Pass #2 - Same material - different approach leading to better understanding!

Pass #1 is an approach that characterizes how an Engineering Physicist thinks, whereas Pass #2 is an approach that characterizes how a theoretical physicist thinks. The lecture notes have all the mathematical details although I will not cover in all detail in class. I have also removed from the lectures many of the examples - they are on the website.

0 - Introduction

In this part of class, re-study classical macroscopic thermodynamics.

Ideas of thermodynamics are very general and mostly independent of any physical models and thus applicable in many different fields of physics.

Task of thermodynamics is to define physical quantities (**state quantities**), which characterize the macroscopic properties of matter (**macrostate**) and to relate these quantities using **equations of state** and **laws of thermodynamics.**

One proceeds from experimental results and sets up relations, the **axiomatic laws of thermodynamics**, which have validity independent of particular physical system under consideration.

Laws supplemented by empirically established relations between state quantities called **equations of state**, which are only valid for particular physical systems.

To create manageable theory (calculational point of view), goal is to only specify a few state quantities from which can determine unique values for all other state quantities.

Thermodynamics cannot and will not give reasons why a certain equation of state describes a system.

It restricts itself to making assertions concerning state quantities, if a particular equation of state is given.

This generality of thermodynamics due to the fact that it is based on only a few empirical theorems, leads to major restriction.

State quantities will, in general, be operationally defined in terms of prescription of how to measure them.

Thermodynamics alone cannot make any assertions concerning reasons and interpretations based on microscopic level, which for most part depend on a physical model.

In particular, interpretation of heat using statistical thermal motion of particles is generally not part of thermodynamics.

Can fully understand such concepts only if use ideas from microscopic regime and will therefore now include such discussions.

Concerned mostly with so-called **equilibrium state.**

Equilibrium thermodynamics is not able to describe time evolution of processes.

However, is possible, by comparison of "before and after" equilibrium states, to decide whether a process can happen or not.

In these special cases, can study systems using concept of infinitesimal changes of state.

In thermodynamics, one mostly deals with functions of more than one variable and use differentials, line integrals and partial derivatives extensively.

Not bother much with mathematical rigor, but concentrate efforts towards understanding physical ideas.

To avoid subject of thermodynamics becoming too “abstract" and "dry", have included many illustrative examples and problems (some in lectures and some only on website).

These clearly illustrate general ideas of thermodynamics.

Systems, Phases and State Quantities

Define thermodynamic system to be arbitrary amount of matter, whose properties uniquely and completely described by specifying certain macroscopic parameters.

Matter(system) under consideration confined by physical walls so that interactions with surroundings/environment modified.

Define further properties of these "walls" or the"container":

a. Isolated systems

These systems do not interact in any way with their surroundings. The container has to be impermeable to any form of energy or matter. The total energy E (all forms) is a conserved quantity for such a system and can be used to characterize the macrostate. The same is true for the particle number N and the volume V.

b. Closed systems

> In this case, one allows only for the exchange of energy with the surroundings, but not for the exchange of matter. Thus, energy is no longer a conserved quantity, that is, it will fluctuate due to energy exchange with the surroundings. If the closed system is in equilibrium with its surrounding, however, then the energy will assume an average value which is related to the temperature of the system or of the surroundings. We will then be able to use the temperature, in addition to N and V, to characterize the macrostate.

c. Open systems

> These systems can exchange energy and matter with their surroundings. Hence, neither the energy nor the particle number are conserved quantities. If the open system is in equilibrium with its surroundings, then average values of the energy and the particle number will be related to the temperature and other macrostate variables (yet to be defined) that can be used to characterize the macrostate.

Clearly, isolated system is an idealization.

In real macroscopic world, an exchange of energy with surroundings cannot be prevented in strict sense.

However, can approximately realize isolated systems using expensive experimental equipment.

If properties of system are same for any part of it, system is **homogeneous.**

If system properties change discontinuously at certain **separating surfaces**, system is **heterogeneous.**

Homogeneous parts of heterogeneous system are **phases** and separating surfaces are **phase boundaries.**

An example of such a system is closed pot containing water, steam and air.

Phase boundary is surface of water.

