]

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{4}$$

that holds on the constraint surface $f(x,y,z) = 0$. To see this we write the differentials with subscripts denoting partial derivatives (E.g. $z_x = \left(\frac{\partial z}{\partial x}\right)_y$, the variable that is held fixed in the partial derivative is not indicated explicitly as it is clear from the context)

$$dz = z_x\,dx + z_y\,dy, \quad dx = x_y\,dy + x_z\,dz, \quad \text{and} \quad dy = y_z\,dz + y_x\,dx. \tag{5}$$

Now we regard x and y as independent variables on the constraint surface & write dz in terms of dx & dy in the formula for dx

$$dx = x_y\,dy + x_z\,(z_x\,dx + z_y\,dy)\,. \tag{6}$$

Since dx and dy are independent differentials on the 2d surface $f = 0$, their coefficients must vanish. The coefficient of dx vanishes provided $x_z z_x = 1$ (i.e., $\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1$). Since we could equally well have taken any other pair as independent variables, we must also have $x_y y_x = y_z z_y = 1$. Now requiring that the coefficient of dy vanish gives $x_z z_y = -x_y$ which becomes $z_x x_y y_z = -1$ upon using the previous result.

- Thermodynamic variables can often be classified as **extensive or intensive**. Extensive quantities are proportional to the amount of material. For example, internal energy (U), the

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[3] Tension is another word for force and thermal tension refers to the change in pressure (force/area) as temperature is varied.

[4] To remember this formula, begin with any of the partial derivatives as the first factor. The latter two factors are obtained by cyclically permuting the variables in the first partial derivative.

various free energies (e.g. Helmholtz free energy F) and entropy (S) are extensive variables, they scale with the volume V (ignoring boundary/surface effects), the number N of particles present or the total mass m. By dividing by N, V or m we obtain the corresponding 'specific' energies or entropy. Intensive quantities such as pressure, temperature and chemical potential (to be introduced later) are independent of the amount of substance. We will see that (p, V), (μ, N) and (t, S) are **canonically conjugate pairs** of intensive and extensive variables.

• **Magnets as thermodynamic systems:** The analogs of pressure and volume for a magnetic material are the external magnetic field ($\mathbf{H}$, intensive) and magnetization ($\mathbf{M}$, by convention dipole moment per unit volume, intensive). A ferromagnet such as an iron bar magnet (a 'magnetic dipole') has a permanent magnetization (pointing, say, in the z direction). The magnetization leads to a magnetic field in the neighbourhood of the magnet, which aligns iron filings. By measuring the magnetic field, one can infer the magnetization. The magnetization of a ferromaget is permanent (more precisely spontaneous) in that it is non-zero even in the absence of an external magnetic field. From a microscopic viewpoint, the magnetization is the vector sum of molecular magnetic moments per unit volume. A paramagnetic substance has no magnetization of its own since thermal fluctuations ensure that the molecular magnetic moments point in random directions and sum to zero. However, in the presence of an external magnetic field $\mathbf{H}$, it acquires a magnetization $\mathbf{M}$ that points along $\mathbf{H}$. Ferromagnets gradually lose their spontaneous magnetization with increase in temperature. The spontaneous magnetization drops to zero above the Curie temperature t_c (770° Celsius for iron) and then ferromagnets become paramagnets. This is a phase transition which bears some resemblance to the liquid to gas vapourization transition. By convention, we will assume that $\mathbf{H}$, and therefore $\mathbf{M}$, point in the z-direction and denote them by their z-components $\mathcal{H}$ and M. Thus, the thermodynamic state space of a uniformly magnetized homogeneous paramagnet is three dimensional with coordinates $\mathcal{H}, M$ and t. $\mathcal{H}$ and M are conjugate variables like the pressure and specific volume (volume per particle) of a gas. In equilibrium, there is an equation of state that relates $\mathcal{H}, M$ and t. For a linear paramagnetic medium $M = \chi \mathcal{H}$ where M is the magnetization per unit volume (V the volume of the magnet is essentially a constant, unlike for a gas). This simply states that the induced magnetization is proportional to the applied magnetic field. The *magnetic susceptibility* χ depends on temperature, it is a measure of how 'magnetizable' a paramagnet is. At high temperatures ($t > t_c$) the paramagnetic susceptibility is given approximately by the Curie-Weiss[5] law $\chi \approx C/(t - t_c)$ for an appropriate temperature scale. C is called Curie's constant.

1.2 Thermodynamic processes

• A **process** is a transformation of a system from an initial state through a continuous succession of intermediate states to a final state. It may sometimes be represented by a curve in the thermodynamic state space, in which case we could call it a thermodynamic process (this may not be possible if the transformation produced inhomogeneities so that, say, the pressure is not constant throughout). A transformation in which the system is always infinitesimally close to an equilibriums state is called a **reversible** or **quasi-static** transformation. For a homogeneous gas, such a process may be represented by a curve that lies entirely on the equilibrium surface in the p-V-t state space; it may also be represented by a curve in a p-V diagram. Starting

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[5] Named after the Polish-French and French physicists Marie Curie and Pierre Weiss.

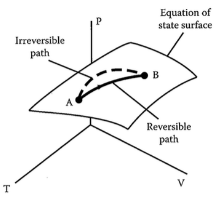

Figure 1.2 The state space in thermodynamics.

Figure 1: From K Huang, Introduction to statistical physics: V, p, t thermodynamic state space of a gas of uniform composition. Reversible processes are curves on the equilibrium EOS surface. Irreversible processes which can be represented in such a diagram go off the equilibrium surface.

from an equilibrium state, a reversible transformation may be realized through a slow variation of external conditions so that the system always has time to adjust itself to the new equilibrium state corresponding to the altered conditions[6]. For example, the slow expansion of a gas in a container fitted with a piston (that can move vertically), as small weights are slowly removed from the piston and kept aside at the same height. The process may be reversed by replacing the weights onto the piston slowly as the gas contracts. If the piston is lowered rapidly, the pressure would not be uniform and there would also be velocity currents set up in the gas, making it pass through non-equilibrium states. A transformation passing through equilibrium states from A to B is called reversible since it can be reversed by applying the changes to the external conditions slowly in the opposite order, so that the system passes through the same intermediate states but from B to A.

• A process that is not reversible (not quasi-static) is called irreversible. Irreversible processes may not always be representable as curves in the pVt state space, since we may need to specify other variables like velocity and there may not be a single pressure that can be assigned to the whole gas.

• Note that a slow process need not be reversible. Examples may be found among dissipative processes such as the slow frictional heating of the suspension of a swing as it executes damped oscillations or the slow heating of a resistor connected to a battery. Even if we try to reverse these processes (by reversing the direction of oscillation of the swing or reversing the direction of current) heat is still produced, not absorbed!

• The spontaneous flow of heat (whether quickly or slowly) from a body at a higher temperature to one at a lower temperature is irreversible. Indeed, we do not see heat spontaneously flowing from a cold body to a hot one.

• Thermodynamic processes in which p, V or T remain constant are called isobaric, isochoric (isopiestic) and isothermal.

• A cycle or cyclic process is a transformation in which the initial and final states are the same. On a p-V diagram, a cycle is represented by a closed curve (which could have self-intersections).

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[6] In other words, for the purposes of the thermodynamic process, we only observe the system at intervals of time that are large compared to the equilibration time of the system. So the 'continuity' of the process needs to be understood in this sense. We will not attempt to understand the dynamical process of how the system approaches equilibrium: this lies outside the purview of thermodynamics and requires a kinetic or dynamical treatment.

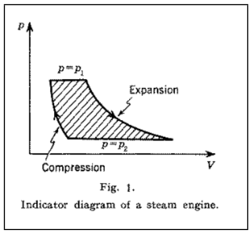

Fig. 1.
Indicator diagram of a steam engine.

Figure 2: From A Sommerfeld, Thermodynamics and Statistical mechanics: pV diagram for a cycle of a steam engine. Work done is equal to shaded area enclosed and is positive as the curve runs clockwise. The isobar at the high pressure p_1 corresponds to the steam in the cylinder expanding while in contact with the boiler. The isobar at the low pressure p_2 corresponds to compression when in contact with the atmosphere or condenser.

Cyclic processes are important in practical applications as they can be repeated, as in a steam engine or refrigerator. Cyclic processes are also of great conceptual value, as we will learn.

1.3 Work

When a gas expands, it does work ΔW on the surroundings; the surroundings do work $-\Delta W$ on the system. Our convention is to take the work done by the gas as positive in the case of an expansion and negative in the case of a contraction. More generally, a system can perform work (mechanical - movement of a piston, electrical/chemical - movement of charges/ions in an electric potential etc.) during a thermodynamic process. For example, consider a gas enclosed in a cylinder with a movable piston of area A. If p is the uniform pressure in the gas, the force exerted on the piston is pA. If the piston moves out a distance Δl, the work done is $\Delta W = pA\Delta l$. In general, if the volume of a gas increases by dV in an infinitesimal expansion, then the work done by the gas is $\delta W = pdV$. This can be shown by breaking up the bounding surface into small pieces and treating each as a small piston.

• Suppose the state can be represented on a p-V diagram, then a transformation from state (V_a, p_a) to (V_b, p_b) is represented by an oriented curve $\gamma_{a\to b}$ joining these points. The work done $W(\gamma) = \int_a^b pdV$ is given by the area under the curve (see figure). Note that the pressure could change during the process and that the area can be negative, as in a compression ($V_b < V_a$). In particular, the work done in a cycle (represented in a p-V diagram) is the area enclosed by the curve. For a simple closed curve, the area is positive if traversed clockwise and vice-versa. dV and δW both vanish in an infinitesimal isochoric transformation.

• In electromagnetic theory it is shown that the work done by the external field $\mathcal{H}$ in increasing the magnetization of a paramagnet from M to $M+dM$ is $\mu_0 \mathcal{H} dM$ where μ_0 is the permeability constant. Thus, the work done by a magnet in the process is $\delta W = -\mu_0 \mathcal{H} dM$. Up to a sign, this is analogous to $\delta W = pdV$ for the work done by a gas.

• It is very important to recognize the empirical fact that the work done during a process $\gamma_{a\to b}$ in general depends on the process and not just on the initial and final states. For example, consider initial and final equilibrium states of water at temperatures t_a and $t_b > t_a$, but at a common pressure, say atmospheric pressure. The corresponding volumes are determined by the equation of state. Now, we can go from state a to b in more ways than one. For instance, we could vigorously stir the liquid for some time and heat it up through friction, thereby doing a significant amount of work (this work is not calculable by integrating 'pdV' since in the intermediate stages, we would have set up a velocity field in the water and we would have to evaluate the work done in setting up the flow etc.). Alternatively, we could simply heat the liquid using a flame, in which case hardly any work is done (the liquid does a little work in expanding against atmospheric pressure). Both these processes are irreversible, but the first one involves a lot more work.

• This path-dependence of the work done is reflected in the fact that areas under different curves joining a to b in a pV diagram are not necessarily the same. In other words, unlike temperature, there is no 'work function' or property of state W such that $W(b) - W(a)$ is the work done during the process. In particular, the work done in an infinitesimal process δW depends on external effects and is not the differential of any state function W. This is why we do not denote it 'dW'. We say that the work done in an infinitesimal process is not an exact differential.

1.4 Exact and inexact differentials

Two independent variables: Given a differentiable function, say of two variables $\sigma(x,y)$, its differential is $d\sigma = \frac{\partial \sigma}{\partial x}\, dx + \frac{\partial \sigma}{\partial y}\, dy$. Under suitable hypotheses (it suffices for σ to have continuous second partial derivatives), the 'mixed' second partials are equal: $\frac{\partial^2 \sigma}{\partial x \partial y} = \frac{\partial^2 \sigma}{\partial y \partial x}$. This is called Schwarz's or Clairaut's theorem.

• On the other hand, suppose we are given a differential expression (also known as a one-form or Pfaffian differential) $\omega = f(x,y)dx + g(x,y)dy$ on the plane. We ask whether ω is the differential of some function σ, i.e., is $\omega = d\sigma$? σ would in a sense be an 'integral' of ω and we would call ω a perfect or exact differential. A necessary condition for this (it is also a sufficient condition on the plane - this is Poincaré's lemma) follows from the above remark: f and g must satisfy $\frac{\partial f}{\partial y} = \frac{\partial g}{\partial x}$. This is called the integrability condition for ω to be exact: if it is satisfied, we can 'integrate' ω to find σ. If we use the components of ω to define a 'coefficient' vector field $\mathbf{v} = (f,g) = f\hat{x} + g\hat{y}$ on the plane, this integrability condition states that $\mathbf{v}$ must be curl free $\nabla \times \mathbf{v} = (g_x - f_y)\hat{z} = 0$. Here, we use subscripts to denote partial derivatives.

• The curl of a vector field measures how much the vector field circulates or swirls around. In 3d if $\mathbf{v} = (f,g,h)$ then $\nabla \times \mathbf{v} = (h_y - g_z, f_z - h_x, g_x - f_y)$. The curl of a vector field on a plane points normal to the plane since $h = 0$ while f and g are independent of z. An example of a curl-free planar vector field is $\mathbf{v} = x\hat{x} + y\hat{y}$. It points radially outwards. The integrability condition is satisfied and indeed we see that $\sigma = (x^2 + y^2)/2$ is a function whose differential equals $\omega = xdx + ydy$. On the other hand $\omega = -ydx + xdy$ is not exact since it does not satisfy the integrability condition and the corresponding vector field $\mathbf{v} = -y\hat{x} + x\hat{y}$ has non-vanishing curl: $\mathbf{v}$ it points azimuthally and describing swirling motion counterclockwise around the origin.

• In passing, we note that given a vector field $\mathbf{v} = (f,g,h)$ we can define another derivative, namely its divergence, which is a scalar $\nabla\cdot\mathbf{v} = f_x + g_y + h_z$. The divergence measures expansion or compression and can sometimes be associated with the presence of sources or sinks. For instance $\mathbf{v} = (x\hat{x} + y\hat{y})$ has divergence $\nabla \cdot \mathbf{v} = 2$ but no curl. However, the integrability condition for exactness is not related to the divergence of the coefficient vector field.

• There is a third notion of derivative, namely the gradient which takes a function $\sigma(x,y,z)$ and produces a vector field $\nabla\sigma = \sigma_x\hat{x} + \sigma_y\hat{y} + \sigma_z\hat{z}$. Our statement on the exactness of ω can then be restated as follows: ω is exact $(\omega = d\sigma)$ if the coefficient vector field $\mathbf{v}$ is curl-free and in that case, $\mathbf{v} = \nabla\sigma$ is the gradient of the scalar function σ.

• In the last section we asserted that the work differential (work that can be done by a gas in an infinitesimal expansion) $\delta W = pdV$ is not exact in general. As another example, consider the Pfaffian differential $\omega = CdT + \frac{nRT}{V}dV$ in the variables T and V. Here n and R are constants while C is independent of V. The above integrability condition is not satisfied since nR/V is not identically zero. Interestingly, notice that ω/T is an exact differential, the integrability condition is satisfied and we can integrate it to find a function σ such that $d\sigma = \omega$. Indeed $\omega/T = CdT/T + nRdV/V = d(C\log T + nR\log V + \sigma_0) \equiv d\sigma$. Notice that σ is defined only up to an additive constant. T is called an integrating factor or integrating denominator for the inexact differential ω. More on this later.

• Now if ω is an exact differential, then its line integral between a pair of points $\mathbf{a}, \mathbf{b}$ on the plane is independent of the path γ connecting them. Indeed, let the path $\gamma : [t_a, t_b] \to \mathbb{R}^2$ be given by $\mathbf{r}(t) = (x(t), y(t))$ with $\mathbf{r}(t_a) = \mathbf{a}$ and $\mathbf{r}(t_b) = \mathbf{b}$. Then the tangent vector to the curve is $\dot{\mathbf{r}}(t)$ and the line element $d\mathbf{l} = \dot{\mathbf{r}}(t)dt$ and

$$\int_\gamma \omega = \int_\gamma f dx + g dy = \int_\gamma \mathbf{v}\cdot d\mathbf{l} = \int_{t_a}^{t_b} (f\dot{x} + g\dot{y})dt = \int_{t_a}^{t_b} (\sigma_x\dot{x} + \sigma_y\dot{y})dt = \int_{t_a}^{t_b} \frac{d\sigma(\mathbf{r}(t))}{dt}dt = \sigma(\mathbf{r}(t_b)) - \sigma(\mathbf{r}(t_a)). \quad (7)$$

The last equality follows from the fundamental theorem of calculus. Path-independence follows since the line integral depends only on the values of the function σ at the end points. Thus, we arrive at a formula for a function $\sigma(\mathbf{r})$ whose differential is ω:

$$\sigma(\mathbf{r}) = \sigma_0 + \int_\gamma \omega \quad (8)$$

where γ is any curve that joins an arbitrary reference point $\mathbf{r}_0$ to $\mathbf{r} = (x, y)$. Notice that σ is not unique: it is determined up to an additive constant which we have taken as $\sigma_0 = \sigma(\mathbf{r}_0)$.

• In particular, the integral of an exact differential around a closed contour C vanishes $\oint d\sigma = 0$. This may also be seen by an application of Green's theorem (2d version of Stokes' theorem)

$$\oint_C f dx + g dy = \int_S (g_x - f_y)\, dx dy = 0 \quad \text{or} \quad \oint_C \mathbf{v}\cdot d\mathbf{l} = \int_S (\nabla\times\mathbf{v})\cdot\hat{z}\, dx dy = 0. \quad (9)$$

Here S is the two-dimensional region bounded by the closed curve C. Conversely, a differential ω whose line integral around every closed curve vanishes is an exact differential. This is easy to show, since the function

$$\sigma_\gamma(x, y) = \sigma_0 + \int_\gamma \omega \quad (10)$$

where γ is any curve from an arbitrary reference point (x_0, y_0) to (x, y) satisfies $d\sigma = \omega$ and is is seen to be independent of the choice of γ. Indeed, the difference $\sigma_\gamma - \sigma_{\gamma'}$ for two curves joining the same points is equal to the line integral of the exact differential ω around the closed curve $\gamma \cup \bar{\gamma}'$ and therefore vanishes ($\bar{\gamma}'$ is the curve γ' traversed in the opposite direction).

Three independent variables: The above statements have a natural generalization to 3D. The differential $\omega = f dx + g dy + h dz$ is locally exact provided the first partials of f, g and h satisfy

$$f_y = g_x, \quad g_z = h_y \quad \text{and} \quad h_x = f_z. \quad (11)$$

Here, for instance, $f_y = \left(\frac{\partial f}{\partial y}\right)_{x,z}$ is the partial derivative with respect to y holding x and z fixed. These three conditions simply state that the coefficient vector field $\mathbf{v} = (f, g, h,)$ is curl-free:

$$\nabla \times \mathbf{v} = (h_y - g_z, f_z - h_x, g_x - f_y) = 0. \qquad (12)$$

So, when $\mathbf{v}$ is curl-free, we may express it as the gradient of a scalar $\mathbf{v} = \nabla\sigma$ or $\omega = d\sigma$. Furthermore, the line integral $\int_a^b \omega$ of the exact differential ω is the difference in values $\sigma(b) - \sigma(a)$ independent of the path.

• The above result can also be obtained from Stokes' theorem in three dimensions. Given a sufficiently smooth vector field $\mathbf{v}$ in a simply connected region, its line integral around a closed curve C can be re-expressed as the surface integral of its curl over any surface S in the region whose boundary is C:

$$\oint_C \mathbf{v} \cdot d\mathbf{l} = \int_S (\nabla \times \mathbf{v}) \cdot d\mathbf{S}. \qquad (13)$$

Now if $\mathbf{v}$ is curl-free, the RHS vanishes, so that its line integral around any (necessarily) contractible closed path vanishes.

1.5 Ideal gas laws

• It is empirically found that many gases in equilibrium satisfy certain common ('ideal' gas) laws at temperatures much higher than their condensation point and at low pressures. At 20° C and atmospheric pressure of one Atm (or 760 mm of Hg or 760 torr), helium, hydrogen, oxygen, carbon dioxide and air to a reasonable approximation behave ideally while water vapour (steam) does not. An ideal gas is what we would get when we expand a real gas to very large volumes. From the molecular standpoint, an ideal gas is one whose molecules are point-like (i.e. occupy negligible volume compared to that of the container) and do not interact with each other (exert negligible forces).

• **Boyle's and Mariotte's Law (1658, 1676):** For a given mass of a gas at a fixed temperature, the product of pressure and volume occupied by the gas in equilibrium is a constant: $p^{(i)}V^{(i)} = \Theta^{(i)}(t,m)$. Based on the investigations of Boyle and Mariotte, the constant $\Theta^{(i)}(t,m)$ could depend (and in fact does depend) on temperature t, mass m of gas and on the chemical nature of the gas (indicated by the species label i).

• **Gas temperature scale:** By a gas thermometer, we mean the following. We select a specified volume (say 1 cc) of a gas (such as Helium) that is far from condensation at a reference temperature (say the freezing point of water at atmospheric pressure of 1 atm). As noted, gases are observed to expand on heating and contract on cooling. We simply define the gas temperature T to be a constant multiple of the volume, with the pressure being held fixed. The constant is often fixed by requiring the difference in gas temperatures at the boiling and freezing points of water to be 100 at atmospheric pressure. Note that fixing the constant through such a specification also removes the dependence on the volume of gas we started with, it could have been 100 cc instead of 1 cc. It is a remarkable empirical fact (see also the Charles-Dalton-Gay-Lussac law below) that a wide variety of gas thermometers (with different gases, but all of which have the same volume at the reference temperature and pressure) agree on their assignment of gas temperatures as long as the gases are far from condensing. The temperature scale T defined this way is called the gas thermometer scale (or absolute gas temperature) or the Kelvin scale. Water freezes at 1 atm pressure at T = 273.16 Kelvin. By construction $T > 0$ since the volume of a gas is a positive number.

- **Charles', Dalton's and Gay-Lussac's Law (1787, 1802):** (See N D Hari Dass, The principles of thermodynamics) *All gases, whatever may be their density and the quantity of water which they hold in solution, and all vapours expand equally between the same degrees of heat.* Here 'same degrees of heat' means 'between the same initial and final temperatures' (freezing and boiling points t_f, t_b of water at atmospheric pressure in Gay-Lussac's experiments). By 'expand equally' he apparently meant the change in volume as a fraction of original volume was the same for all gases. The expansion of all gases was carried out at the same fixed pressure p (atmospheric pressure). If the species of gas is labelled i, we may summarize the law by

$$\frac{V_{t_b}^{(i)} - V_{t_f}^{(i)}}{V_{t_f}^{(i)}} = c(p; t_f, t_b) \tag{14}$$

for all gases. In other words, the fractional change in volume is independent of species, but we have allowed for a dependence on the pressure and initial and final temperatures through $c(p; t_f, t_b)$. Note that though the volumes $V_{t_b}^{(i)}, V_{t_f}^{(i)}$ depend on the mass of gas present, the ratio on the left is independent of the mass, since it is found that twice the mass of a gas occupies twice the volume at a fixed temperature and pressure. So the RHS is also independent of mass of gas used.

- Now applying the Boyle-Mariotte law, we get

$$\frac{\Theta^{(i)}(t_b, m) - \Theta^{(i)}(t_f, m)}{\Theta^{(i)}(t_f, m)} = c(p; t_f, t_b). \tag{15}$$

The dependence on pressure cancels between numerator and denominator on the LHS since the expansion is carried out at a fixed pressure. Thus the RHS must be independent of pressure and $c = c(t_f, t_b)$. Moreover, the RHS is independent of species. The simplest way for the LHS to be independent of species is for $\Theta^{(i)}(t, m)$ to be species independent. However, this contradicts experiment: putting this in Boyle's law, we would find that the product pV for mass m of any gas is the same function of temperature $\Theta(t, m)$. However, it is found that a common mass m of different gases at the same temperature have *different* constant values for the product pV. This is also why in setting up the gas thermometer, we did not take equal masses of different gases but rather equal volumes at a common temperature and pressure. The next simplest possibility is that $\Theta^{(i)}(t, m) = \nu^{(i)}(m)\, \Theta(t)$ is the product of a species-dependent function $\nu^{(i)}(m)$ and a species-independent function of temperature. The constant $\nu^{(i)}(m)$ cancels in the quotient on the LHS of (15), ensuring that the RHS is independent of both i and m.

Putting this in the Boyle-Mariotte law, we deduce that for a fixed mass m of any gas (labeled i) at a fixed temperature t,

$$p^{(i)} V^{(i)} = \nu^{(i)}(m)\, \Theta(t). \tag{16}$$

Here $\Theta(t)$ is a universal function of temperature. Now we are free to choose our temperature scale. The law takes its simplest form when we use the gas thermometer scale of temperature, in which case $\Theta(T)$ is a universal constant multiple, say R, of T (since we defined the gas thermometer temperature to be a multiple of the volume of the gas holding p, m fixed). Thus the simplest way of satisfying the observations of Boyle-Mariotte-Charles-Dalton-Gay-Lussac is for gases to obey

$$p^{(i)} V^{(i)} = \nu^{(i)}(m)\, RT \tag{17}$$

where T is the gas thermometer temperature. As we will see, $\nu^{(i)}(m)$ depend on the species via a characteristic property which we now recognize as their molecular masses. This brings us to Avogadro's postulate.

• **Avogadro's postulate (1811):** *Equal volumes of all gases at the same temperature and pressure have the same number of corpuscles (molecules), but (in general) different masses.* However, the molecular constitution of matter took nearly a century to be confirmed. In the interim, it made sense to reformulate Avogadro's postulate in terms of measurable quantities. Ostwald introduced the concept of moles for this purpose. A gram-mole or gram molar mass μ of a gas was defined as a definite number of grams of a gas. For example, one gram-mole of hydrogen is 2 grams of the gas (i.e. $\mu = 2$ for H_2). A gram mole of oxygen is 32 grams (i.e. $\mu = 32$ for O_2).

• These assignments were based on the proportions in which elements combined to form chemical compounds (the subject of Dalton's and Gay-Lussac's laws of multiple proportions[7] and integral volume ratios[8]), but could also be deduced from calibrating gas thermometers with the same mass of different gases with each other. In current language, one gram mole of a compound is as many grams as there are units in the sum of atomic weights of the constituent elements, with the Hydrogen atom being assigned an atomic weight of one since it is the lightest known element. We often refer to one gram mole of a gas as simply one mole of the gas. Avogadro's law in Ostwald's formulation states that *equal volumes of all gases at a common pressure and temperature contain equal numbers of moles of the gas.* So suppose we consider one gram-mole of gas i (i.e. μ_i grams) as well as one gram mole of gas j (i.e. μ_j grams) at the same pressure and temperature. The Avogadro-Ostwald postulate along with the Boyle-Mariotte-Gay-Lussac-Charles law implies

$$V^{(i)} = V^{(j)} \quad \text{or} \quad \frac{\nu^{(i)}(\mu_i)RT}{p} = \frac{\nu^{(j)}(\mu_j)RT}{p} \qquad \text{or} \quad \nu^{(i)}(\mu_i) = \nu^{(j)}(\mu_j) \quad \forall\, i,j. \tag{18}$$

Thus the constants $\nu^{(i)}(\mu_i)$ are independent of species if we consider one gram mole of each species. We can take this universal constant to be one, by a rescaling of R. Thus, for one mole of an ideal gas, $pV = RT$. If we had considered n gram moles instead of one gram mole, the volume occupied at a fixed temperature and pressure is found to be multiplied by n, so we arrive at $pV = nRT$ for n gram moles of any sufficiently ideal gas. In other words, $\nu^{(i)}(m) = m/\mu_i$. To see this, we first note by the property just noted that $\nu^{(i)}(m) \propto m$ is proportional to the mass of the gas, so for some proportionality constant k_i (depending on species),

$$\nu^{(i)}(m) = k_i\, m. \tag{19}$$

Taking one gram mole of gas i we have $m = \mu_i$. Now, using our observation that

$$\nu^{(i)}(\mu_i) = 1 \quad \text{we get} \quad k_i\mu_i = 1 \quad \text{or} \quad k_i = \frac{1}{\mu_i}. \tag{20}$$

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[7] **Dalton's law of multiple proportions:** When two elements combine with each other to form more than one compound, the masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers. *E.g. 24g of carbon combine with 32g of oxygen to form 56g of carbon monoxide. 24g of C also combine with 64g of oxygen to give 88g of carbon dioxide. So the ratio of oxygen masses that combine with the same mass of carbon is* $1:2$.

[8] **Gay-Lussac's law of integral volume ratios:** The ratio between the volumes of the reactant gases and the products can be expressed in simple whole numbers. *E.g. 4g of hydrogen gas combine with 32g of oxygen to give 36g of water vapour. It is found that two litres of hydrogen combines with one litre of oxygen to give 2 litres of water vapour. The ratio of volumes of reactants to product is* $3:2$.

• **Ideal gas law:** Combining Avogadro's postulate with the Boyle-Mariotte and Charles-Dalton-Gay-Lussac laws in the manner above, it is found that the equation of state of an ideal gas takes a particularly simple form when we use the gas thermometer scale. For m grams of a gas with gram molecular mass[9] μ,

$$pV = (m/\mu)RT. \tag{21}$$

• Here $R = 8.314$ Joules/Kelvin per mole is the universal gas constant. From Ostwald's definition, the quotient $n = m/\mu$ is the number of moles of the gas. By Avogadro's law, one mole of all (nearly ideal) gases contain the same number of molecules, namely $N_A = 6.023 \times 10^{23}$ (Avogadro's number, estimated by J J Loschmidt in 1856 and more accurately measured by J B Perrin in 1909 after Einstein's work on Brownian motion).

• The ideal gas EOS may also be expressed as a relation among pressure, density $\rho = m/V$ and temperature $p = \rho RT/\mu$. Alternative forms are $pV = nRT$ and $pV = Nk_BT$ where $N = N_A n$ is the number of molecules and $k_B = R/N_A = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. If we introduce the specific volume $v = V/m$ which is the reciprocal of density, then the ideal gas law states that $pv = RT/\mu$.

• As noted, from a microscopic viewpoint, an ideal gas is a collection of molecules of a given chemical species occupying a volume much larger than the size of the molecules and whose inter-molecular forces can be ignored. The Hamiltonian for such a collection of molecules is the sum $(1/2M)\sum_a (p_a^2)$ where the various molecules are labelled by a and M is the mass of each molecule. It is not surprising, then, that all gases that can be approximated by such a treatment behave in the same way except for the difference in the masses of the molecules. The molecular mass enters the ideal gas law through μ $(M = \mu/N_A)$ and is the only way in which the gas manifests its chemical identity.

• For an isothermal transformation of a fixed amount of an ideal gas, pV is a constant. Thus, on a p-V diagram, an isotherm is represented by a hyperbola with the p and V axes as asymptotes. The work done by the gas in a reversible isothermal expansion from volume V_1 to V_2 is

$$W = \int_{V_1}^{V_2} p(V) dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \log(V_2/V_1) = nRT \log(p_1/p_2). \tag{22}$$

2 Heat transferred and the first law of thermodynamics

2.1 Heat transferred and its mechanical equivalent

• **Caloric theory of heat:** Prior to the mid 1800s heat was regarded as a substance, the 'caloric' which was thought to be like a fluid that flowed while its amount was conserved[10]. This is in contrast to the current view that heat is a form of energy that can be transformed (partly) into (or arise from) other forms of energy. The heating of water by a flame was assumed to involve flow of the caloric (heat-fluid) from the fire to the water. When a bottle of hot water was brought into contact with a bottle of cold water, it was supposed that the heat fluid flowed from hot to cold water till the temperatures were equalized. The theory was not without merit. Carnot (1824) correctly deduced limits to the conversion of heat into work based on the caloric theory.

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[9] For example, the gram molecular mass of H_2 molecule is 2 while that of that of He_2^4 atom is 4.

[10] An even earlier (now discarded) theory of combustion was the *Phlogiston* theory, developed from 1667 onwards.

However, the caloric theory had to be replaced since it contradicted experiment. The amount of heat fluid was not conserved: heat could be produced entirely from mechanical or electrical work, as in the heating of a resistor/filament of a light bulb or the melting of two pieces of ice when rubbed together. The caloric theory of heat was replaced by a more mechanical theory of heat.

• The amount of heat transferred in a process may be quantified through temperature measurements. **One calorie of heat transferred** is defined as the quantity of heat required to raise the temperature of one gram of water from 14° to 15° C at atmospheric pressure. It is important to recognize that while we can measure and define the heat exchanged between systems, we have not defined the 'heat content' of a system.

• **Mechanical equivalent of heat** Count Rumford (also known as Benjamin Thompson, 1798) famously demonstrated that water could be made to boil while the shaft of a canon was being mechanically bored. Water could also be heated through stirring using immersed paddles that were made to rotate by letting a weight descend under gravity. Several careful experiments showed that the heat transferred (in calories) was proportional to the work done (say in Joules or ergs), through a universal proportionality constant $\delta Q = (1/J)\delta W$. Precisely, to transfer one calorie of heat, the same amount of work, i.e. $J = 4.186$ Joules had to be done. Thus 4.186 Joules of work done is the mechanical equivalent of one calorie of heat transferred.

2.2 First Law of Thermodynamics

• In 1842 Robert Mayer presented a mechanical theory of heat, based on the transformability of heat into mechanical energy (and vice versa), and formulated the 1st law of thermodynamics. We will state the first law and later describe the cyclic process he used to determine the mechanical equivalent of heat. A similar process had been considered by Sadi Carnot somewhat earlier. Hermann Helmholtz (1847) made Mayer's ideas on the first law mathematically more precise. The first law was the work of these and several other scientists.

• The first law postulates the existence of the internal energy as a state function of a thermodynamic system. It posits that the heat added to a system is equal to the sum of the increase in its internal energy (denoted U by Rudolf Clausius) and the work done by the system.

$$\Delta Q = \Delta U + \Delta W. \tag{23}$$

We may regard the first law as a generalization of the statement of conservation of energy. For an isolated system (thermally and mechanically/electromagnetically etc), the internal energy is conserved. For a thermally insulated system, the work done by the system is equal to the drop in its internal energy $\Delta W = -\Delta U$.

• Given the state of a system, we can speak of the internal energy of that state, but not the 'heat content' or 'work' of the system in that state, heat and work are not state functions, they are measures of external effects. *If the caloric theory was true, heat would be a state function, equal to the amount of caloric fluid.*

• For a cyclic process, the initial and final states are the same so $\Delta U = 0$ and the 1st law becomes $\Delta Q = \Delta W$, i.e., the work done is equal to the heat absorbed.

• For an infinitesimal reversible expansion of system volume dV against a pressure p, the work done is $\delta W = pdV$. So for infinitesimal reversible processes, we write

$$\delta Q = dU + pdV. \tag{24}$$

Unlike the heat and work differentials δQ and δW which are not exact, the internal energy differential dU is an exact differential. So for a cyclic process $\oint dU = 0$. On the other hand, there is no state function Q such that δQ is equal to dQ.

• The 1st law allows us to measure heat exchanged in energy units. It is found that 1 calorie of heat exchanged is equivalent to 4.186 Joules of energy.

• The first law is sometimes interpreted as stating the impossibility of constructing a machine (perpetuum mobile or perpetual motion machine of the first kind) that can create or destroy energy. Rather, energy can be transformed into other forms such as mechanical/electrical work and heat.

• When the number of particles N in the system can change, the internal energy of a system could change even if no mechanical work is done on the system nor any heat transferred to it. It is conventional to define the chemical potential μ as the energy required to add one particle to a thermally and mechanically isolated system. The first law is then generalized to

$$\Delta Q = dU + \Delta W - \mu\,\Delta N \quad \text{or} \quad \delta Q = dU + pdV - \mu dN \tag{25}$$

for an infinitesimal process. We may interpret this equation as saying that the heat added to a cup of water by a flame is equal to the sum of the increase in its internal energy, the work the water does in expanding against atmospheric pressure and the energy lost to particles expelled from the container ($dN < 0, \mu > 0$, here N is).

• Based on the manner they enter the equation for energy conservation, we say that p and V are conjugate variables as are μ and N. In each pair we have one intensive and one extensive variable. Notice that the product of conjugate variables has dimensions of energy.

2.3 First law for systems with (p, V, T) state space, three δQ equations and specific heats

• If the state of a thermodynamic system (such as a homogeneous gas) can be represented by a point in PVT space (subject to the equation of state), then we may express the state function U in terms of any one of the three pairs of independent variables. For instance, taking (T, p) as independent variables, the infinitesimal increase in volume and internal energy are

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \quad \text{and} \quad dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp. \tag{26}$$

Then the 1st law $\delta Q = dU + pdV$ implies the following three 'δQ equations' for the infinitesimal heat added to a system with the indicated variables taken as independent:

$$\begin{aligned}
(T, V) \quad &\longrightarrow \quad \delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV,\\
(T, p) \quad &\longrightarrow \quad \delta Q = \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] dT + \left[\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right] dp,\\
(p, V) \quad &\longrightarrow \quad \delta Q = \left(\frac{\partial U}{\partial p}\right)_V dp + \left[\left(\frac{\partial U}{\partial V}\right)_p + p\right] dV.
\end{aligned} \tag{27}$$

- We define the heat/thermal capacity of a system as the ratio $C = \delta Q/dT$ of infinitesimal heat added (usually reversibly) to the consequent increase in temperature. The heat capacity generally depends on how the system is heated. Of particular significance are the principal heat capacities C_V, C_p at constant volume and pressure. Taking (T,p) and (T,V) as independent variables in (27) we obtain expressions for C_V, and C_p in terms of derivatives of state functions

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{28}$$

We may intuitively argue that C_p should generally exceed C_V since at constant pressure, additional heat must be supplied for the gas to do work while expanding while at constant volume, all the heat added goes into increasing the internal energy and temperature.

- Note that C_P can also be written as $C_P = \partial_T(U + pV)$ where the partial derivative is evaluated at constant pressure. It is therefore natural to introduce the new extensive state function 'enthalpy' $H = U + pV$ and express C_p as the temperature derivative of H at constant pressure, just as C_V is the temperature derivative of U at constant volume. The formula $H = U + pV$ is reminiscent of the rough formula $H = -L + p\dot{q}$ relating the Hamiltonian to the Lagrangian in mechanics. More on this analogy later.

- The heat capacities are extensive as U and V are. It is often convenient to define the corresponding intensive quantities c_V, c_p by considering the heat exchanged per unit mass (specific heats) or per mole or molecule (molecular heats).

2.4 First law for paramagnet

Recall that the thermodynamic state space of a paramagnet is three dimensional with coordinates given by external magnetic field $\mathcal{H}$ (z component), z-component of magnetization M and temperature T. From electromagnetic theory, the work done by the external field in increasing the magnetization from M to $M + dM$ is $\mu_0 \mathcal{H} dM$. Thus the first law takes the form (Paul Langevin, 1905)

$$\delta Q = dU - \mu_0 \mathcal{H} dM \tag{29}$$

Comparing with $\delta Q = dU + pdV$ for a gas, we see that roughly, p and $-\mu_0\mathcal{H}$ play similar roles while volume and magnetization are analogous. The equation of state for a paramagnet bears some resemblance to the ideal gas law. Indeed, comparing the Curie-Weiss law with the ideal gas law,

$$M = \chi\mathcal{H} = \frac{C\mathcal{H}}{(T - T_c)} \quad \text{and} \quad \rho = \frac{\mu p}{RT}, \tag{30}$$

we see that Curie's constant C plays the role of μ/R while magnetization (per unit volume) is like density and $\mathcal{H}$ is like pressure. $T - T_c$ for the paramagnet is replaced with the gas thermometer temperature.

- As for a gas, we may define heat capacities and specific heats of a paramagnet at constant magnetic field or constant magnetization. See Haridass or Sommerfeld for further discussion.