Say there is liquid phase(water) and gaseous phase(air and steam).

Macroscopic quantities which describe system called **state quantities.**

Besides energy E, volume V, particle number N, also have (to be defined) entropy S, temperature T, pressure p, chemical potential μ and so on.

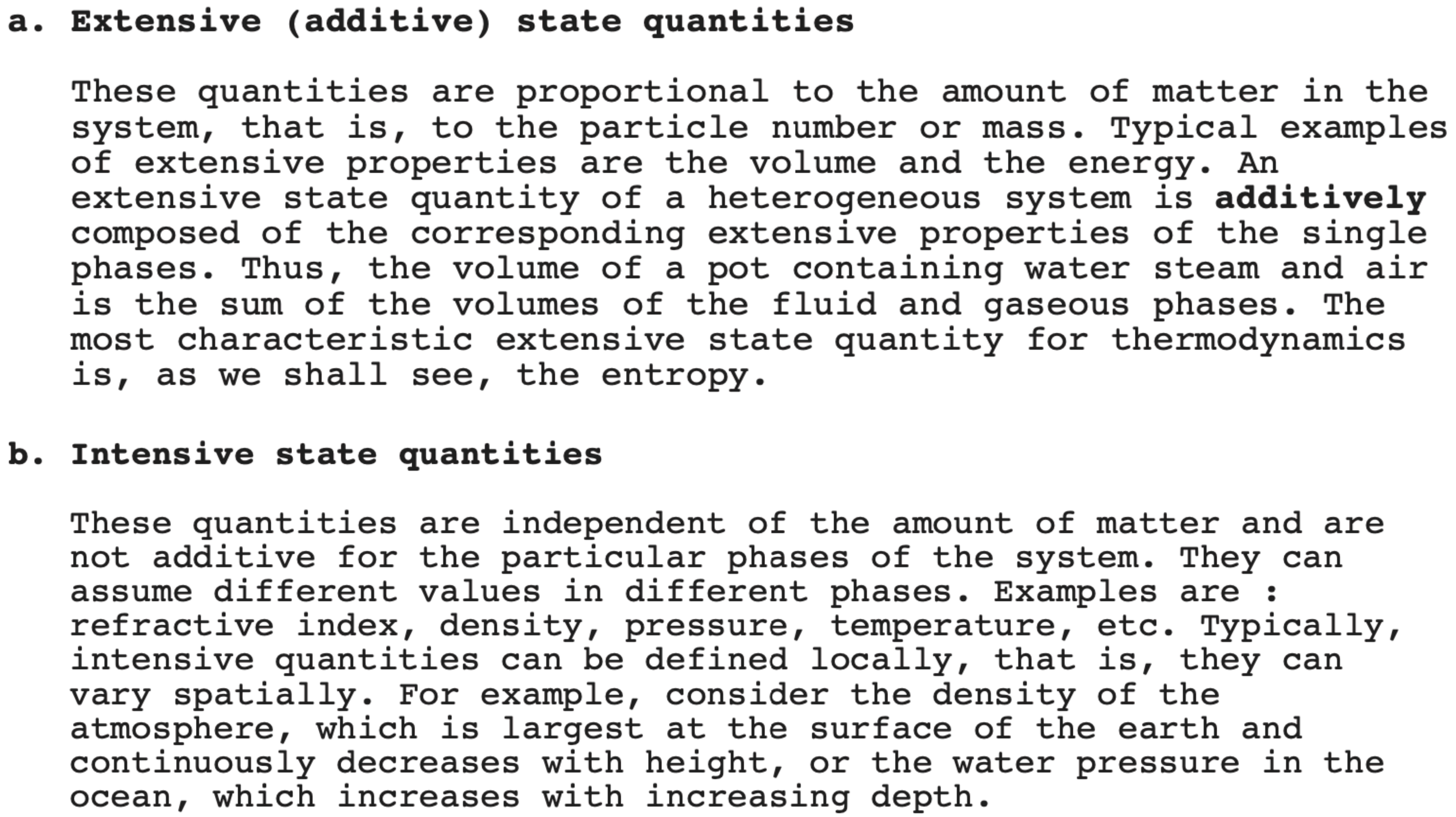
Microscopic properties such as positions and momenta of individual particles are **not** state quantities in thermodynamics.

Can choose few state quantities (state variables given by equations of state) such that all other state quantities have values dependent on these state variables.

As stated earlier, equations of state are determined by experiment.

Example is concept of an ideal gas, which shall often use as model for real gases(but only valid in limit of low gas density).

In general, distinguish two classes of state quantities:



a. Extensive (additive) state quantities

These quantities are proportional to the amount of matter in the system, that is, to the particle number or mass. Typical examples of extensive properties are the volume and the energy. An extensive state quantity of a heterogeneous system is **additively** composed of the corresponding extensive properties of the single phases. Thus, the volume of a pot containing water steam and air is the sum of the volumes of the fluid and gaseous phases. The most characteristic extensive state quantity for thermodynamics is, as we shall see, the entropy.

b. Intensive state quantities

These quantities are independent of the amount of matter and are not additive for the particular phases of the system. They can assume different values in different phases. Examples are : refractive index, density, pressure, temperature, etc. Typically, intensive quantities can be defined locally, that is, they can vary spatially. For example, consider the density of the atmosphere, which is largest at the surface of the earth and continuously decreases with height, or the water pressure in the ocean, which increases with increasing depth.

One can easily move from extensive to intensive state quantities where both essentially describe very similar physical properties.

For example, energy, volume and particle number are extensive state quantities, while energy per unit volume (energy density)or energy per particle, are intensive state quantities.

1 - Energy in Thermal Physics

1.1 Thermal Equilibrium

Temperature is a state quantity which is unknown in mechanics and electrodynamics.

It is specially introduced in thermodynamics and its definition is closely connected with concept of thermal equilibrium.

Operational definitions:

> **Temperature is what you measure with a thermometer.**
>
> **Temperature is the thing that is the same for two systems (objects) after they have been in contact long enough.**

These simple sounding definitions are more complicated than they sound.

They are vague and contain many ill-defined quantities.

This first definition says that can precisely define notion of temperature by specifying how and in which units temperature is measured.

Equality of temperature of two bodies is condition for thermal equilibrium between these bodies.

Important because **thermodynamic state quantities are defined and measurable only in equilibrium.**

Define **equilibrium state** as one macroscopic state of closed system to which system evolves after sufficiently long period of time; in equilibrium state, state quantities no longer change with time.

Restrict our considerations to situations where existence of an equilibrium state is obvious.

Often reasonable to speak of thermodynamic equilibrium even if state quantities still change very slowly.

For example, our sun is by no means in an equilibrium state (it continuously loses energy through radiation).

Nevertheless, application of thermodynamic state quantities makes sense in this case because changes proceed very slowly.

So-called "quasi-stationary" system is effectively in an equilibrium state for a reasonable length of time and thermodynamics can be applied during that period.

Suppose that, in an isolated system, bring two subsystems, each previously in equilibrium, into thermal contact(no exchange of matter) with each other.

Then, one observes, in general, various processes associated with a change of state quantities, until after a sufficiently long time a new equilibrium state is attained.

One calls this new state **thermal equilibrium.**

Experiment shows that all systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other.

Use this empirical fact as foundation of definition of temperature and therefore, important enough to call it **zeroth law of thermodynamics.**

Therefore, systems in thermal equilibrium with each other have common intensive property, which denote as **temperature** and systems not in equilibrium with each other will have different temperatures.

Measurement of temperature is done as follows:

System whose thermal equilibrium state is uniquely connected with an easily observable state quantity, that is, **a thermometer**, is brought into thermal equilibrium with system whose temperature is to be measured.

State quantity to be observed can be, for example, volume of a fluid (fluid thermometer) or volume of a gas (gas thermometer) or resistance of certain conducting material(resistance thermometer).

Not necessary to put measuring apparatus (thermometer) in direct contact with system (in thermal equilibrium).

For example, surface temperature of sun or temperature of a flame can be determined by measuring spectrum(distribution of power or intensity as a function of wavelength or frequency) of emitted electromagnetic radiation.