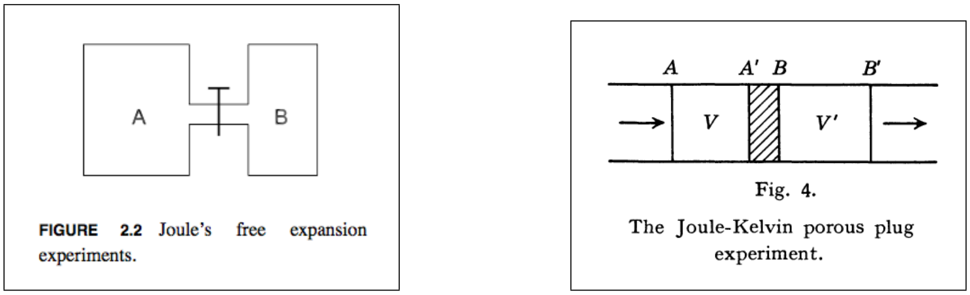

FIGURE 2.2 Joule's free expansion experiments.

Fig. 4. The Joule-Kelvin porous plug experiment.

Figure 3: Joule free expansion experiment and Joule-Kelvin porous plug experiment (from Sommerfeld)

3 Applications of the first law

3.1 Gay-Lussac and Joule experiment: irreversible adiabatic expansion

• Gay-Lussac (1807) confined a gas in a thermally insulated cylindrical container fitted with a movable piston. Initially, the gas was in equilibrium at temperature T_1, pressure p_1 and occupied volume V_1. The piston was suddenly moved outwards, increasing the available volume to V_2. The gas expanded (through a complicated flow) and eventually reached equilibrium at a lower pressure p_2 in volume V_2. Remarkably, there wasn't much change in temperature $T_2 \approx T_1$. This was confirmed by J P Joule (1845) who repeated the experiment more carefully, this time with two glass jars connected by a tube with a stop-cock. When the cock was released, gas (air, hydrogen) from the filled jar flowed into the evacuated jar and a new equilibrium was established, with barely any change in temperature.

• Though the experiment pre-dates the first law, let us apply the first law to the initial and final states. Since the gas expands into a vacuum (zero pressure), we may assume it does not do any work. Insulation ensures the gas does not exchange any heat. Thus the internal energy must be unchanged. Taking volume and temperature as independent variables (with pressure determined by the ideal gas equation of state), $U(V_1, T_1) = U(V_2, T_1)$. We conclude that the internal energy of an ideal gas is independent of volume, $U = U(T)$.

3.2 Joule-Kelvin (or Joule-Thomson) porous plug experiment and enthalpy

• This was a successor to Gay-Lussac's and Joule's free expansion experiments. It lent greater credence to the conclusion that the internal energy of a gas obeying the ideal EOS (air, hydrogen etc.) is a function of temperature but not volume. Interestingly, the results of the experiment could be interpreted in terms of enthalpy.

• Gas at a higher pressure p_1 is forced slowly[11] from the left chamber through a pipe (filled with a porous plug made of cotton wool) to the right chamber at lower pressure p_2 (the pressures are maintained at the same values throughout). Both chambers were insulated and had the same cross-sectional area A. The pipe was made of beechwood, a thermal insulator. Consider a volume V_1 of gas between two vertical cross-sections on the left, that emerges on the right and occupies volume V_2 between two vertical cross-sections. The distance traversed by the gas

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[11] When done slowly, this would give another example of a slow but irreversible process.

on the left is V_1/A and V_2/A on the right. On the left, the force $p_1 A$ on the gas does work $p_1 A V_1/A = p_1 V_1$. On the right, the opposing force $p_2 A$ does work $-p_2 A V_2/A = -p_2 V_2$ on the gas. Thus the total work done on this mass of gas is $p_1 V_1 - p_2 V_2$. The process may be assumed adiabatic. Denoting the initial and final internal energies of the gas by U_1 and U_2, the first law implies

$$U_2 - U_1 = p_1 V_1 - p_2 V_2 \quad \text{or} \quad U_1 + p_1 V_1 = U_2 + p_2 V_2. \tag{31}$$

The enthalpy $H = U + pV$ of a given mass of gas is conserved as it passes through the insulated plug.

• Furthermore, it was found that the temperature of the gas was almost unchanged. Assuming the ideal gas law,

$$U_2 - U_1 = p_1 V_1 - p_2 V_2 = nR(T_1 - T_2) \approx 0. \tag{32}$$

Though the volume has changed, U has not, so the internal energy of an ideal gas may be taken independent of volume $U = U(T)$. Since the gas is pushed down a pressure gradient ($p_1 > p_2$), $T_2 \approx T_1$ implies $V_2 > V_1$, i.e. the gas expands.

• Careful measurements indicate that T_1 and T_2 are not quite the same (under ordinary conditions $T_2 < T_1$ for air but $T_2 > T_1$ for hydrogen). In fact, many real (as opposed to ideal) gases can be cooled as they expand while passing down a pressure gradient. This is the basis of the Joule-Thomson effect.

3.3 Heat capacities of ideal gases

• We concluded from Joule's experiment that the internal energy of a fixed mass of an ideal gas could be taken independent of volume. This is sometimes called the **caloric condition**. It follows that $C_V(T) = \frac{dU}{dT}$ or $dU = C_V(T)dT$. This, along with the ideal gas EOS and 1st law leads to the useful relation $C_p - C_V = nR$ between heat capacities at constant pressure and volume. To see this, we write the first law in form $\delta Q = C_V dt + pdV$ and substitute for pdV from the differential of the EOS $pV = nRT$:

$$pdV + Vdp = nRdT. \tag{33}$$

Thus we get

$$\delta Q = (C_V + nR)dT - Vdp. \tag{34}$$

We may now read off the heat capacity at constant pressure

$$C_p = (\delta Q/dT)_p = C_V + nR. \tag{35}$$

This is consistent with our earlier observation that c_p must exceed c_V: at constant pressure part of the heat supplied goes into expanding the gas leaving less heat to raise its temperature. The relation is often expressed in terms of molar specific heats $c_p - c_V = R$ ($c_p = C_p/n$ is the heat capacity per mole or molecular heat at constant pressure) and is in good agreement with experiments.

• While thermodynamics has allowed us to find a relation among heat capacities, it does not give us a way of determining their values. The kinetic theory of gases, which takes into account the molecular structure of matter allows us to estimate c_V. For monoatomic gases (such as helium and neon and other Noble gases and mercury vapour) one finds the molar specific heat $c_V =$

$(3/2)R$. For diatomic molecules (such as hydrogen, nitrogen and oxygen and air), $c_V = (5/2)R$. Now a monoatomic species, approximated as a point mass has three translational degrees of freedom. A diatomic molecule, regarded as a rigid rod of zero thickness has three translational and two rotational degrees of freedom. It is thus plausible that $c_V = (f/2)R$ where f is the number of such degrees of freedom. In fact, kinetic theory leads to the law of equipartition of energy, whereby each such degree of freedom contributes $R/2$ to c_V. A non-collinear polyatomic molecule (such as NO_2) has three rotational and three translational degrees of freedom so that $c_V = 3R$.

• Using the thermodynamic relation $c_p - c_V = R$ we have $c_p = (1 + f/2)R$.

• The ratio of specific heats $\gamma = c_p/c_V = C_p/C_V$ ('adiabatic index') plays an important role in adiabatic transformations to be discussed shortly. Thermodynamics and kinetic theory together predict that $\gamma = 1 + 2/f$. In particular, $\gamma > 1$. For mono-, di- and generic polyatomic gases, $\gamma = 5/3, 7/5$ and $4/3$.

3.4 Mayer's cycle for mechanical equivalent of heat

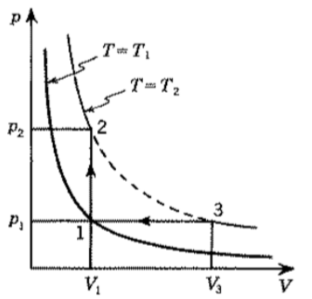

Fig. 3.
Cycle for the determination of the mechanical equivalent of heat.

Figure 4: From Sommerfeld Thermodynamics and Statistical Mechanics. Mayer's cycle for the mechanical equivalent of heat.

• To appreciate the historical and physical significance of the formula for the difference between heat capacities of an ideal gas we study Mayer's cycle (see Fig. 4). This was a cyclic process considered by R Mayer in his discovery of the first law of thermodynamics and in calculating the mechanical equivalent of heat. Consider n moles of an ideal gas in state 1 at atmospheric pressure p_1 and occupying volume V_1 at temperature T_1. It is reversibly heated at constant volume to state 2 at temperature $T_2 > T_1$, pressure $p_2 > p_1$ and volume $V_2 = V_1$. In this process, the gas does no work, but its internal energy is increased by

$$\Delta U_1 = \Delta Q_1 = \int_{T_1}^{T_2} C_V dT. \tag{36}$$

Next, the gas is expanded isothermally to state 3 with volume V_3 so as to reduce its pressure back to p_1. By the caloric condition, there is no change in internal energy. Finally, the gas is compressed at constant pressure p_1 from volume V_3 to V_1, thereby returning it to its initial state at temperature T_1. In this final stage the work done by the gas is negative $p_1(V_1 - V_3)$

and the heat added to the gas is $\int_{T_2}^{T_1} C_p dT$. Thus, the increase in internal energy in the third process is

$$\Delta U_3 = \Delta Q - \Delta W = p_1(V_3 - V_1) - \int_{T_1}^{T_2} C_p dT. \tag{37}$$

Being a cycle, there is no net change in internal energy $\Delta U_1 + \Delta U_2 + \Delta U_3 = 0$ or

$$\int_{T_1}^{T_2} (C_p - C_V) dT = p_1(V_3 - V_1). \tag{38}$$

Now suppose we make each of the processes infinitesimal, so that $T_2 - T_1 = dT$ and $V_3 - V_1 = dV$, then

$$p_1 dV = (C_p - C_V) dT. \tag{39}$$

Looked at in isolation, we may interpret this as a relation valid for a process at constant pressure p_1. However, from the ideal gas law $pV = nRT$, at constant pressure we must have $pdV = nRdT$. Thus, the difference between heat capacities must satisfy

$$C_p - C_V = nR = (m/\mu)R \quad \text{or} \quad c_p - c_V = R/\mu. \tag{40}$$

where μ is the molar mass and c_p, c_V are the specific heats per mole. Now, the specific heats had been measured (and expressed in calories per gram). The gas constant had also been measured (and expressed in ergs per degree per mole or Joules per degree per mole). By equating the two we arrive at the mechanical equivalent of heat: 1 calorie of heat added is equivalent to 4.186 Joules of work done.

3.5 Adiabatic transformation of an ideal gas

• Previously, we argued that a reversible isothermal expansion/contraction of an ideal gas is represented by a hyperbola $pV =$ constant on the pV plane.

• It is similarly interesting to find the curves on the pV plane representing reversible transformations in which no heat is exchanged, i.e., adiabatic transformations. A gas expands adiabatically if it is enclosed in a thermally insulated container and does work slowly pushing out a movable piston. Since $\delta Q = 0$ the first law gives $dU + pdV = 0$. Taking T, V as independent variables, Joule's experiment implies that $dU = C_V dT$ is independent of the change in volume. Eliminating $p = nRT/V$ using the ideal gas law, we get

$$C_V dT + \frac{nRT}{V} dV = 0 \quad \text{or} \quad C_V \frac{dT}{T} + (C_p - C_V)\frac{dV}{V} = 0 \quad \text{or} \quad \frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0 \tag{41}$$

where we used $C_p - C_V = nR$ and $\gamma = C_p/C_V$. Now assuming γ is independent of temperature (as is found to be approximately the case), we may integrate to get $\log(TV^{\gamma-1}) =$ constant. Thus for adiabatic transformations of an ideal gas we must have

$$TV^{\gamma-1} = \text{constant} \quad \text{or} \quad pV^{\gamma} = \text{constant} \quad \text{or} \quad T \propto p^{\frac{\gamma-1}{\gamma}}. \tag{42}$$

Thus, adiabats are defined by curves on the pV plane along which pV^γ is constant. Since $\gamma > 1$ we see that adiabats are steeper than isotherms if V and p are taken as abscissa and ordinate respectively.

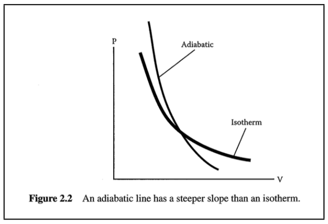

Figure 5: From K. Huang Introduction to Statistical Physics. Adiabat is steeper than an isotherm for an ideal gas.

3.6 Pressure and temperature in the atmosphere

The pressure and temperature are known to drop with height in the atmosphere. Hot air at the Earth's surface rises while cooler air drops down in convection currents. Since air is a poor conductor of heat, its motion can be taken to be adiabatic (i.e. $p \propto \rho^\gamma$ or $TV^{\gamma-1} =$ constant). We will not attempt to model this flow, but instead assume a steady state where the pressure and density are nevertheless related by the adiabatic relation. To get a crude estimate of the temperature and pressure variation with height, we consider a thin horizontal layer of gas of height dz and area A in mechanical equilibrium. The weight of the air in the layer is $A\,\rho\,g\,dz$. In equilibrium, the pressure at the bottom of the layer exceeds that on the top of the layer by the weight per unit area: $dp = -\rho g dz$. The negative sign is because pressure drops with increasing z. It turns out that the temperature variation with height is simpler (essentially linear) than that of pressure or density. So we eliminate density in favour of temperature using the EOS $p = \rho RT/\mu$ where μ is the mean molecular mass of air (between 28 and 32 for N_2 and O_2). Thus

$$\frac{dp}{p} = -\frac{\mu g}{RT} dz \tag{43}$$

We may now eliminate pressure in favour of temperature by use of the adiabatic condition $pT^{\frac{\gamma}{1-\gamma}} =$ constant. Differentiating, we get

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1}\frac{dT}{T}. \tag{44}$$

Thus we arrive at a constant rate of change of temperature with height

$$\frac{dT}{dz} = -\frac{\mu g}{R}\left(\frac{\gamma-1}{\gamma}\right). \tag{45}$$

Find the numerical value of the temperature gradient. Also find an equation for dp/dz and solve it.

3.7 Carnot Cycle

• A **reservoir or source of heat or heat bath** at a given temperature is an idealized body that can exchange heat with other thermodynamic systems without suffering a change in temperature and without performing work. A large body of water at a common temperature throughout behaves as a reservoir. Its temperature and volume may be taken to be roughly constant as it comes into contact with other small systems.

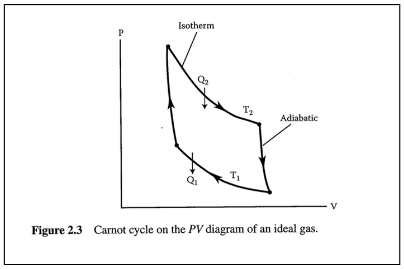

Figure 6: From K Huang: Carnot cycle on a pV diagram.

• The engine of a car provides an example of a cyclic heat engine. It absorbs heat at a high temperature t_2 (generated from combustion of fuel), does some work in moving the car, expels waste heat via the exhaust to the low temperature (t_1) reservoir (surroundings) and returns to its initial state. Here t denotes some empirical temperature scale, such as given by a mercury thermometer.

• A reversible engine is one that operates around a reversible cycle, this is of course an idealization since no real engine is truly reversible.

• The Carnot engine is a reversible cyclic heat engine that converts heat Q_2 absorbed at a high temperature (t_2) reservoir to work W while also expelling some waste heat Q_1 at a low temperature (t_1) reservoir. It is of great importance in understanding the limits of conversion of heat into work. Consider a fluid (e.g. an ideal gas) whose state can be represented by a point in the $p-V$ plane. A Carnot cycle is a clockwise oriented closed curve $ABCDA$ consisting of two isotherms and two adiabats (recall that adiabats are steeper than isotherms for an ideal gas).

• A simple example of a Carnot engine consists of a gas enclosed in a cylindrical container whose lateral walls are thermally insulated. A thermally insulated movable piston on the top of the cylinder allows work to be done by/on the gas while the diathermic base of the cylinder allows heat to be exchanged. One cycle of the engine consists of the following four stages. To begin with, the gas in the container is placed on the heat source at t_2 and brought to equilibrium at temperature t_2 while occupying a volume V_A.

AB: The container is placed on a heat source (reservoir) at t_2 and the piston is raised slowly causing the gas to expand isothermally from $V_A \to V_B$ and absorb heat Q_2.

BC: The container is placed on an insulator and the gas is allowed to expand adiabatically (reversibly) from volume V_B to V_C while its temperature drops from t_2 to t_1.

CD: The container is placed on a heat reservoir at temperature t_1 and slowly compressed isothermally from V_C to V_D while expelling heat Q_1.

DA: The container is placed on an insulator and the gas is slowly compressed from V_D back to the initial volume V_A, raising its temperature from t_1 to t_2.

• Let us apply the 1st law to one cycle of the Carnot engine. Since it has returned to its initial state, there is no change in internal energy (we do not assume here that the fluid is an ideal gas). Thus the work W done by the gas must equal the net heat absorbed: $W = Q_2 - Q_1$. It is an empirical observation (that we will prove later using the 2nd law of thermodynamics) that if $W > 0$, Q_1 cannot be zero or negative, i.e., some 'waste' heat must be surrendered at the low temperature reservoir ('exhaust'). The work done is also given by the area $W = \oint pdV$ enclosed by the closed curve ABCDA in the $p - V$ plane.

• The efficiency of the Carnot cycle is defined as the ratio of work done $W = Q_2 - Q_1$ to heat Q_2 absorbed at the high temperature reservoir

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}. \tag{46}$$

No real engine with $\eta = 1$ has been constructed. We will show later that the 2nd law implies $\eta < 1$.

• Since the Carnot cycle is reversible, we can run it in reverse $ADCBA$ to get a refrigerator. In this case the signs of Q_2, Q_1 and W are all reversed. Since the curve is traversed counterclockwise $\oint pdV$ is also negative. In other words, work W is performed on the refrigerator, allowing it to absorb heat Q_1 from the low temperature reservoir (at T_1, the interior of the fridge) and deposit heat $Q_2 = W + Q_1$ at the high temperature reservoir (at T_2, the environment outside the fridge). If E is a Carnot engine, then we will denote the corresponding refrigerator by $\bar{E}$.

4 Second law of thermodynamics

• The second law is a postulate built on the observation that heat is not conducted (spontaneously) from lower to higher temperatures, though we do observer spontaneous heat transfer from a hot to a cold body. This leads to Clausius' formulation. Interestingly there is an equivalent formulation of the second law due to Kelvin, that puts limits on the conversion of heat into work. Recall that while the first law precludes creation of energy, it does not place restrictions on the conversion of heat into work or vice versa. Empirically, there is no restriction on the conversion of work completely into heat. Indeed, a body at any temperature can be heated by friction, thereby converting mechanical work entirely into heat (electrical energy can similarly be converted into heat using a resistor). However, there *are* limits to the conversion of heat into work. If not, it would be possible to do essentially an unlimited amount of work using a device that extracts heat from our surroundings. The second law states the impossibility of creating such a 'perpetuum mobile of the second kind'. Thus, we may regard the 2nd law as placing restrictions on energy conserving processes that would otherwise be allowed by the 1st law.

4.1 Kelvin and Clausius postulates and their equivalence

• **Clausius postulate:** There is no thermodynamic process whose *only final result* is to transfer heat from a reservoir at a lower temperature to a reservoir at a higher temperature.

• **Kelvin postulate:** There does not exist a thermodynamic process whose *only final result* is to extract heat from a reservoir which is at the same temperature throughout the process and convert it entirely into work.

• A useful re-statement of the Kelvin postulate is this: If the only final result of a thermodynamic process is to extract heat Q from a reservoir at temperature t and convert it entirely into work

W then $W = Q \leq 0$. In other words, work was done on the system and converted into an equal amount of heat.

• The Kelvin postulate precludes the construction of an engine that converts heat from one reservoir at a fixed temperature into work. Loosely, a Carnot engine is the next best thing, it does work by operating between reservoirs at two different temperatures.

• We will now show the **equivalence of the Clausius and Kelvin postulates**. Convince yourself that to show $A \Rightarrow B$ it is enough to show that the falsehood of B implies the falsehood of A.