Only assumption, in this case, is that local thermal equilibrium(at source of radiation) is not disturbed in any major way by emission processes.

Clearly, procedure of measuring temperature is connected with an equation of state, that is, relationship between observed state quantity (volume, resistance, etc) and temperature.

Experiment indicates that when two objects are able to exchange energy (there are many forms of energy as we shall see) and energy is able to move spontaneously from one object to the other, define object giving energy to be at "higher" temperature and object that absorbing energy to be at "lower" temperature.

Stating this formally, have restatement of theoretical definition of temperature

> **Temperature is a measure of the tendency of an object to spontaneously give up energy to it surroundings. When two objects are in thermal contact, the one that tends to spontaneously lose energy is at the higher temperature.**

To fix a general temperature scale, have to choose a **standard system.**

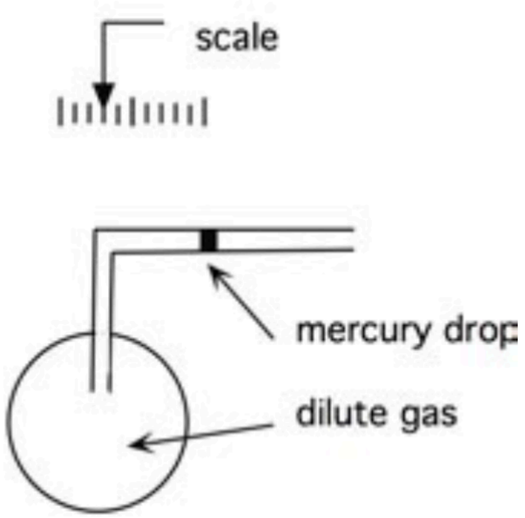
In particular, exploit fact that many different gases behave similarly if dilute (have low density).

Can use volume of certain definite amount of such gas (at certain nonvanishing pressure) as measure of temperature and then calibrate other thermometers accordingly.

Suppose define thermodynamic temperature T with help of volume of such a dilute gas as

$$T = T_0 \frac{V}{V_0} \tag{01.01}$$

at constant pressure and constant particle number as shown in figure.