• **Clausius $\Rightarrow$ Kelvin**: Suppose the Kelvin postulate is false. It would then be possible to extract heat Q_1 from a reservoir at temperature t_1 and convert it to entirely into work $W = Q_1$. Now we could use this work W to deliver an equal amount of heat (e.g. via friction) to a reservoir at any temperature, say one at temperature $t_2 > t_1$. We would thus have transferred heat from low to high temperature with no other effect, in violation of Clausius's postulate.

• **Kelvin $\Rightarrow$ Clausius**: Conversely, suppose the Clausius postulate is false and we have a device that delivers heat Q_2 from a reservoir at t_1 to a reservoir at t_2 with $t_2 > t_1$. Then we could run a Carnot engine between the reservoirs at t_2 and t_1 to extract heat Q_2 from the reservoir at t_2 and deliver $Q_1 < Q_2$ to the reservoir at t_1 while performing work $Q_2 - Q_1 > 0$. In effect, we would have a machine whose only final effect is to extract heat $Q_2 - Q_1$ from a reservoir at t_1 and convert it entirely into work, in violation of Kelvin's postulate.

• **Cautionary remarks:** In applying the second law, care must be taken in checking the hypotheses. In particular, the second law does not prohibit complete conversion of heat into work, if that is not all that happens. (1) For instance, in isothermal expansion of an ideal gas, the heat supplied to the gas is equal to the work done by the gas. There is no change in internal energy of the gas. However, at the end of the process, the gas has expanded and occupies a larger volume. This violates the assumption in Kelvin's postulate that 'there is no other final effect ...' So isothermal expansion of an ideal gas does not contradict the second law. (2) On the other hand, a Carnot engine, being cyclic, is able to do work without any net change in state of the gas! But this clever device comes at a cost: it needs a second reservoir to accept waste heat!

4.2 Consequences of the 2nd law for efficiency of engines

• **A cyclic engine cannot *absorb* heat at two reservoirs *and* do work.** If a cyclic heat engine (not necessarily a Carnot engine nor even a reversible one) operating between temperatures $t_2 > t_1$ does work $W > 0$ by absorbing heat $Q_2 > 0$ at t_2 and expelling heat Q_1 at t_1, then Q_1 must be strictly positive. This seemingly obvious but non-trivial statement is a consequence of the 2nd law. In particular, it means a cyclic engine cannot *absorb* heat at both reservoirs *and* do work. *Proof:* To see why, suppose $Q_1 \leq 0$ so that the engine absorbs heat $|Q_1|$ at t_1. If $Q_1 = 0$ then we already have a contradiction with Kelvin's postulate, so we may assume $|Q_1| > 0$. Then we could bring the two reservoirs into thermal contact and allow heat of magnitude $|Q_1|$ to be conducted from t_2 to t_1 so that the low temperature reservoir would suffer no net heat gain/loss. After one cycle, the engine would have taken heat $Q_2 - |Q_1|$ from the reservoir at t_2 and converted it completely into work, contradicting the Kelvin postulate. (An alternate argument is to convert part of the work done into heat amounting to $|Q_1|$ and deliver it to the low temperature reservoir, so that the latter suffers no net heat exchange. Again, we arrive at a contradiction with the Kelvin postulate.)

• **Fundamental theorem on heat engine efficiencies:** Now consider two cyclic engines ('unprimed' and 'primed') working between the same temperatures $t_2 > t_1$. Let the amounts of heat absorbed and expelled at t_2 and t_1 and the work done be denoted Q_2, Q_1, W and Q_2', Q_1', W' respectively. Taking $W, W' > 0$ all the heats exchanged are positive by the previous result. Then the second law implies that if the first (unprimed) engine is reversible, then

$$\frac{Q_2}{Q_1} \geq \frac{Q_2'}{Q_1'} \quad \text{or} \quad \eta \geq \eta'. \tag{47}$$

In other words, the efficiency $\eta' = 1 - Q_1'/Q_2'$ of any cyclic engine is bounded above by the efficiency $\eta = 1 - Q_1/Q_2$ of the reversible cyclic engine between the same pair of temperatures. We will prove this shortly.

Corollary: If both engines are reversible, then

$$\frac{Q_2}{Q_1} = \frac{Q_2'}{Q_1'} \quad \text{or} \quad \eta = \eta'. \tag{48}$$

This is a consequence of the fundamental theorem. Indeed, if the primed engine is reversible we have $Q_2'/Q_1' \geq Q_2/Q_1$. Combining with $Q_2/Q_1 \geq Q_2'/Q_1'$ on account of the reversibility of the first engine, the result follows. In other words, all reversible cyclic engines operating between the same pair of temperatures have the same universal efficiency (though they might absorb/expel different amounts of heat). The Carnot engine is a special cyclic reversible engine that uses an ideal gas as its working substance, but its efficiency is universal.

Proof of the fundamental theorem in the special case $Q_2 = Q_2'$: We will run the reversible engine in reverse as a refrigerator. Thus the total work done by the cyclic process defined by combining the engines is

$$W_{\text{tot}} = Q_2' - Q_1' - (Q_2 - Q_1). \tag{49}$$

For simplicity, let us assume that $Q_2 = Q_2'$ so that there is no net heat exchanged with the high temperature reservoir t_2. It follows that the combined engine absorbs heat $Q_1 - Q_1'$ from reservoir t_1 and does an equal amount of work $W_{\text{tot}} = Q_1 - Q_1'$. This would violate the second law unless $Q_1 \leq Q_1'$ so that the combined engine simply converts work into heat. Dividing by $Q_2 = Q_2'$ we get

$$\frac{Q_1}{Q_2} \leq \frac{Q_1'}{Q_2'} \quad \text{or} \quad \frac{Q_2}{Q_1} \geq \frac{Q_2'}{Q_1'} \quad \text{or} \quad \eta \geq \eta'. \tag{50}$$

• The above proof may be generalized to treat the case $Q_2 \neq Q_2'$.

4.3 Absolute thermodynamic temperature

• We concluded above that all reversible cyclic engines working between the same pair of temperatures $t_2 > t_1$ have the same Q_2/Q_1 ratio (or efficiency $\eta = 1 - Q_1/Q_2$), irrespective of the heats absorbed/expelled or work done. Thus for a reversible cycle, Q_2/Q_1 is some universal function of the temperatures

$$\frac{Q_2}{Q_1} = f(t_1, t_2). \tag{51}$$

Note that $f(t_1,t_2) > 0$ since $Q_{1,2} > 0$ assuming the engine does positive work. We will show now that the function $f(t_1,t_2)$ satisfies the reproducing/multiplicative property

$$f(t_0,t_1)f(t_1,t_2) = f(t_0,t_2) \tag{52}$$

where t_0 is any temperature (below t_1). To see this, suppose $C_1(t_0,t_1)$ and $C_2(t_0,t_2)$ are two reversible cycles working between the indicated temperatures. For $i = 1,2$, C_i absorbs heat Q_i at t_i and expels heat Q_0 at t_0. Then we must have

$$\frac{Q_2}{Q_0} = f(t_0,t_2) \quad \text{and} \quad \frac{Q_1}{Q_0} = f(t_0,t_1). \tag{53}$$

Now consider the combined reversible cycle C consisting of one cycle each of C_2 and the reverse of C_1. C absorbs heat Q_2 at t_2 and expels Q_1 at t_1 with no net heat exchanged at t_0. Thus we must have

$$\frac{Q_2}{Q_1} = f(t_1,t_2). \tag{54}$$

Combining, we get the advertised multiplicative property

$$\frac{Q_2}{Q_1} = f(t_1,t_2) = \frac{f(t_0,t_2)}{f(t_0,t_1)}. \tag{55}$$

Since t_0 is an arbitrary temperature, we may treat it as a fixed reference temperature and regard $f(t_0,t_i)$ as a function θ of t_i alone. Thus we write

$$f(t_0,t) = \theta(t) > 0. \tag{56}$$

It follows that $f(t_1,t_2)$ can be expressed in terms of the single function of one variable θ:

$$\frac{Q_2}{Q_1} = f(t_1,t_2) = \frac{\theta(t_2)}{\theta(t_1)}. \tag{57}$$

Note that $\theta(t)$ is not uniquely defined: we may redefine $\theta(t)$ by a positive multiplicative constant without affecting Q_2/Q_1.

• It now makes sense to switch from the empirical temperature t (which is defined using the special properties of a thermometric material, say mercury, used in a thermometer) to the so-called absolute thermodynamic temperature $\theta(t)$. It is conventional to choose the multiplicative constant in θ so as to ensure that the boiling and freezing points of water at atmospheric pressure differ by 100: $\theta(t_b) - \theta(t_f) = 100$. The existence of this absolute thermodynamic temperature is a consequence of the 2nd law. It is independent of the properties of the working substance in the heat engine, as it is defined in terms of the universal efficiency of reversible cycles.

We may now write this universal efficiency as

$$\eta_{\text{rev}} = 1 - \frac{Q_1}{Q_2} = \frac{\theta_2 - \theta_1}{\theta_2}. \tag{58}$$

• We may also express the ratio of work done to heat expelled at the low temperature reservoir:

$$\frac{W}{Q_1} = \frac{Q_2 - Q_1}{Q_1} = \frac{\theta_2 - \theta_1}{\theta_1} = \frac{\theta_2}{\theta_1} - 1. \tag{59}$$

Now running the engine in reverse, the signs of Q_1, Q_2 and W are reversed. W/Q_1 is then the work required to extract a unit amount of heat from the interior of the (reversible) refrigerator. θ_2 is typically room temperature, and is fixed. As expected, the work (supplied through electrical energy) required grows as the temperature of the interior θ_1 falls.

4.4 Equality of absolute thermodynamic and gas temperatures

The absolute thermodynamic temperature θ coincides with the ideal gas thermometer temperature T defined earlier. To see this, we consider a Carnot cycle, i.e. a reversible engine with n moles of an ideal gas as working substance composed of the following four stages. (A-B) isothermal expansion absorbing heat Q_2 from reservoir at gas temperature T_2; (B-C) adiabatic expansion; (C-D) isothermal compression at gas temperature T_1 expelling heat Q_1 and (C-A) adiabatic compression. We will now show that $Q_2/Q_1 = T_2/T_1$.

Proof: The heat Q_2 absorbed during the isothermal expansion is equal the work done W_{AB} since the internal energy of the ideal gas is unchanged (by Joule's experiment, internal energy of an ideal gas depends on temperature an not volume, so $U_A = U_B$). Thus from (22)

$$Q_2 = W_{AB} = nRT_2 \log \frac{V_B}{V_A}. \tag{60}$$

Similarly, the heat Q_1 expelled during the isothermal compression is

$$Q_1 = -W_{CD} = nRT_1 \log \frac{V_C}{V_D} \tag{61}$$

Thus

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \frac{\log(V_B/V_A)}{\log(V_C/V_D)}. \tag{62}$$

It turns out that the ratios of volumes are equal, $V_B/V_A = V_C/V_D$. To see this, recall that in an adiabatic process, $TV^{\gamma-1}$ is constant where $\gamma = c_p/c_V$. Thus

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \quad \text{and} \quad T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}. \tag{63}$$

Dividing one by the other, we get $V_B/V_A = V_C/V_D$. Thus the ratio of heat absorbed to heat expelled is the ratio of gas thermometer temperatures

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}. \tag{64}$$

Previously, we found that $Q_2/Q_1 = \theta_2/\theta_1$ is the ratio of absolute thermodynamic temperatures. Thus T and θ can differ at most by a multiplicative constant. However we must have $T = \theta$ since both temperature scales have been chosen so that the boiling and freezing points of water are 100 degrees apart at atmospheric pressure. We will denote this common absolute temperature scale by T, the Kelvin scale. In particular, the efficiency of a Carnot engine is

$$\eta = \frac{T_2 - T_1}{T_2}. \tag{65}$$

4.5 Clausius' Theorem

Consider a system S that undergoes a cyclic process P in which it comes into contact with reservoirs at temperatures $T_1, \cdots, T_n$ from which it absorbs heat in the amounts $Q_1, \ldots, Q_n$ and performs work $W = \sum_i Q_i$. By the 2nd law, some of the $Q_i's$ must be negative (heat expelled), otherwise, heat would have been completely converted into work without other net effect. Clausius' theorem states that

$$\sum_i \frac{Q_i}{T_i} \leq 0 \tag{66}$$

with equality for a reversible cycle. It is important here that T be the absolute thermodynamic temperature. By taking a limit as $n \to \infty$ we may arrive at a cycle in which the system absorbs heat $\delta Q(T)$ from a distribution of sources with temperatures T. Clausius' theorem then becomes

$$\oint \frac{\delta Q}{T} \leq 0 \tag{67}$$

with equality for a reversible cycle. Note here that T is the temperature of the particular reservoir from which the system S receives heat δQ, it is not necessarily the temperature of S while it receives that heat. After all, in general heat cannot naturally be conducted from a cold to hot body, so the temperature of S must be bounded above by that of the reservoir if it is to receive heat (and must be greater than or equal to T if it is to give up heat). If the heat is received reversibly, then the temperatures of the system and reservoir coincide.

• **Proof:** Clausius' theorem is a consequence of the 2nd law and makes elegant use of Carnot cycles. In addition to the n reservoirs at T_i $(i = 1, \ldots, n)$, it is convenient to introduce a reference reservoir at an arbitrary temperature $T_0 > 0$ and a sequence of Carnot engines C_i operating between temperatures T_0 and T_i. C_i is chosen to absorb heat Q_i^0 at T_0 and expel heat Q_i to the reservoir at T_i. Since S absorbs Q_i at T_i during the process P, there is no net heat exchanged at the n reservoirs in the combined cycle consisting of $P, C_1, \cdots C_n$. In this combined cycle, an amount of heat

$$Q_0 = \sum_i Q_i^0 = T_0 \sum_i \frac{Q_i}{T_i} \tag{68}$$

is absorbed at T_0. Now the work done by S in process P is $W = \sum_i Q_i$ while the work done in C_i is $Q_i^0 - Q_i$. Thus the total work done in the combined cycle is

$$W_{\text{total}} = \sum_i Q_i + \sum_i (Q_i^0 - Q_i) = Q_0. \tag{69}$$

Thus, the only final result of the combined cycle is to convert heat Q_0 from T_0 entirely into work. This would violate the 2nd law unless $Q_0 \leq 0$, i.e.,

$$T_0 \sum_i \frac{Q_i}{T_i} \leq 0. \tag{70}$$

Clausius' inequality follows since T_0 is a fixed positive temperature.

• Now if P is a reversible process, we can run it as well as each of the C_i backwards. In the reversed combined cycle, the signs of all the $Q's$ would be reversed leading to the reversed Clausius inequality

$$\sum_i \frac{Q_i}{T_i} \geq 0. \tag{71}$$

Combining the inequalities for the forward and backward process we conclude that $\sum_i Q_i/T_i = 0$ for a reversible process.

5 Entropy and some consequences of the 2nd law

• The most important consequence of the second law is the existence of a new state function called entropy.

5.1 Absolute temperature as an integrating denominator and the entropy

• Clausius' theorem states that for any reversible cyclic process,

$$\oint_{\text{rev}} \frac{\delta Q}{T} = 0. \tag{72}$$

Thus the line integral of the differential $\delta Q/T$ vanishes around any closed curve lying on the space of equilibrium states. Now suppose P and P' are two reversible processes between the same pair A, B of initial and final equilibrium states, and let us denote by $\bar{P}'$ the reverse of process P'. Then $P \cup \bar{P}'$ is a reversible cyclic process ($A \to B \to A$) to which Clausius' theorem applies

$$0 = \oint_{P \cup \bar{P}'} \frac{\delta Q}{T} \quad \Rightarrow \quad \oint_P \frac{\delta Q}{T} = \oint'_P \frac{\delta Q}{T}. \tag{73}$$

In other words, the line integral of $\delta Q/T$ is independent of the (reversible) path chosen. On the other hand, we have observed that the heat change $\int_P \delta Q$ is generally path-dependent (even for reversible processes). This means that though the infinitesimal heat change δQ is not an exact differential on the space of equilibrium states, dividing it by the 'integrating factor' T turns it into the exact differential $\delta Q/T$.

• **Entropy of equilibrium states:** The second law of thermodynamics has allowed us to define an absolute temperature T which is an integrating denominator for the heat δQ added in an infinitesimal reversible process. The exact differential $\delta Q/T = dS$ defines an extensive state function (entropy) upto an additive constant. Thus, with respect to a 'reference' equilibrium state A, the entropy of any equilibrium state B that can be reached from A by a reversible process is given by

$$S(B) = S(A) + \int_{R(A \to B)} \frac{\delta Q}{T}. \tag{74}$$

$R(A \to B)$ is any reversible path from A to B. By the exactness of $\delta Q/T$, $S(B)$ is independent of the choice of reversible path. A different choice of reference state will add a common constant to the entropy of all equilibrium states. Note that we have not defined the entropy of states that are not in equilibrium, we will address this later.

• The name entropy was coined by Rudolf Clausius (1850s-1860s) (who also used the letter S for it) in the context of thermodynamics. Entropy derives from the Greek word for transformation ($\tau\rho o\pi\eta$). Clausius was studying the changes that occur in a system especially in dissipative processes as well as the transformation of heat into work and vice versa. He apparently wanted a word that sounded like energy (derived from the Greek $\varepsilon\rho\gamma o$) because entropy and energy had some similarities – they are both state functions.

• Thus, loosely we may say that the zeroth, first and second laws of thermodynamics each postulates the existence of a new state function: temperature, internal energy and entropy.

• For an infinitesimal reversible process[12], we may write the heat added to the system as

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[12] For irreversible infinitesimal processes, δQ is well-defined, but we have not defined TdS.

$\delta Q = TdS$. Thus an infinitesimal reversible adiabatic process is the same as an isentropic process. In particular, the heat capacities may be expressed as

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{and} \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p . \tag{75}$$

For infinitesimal processes we have a new form of the 1st law:

$$TdS = dU + pdV \quad \text{or} \quad dU = TdS - pdV. \tag{76}$$

In this form, S and V are the 'natural' variables that the internal energy depends on.

- In particular, if the function $U(S,V)$ is known, then we may compute the temperature and pressure, as functions of S and V:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad p = -\left(\frac{\partial U}{\partial V}\right)_S . \tag{77}$$

However, the internal energy is often not directly measurable and we seldom have an explicit formula for U as a function of S and V (e.g. for an ideal gas it is easier to express U as a function of T: for constant C_V, $U = C_V T$ upto an additive constant). Remarkably, we can eliminate the internal energy from (77). Indeed, taking one more partial derivative and equating mixed partials $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$ we arrive at the 'Maxwell relation'

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{78}$$

which is the integrability condition for exactness of the differential expression for the change in internal energy. We will say more about Maxwell's relations later.

5.2 Exactness of $dS = \delta Q/T$ and the energy equations

Energy equation: The fact that dS is an exact differential implies that its components (regarded as a vector) must have zero curl. Choosing T and V as independent variables we have

$$dS = \frac{1}{T}\frac{\partial U}{\partial T}dT + \left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{p}{T}\right)dV \tag{79}$$

Thus we must have

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{p}{T}\right) \quad \text{or} \quad \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{p}{T^2} + \frac{1}{T}\frac{\partial p}{\partial T}. \tag{80}$$

The mixed partials cancel by Schwarz's theorem leaving the so-called TV-form of the energy equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \tag{81}$$

The energy equation expresses the volume derivative of internal energy at constant T (which is difficult to measure) in terms of the more easily measurable variation of pressure with temperature.

- For a fluid satisfying the ideal gas EOS $pV = nRT$ the energy equation becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = T(nR/V) - p = 0. \tag{82}$$

This is consistent with our earlier assumption (based on Joule's experiment), that the internal energy of an ideal gas is a function of temperature and not volume. It now seems as if we can drop this assumption and instead *derive* the volume-independence of U using the energy equation. However, this is not quite true, because the assumption that U is independent of volume has already crept into the derivation of the energy equation. Strictly speaking, the temperature that appears in the energy equation (or as an integrating factor for δQ) is the absolute thermodynamic temperature. To show the equality of gas and thermodynamic temperatures (see §4.4), we assumed that the internal energy of an ideal gas is a function of temperature alone, so that it does not change during an isothermal compression in a Carnot cycle. Thus, the volume-independence of the internal energy of an ideal gas and the functional form of $U(T)$ (e.g. that C_V is a constant (independent of temperature) for a calorically perfect gas) are independent postulates on the nature of an ideal gas, that do not follow from the application of the first and second laws of thermodynamics to the EOS $pV = nRT$.