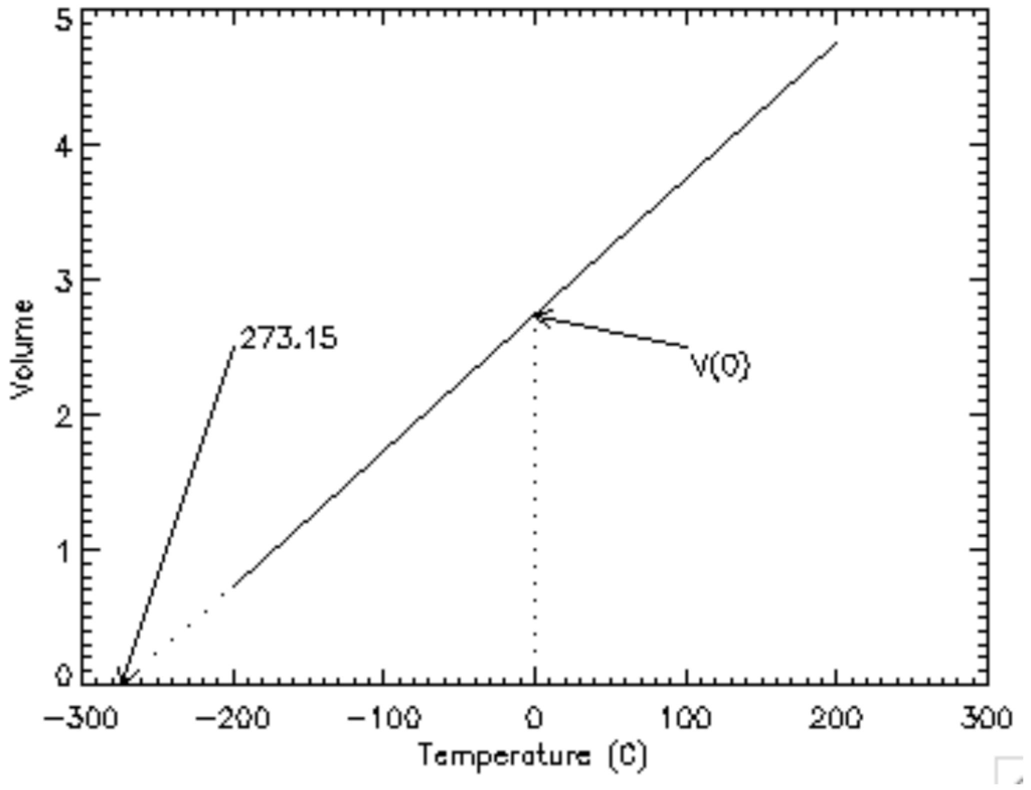
Gas Thermometer

Note that open end of tube means have atmospheric pressure and plug means have constant particle number.

By defining particular temperature T_0 for standard volume V_0 (e.g., at pressure of one atmosphere) can fix scale.

Today one takes melting point of ice as $T = 273.15K$, where unit K is "kelvin".

If plot volume of dilute gas versus temperature in $^\circ C$, find crossing point with abscissa at temperature $-273.15^\circ C$ as shown in figure below.



VT diagram of a dilute gas

Of course, one cannot experimentally measure volume of a gas at very low temperatures, since will liquefy, but one can extrapolate to crossing point.

Therefore, have constructed an idealized system (an ideal gas), volume of which is just $V = 0\, m^3$ at absolute temperature (which we just call temperature from now on) $T = 0\, K$.

At first sight, may seem impractical to use such an idealized system, which can never serve as a real thermometer (at low temperatures) to define unit.

From statistical point of view, however, will see that this notion of temperature yields very simple relationships in kinetic theory of gases.

For example, will see that absolute temperature defined here is directly proportional to average kinetic energy of gas particles.

In particular, observe that there are no negative absolute temperatures in thermodynamic equilibrium, since if all particles are at rest (zero kinetic energy), average energy is zero and thus, temperature is also zero.

Of great importance to separate notion of **equilibrium** from that of a **stationary state.**

In **stationary state** macroscopic state quantities are also **independent of time**, but these states are always connected with an energy flux, which is not case for equilibrium states.

For example, let consider an electric hot plate. If put a pot with meal on top to it, after some time a stationary state will be attained where temperature of meal will not change any longer.

This, however, is not a state of thermal equilibrium as long as surroundings have different temperature.

One must continuously supply system with (electrical) energy to prevent cooling of the dish, which continuously radiates energy (heat) into surroundings.

System is not isolated, since energy is supplied as well as emitted.

1.2 The Ideal Gas

To illustrate basic concepts of thermodynamics, consider an ideal gas in greater detail.

Such an ideal gas is characterized by fact that particles are considered (as in classical mechanics) to be noninteracting, pointlike particles.

Obvious that this is simple model of real gas, particles of which have atomic dimensions and do interact.