- Later, we will apply the energy equation to understand the slope of phase boundaries in a pT diagram for first order phase transitions (Clapeyron equation).

- Two other forms of the energy equation may be obtained as above by choosing (T, p) and (V, p) as independent variables.

5.3 Entropy of an ideal gas

The second law guarantees that T is an integrating denominator for the infinitesimal heat δQ absorbed in a reversible process. Let us demonstrate this for an ideal gas and thereby identify the state function (entropy) S such that $\delta Q/T = dS$. For n moles of an ideal gas $p = nRT/V$ and $dU = C_V dT$ with C_V independent of V (this is called the caloric condition, $U(T,V) = U(T)$ is independent of volume). So the first law $\delta Q = dU + pdV$ implies

$$dS = \frac{\delta Q}{T} = C_V \frac{dT}{T} + nR\frac{dV}{V}. \tag{83}$$

To carry out explicit integration, we assume that C_V is independent of temperature, which is usually a good approximation (such a gas is said to be calorically perfect). It follows that

$$dS = d\left(\log T^{C_V} + \log V^{nR}\right) = d \log\left(T^{C_V} V^{nR}\right). \tag{84}$$

Thus, the entropy of an ideal gas is

$$S(T,V)_{\text{ideal gas}} = C_V \log T + nR \log V + S_0 = \log\left(T^{C_V} V^{nR}\right) + S_0 \tag{85}$$

where S_0 is an additive constant of integration. The dimensional constants in S_0 must ensure that the argument of the logarithm is dimensionless and that S is extensive (the term $nR \log V$ entails logarithmic violation of extensivity under $n \to \lambda n, V \to \lambda V$). It turns out that the third law of thermodynamics constrains the value of S_0.

- For a monoatomic ideal gas $C_V = (3/2)nR$ from kinetic theroy, so

$$S(T,V)_{\text{monoatomic}} = nR\log(T^{3/2}V) + S_0. \tag{86}$$

- Notice that if an ideal monatomic gas undergoes an isentropic process, then $T^{3/2}V$ must be constant. More generally, using $nR = C_P - C_V$ we find that $T^{C_V}V^{C_P - C_V}$ must be a constant. Taking the C_V^{th} root this means $TV^{\gamma-1}$ must be constant.

- Entropy may also be expressed in terms of p and T or p and V by using the EOS $V = nRT/p$ and the relation $C_p = C_V + nR$:

$$S(p,T) = C_p\log T - nR\log(p/nR) + S_0 \quad \text{and} \quad S(p,V) = C_V\log(p/nR) + C_p\log V + S_0. \tag{87}$$

- **Entropy rise in free Joule expansion of an ideal gas.** In thermally insulated free Joule expansion of an ideal gas from a container of volume V to one of volume $V' > V$, no work is done and no heat is added to the gas. Though its final pressure is less than the initial pressure, its final temperature and internal energy are the same as their initial values. Though the process is irreversible, the initial and final states are equilibrium states, so we may evaluate their entropies. The constant S_0 cancels out and we obtain a simple formula for entropy rise in free expansion of an ideal gas:

$$S(T,V') - S(T,V) = nR\log(V'/V). \tag{88}$$

Notice that this increase is independent of the temperature T. This entropy rise cannot be calculated by integrating $\delta Q/T$ since it is not a reversible process. We note that in this example, the entropy of a thermally insulated system has increased. We will see that this is more generally true.

5.4 Properties of entropy and examples

- **Clausius inequality:** Recall that we defined the entropy of an equilibrium state B with reference to an equilibrium state A as the line integral of the exact differential $\delta Q/T$ along any reversible path R from A to B. Suppose in addition to the reversible path $R(A \to B)$, the equilibrium states A and B are also connected by a (not necessarily reversible) path P. Then the closed path $P \cup \bar{R}$ represents a cyclic process to which we may apply Clausius' theorem[13]

$$\oint_{P\cup\bar{R}} \frac{\delta Q}{T} \leq 0 \quad \Rightarrow \quad \int_P \frac{\delta Q}{T} \leq \int_R \frac{\delta Q}{T} = S(B) - S(A). \tag{89}$$

Thus the line integral of $\delta Q/T$ along any path P joining equilibrium states A and B is bounded above by the entropy difference. Equality holds if (and only if) P is reversible.

- Since S is a state function, the entropy change in any process P between equilibrium states A and B is always given by $S(B) - S(A)$. It may also be expressed as the line integral $\int_P \delta Q/T$ only if P is reversible.

- **Law of non-decreasing entropy for insulated systems:** For a thermally insulated system, δQ is identically zero during any process. Thus we must have $S(B) \geq S(A)$: the final entropy

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[13] Note that in general we may not consider $R \cup \bar{P}$ since P may not be reversible!

of a thermally insulated system must be at least as large as its initial value. This is often loosely stated as the law of 'increase' of entropy of an isolated system. We note that this is not an independent law but a consequence of the second law of thermodynamics. On the other hand, the entropy of systems that can exchange heat with their surroundings could increase or decrease. For example, we might reduce the entropy of a body at temperature T_h by letting heat ΔQ be conducted from it to another body at a lower temperature $T_l < T_h$.

(1) Heat conduction: Suppose an isolated system consists of two large bodies at temperatures T_h and T_l with $T_h > T_l$. A small amount of heat $\Delta Q > 0$ is conducted from the hotter one to the colder one. From Clausius' theorem, the changes in entropy satisfy the following inequalities

$$(\Delta S)_h \geq \int \frac{\delta Q}{T} \approx -\frac{\Delta Q}{T_h} < 0 \quad \text{and} \quad (\Delta S)_l \geq \int \frac{\delta Q}{T} \approx \frac{\Delta Q}{T_l} > 0. \tag{90}$$

Here we have assumed that the small heat transferred does not significantly change the temperatures of either of the big bodies. Thus, the change in entropy of the system is given by

$$\Delta S = (\Delta S)_h + (\Delta S)_l \geq \Delta Q \left(\frac{1}{T_l} - \frac{1}{T_h} \right) > 0 \quad \text{as} \quad T_h > T_l. \tag{91}$$

We see that entropy is produced in heat conduction. The entropy of the colder body has increased. The entropy of the hotter body may decrease, though our inequality allows it too to increase.

(2) Heating through friction: The initial energy in a swing is dissipated as it executes damped oscillations, heating up the suspension through friction. In this process, mechanical work ΔW done on the swing is completely converted into heat $\Delta Q = \Delta W$ and the temperature of the suspension is raised from T_i to $T_f > T_i$. The change in entropy of the suspension must satisfy

$$\Delta S \geq \int_i^f \frac{\delta Q}{T} > \int_i^f \frac{\delta Q}{T_f} = \frac{1}{T_f} \int_i^f \delta Q = \frac{\Delta Q}{T_f} > 0. \tag{92}$$

So heating through friction is an entropy raising process.

• **Remark:** Suppose equilibrium states A and B of a thermally insulated system are connected by a reversible process (which must necessarily be adiabatic $\delta Q = 0$). Then $S(B) = S(A)$. On the other hand, if they are connected by an irreversible process (again with no heat exchange) then $S(B) > S(A)$. Evidently, the same pair of equilibrium states of a thermally insulated system cannot be connected by both a reversible and irreversible process with no heat change. E.g. Free Joule expansion of an ideal gas from equilibrium state (T, V_1) to equilibrium state (T, V_2) with no heat exchange is an irreversible process between two states of an ideal gas that differ in volume $V_2 > V_1$ but have the same temperature. It involves an entropy increase of $nR \log(V_2/V_1)$. Can we find a reversible way of adiabatically expanding the same ideal gas between the same equilibrium states? This is not possible. An adiabat $pV^\gamma = \text{const}$ cannot intersect an isotherm at more than one point, so it cannot connect two distinct states with the same temperature. Note that there are reversible ways of expanding such a gas isothermally, but they involve work and hence heat exchange and therefore cannot be adiabatic. E.g. let the gas expand while compressing a spring connecting the piston to a fixed wall, the process can be reversed by expanding the spring while compressing the gas.

• **Entropy of composite systems** Suppose a system s is composed of two homogeneous parts s_1 and s_2, each in equilibrium with its own entropy. Then it is often (though not always) the case that we can define the entropy of s to be the sum $S = S_1 + S_2$. For instance, suppose the internal energies are additive, $U = U_1 + U_2$ and the work done by s is the sum of the works done $\Delta W = \Delta W_1 + \Delta W_2$. Then the heat added to s would also be additive $\delta Q = \delta Q_1 + \delta Q_2$. If T is the *temperature of the reservoir from which heat δQ is received*, then the entropy $S(B)$ (defined as $\int_A^B \delta Q/T$) of the state B of the combined system (relative to state A) satisfies the

$$\textbf{additive property:} \quad S(B) = \int_A^B \frac{\delta Q}{T} = \int_{A_1}^{B_1} \frac{\delta Q_1}{T} + \int_{A_2}^{B_2} \frac{\delta Q_2}{T} = S_1(B_1) + S_2(B_2). \tag{93}$$

Here A_1 and B_1 are the states of subsystem s_1 when the total system is in states A and B, the same applies to A_2 and B_2. The additivity of internal energies may fail for instance if the energy of the interface (common boundary surface) of the two systems is comparable to the energy of either s_1 or s_2 in isolation. It could also fail if there are long-range forces in operation between the constituents of s_1 and those of s_2 so that the interaction energy cannot be ignored compared to U_1 and U_2. For neutral gases there are no long-range forces since the electromagnetic forces are screened due to the neutrality of matter on macroscopic scales (despite the long-range nature of Coulomb forces between individual charges). On the other hand, this assumption can fail in systems of gravitating masses (e.g. a galaxy) since gravity is always attractive and there is no screening.

• When the above additivity property holds, we may use it to define the entropy of non-homogeneous systems that are not in equilibrium. We subdivide the system s into homogeneous parts $s = \cup_i s_i$ each of which is in equilibrium (say at temperature T_i and pressure p_i) and define the entropy of s to be the sum of entropies. In this manner we may try to define the entropy of a flowing fluid, which is evidently not in equilibrium.

• **Infinitesimal version of Clausius inequality:** Specializing the Eq. (89) to an infinitesimal process P we may write $S(B) - S(A) \approx dS$ and $\int_P \delta Q/T \approx \delta Q/T$. So for an infinitesimal process in which a system absorbs heat δQ from a reservoir at temperature T,

$$TdS \geq \delta Q. \tag{94}$$

If the process is irreversible, then $TdS > \delta Q$. Equality holds for a reversible process. We had initially assumed that the process P begins and ends at equilibrium states. This assumption may be relaxed in situations where we can define the entropy for non-equilibrium states.

• **Entropy and loss:** The entropy increase in an irreversible process of an isolated system may be interpreted as a loss in the ability to do useful work. To see this, we consider two processes: (a) free Joule expansion of n moles of a thermally insulated ideal gas from (T, V_1) to (T, V_2) with $V_2 > V_1$ and (b) slow (reversible) isothermal expansion of the same ideal gas between the same initial and final states while compressing a spring. In free expansion, no work is done, but the entropy of the gas rises by $\Delta S = nR\log(V_2/V_1)$. In the slow isothermal expansion, there is no change in U as T does not change (the gas is kept in contact with a reservoir at temperature T from which it receives heat in order to expand), so the work done $\Delta W = nRT\log(V_2/V_1)$ must equal the heat ΔQ absorbed. Thus the increase in entropy of the gas in this isothermal expansion is $\Delta S = \int \delta Q/T = nR\log(V_2/V_1)$. We see that in both free and reversible expansion, there is an identical increase in the entropy of the gas. This had to be the case as both processes have the same initial and final states, and entropy is a state function. How do the processes differ?

• (a) Free expansion is irreversible, the entropy of the system as a whole (gas + insulated container) increases by ΔS. In (b), the entropy of the surroundings of the gas (the spring and reservoir) decrease, as they give up heat ΔQ at a fixed temperature T. In fact, since the gas + surroundings form an isolated system undergoing a reversible process, the total entropy is unchanged. Indeed, the process can be reversed by isothermally compressing the gas slowly by letting the spring expand. Thus we may interpret the increase in entropy in free expansion as a loss in useful work that the gas could do. In (b) there is no increase in entropy for the system as a whole, and 'useful' work done by the gas is stored in the spring.

• **Increasing entropy and stability:** An isolated system (thermally and mechanically isolated) must have a fixed internal energy (as $\delta Q = \delta W = 0$). We showed above that its entropy is a non-decreasing function of time. So if an isolated system is in a state of maximal entropy consistent with its energy then it can undergo only those transformations to other states with the same energy and maximal value of entropy. In practice, all macroscopic processes are irreversible (running of engines etc.). In other words, in 'real' isolated physical systems, entropy is strictly increasing with time. So even if there is another state with the same maximum entropy, a real system cannot access it. Thus, a maximum entropy state of an isolated system is a stable state: once in such a state, the system remains in it if isolated.

5.5 Boltzmann's statistical interpretation of entropy

• Thermodynamics provides a macroscopic description of systems independent of their microscopic structure (atomic/molecular structure of matter). Statistical mechanics (SM) is a framework based on the dynamics of microscopic constituents. Boltzmann gave a statistical interpretation for entropy and the law of its increase for isolated systems.

• SM begins with the microscopic dynamical state of a system (say a gas), specified by positions and momenta of a large number of molecules. On the other hand, the thermodynamic state of the same system is defined by the values of a few macroscopic variables such as p, V, T (or p, V, U). There are typically very many microstates that correspond to a given macrostate, since for example, different molecular motions can result in the same total energy and pressure in a fixed volume. Suppose π is the fraction of microscopic states corresponding to a given macrostate, it is interpreted as the statistical probability of the given macrostate, assuming that all microstates with a common energy are equally probable (this is one of the postulates of statistical mechanics). Boltzmann related the probability π of a macrostate to its entropy: $S = k_B \log \pi$ where $k_B = R/N_A$ is Boltzmann's constant. Based on this relation, we see that the entropy of an isolated system is non-decreasing provided transformations of the system to states of lower probability are forbidden.

• We can be a bit more precise. The microscopic state space is the phase space of the gas. If the gas has N molecules and is in a three-dimensional room, then the phase space is $M = \mathbb{R}^{3N} \times (\text{room})^{3N}$. There is a many-to-one projection map Π from this mechanical state space to the thermodynamic state space. If we take p, V, U as coordinates on the thermodynamic state space, then the inverse image of a macrostate $\Pi^{-1}(p, V, U)$ is the set of all microstates that correspond to those values of macroscopic variables.

• There is a natural Liouville volume element (measure) on this phase space,

$$d\mu = \Pi_{i=1}^{N} dp_i^x dq^{xi} dp_i^y dq^{yi} dp_i^z dq^{zi} \tag{95}$$

that allows us to assign volumes to subsets Ω of the phase space

$$\mathrm{Vol}(\Omega) = \int_\Omega d\mu. \tag{96}$$

Though the volume of the whole phase space M is typically infinite, the volume of the set of macrostates of a fixed energy U is finite since the positions are confined inside the room and the momenta cannot become too large in magnitude. Then Boltzmann's statistical probability π is defined as the ratio

$$\pi(p,V,U) = \frac{\mathrm{Vol}(\Pi^{-1}(p,V,U))}{\mathrm{Vol}(M_U)}. \tag{97}$$

Notice that π (and consequently the statistical entropy) has only been defined for macrostates. Unlike the energy of a microstate, we do not define the entropy of a microstate.

• To make Boltzmann's relation plausible, let us show that if there is a functional relation $S = f(\pi)$ between entropy and probability, then assuming f is differentiable, it must be of the logarithmic form given by Boltzmann. Following Fermi, consider a thermodynamic system s in a particular state with entropy $S = f(\pi)$ where π is the probability of the state. Suppose s is composed of two separate parts s_1 and s_2 with entropies $S_1 = f(\pi_1)$ and $S_2 = f(\pi_2)$ where $\pi_{1,2}$ are the probabilities of the corresponding states. Then under the conditions for extensivity, $S = S_1 + S_2$ while $\pi = \pi_1\pi_2$ so that $f(\pi_1\pi_2) = f(\pi_1) + f(\pi_2)$. This functional relation must hold for any probabilities $\pi_{1,2} = x, y$, i.e. $f(xy) = f(x) + f(y)$ for all $0 \leq x, y \leq 1$. To determine f we assume it is differentiable and suppose that $y = y_0 + \epsilon$ for small ϵ. Then Taylor expanding,

$$f(x(y_0+\epsilon)) = f(x) + f(y_0+\epsilon) \quad \Rightarrow \quad f(xy_0) + \epsilon x f'(xy_0) = f(x) + f(y_0) + \epsilon f'(y_0). \tag{98}$$

By the functional relation $f(xy_0) = f(x) + f(y_0)$ so we have

$$x f'(y_0 x) = f'(y_0) \quad \text{or} \quad y_0 x f'(y_0 x) = y_0 f'(y_0) = \text{const.} = k. \tag{99}$$

Now denoting $y_0 x$ as χ and integrating we have

$$\chi f'(\chi) = k \quad \text{or} \quad f(\chi) = k \log \chi + \text{const.} \tag{100}$$

As desired, we find that $S = f(\pi) = k \log \pi$ upto an undetermined additive constant. The constant k can be fixed by requiring that this formula agrees with the thermodynamic one already derived for an ideal gas, one finds that $k = k_B$. The actual task of calculating Boltzmann's entropy of an ideal gas starting from the mechanics of free particles is left to a course on statistical mechanics.

5.6 Thermal expansion, compressibility and tension coefficients for an ideal gas

• Some measurable coefficients we have defined for a gas/fluid are (here $H = U + pV$ is enthalpy):

$$\begin{aligned}
&\text{heat capacity at constant volume} && C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and pressure} \quad C_p = \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \\
&\text{compressibilities: isothermal} && \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \text{and isentropic} \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \\
&\text{coefficient of thermal expansion} && \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \text{and tension} \quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V .
\end{aligned} \tag{101}$$

• For an ideal gas we may determine the coefficients of thermal expansion α and tension β as well as the isothermal compressibility κ_T directly from the EOS $pV = nRT$:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{pV} = \frac{1}{T}, \quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{pV} = \frac{1}{T} \quad \text{and} \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{nRT}{Vp^2} = \frac{1}{p}. \tag{102}$$

We see that an ideal gas is more compressible at low pressures. At very high pressures, gases liquify and may often be treated as incompressible. The coefficients of thermal expansion and tension are both equal to $1/T$. At high temperatures, there is hardly any fractional change in volume or pressure of an ideal gas when the temperature is slightly increased. Exercise: Find a formula for the adiabatic compressibility κ_S of an ideal gas.

6 Thermodynamic potentials

A potential (in mechanics, fluid mechanics and electrostatics) is a function whose derivative gives the force, velocity or electric field. Thermodynamic potentials such as the internal energy, Helmholtz free energy, Enthalpy and Gibbs free energy play a similar role. They differ in the independent variables that they depend on.

6.1 Legendre transform from internal to free energies and enthalpy

Combining the first and second laws of thermodynamics for infinitesimal reversible transformations of a gas, the increase in internal energy is $dU = TdS - pdV$. Thus the internal energy, which is our first example of a thermodynamic potential, is naturally a function of entropy and volume[14]. The other two conjugate variables are given by its partial derivatives $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $p = -\left(\frac{\partial U}{\partial V}\right)_S$. The change in internal energy is particularly simple for adiabatic ($dS = 0$) or isochoric ($dV = 0$) processes. However, many processes take place at constant temperature (room temperature) or at constant pressure (atmospheric pressure). Thus, it would be convenient to have thermodynamic potentials with other independent variables.

• The Legendre transform (LT), familiar from Lagrangian and Hamiltonian mechanics[15] allows us to change independent variables[16]. For instance, to switch from (S,V) to (T,V) as independent variables, we define the Helmholtz free energy $F = U - TS$. It follows that $dF = dU - TdS - SdT = -pdV - SdT$. Thus F is naturally a function of (V,T) with the other two given by[17]

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_T. \tag{103}$$

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[14] Of course, we may view U as a function of p and V as we did in deriving the TdS equations. What we mean here are the independent differentials that appear in dU directly as a consequence of the 1st and 2nd laws.

[15] The Lagrangian is a function of coordinates q and velocities $\dot{q}$, while the Hamiltonian is a function of coordinates and momenta p. $H = p\dot{q} - L$ with $p = \frac{\partial L}{\partial \dot{q}}$ or $H(q,p) = \text{ext}_{\dot{q}}(p\dot{q} - L(q,\dot{q}))$. Calculate the Legendre transform of $L = \frac{1}{2}m\dot{q}^2 + V(q)$. In particular, show that the Legendre transform of a quadratic function velocities is again a quadratic function of momenta.

[16] Changing independent variables here does not simply mean expressing the same scalar function, say $f(p,T)$ in terms of V and T using the equation of state. In particular, at a given equilibrium state the numerical values of the state function U and its Legendre transform F are in general unequal.

[17] In statistical mechanics one derives a formula for the Helmholtz free energy by averaging over microscopic motions. The thermodynamic relation $p = -\left(\frac{\partial F}{\partial V}\right)_T$ then gives a relation among p, V and T and thus gives a way of deriving the equation of state from microscopic considerations.

We will see that the free energy may be interpreted in terms of the work that a system can do at constant temperature. To obtain $F = U(S,V) - TS$ as a function of T, V we must express S in terms of T and V using the relation $T = \frac{\partial U}{\partial S}$. Since this is just the condition for $U - TS$ to be extremal, we may write

$$F(T,V) = \text{ext}_S \left(U(S,V) - TS \right) \tag{104}$$

• Enthalpy is the thermodynamic potential that depends on (S,p). It is defined via the relation $H = U + pV$ so that $dH = dU + pdV + Vdp = TdS + Vdp$ and

$$T = \left(\frac{\partial H}{\partial S} \right)_p \quad \text{and} \quad V = \left(\frac{\partial H}{\partial p} \right)_S . \tag{105}$$

It is a Legendre transform of the internal energy

$$H(S,p) = \text{ext}_V \left(U(S,V) + pV \right) \tag{106}$$

• Gibbs free energy is the last thermodynamic potential, with independent variables (T,p). It may be obtained from $U(S,V)$ by a succession of two Legendre transforms

$$G = U - TS + pV = F + pV = H - TS \tag{107}$$

Evidently $dG = dF + pdV + Vdp = -SdT + Vdp$ so that

$$S = -\left(\frac{\partial G}{\partial T} \right)_p \quad \text{and} \quad V = \left(\frac{\partial G}{\partial p} \right)_T . \tag{108}$$

Gibbs free energy may be obtained as a Legendre transform of U, F or H:

$$G(T,p) = \text{ext}_{V,S} \left(U(S,V) - TS + pV \right) = \text{ext}_V \left(F(T,V) + pV \right) = \text{ext}_S \left(H(S,p) - TS \right) \tag{109}$$

• In summary, we have defined three new state functions (thermodynamic potentials) via Legendre transforms from the internal energy:

$$F = U - TS, \quad H = U + pV \quad \text{and} \quad G = U - TS + pV. \tag{110}$$

Note that we cannot obtain thermodynamic potentials with (p,V) or (T,S) as natural independent variables via Legendre transformation from $U(S,V)$. This is because the LT only allows us to replace a variable by its conjugate, i.e., $p \leftrightarrow V$ or $T \leftrightarrow S$. Note also that U and H are defined up to additive constants. On the other hand, the Helmholtz and Gibbs free energies are defined up to a linear function of temperature, since entropy has been defined only up to an additive constant. We will return to this issue when we discuss the third law of thermodynamics.

• The first and second laws of thermodynamics for infinitesimal reversible processes may be expressed in terms of any one of the four thermodynamic potentials:

$$\begin{aligned} dU(S,V,N) &= TdS - pdV + \mu dN, & dF(T,V,N) &= -SdT - pdV + \mu dN, \\ dH(S,p,N) &= TdS + Vdp + \mu dN \quad \text{and} & dG(T,p,N) &= -SdT + Vdp + \mu dN. \end{aligned} \tag{111}$$

Ideal gas: Let is consider a calorically perfect ideal gas. Its internal energy is given by $U = C_V T + U_0$. To express U in terms of the natural variables S and V we recall the formula for entropy

$$S = S_0 + C_V \log T + nR \log V \tag{112}$$

and use it to express T as a function of S an V:

$$T = \exp[(S - S_0 - nR \log V)/C_V]. \tag{113}$$

Thus we obtain

$$U(S, V) = C_V \exp[(S - S_0 - nR \log V)/C_V]. \tag{114}$$

We may now obtain the Helmholtz free energy via a Legendre transform. Show that

$$F_{\text{perfect gas}}(T, V) = U - TS = C_V T - T(C_V \log T + nR \log V) + U_0 - S_0 T. \tag{115}$$

In particular, the Legendre transform of an exponential function of S is T times a logarithm of T. It is easily verified that $p = -\left(\frac{\partial F}{\partial V}\right)_T$ leads to the ideal gas equation of state while its entropy is recovered by computing $-\left(\frac{\partial F}{\partial T}\right)_V$. Similarly, the Gibbs free energy $G(T, p)$ of perfect gas is

$$\begin{aligned} G &= U - TS + pV = C_V T + U_0 - T(C_V \log T + nR \log V + S_0) + nRT \\ &= C_p T + U_0 - T(C_p \log T - nR \log(p/nR) + S_0). \end{aligned} \tag{116}$$

Notice that both free energies are undetermined upto a linear function of temperature due to additive constants in S and U.

- Why are F and G called free energies? Let us find out.

6.2 Interpretation of Helmholtz free energy

- For a mechanical system, the law of conservation of energy says that the work done is equal to the decrease in internal energy. For a thermodynamic system, the work done $\Delta W = -\Delta U + \Delta Q$ may be less/more than the decrease in internal energy depending on whether heat is absorbed or given up by the system. We seek a replacement for internal energy that will allow us to give a bound on the work that a thermodynamic system can do. The second law allows us to use the Helmholtz free energy to get an upper bound on the work that a system in contact with a reservoir at constant temperature can do.

- Consider a transformation of a system from state A to B while in contact with a heat reservoir at temperature T_{res}. By the second law

$$\int_A^B \frac{\delta Q}{T_{\text{res}}} \leq S(B) - S(A). \tag{117}$$

Since the temperature T_{res} of the reservoir is fixed, we have an upper bound on the heat received by the system

$$\Delta Q = \int_A^B \delta Q \leq T_{\text{res}}(S(B) - S(A)). \tag{118}$$

Note that the temperature of the system need not equal $T_{\rm res}$, and the process need not be isothermal. By the first law $\Delta W = \Delta Q - \Delta U$, so we get an upper bound on the work done

$$\Delta W \leq -U(B) + U(A) + T_{\rm res}(S(B) - S(A)). \tag{119}$$

This about as much as we can say in general. However, it is tempting to write the RHS in terms of the Helmholtz free energy of the system. If we *assume* that the initial and final absolute temperatures (T_A, T_B) of the system are equal to $T_{\rm res}$, then the RHS is just the difference in Helmholtz free energies

$$\Delta W \leq F(A) - F(B) = -\Delta F. \tag{120}$$

Thus the maximum work that a system can do while in contact with a reservoir at constant temperature is the decrease in free energy. In this sense, F is the energy freely available to do work, hence the name. If the process is reversible, then the inequality is saturated and $F(A) - F(B)$ is the actual amount of work done. Note that to be reversible, the system would have to have the same temperature T as the reservoir throughout. If the process is irreversible, we have a strict upper bound on the work done.

6.3 Gibbs' criteria for thermodynamic equilibrium

• We observed that the entropy of an isolated system is a non-decreasing function of time. What is more the change in entropy of an isolated system $\Delta S > 0$ if the process is irreversible, with equality for reversible processes. All macroscopic natural processes are found to be irreversible and are observed to proceed towards increasing entropy. What is more, any state of an isolated system with maximal entropy consistent with its conserved internal energy is particularly stable since there is no thermodynamic process that can further increase its entropy. The foregoing considerations lead us to Gibbs' criterion for thermodynamic equilibrium: an isolated system with fixed energy and number of particles is in equilibrium if its entropy is maximal. Gibbs also gave another criterion for thermodynamic equilibrium that traces its origins to mechanical equilibrium. We are familiar with the fact that a particle moving in a potential is in equilibrium if it is at a minimum of the potential. Gibbs' second criterion states that if the entropy of an isolated system is held fixed, then it is in equilibrium when its energy is minimized.

• Neither entropy nor internal energy is an easily measured property of thermodynamic systems. Moreover, U is naturally a function of S and V, but entropy is not easily controlled in the lab. Properties that are more easily controlled are temperature, pressure and volume. This is where the other thermodynamic potentials come in handy. Recall that the natural variables of Helmholtz free energy, and Gibbs free energy are (T, V) and (p, T) respectively. Thus it is useful to reformulate the condition for thermodynamic equilibrium in terms of F and G.

• Now in an infinitesimal process, $dS \geq \delta Q/T$ (irrespective of whether the system is isolated or not, with equality if it is reversible. Here T is the temperature of the reservoir). So by the first law, $TdS \geq dU + pdV$. If the system is mechanically isolated, then no work is done and so $TdS \geq dU$ or $dU - TdS \leq 0$. But this is just the condition $dF(T, V) \leq 0$ for a system at constant temperature (equal to that of the reservoir). Thus we see that the Helmholtz free energy is a decreasing (precisely non-increasing) function of time for a mechanically isolated system at constant temperature. The same applies to finite transformations of a mechanically isolated system at constant temperature: from the previous section, $\Delta W = 0 \leq F(A) - F(B)$. As a consequence, a system at constant temperature (equal to that of its environment) undergoing isochore transformations (mechanically isolated, e.g. if p is constant and $dV = 0$) is in equilibrium when its free energy is a minimum. Recall that a mechanical system is in equilibrium when the potential is a minimum. F being a thermodynamic analogue, is sometimes called the thermodynamic potential at constant volume.

• We may also view the principle of minimization of Helmholtz free energy as a constrained minimization problem. Recall Gibbs' second criterion for equilibrium: minimize internal energy holding entropy fixed. This is equivalent to minimizing $U - TS$ where T is a Lagrange multiplier enforcing the constraint on entropy.

• Similarly, let us consider a system at constant pressure and temperature. This applies to chemical reactions happening at room temperature and at atmospheric pressure. Now $G = U - TS + pV$, so at constant T, p,

$$dG = dU - TdS - SdT + pdV + Vdp = dU - TdS + pdV \leq 0 \tag{121}$$

as $TdS \geq \delta Q$. Thus, Gibbs' free energy decreases for infinitesimal transformations of a system at constant T and p. [Note: We cannot use $dG = -SdT + Vdp$ (which would suggest $dG = 0$) here, since this formula is only valid for reversible transformations.]

• We could arrive at the same result by considering finite transformations. Suppose our system undergoes a thermodynamic transformation $A \to B$ at constant temperature T and pressure p. The work done is simply $\Delta W = \int_A^B pdV = p(V(B) - V(A))$, which must be bounded above by the drop in free energy: $\Delta W \leq F(A) - F(B)$. So

$$F(B) + pV(B) \leq F(A) + pV(A) \quad \text{or} \quad G(B) \leq G(A). \tag{122}$$

In particular, a system at constant T and p is in equilibrium if G is a minimum.

6.4 Maxwell relations

The first law for infinitesimal reversible processes $dU = TdS - pdV$ implies $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -p$. The equality of second mixed partials of U leads to the first Maxwell identity:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{123}$$

The differential of Helmholtz free energy $dF = -SdT - pdV$ implies $\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $\left(\frac{\partial F}{\partial V}\right)_T = -p$. Thus we get a second Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{124}$$

Enthalpy is naturally a function of S and p with $dH = TdS + Vdp$. Thus $\left(\frac{\partial H}{\partial S}\right)_p = T$ and $\left(\frac{\partial H}{\partial p}\right)_S = V$ which implies the Maxwell relation

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p . \tag{125}$$

Finally, for the Gibbs free energy, $dG = Vdp - SdT$, so $\left(\frac{\partial G}{\partial p}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_p = -S$ and

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T. \tag{126}$$

- We may obtain **additional Maxwell relations** by allowing the number of particles to vary by including a chemical potential term in the first law $dU = TdS - pdV + \mu dN$.
- The Maxwell relations provide surprising connections among thermodynamic coefficients. We will see an application in the context of the third law of thermodynamics.

6.5 Extensivity, Euler equation and Gibbs-Duhem relation

- We have mentioned before that if surface effects can be ignored, then the internal energy, work done, heat absorbed and entropy may be taken to be extensive. What this means is that if the volume (and consequently the number of particles) is doubled, then U, S etc are also doubled. More precisely, extensivity of internal energy is the condition

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad \text{for any real} \quad \lambda > 0. \tag{127}$$

Such a function is called homogeneous of degree one.

- **Euler's theorem on homogeneous functions:** More generally, $f(x, y, \cdots)$ is a homogeneous function of degree n, if for all $x, y, \cdots$ for which f is finite, it satisfies

$$f(\lambda x, \lambda y, \cdots) = \lambda^n f(x, y, \cdots) \quad \forall \quad \lambda. \tag{128}$$

Euler's theorem on homogeneous functions gives an alternate characterization of homogeneous functions, assuming differentiability. For definiteness, consider two independent variables. Examples of homogeneous functions include $f(x, y) = 2x^2 - 7y^2 + xy$ (degree two) and $g(x, y) = 4x - 7y$ or $g = x^2/y$ (degree one) or $h(x) = \log(x) - \log(y) + \exp(x/y)$ (degree zero). Now define the scaling or dilatation/dilation operator $D = x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y}$. Notice that $Df = 2f$ and $Dg = g$. Euler's theorem states that a homogeneous function is an eigenfunction of the scaling operator with eigenvalue equal to the degree of homogeneity.

$$Df = \left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y}\right) f(x, y) = nf(x, y). \tag{129}$$

Let us sketch a proof for one variable, essentially the same applies to any number of variables. So suppose $f(\lambda x) = \lambda^n f(x)$ for all λ, x. Differentiating in λ and putting $\lambda = 1$ we get $xf'(x) = nf(x)$. What this means is that we consider an infinitesimal scaling by taking $\lambda = 1+\epsilon$ where ϵ is small. Then we must have

$$f(x + \epsilon x) = (1 + \epsilon)^n f(x) \approx (1 + n\epsilon) f(x) \tag{130}$$

Rearranging,

$$f(x + \epsilon x) - f(x) = n\epsilon f(x) \quad \text{or} \quad x\left(\frac{f(x + \epsilon x) - f(x)}{\epsilon x}\right) = nf(x). \tag{131}$$

Taking $\epsilon \to 0$ holding $x \neq 0$ fixed, the LHS tends to $xf'(x)$. Thus, we get $Df(x) = nf(x)$ as advertised. Alternatively we may use the Taylor expansion on the LHS

$$f(x) + \epsilon x f'(x) + \mathcal{O}(\epsilon^2) = f(x) + n\epsilon f(x) + \mathcal{O}(\epsilon^2) \tag{132}$$

to conclude that $xf' = nf$.

• Now, extensivity implies that the internal energy is homogeneous of degree one, so it must satisfy

$$\left(S\frac{\partial}{\partial S} + V\frac{\partial}{\partial V} + N\frac{\partial}{\partial N} \right) U = U. \tag{133}$$

The above three partial derivatives of U may be obtained from the first law:

$$dU = TdS - pdV + \mu dN \quad \Rightarrow \quad \frac{\partial U}{\partial S} = T, \ \frac{\partial U}{\partial V} = -p, \ \frac{\partial U}{\partial N} = \mu. \tag{134}$$

Thus

$$U = ST - pV + \mu N. \tag{135}$$

Now recall that we had defined the Helmholtz free energy, enthalpy and Gibbs free energy via successive Legendre transforms of the internal energy:

$$F = U - TS, \quad H = U + pV, \quad G = F + pV = U - TS + pV. \tag{136}$$

As a consequence, when energy is extensive

$$F = \mu N - pV, \quad H = TS - \mu N \quad \text{and} \quad G = \mu N \tag{137}$$

In other words, the chemical potential is simply the Gibbs free energy per particle.

• The above formulae for thermodynamic potentials (in particular $G = \mu N$) leads to the **Gibbs-Duhem relations**. Indeed, equating $dG = \mu dN + Vdp - SdT$ with $dG = \mu dN + Nd\mu$ we get the Gibbs Duhem relation in the **energy representation**

$$d\mu = \frac{V}{N}dp - \frac{S}{N}dT = vdp - sdT \tag{138}$$

Here $v = V/N$ is the specific volume and $s = S/N$ is the entropy per particle. We could also obtain this relation by equating dU computed from $U = TS - pV + \mu N$ with the expression given by the first law.

7 Phase transitions

7.1 General features of 1st and 2nd order transitions

• When water freezes or boils, it undergoes a phase transition. We have also encountered the transition from the ferro- to paramagnetic phases of iron. These are examples of so-called first and second-order phase transitions. A first order transition is characterized by a non-zero latent heat which vanishes for a 2nd order transition. For instance, suppose we start with water at 30° C and heat it at constant atmospheric pressure, its temperature rises till we hit 100° C. The water starts to boil, with water being converted to vapour. However, the temperature remains constant till all the water has been converted to vapour. The amount of heat required to vapourize unit mass of water at 100° C is the latent heat of vaporization. The ice to water melting transition also involves a latent heat. The boiling/condensation transitions can also be examined at constant temperature rather than pressure (See Fig 7(b)). For instance, suppose we begin with water vapour at $T = 105^\circ$ C and atmospheric pressure. As we isothermally compress the vapour (decrease the volume of the container), the pressure increases until it reaches the so-called saturated vapour pressure, when the vapour starts condensing. Further compression does not lead to an increase in pressure. Instead, more and more of the vapour condenses isothermally at the fixed vapour pressure. At this stage, the vapour and liquid phases coexist in equilibrium. Phase coexistence is another characteristic feature of first order transitions. When all the vapour has condensed, further compression results in an a steep increase in pressure, since liquids are not as compressible as gases.

• Fig 7 shows the equation of state surface in the pVT thermodynamic state space showing both the melting and boiling transitions. Note that the gas and liquid phases is each described by an equation of state, though the EOS relation $f(p, V, T) = 0$ is different for the two phases. Isotherms for a liquid to vapour transition are shown in a pV diagram.

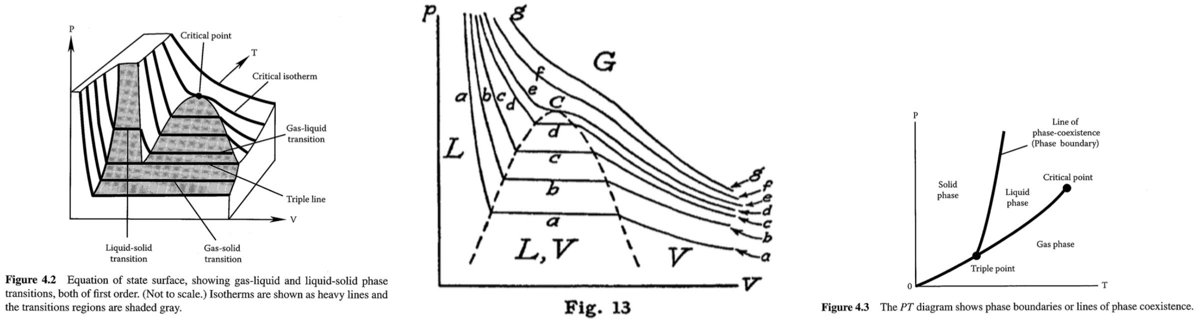

Figure 4.2 Equation of state surface, showing gas-liquid and liquid-solid phase transitions, both of first order. (Not to scale.) Isotherms are shown as heavy lines and the transitions regions are shaded gray.