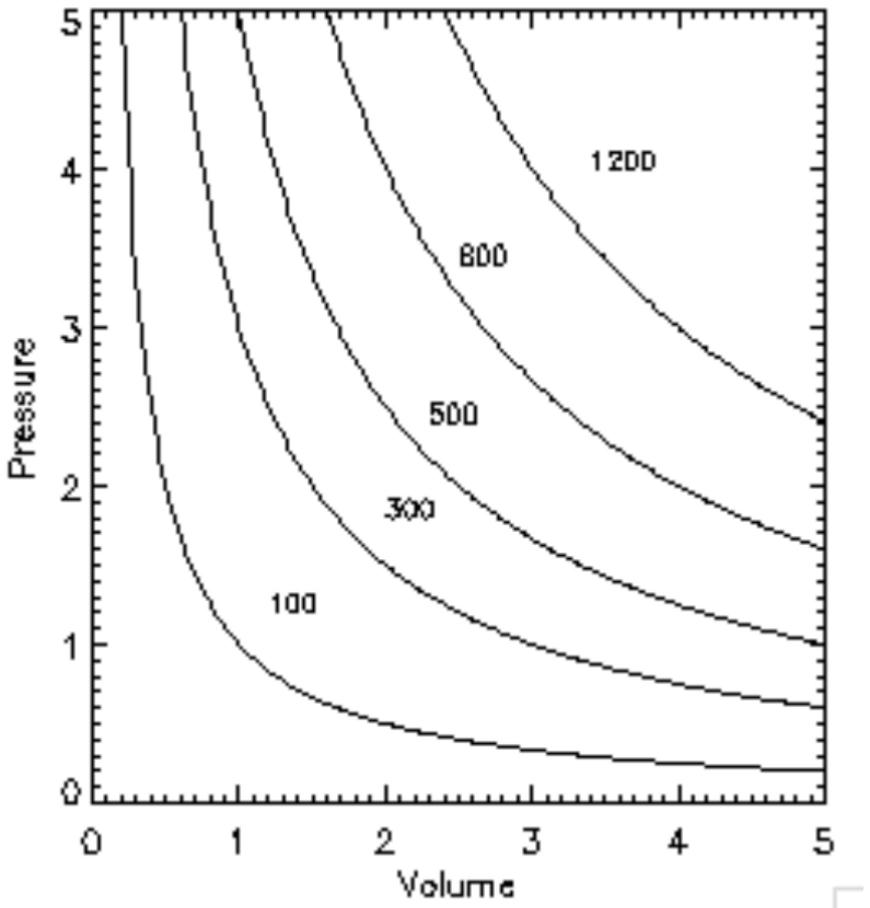
Approximation is better the more dilute the gas.

General relationship between pressure and volume of gas at constant temperature (see the figure at right) is given by

$$pV = p_0 V_0 \quad , \quad T = \text{constant} \qquad \text{(hyperbola)}$$

$p_0 V_0$ depends on T

where define pressure as force per unit area which acts on walls of container.



PV diagram for an ideal gas

Microscopically, origin of pressure is fact that particles hit walls, where are reflected and transfer momentum.

Can also consider dependence of volume on temperature.

Corresponding equation is identical with definition of absolute temperature, namely,

$$V = V_0 \frac{T}{T_0} \quad , \quad p = \text{constant}$$

Quantities p_0, V_0, and T_0 are pressure, volume and temperature of an arbitrary fixed state (reference state).

Now determine relationship that holds between pressure, volume and temperature if move from state (p_0, V_0, T_0) to final state (p, V, T).

First change pressure at constant temperature until we reach the desired pressure p, where a volume V_0' is attained

$$pV_0' = p_0 V_0 \quad , \quad T_0 = \text{constant}$$

Now change temperature at constant pressure to obtain

$$V = V_0' \frac{T}{T_0} \quad , \quad p = \text{constant}$$

If eliminate intermediate volume V_0' from both equations we have

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0} = \text{constant}$$

Since expression $\frac{pV}{T}$ is an extensive quantity it must, under same conditions, increase proportional to particle number, that is, it must equal kN, where we introduce Boltzmann's constant of proportionality $k = 1.380658 \times 10^{-23}\ J \cdot K^{-1}$.

We then obtain $$\frac{pV}{T} = \frac{p_0 V_0}{T_0} = Nk \rightarrow pV = NkT \text{ or } p = \rho kT \qquad (01.02)$$

This is **ideal gas law.**

Also an example of equation of state where pressure is proportional to product of particle density $\rho = N / V$ and temperature.

Example: The Exponential Atmosphere

Kinetic Theory of Ideal Gas

Now show that temperature of ideal gas(as defined above) can be understood as average kinetic energy of particles in gas.

Each particle of gas has velocity vector $\vec{v}$ which will be changing with time.

Although individual particles change their velocities, in an equilibrium state, on average, there will always be **same number** of particles in certain interval(volume) $d^3\vec{v} = dv_x\, dv_y\, dv_z$ in velocity space.

That is **real meaning** of term **equilibrium state.**

Therefore, makes sense to ask for probability that particle is in interval $d^3\vec{v}$, that is, to speak of a **velocity distribution** in the gas which does not change with time in thermodynamic equilibrium (although individual particles are still changing).

Do not need to know its exact form.

Sufficient at this point to know that such a distribution exists.