Fig. 13

Figure 4.3 The *PT* diagram shows phase boundaries or lines of phase coexistence.

(a) (b) (c)

Figure 7: (a) From K Huang: (b) From E Fermi: Isotherms for liquid to vapour transition in a pV diagram (c) From K Huang: Phase boundaries for solid-liquid-gas system in a pT diagram. The line of first order transitions ends at the critical point representing a second order transition. At the triple point, all three phases coexist.

• Notice from the pVT and pV diagrams that the range of volumes over which the liquid and vapour coexist shrinks as we move to isotherms at higher temperatures. At the critical temperature T_c (374°C for water) the coexistence region of the isotherm shrinks to a point with the critical saturated vapour pressure p_c (217.7 atm for water). At this critical point, vapour and liquid coexist with the same density and specific entropy and the latent heat vanishes. The transition changes from first to second order. This may be seen in a pT diagram (Fig 7(c)) showing coexistence curves that demarcate the boundaries between the various phases. The phase boundaries correspond to first order phase transitions. It is seen that the line of first order liquid-gas phase transitions ends at the critical point. A line of first order phase transitions often ends at a second order transition. At temperatures higher than T_c, water exists in a single phase with continuously varying properties. Note that the melting transition is always first order, there is no critical point for the solid to liquid transition. Instead we have a triple point on the pT diagram (projection of the triple-line isotherm in pVT space) where solid, liquid and vapour can coexist at a first order transition. At temperatures less than the triple point temperature, there is no liquid phase and vapour directly condenses to a solid via a first order transition (this sublimation transition may be familiar from the vapourization of solid camphor when heated).

• We will see that for two phases to coexist in equilibrium, their free energies (Gibbs or Helmholtz depending on context) must be equal. Thus, free energies are continuous across a first order phase transition. On the other hand, the densities and specific entropies of vapour and liquid phases that coexist at a common temperature and pressure are vastly different. Specific entropy of a gas is significantly more than that of the liquid (or solid): there are many more microstates corresponding to a given macrostate of a gas. Since specific volume and specific entropy are derivatives of the specific Gibbs free energy with respect to pressure and temperature, we infer that the first derivatives of the free energy are discontinuous across a first order phase transition.

• This motivates Ehrenfest's classification of phase transitions. A phase transition is of order $n = 1, 2, \ldots$ if an n^{th} partial derivative of free energy is the first one to be discontinuous.

• Specific heats typically diverge at a second order phase transition ($T = T_c$). Recall that $c_V = T\left(\frac{\partial s}{\partial T}\right)_V$ where s is specific entropy and that entropy $S = -\left(\frac{\partial F}{\partial T}\right)_V$. Thus specific heats are given by second derivatives of the free energy. In a second order transition, the free energy and its first derivative are continuous across the transition but its second derivative suffers a divergence. Interesting phenomena in the neighbourhood of the critical point of water were discovered in building and working with steam engines (detailed measurements were collected in steam tables, which are like star charts in celestial mechanics). One such phenomenon is critical opalescence, steam at the critical temperature was found to be opaque to light of practically any wave length. Usually, a medium is transparent to light of wavelengths different from the typical length scales of disturbances in the medium. Critical opalescence is interpreted as a demonstration of the existence of fluctuations on all length scales in steam at T_c. It turns out that specific heats measure fluctuations[18], so diverging specific heats go hand in hand with fluctuations on all length scales (we say that 2nd order phase transitions display scale-invariance, there is no characteristic length scale).

• The ferromagnetic to paramagnetic transition as T is increased beyond the Curie-Weiss temperature is another example of a second order phase transition. In this case, the Helmholtz free energy and its first derivative (the spontaneous magnetization) are continuous, but the second derivatives of free energy, (the magnetic susceptibility and specific heat) diverge at the critical temperature.

7.2 Clausius-Clapeyron equation from energy equation

• The Clapeyron equation (developed by French engineer and physicist Benoit Clapeyron extending work of Clausius) gives a formula for the variation of saturation vapour pressure with temperature when liquid and saturated vapour coexist at the boiling point (in terms of the latent heat of vaporization associated to the first order transition). It determines the shape of the phase boundary between vapour and liquid phases in a pT diagram.

The key idea is to use the energy equation to express $\frac{\partial p}{\partial T}$ at constant volume in terms of $\frac{\partial U}{\partial V}$

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[18] Roughly, equilibrium is determined by a local minimum of free energy. To study fluctuations around equilibrium, we may Taylor expand the free energy around its minimum $F = F_0 + (\partial F/\partial T)_0(T - T_0) + \frac{1}{2}(\partial^2 F/\partial^2 T)_0(T - T_0)^2 + \cdots$. As in mechanics, the curvature of the graph of the thermodynamic potential around its minimum controls oscillations/fluctuations. This curvature is proportional to the second derivative of free energy, which is the specific heat.

at constant temperature. Following Fermi, we consider the region (below the critical point) of the pV diagram where vapour and liquid coexist. The isotherms are horizontal, so the pressure (saturated vapour pressure $p(T)$, which is also the pressure of the coexisting liquid) is a constant, depending only on temperature (and not volume). Similarly, the densities (or specific volumes v_g and v_l) of the vapour and liquid are functions only of temperature. As the mixture is compressed isothermally, vapour condenses without changing the density of either phase. Similarly, let u_g and u_l be the specific internal energies. At a particular volume along the horizontal isotherm, suppose m_g and m_l are the masses, so that the total mass $m = m_g + m_l$. The total volume and internal energy are given by

$$V = m_g v_g(T) + m_l v_l(T) \quad \text{and} \quad U = m_g u_g(T) + m_l u_l(T). \tag{139}$$

Now, if the system is expanded, the pressure and temperature do not change but a mass dm of the liquid is converted to vapour. To apply the energy equation to this transformation, we find the change in volume and internal energies:

$$V + dV = (m_l - dm)v_l + (m_g + dm)v_g = V + (v_g - v_l)dm \quad \Rightarrow \quad dV = (v_g - v_l)dm. \tag{140}$$

Similarly $dU = (u_g - u_l)dm$. Since both these are under isothermal conditions,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{u_g - u_l}{v_g - v_l}. \tag{141}$$

By the energy equation,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{p}{T}. \tag{142}$$

In our case, the pressure is independent of volume so we may write dp/dT in the energy equation. It is possible to express $\left(\frac{\partial U}{\partial V}\right)_T$ in terms of the latent heat. The heat needed to vapourize a mass dm of liquid that coexists with saturated vapour at temperature T is

$$\delta Q = dU + pdV = \left(u_g - u_l + p(v_g - v_l)\right) dm \tag{143}$$

The heat of vapourization per unit mass is called the latent heat λ. Thus

$$\lambda(T) = \frac{\delta Q}{dm} = u_g(T) - u_l(T) + p(T)(v_g(T) - v_l(T)) \quad \text{or} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{\lambda}{v_g - v_l} - p. \tag{144}$$

Combining with the energy equation, we arrive at the Clapeyron equation

$$\frac{dp}{dT} = \frac{\lambda(T)}{T(v_g - v_l)}. \tag{145}$$

The latent heat and $v_g - v_l$ are positive, so the slope of the liquid-gas phase boundary is positive. The Clapeyron equation may also be applied to the solid to liquid transition, with λ denoting the latent heat of melting and $v_g - v_l$ replaced with $v_l - v_s$. For most materials the slope is again positive. Water is an exception, it expands on freezing, so that the slope is negative in this case.

- In the liquid to gas case, the Clapeyron equation may be simplified. We assume, following Clausius, that the density of the gas is much less than that of the liquid $v_g \gg v_l$ and treat the vapour as an ideal gas satisfying $pv_g = RT/M$ where M is mass per mole of the vapour. The resulting Clausius-Clapeyron equation is

$$\frac{dp}{dT} \approx \frac{M\lambda(T)p}{RT^2} \quad \text{or} \quad \frac{d\log p}{dT} \approx \frac{M\lambda(T)}{RT^2}. \tag{146}$$

If we further assume that the latent heat does not vary much with temperature, we may integrate to get an approximate formula for the saturated vapour pressure as a function of temperature

$$p(T) \approx p_0 e^{-\lambda M/RT}. \tag{147}$$

7.3 Condition for phase coexistence and Clapeyron's equation from Gibbs free energy

- We will apply the principle that the Gibbs free energy is an extremum in equilibrium to rederive the Clapeyron equation. As before, we have a liquid and its saturated vapour coexisting at a constant temperature T and vapour pressure $p(T)$. Let $u_l, u_g, s_l, s_g, v_l, v_g, g_l, g_g$ (all functions of T) be the specific internal energies, entropies, volumes and Gibbs potentials of the liquid and gas per unit mass. If m_l, m_g are the masses of the two phases, then the total Gibbs potential is the sum $G = m_l g_l + m_g g_g$. If the volume is slightly increased isothermally, the pressure is unchanged but a mass δm of liquid is converted to gas. The change in Gibbs potential $\delta m(g_g - g_l)$ must vanish since the mixture was in equilibrium. Thus, the specific Gibbs potentials of the two phases must be equal in equilibrium, i.e., the Gibbs potential is continuous across a first order phase transition[19]. This is the **condition for phase coexistence**. In other words, using $g = u - Ts + pv$ we get at any given temperature:

$$g_g - g_l = (u_g - u_l) - T(s_g - s_l) + p(v_g - v_l) = 0. \tag{148}$$

- Since we seek a formula for dp/dT, we differentiate with respect to temperature:

$$\frac{d}{dT}(u_g - u_l) - T\frac{d}{dT}(s_g - s_l) - (s_g - s_l) + \frac{dp}{dT}(v_g - v_l) + p\frac{d}{dT}(v_g - v_l) = 0. \tag{149}$$

By the first law, $Tds = du + pdv$, so dividing by dT three of the terms cancel leaving

$$\frac{dp}{dT}(v_g - v_l) = (s_g - s_l) \quad \text{or} \quad \frac{dp}{dT} = \frac{T(s_g - s_l)}{T(v_g - v_l)}. \tag{150}$$

However, $T(s_g - s_l)$, the heat required to vapourize unit mass of liquid is simply the latent heat λ, so we arrive at Clapeyron's equation

$$\frac{dp}{dT} = \frac{\lambda}{T(v_g - v_l)}. \tag{151}$$

7.4 van der Waals gas

7.4.1 vdW equation of state, virial expansion, isotherms

The ideal gas EOS works well at high temperatures and low pressures. However, significant deviations are observed as the gas gets closer to condensation. van der Waals proposed the

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[19] Note that the derivatives of the specific Gibbs potential with respect to temperature and pressure (negative specific entropy and specific volume) are discontinuous across the phase boundary for a first order phase transition.

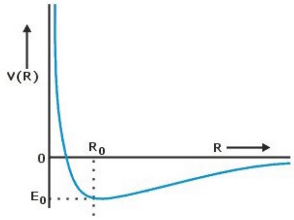

Figure 8: Interatomic potential energy $V(R)$ between two identical atoms as a function of separation R between their nuclei.

simplest equation of state that qualitatively accounts for the first order vapour to liquid condensation transition. Condensation is due to intermolecular forces. Recall that the molecules of an ideal gas are assumed point-like and to not interact with each other. Real gas molecules strongly repel when they get closer than about a tenth of a nanometer (sometimes modeled as a 'hard-sphere' core). The intermolecular potential is attractive ('cohesive forces') at slightly larger separations (which can lead to condensation) and goes to zero asymptotically. The arbitrary additive constant in the potential is chosen so that the potential vanishes at infinite separation.

• Consider n moles of a gas in a container of volume V. Suppose nb is the total volume occupied by the hard cores of the molecules (b is the volume of the cores of a mole of the gas). The molecules therefore have only an effective volume $V_{\text{eff}} = V - nb$ to move around. The pressure of the gas on an outer wall (or a membrane in the gas) is due to the force exerted by molecules as they collide with the wall. The attractive interaction between pairs of molecules could be expected to reduce this pressure compared to its ideal gas value p_{ideal}. van der Waals argued that the reduction in pressure would thus be proportional to the number of pairs[20] of particles, i.e., $\sim n^2$. However, since pressure is intensive, we must divide by the square of an extensive quantity. Thus, van der Waals proposed that the actual pressure is given by

$$p = p_{\text{ideal}} - \frac{n^2 a}{V^2}. \tag{152}$$

Here, a is a (dimensional) constant depending on the strength of the inter-molecular force, but independent of n. We may call $n^2 a/V^2$ the cohesion pressure.

• van der Waals *postulated* that in such a real gas, the ideal pressure and the available volume continue to be related via the ideal equation of state:

$$p_{\text{ideal}} V_{\text{eff}} = nRT \quad \text{or} \quad \left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT. \tag{153}$$

What we measure and control are the actual pressure and volume of container. When the EOS is expressed in terms of these, interesting new phenomena become possible. When a and b vanish, the effects of intermolecular forces and molecular size are not accounted for and we return to the ideal EOS.

Virial expansion of vdW EOS: At low density n/V the vdW EOS should approach that of the ideal gas. The virial expansion quantifies the deviations from ideal behavior through an

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[20] Of course, only a fraction of the total number of molecules which are close enough to a given molecule would have a significant attractive influence. The information in this fraction is absorbed into the constant a.

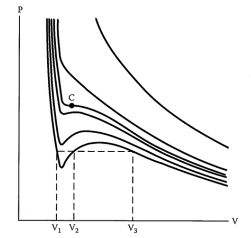

Figure 4.6 Isotherms of the van der Waals gas. The critical point is at C.

Figure 9: From K Huang: vdW isotherms in a PV diagram.

expansion in powers of n/V. To obtain it, we rewrite the vdW EOS

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb)=nRT \quad \text{as} \quad p=\frac{nRT}{V-nb}-\frac{n^2a}{V^2} \quad \text{or} \quad \frac{pV}{nRT}=\left(1-\frac{nb}{V}\right)^{-1}-\frac{na}{VRT}. \tag{154}$$

Expanding in powers of the small dimensionless quantity nb/V we get

$$\frac{pV}{nRT}=1+\frac{nb}{V}\left(1-\frac{a}{bRT}\right)+\left(\frac{nb}{V}\right)^2+\left(\frac{nb}{V}\right)^3+\cdots \tag{155}$$

When the molecular volume $nb \ll V$ we recover the ideal gas law. The first deviation is encoded in the 'virial coefficient' $b-a/RT$, which can be measured. Its temperature dependence contains information on the molecular parameters a and b.

van der Waals isotherms: The vdW isotherms are plotted on the p-V plane in Fig 9. For large T they approach the hyperbolae pV = constant of the ideal gas. It is convenient to multiply (153) by V^2 and regard the vdW EOS as a cubic equation for V for any given p, n and T:

$$(pV^2+n^2a)(V-nb)=nRTV^2 \quad \text{or} \quad f(V)=pV^3-(nbp+nRT)V^2+n^2aV-n^3ab=0. \tag{156}$$

Being a cubic with real coefficients, there is either one or three real roots V (the latter possibility includes cases where two or all three roots coincide). To analyze the possibilities, we sketch a graph of $f(V)$ based on the following observations: (a) $f(V)\to\pm\infty$ as $V\to\pm\infty$, (b) $f(0)=-n^3ab<0$, (c) $f(V)$ is monotonically decreasing for $V<0$ so real roots of f are non-negative, (d) $f'(0)=n^2a>0$ so f has a positive slope near $V=0$, (e) the coefficient of the V^2 term $(-n(bp+RT))$ is negative, so f increases with V from negative values and eventually reaches a maximum (f) f has a root before this local maximum if T is small and no such root if T is large: this is due to a competition between the linear and quadratic terms, which increase/decrease with V, (g) f then decreases due to the negative quadratic term and could encounter another zero (g) as the effects of the V^3 term kick in, f reaches a local minimum and then monotonically increases ($f\to\infty$) as $V\to\infty$. Thus for large T there is a unique root V for any p while for small T there may be either one or three roots V. It is instructive to plot $f(V)$ for different values of p and T to better understand the various possibilities.

For high temperatures, there is a unique volume for any given pressure. As the temperature is decreased, this continues to be true till we approach a critical temperature T_c and a critical isotherm with a horizontal point of inflection C. As the temperature is further lowered, there

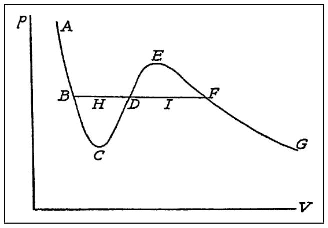

Figure 10: van der Waals isotherm on a PV diagram and Maxwell construction from E Fermi, Thermodynamics. The saturated vapour pressure for the temperature of the indicated vdW isotherm $GFEDCBA$ is the one for which the areas above and below the horizontal coexistence line $FIDHB$ are equal.

are three volumes corresponding to a given pressure. Comparing with the isotherms of a real gas shown in Fig. (7) we see that they are qualitatively similar to the vdW isotherms for $T \geq T_c$. For $T < T_c$ the vdW isotherms have a local maximum and minimum pressure while the real isotherms have a constant saturated vapour pressure corresponding to an inhomogeneous stable phase with vapour and liquid coexisting. If an unsaturated gas is compressed isothermally, till the saturated pressure is reached, condensation normally sets in and the gas phase separates into a liquid-vapour mixture. Under further compression, the pressure remains constant with more and more of the vapour condensing until the system consists of pure liquid. It is only on further isothermal compression that the pressure again starts to rise.

• What then is the nature of the physical states along vdW isotherms for $T < T_c$? If a saturated vapour is free of impurities[21] and is carefully compressed, it is possible for higher pressures to be reached without condensation setting in. This corresponds to a homogeneous but labile (somewhat unstable) supersaturated gas which would condense if perturbed (the portion FE in Fig. 10). The corresponding homogeneous labile state approached from the liquid end of the vdW isotherm is called undercooled (the portion BC in Fig. 10). It may be achieved by heating a liquid in a container that is free of vibration to a temperature a little higher than the boiling point. The vdW isotherm thus corresponds to homogeneous but somewhat unstable states.

• Remarkably, it is possible to apply Maxwell's construction to the vdW isotherms to obtain the stable horizontal isotherms. Before discussing this, let us analytically find the critical values of T, p and V.

7.4.2 Critical isotherm and critical point

• The isotherms for n moles of a vdW gas are curves of constant T on the pV plane defined by the EOS

$$(p + \frac{n^2 a}{V^2})(V - nb) = nRT. \tag{157}$$

It is convenient to multiply by V^2 and regard this as a cubic equation for V for any given p and T:

$$(pV^2 + n^2 a)(V - nb) = nRTV^2 \quad \text{or} \quad f(V) = pV^3 - n(bp + RT)V^2 + n^2 aV - n^3 ab = 0. \tag{158}$$

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[21] Impurities like dust would serve as nucleation sites for condensation. Supersaturated vapour is used in a Wilson cloud chamber to detect tracks of elementary particles, the particles serve as nucleation sites for condensation.

For sufficiently high T the graph of the isotherm $p(V)$ must reduce to the hyperbola $p = nRT/V$ characteristic of an ideal gas. So for large T the isotherm has no local extrema and there is a unique volume corresponding to any given pressure (see Fig. 9). For sufficiently low T, an isotherm has both a local minimum pressure $p_{\min}$ and a local maximum pressure $p_{\max}$ and three volumes $V_{1,2,3}$ corresponding to any pressure in between ($p_{\min} < p < p_{\max}$). The critical isotherm (at the critical temperature T_c) is the one where the three roots $V_{1,2,3}$ coalesce at a critical volume V_c, in other words, the critical isotherm has an inflection point:

$$\frac{\partial p}{\partial V} = 0, \quad \text{and} \quad \frac{\partial^2 p}{\partial V^2} = 0. \tag{159}$$

The corresponding pressure is p_c and temperature T_c. To find these values, we put

$$\frac{\partial p}{\partial V} = -\frac{nRT}{(V - nb)^2} + \frac{2n^2 a}{V^3} = 0 \quad \text{or} \quad \frac{RT}{(V - nb)^2} = \frac{2na}{V^3} \tag{160}$$

and

$$\frac{\partial^2 p}{\partial V^2} = \frac{2nRT}{(V - nb)^3} - \frac{6n^2 a}{V^4} = 0 \quad \text{or} \quad \frac{RT}{(V - nb)^3} = \frac{3na}{V^4}. \tag{161}$$

Combining we get

$$\frac{2na}{V^3(V - nb)} = \frac{3na}{V^4} \quad \text{or} \quad \frac{2}{V - nb} = \frac{3}{V} \quad \Rightarrow \quad V_c = 3nb. \tag{162}$$

Putting this in the first condition we get $RT_c = \frac{8a}{27b}$ and finally from the vdW EOS, $p_c = a/2nb^2$. Thus the critical pressure, volume and temperature for n moles of a vdW gas are

$$p_c = \frac{a}{27b^2}, \quad V_c = 3nb \quad \text{and} \quad T_c = \frac{8a}{27Rb}. \tag{163}$$

The critical volume is thrice the excluded volume nb, so the gas/liquid is quite dense at the critical point.