Write $dN(\vec{v})$ for number of particles in velocity interval (volume) $d^3\vec{v}$ **centered around** velocity value $\vec{v}$. Then have

$$dN = Nf(\vec{v})d^3\vec{v} \quad , \quad f(\vec{v}) = \frac{1}{N}\frac{dN}{d^3\vec{v}} \tag{01.03}$$

where $f(\vec{v})$ is velocity distribution(probability) function (this is basically a **definition** of $f(\vec{v})$).

Since every particle has some velocity value, must have

$$\int_{-\infty}^{\infty} f(\vec{v})d\vec{v} = 1$$

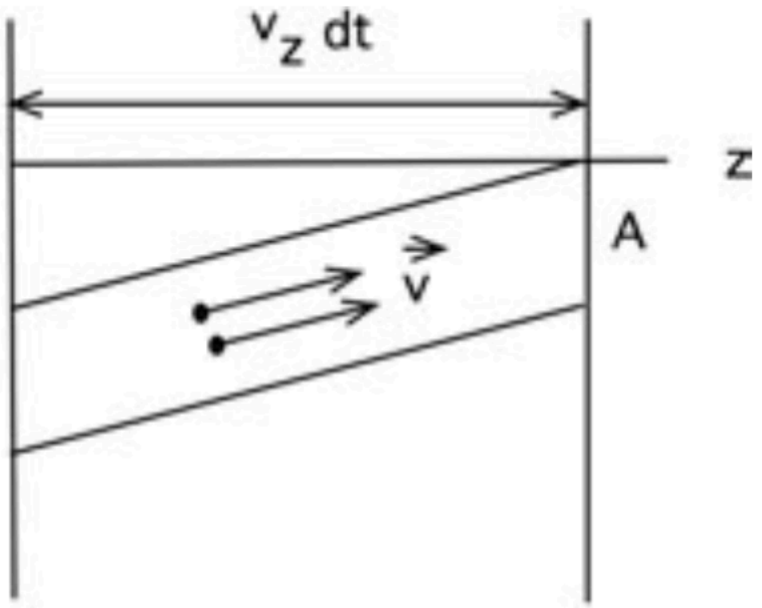
that is, probability for particle to have **some** velocity equals unity(only way to make physical sense).

As mentioned earlier, pressure of gas originates from momentum transfer by particles when they are reflected at some surface A (corresponding to walls of container).

If assume the z-axis of our coordinate system is perpendicular to wall area A, a particle of velocity $\vec{v}$ which hits that area transfers (elastic collision) momentum $p = 2mv_z$.

Now question is, how many such particles with velocity vector $\vec{v}$ hit surface area A during time dt?

As one can see from figure below answer is just particles inside parallelepiped with base area A and height $v_z\,dt$, that is,



Scheme for calculating the pressure

all particles with velocity $\vec{v}$ travel distance $d\vec{r} = \vec{v}dt$ during time dt and therefore hit surface if they are anywhere inside parallelepiped at beginning of time interval.

On other hand, number of particles with velocity $\vec{v}$ inside parallelepiped is just

$$dN = N\frac{dV}{V}f(\vec{v})d^3\vec{v} \qquad (01.04)$$

if dV/V is fraction of total volume occupied by parallelepiped, where $dV = Av_Z dt$.

Each particle transfers momentum $2mv_Z$, so that impulse per area A is

$$dF_A dt = 2mv_z dN = 2Nv_z^2 f(\vec{v})d^3\vec{v}\,\frac{Adt}{V} \qquad (01.05)$$

where dF_A is "force" on A due to this volume.

Canceling dt on both sides, this is just contribution of particles with velocity $\vec{v}$ to pressure.

Then calculate total pressure by integrating over all possible velocities with a positive component v_Z (since otherwise particles move in opposite direction and do not hit wall).