7.4.3 Maxwell construction

As discussed, the vdW isotherms describe unstable homogeneous states (supersaturated vapour for instance) in the region between volumes V_B and V_F (see Fig 10) where the vdW isotherms display a local minimum and a local maximum. In this region, the stable equilibrium state is a liquid-vapour mixture at the constant saturation vapour pressure. The Maxwell construction gives an elegant method of identifying the constant saturated vapour pressure that corresponds to a given vdW isotherm. The height of the horizontal coexistence isotherm BF is determined by the condition that the areas $DEFD$ and $BDCB$ bounded by the horizontal and the the vdW isotherm must be equal. To show this, we follow Maxwell (see Fermi) and consider the reversible isothermal cycle $BCDEFIDHB$. In other words, we first expand the liquid from B along the vdW isotherm $BCDEF$ passing through homogeneous states ending with saturated vapour at F. Then we return from F to B by compressing the vapour at constant saturated vapour pressure via liquid-vapour mixtures $FIDHB$. Note that the point D corresponds to two different states: a liquid-vapour mixture when approached horizontally and a labile homogeneous state when approached via the vdW isotherm[22]. Being a reversible cyclic process $\oint \delta Q/T = 0$

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[22] The closed curves $DHBCD$ and $DIFED$ do not represent reversible cyclic processes.

by Clausius' theorem. Since it is isothermal as well, T is a constant, and the heat added $\oint \delta Q$ must be zero. By the first law for a cycle, the work done is also zero. Since $DEFID$ is traversed clockwise while $BCDHB$ us traversed anti-clockwise, the total work done is zero provided the magnitudes of the areas are equal. In real gases, these areas are quite small. Note that the Maxwell construction applies to any equation of state, not just the vdW gas.

7.4.4 Entropy and Caloric condition for vdW gas

Recall the caloric condition $(\frac{\partial U}{\partial V})_T = 0$ for an ideal gas that followed from the Joule free expansion experiment. We may view this as a consistency condition for $\delta Q/T$ to be an exact differential. Indeed, taking T, V as independent variables for an ideal gas, we have

$$\frac{\delta Q}{T} = \frac{dU + pdV}{T} = \frac{1}{T}\frac{dU}{dT}dT + \left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{nR}{V}\right) dV. \tag{164}$$

The integrability condition

$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{1}{T}\frac{\partial U}{\partial V} + \frac{nR}{V}\right) \quad \Rightarrow \quad \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} \quad \text{or} \quad \left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{165}$$

Similarly, let us derive the caloric condition for a vdW gas:

$$\frac{\delta Q}{T} = \frac{dU + pdV}{T} = \frac{1}{T}\frac{\partial U}{\partial T}dT + \frac{1}{T}\left(\frac{\partial U}{\partial V} + \frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV \tag{166}$$

As before, we get

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\frac{\partial U}{\partial V} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{an^2}{V^2 T^2} \quad \text{or} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}. \tag{167}$$

So, for entropy to exist as a state function for a vdW gas, the caloric condition must be satisfied. In particular, the EOS does not completely determine the thermodynamic nature of a vdW gas, it must be supplemented by the caloric condition.

- The above caloric condition implies that the internal energy of a vdW gas is not independent of volume, unlike for an ideal gas ($a \to 0$). However, it is possible to show that the heat capacity at constant volume is independent of volume $C_V = C_V(T)$, just as for an ideal gas!

Entropy of vdW gas: Assuming the caloric condition is satisfied, the entropy of a vdW gas is determined by

$$dS = \frac{\delta Q}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{nR}{V - nb}dV = \frac{C_V(T)}{T}dT + \frac{nR}{V - nb}dV. \tag{168}$$

As in the case of an ideal gas, the temperature dependence of C_V is not fixed by thermodynamics. If it is assumed roughly constant, then we may integrate from T_0, V_0 to T, V to obtain

$$S(T, V) \approx C_V \log\left(\frac{T}{T_0}\right) + nR \log\left(\frac{V - nb}{V_0 - nb}\right). \tag{169}$$

7.5 Remarks on paramagnetic to ferromagnetic phase transition

• Consider a magnetic material like iron. Recall that the magnetization $\mathbf{M}$ is the total dipole moment of the sample per unit volume. The thermodynamic state space of a magnet is parametrized by three variables $\mathbf{H}, \mathbf{M}, T$, the applied external magnetic field, magnetization and temperature. A paramagnet is one which has zero magnetization in the absence of an external magnetic field $\mathbf{H}$, but which develops an induced magnetization when an external $\mathbf{H}$ is turned on. For small $|\mathbf{H}|$, the induced $\mathbf{M}$ is linear in $\mathbf{H}$ and satisfies the Curie-Weiss law $\mathbf{M} = \chi \mathbf{H}$ where χ is the temperature-dependent susceptibility. In other words, the external field tends to align[23] the atomic dipoles in the direction of $\mathbf{H}$. This linear relation ceases to hold for large $|\mathbf{H}|$, indeed there is a non-linear saturation (see Fig. 11). The magnetization cannot increase indefinitely, it has a maximal value, which is attained when all the atomic dipoles are aligned. Now χ is a function of temperature. If the temperature of the paramagnet is increased χ decreases: thermal agitation decreases the alignment brought about by the external field. For convenience let us suppose $\mathbf{H} = H\hat{z}$ and $\mathbf{M} = M\hat{z}$ are in the z-direction. Then the isotherm $M(H)$ for a higher temperature lies below the earlier one, with saturation occurring at a higher H (see Fig.11). On the other hand, if the temperature is decreased, the susceptibility (slope of $M(H)$ at $H = 0$) grows and in fact diverges at a critical Curie temperature T_c (see Fig. 12). Below T_c, the sample possesses a non-zero residual 'spontaneous magnetization' $M_{\rm sp}(T)$ even when the external field $H \to 0^+$: it is a ferromagnet like the familiar bar magnet. The spontaneous magnetization grows as the temperature is decreased below T_c. We have just described a second order phase transition from a paramagnet to ferromagnet. The free energy, internal energy, specific entropy and magnetization are continuous across the transition[24], but the susceptibility and specific heat (which are second derivatives of the Helmholtz free energy with respect to H and T respectively) diverge at the critical point.

• It is found that in the neighbourhood of T_c, there are fluctuations on a whole variety of length scales in the sample and even far separated atomic spins are strongly correlated - this is the analogue of critical opalescence at the critical point in the vapour to liquid transition in water. Moreover, the spontaneous magnetization, specific heat and susceptibility have power law behaviors for $T \lesssim T_c$. For instance:

$$M(T, H=0) \sim (T_c - T)^\beta, \quad C(T, H=0) \sim (T_c - T)^\alpha, \quad \text{and} \quad \chi(T, H=0) \sim (T_c - T)^\gamma. \tag{170}$$

The exponents α, β, γ are called critical exponents (there are similar exponents for $T > T_c$). These exponents have been measured and found to display universality - they are the same for a wide variety of materials undergoing the second order phase transition. A remarkably successful theory of second order phase transitions (which predicts the values of critical exponents and much more, based on the method of the 'renormalization group') has been developed beginning in the 1960s (Nobel prize to American physicist Kenneth G Wilson in 1983).

• A simple microscopic model for a magnet was proposed by Heisenberg[25]. In the Heisenberg model we have a crystal with atomic magnetic dipole moments $\mathbf{m}_i$ located at the sites of the crystal lattice; i labels the sites. The magnetic moments arise from the electronic spin (and

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[23] A diamagnet is one where the induced magnetization points in the direction opposite to $\mathbf{H}$.

[24] Second order phase transitions are often referred to as continuous phase transitions. There is no latent heat.

[25] A related simplified model is called the Ising model, in which the magnetic moment on each site can only take the values ±1 in appropriate units, these are the z-components of the magnetic moment.

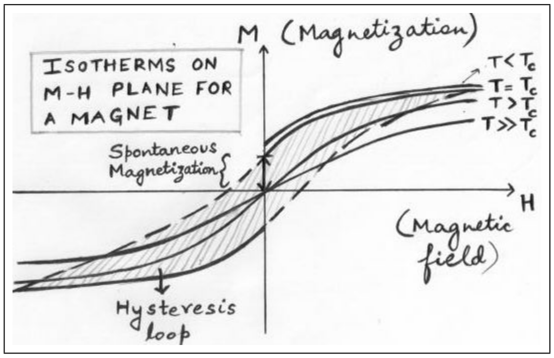


Figure 11: Plot of magnetization vs applied magnetic field for various temperatures in a magnetic domain. For $T > T_c$ (paramagnetic phase) $M = \chi H$ for small H (linear response regime) while M saturates for large H. For $T \leq T_c$ (ferromagnetic phase) there is a residual (spontaneous) magnetization even when $H \to 0^{\pm}$. The memory effect (hysteresis loop) is also shown.

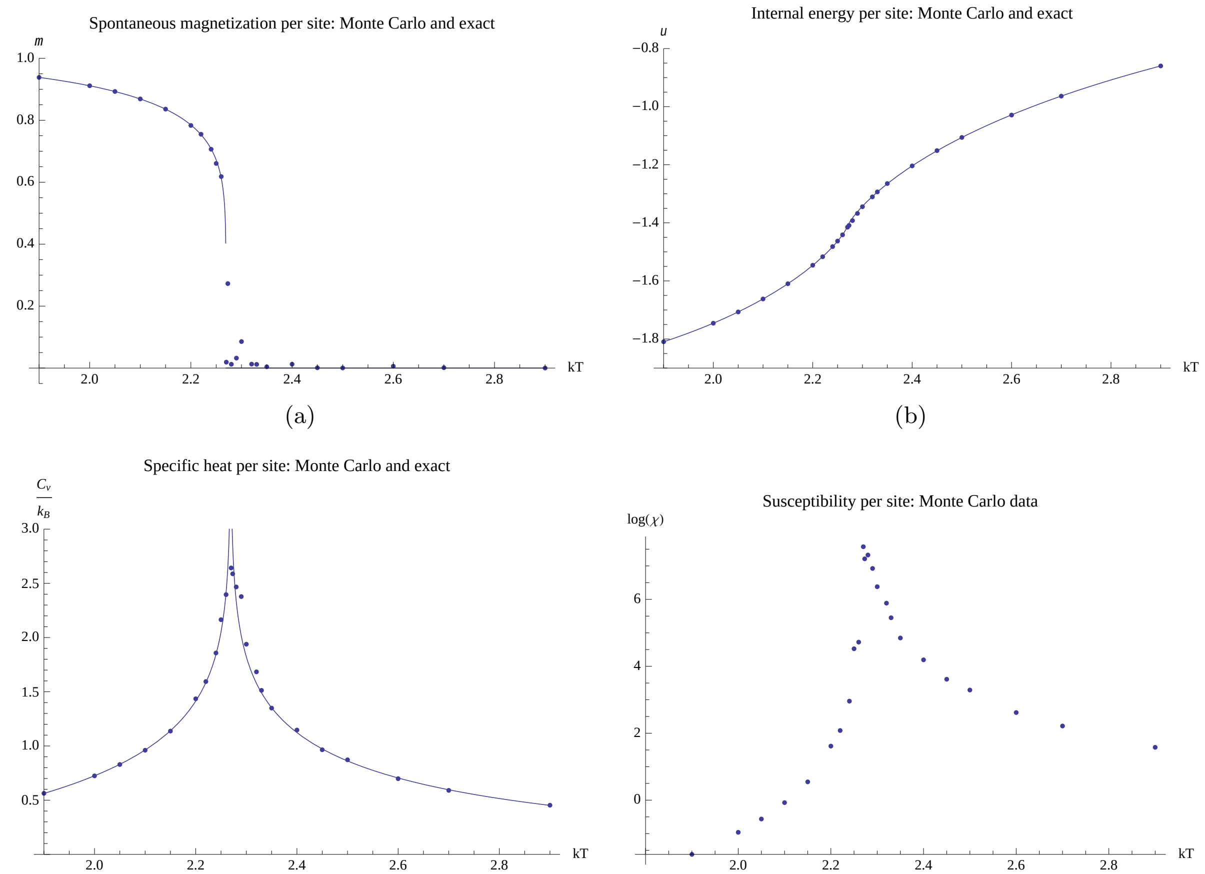
orbital motion). The Hamiltonian is

$$H = -\sum_i \mathbf{H}_i \cdot \mathbf{m}_i - \sum_{\langle i,j \rangle \text{ n.n}} J\, \mathbf{m}_i \cdot \mathbf{m}_j. \tag{171}$$

The first term represents the magnetic dipole energy due to the external magnetic field. Here, $\mathbf{H}_i$ is the external magnetic field at the location of the i^{th} dipole. The dipole energy is minimized when the dipoles are aligned with the external field, as we expect for a paramagnet (reversing the sign of this term would be relevant to a diamagnet). The second term represents the energy of interaction between nearest neighbor atomic dipoles (denoted n.n or $\langle ij \rangle$). J is an interaction strength. We have assumed that the dipolar interactions decay rapidly with separation, so that we may restrict attention to nearest neighbors. Notice that for $J > 0$, the interaction energy is minimized when all the dipoles point in the same direction, as we expect for a ferromagnet (if $J < 0$ we have an anti-ferromagnet, whose energy is lowest when neighboring dipoles point in opposite directions). Since the interaction energy involves dot products of dipoles, it is rotation invariant (the dot product of two vectors does not depend on the orientation of the frame, but only on the angle between the vectors and their lengths). The direction of the external magnetic field $\mathbf{H}$ breaks this rotation symmetry and determines the direction in which the dipoles align.

8 Third law of thermodynamics

• Our definition of the entropy of a state B depended on the choice of a reference state A: $S(B) = \int_A^B \delta Q/T$ where the integral is along any reversible process. The arbitrariness in the choice of reference state leads to an undetermined constant S_0 in the entropy. This does not matter as long as we are only concerned with differences in entropies. On the other hand, the free energies $F = U - TS$ and $G = U - TS + pV$ are undetermined up to a linear function of temperature, reducing their utility in dealing with states at different temperatures. We also noticed that an appropriate choice of S_0 (depending on some dimensional physical quantities) would be necessary to make the formula for the entropy of an ideal gas dimensionally consistent as well as extensive. There are other situations where the value of S_0 is important (E.g. the equations for chemical and gaseous equilibria).



(a) (b) (c) (d)

Figure 12: Numerically and analytically calculated (dots/solid curve) spontaneous magnetization, internal energy, specific heat and susceptibility at zero external field for a planar square lattice Ising magnet with $J = 1$ plotted as a function of kT. The transition temperature is at $kT_c = 2.27$. From H. Senapati, B.Sc. thesis CMI (2013).

• The third law was originally formulated by Walther Nernst (1912) in terms of the maximum available work or Helmholtz free energy. He discovered it in the context of electrochemical reactions and experimentally verified its consequences for the behavior of specific heats.

• The third law of thermodynamics, as reformulated by Planck, states that as the temperature of a system approaches absolute zero, its entropy approaches a constant value independent of pressure/volume/density, state of aggregation etc. This constant value may be taken to be zero. In particular, all states of the system at $T = 0$ have $S = 0$. We consider some simple consequences of the third law.

• Since S approaches a constant independent of volume and pressure as $T \to 0$, its derivatives with respect to p, V must vanish. We may use the Maxwell relations to relate derivatives of entropy to certain measurable coefficients. For example

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -\alpha V \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = p\beta. \tag{172}$$

Thus, the coefficients of thermal expansion α and tension β must vanish at absolute zero (assuming V and p do not).

- **Specific heats approach zero at absolute zero.** Consider the specific heats at constant pressure and volume expressed as derivatives of the specific entropy

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \quad \text{and} \quad c_V = T\left(\frac{\partial s}{\partial T}\right)_V \tag{173}$$

Now by the third law, $s \to 0$ as $T \to 0$. Assuming a power law behavior, $s \to T^{\epsilon}$ for some $\epsilon > 0$ as $T \to 0$. It follows that the specific heats also go to zero as T^{ϵ}.

- Alternatively, integrating from $T = 0$, we may express the specific entropy at temperature T as

$$s(T,p) = \int_0^T \frac{c_p(T')}{T'}\, dT' + \tilde{s}_0(p) \quad \text{and} \quad s(T,v) = \int_0^T \frac{c_v(T')}{T'}\, dT' + \tilde{\tilde{s}}_0(v). \tag{174}$$

In the first case we regard s as a function of T, p and in the second as a function of temperature and specific volume. For the integrals to be finite, c_p and c_v must vanish as $T \to 0$ in view of the division by T'. The 'constants' of integration $\tilde{s}_0(p)$ and $\tilde{\tilde{s}}_0(v)$ are independent of temperature, we will assume they are finite. For s to have a finite limit (independent of p and v) as $T \to 0$, both $\tilde{s}_0(p)$ and $\tilde{\tilde{s}}_0(v)$ must vanish.

- As a consequence, the simplifying assumption of temperature-independent specific heats is not consistent with the third law. There are significant deviations at low temperatures. At low T, quantum effects become important since the intermolecular spacing can become comparable to the (thermal) de Broglie wavelength of the molecules. The exponent ϵ in the power-law above depends on the nature of the material (i.e. whether the particles are fermions or bosons and the forces between them). The vanishing of specific heats as $T \to 0$ is in agreement with experiments.

9 Fourier's equation for heat conduction

- We have largely dealt with thermodynamic systems in equilibrium, where the temperature is the same throughout the system. However, it is also interesting to know how a system approaches equilibrium. For example, a metal rod (or a fluid) may be heated at one end and left to itself (and thermally insulated). It is observed that the initially inhomogeneous distribution of temperature gradually tends to a uniform distribution through the conduction or diffusion of heat. We seek to determine the time dependence of the distribution of temperature.

- Empirically it is found that the heat flux between bodies (or parts of a body) grows with the temperature difference and is in the direction of decreasing temperature. Joseph Fourier's law (1822) of heat conduction/diffusion states that the heat flux density vector (energy crossing unit area per unit time) is proportional to the negative gradient in temperature

$$\mathbf{q} = -k\nabla T \quad \text{where} \quad k = \text{thermal conductivity}. \tag{175}$$

- Consider material in a fixed volume V. The rate of increase in internal energy per unit time

$$\frac{dU}{dt} = \int_V \rho c_v \frac{\partial T}{\partial t} d\mathbf{r} \tag{176}$$

must equal the rate of influx of heat across the surface S that bounds V.

$$\int_V \rho c_v \frac{\partial T}{\partial t} d\mathbf{r} = \int_S k\nabla T \cdot \hat{n}\, dS = k \int_V \nabla \cdot \nabla T\, d\mathbf{r}. \tag{177}$$

Here c_v is the specific heat/mass (at constant volume, no work) and $\rho =$ mass density, both of which are assumed constant during the process.

- V is arbitrary, so the integrands must be equal. The heat equation follows:

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T \quad \text{where} \quad \kappa = \frac{k}{\rho c_v} \quad \text{is thermal diffusivity.} \tag{178}$$

Heat diffusion/conduction is dissipative, temperature differences even out (subject to boundary conditions) and heat flow stops at an equilibrium temperature. The heat equation is a linear partial differential equation that is second order in space derivatives and first order in time derivatives. Fourier used the series that now bear his name to solve the heat equation.