Therefore,

$$p = \frac{1}{A}\int_{v_z>0} dF_A = \frac{N}{V}\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{0}^{\infty} dv_z f(\vec{v}) 2mv_z^2 \qquad (01.06)$$

Since, on average, gas is at rest, that is, average values of velocity components are equal to zero, $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$ and distribution $f(\vec{v})$ cannot depend on direction of $\vec{v}$, but only on its magnitude $|\vec{v}|$, then can write integral $\int_0^\infty dv_z$ as $\frac{1}{2}\int_{-\infty}^\infty dv_z$ and thus obtain

$$pV = mN\int_{-\infty}^{\infty} d^3v f(\vec{v}) v_z^2 \qquad (01.07)$$

Integral corresponds to mean (or average) value of square of velocity in direction perpendicular to surface.

This mean value has to be same in all spatial directions because gas is isotropic (independent of direction), that is,

$$\int d^3\vec{v} f(\vec{v}) v_z^2 = \langle v_z^2 \rangle = \langle v_x^2 \rangle = \langle v_y^2 \rangle \tag{01.08}$$

or since $v^2 = v_x^2 + v_y^2 + v_z^2$,

$$\langle v_z^2 \rangle = \frac{1}{3} \langle \vec{v}^2 \rangle = \frac{1}{3} \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right) \tag{01.09}$$

so that end up with result

$$pV = mN \frac{1}{3} \langle \vec{v}^2 \rangle = \frac{2}{3} N \langle \varepsilon_{kinetic} \rangle \tag{01.10}$$

where

$$\langle \varepsilon_{kinetic} \rangle = \frac{1}{2} m \langle \vec{v}^2 \rangle$$

is mean kinetic energy of **a particle.**

If compare this with ideal gas law eq (01.02) have

$$\langle \varepsilon_{kinetic} \rangle = \frac{3}{2} kT \tag{01.11}$$

that is, quantity kT is measure of mean kinetic energy of a particle in an ideal gas and get ideal gas law back!

Maxwell's velocity distribution

Now determine form of velocity distribution(probability) function in detail.

Because of isotropic nature of gas, $f(\vec{v})$ can only be function of $|\vec{v}|$ or equivalently v^2.

Can also assume that velocity distributions of single components (v_x, v_y, v_z) are independent of each other, that is, must have

$$f(v^2) = f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)f(v_y^2)f(v_z^2) \tag{01.12}$$

Can justify this assumption and equation in following way.

Function $f(\vec{v})$ corresponds to probability density of finding particle with velocity $\vec{v}$.

This, however, has to be proportional to probability densities of finding particle at v_x, v_y and v_z, as long as these are statistically independent events.

Only mathematical function which satisfies eq (01.12) is the exponential function, so that we can write $f(\vec{v}^2) = Ce^{a\vec{v}^2}$, where C is a constant and a cannot depend on $\vec{v}$, but is otherwise arbitrary.

If assume that function $f(\vec{v})$ is normalizable (see below), must have $a < 0$, which corresponds to a **Gaussian** distribution of velocity components.

Constant C is determined by normalization of function $f(v_i)$ for each component,

$$1 = \int_{-\infty}^{\infty} f(v_i) dv_i = C \int_{-\infty}^{\infty} e^{-av_i^2} dv_i = C\sqrt{\frac{\pi}{a}} \rightarrow C = \sqrt{\frac{a}{\pi}}$$

where have now written $-a$ with $a > 0$.

Can then calculate constant a for an ideal gas.

From (01.11) we have

$$\langle E_{kinetic} \rangle = \frac{3}{2} kT = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} m \langle v_z^2 \rangle$$

Since $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ this says that

$$kT = m\langle v_z^2 \rangle = m\int v_z^2 f(\vec{v}) d^3\vec{v} = m\int_{-\infty}^{\infty} f(v_x) dv_x \int_{-\infty}^{\infty} f(v_y) dv_y \int_{-\infty}^{\infty} v_z^2 f(v_z) dv_z$$

$$= m\int_{-\infty}^{\infty} v_z^2 f(v_z) dv_z = m\sqrt{\frac{a}{\pi}} \int_{-\infty}^{\infty} v_z^2 e^{-av_z^2} dv_z = 2m\sqrt{\frac{a}{\pi}} \int_{0}^{\infty} v_z^2 e^{-av_z^2} dv_z$$

If substitute

$$x = av_z^2 \rightarrow dv_z = \frac{1}{2\sqrt{a}}\frac{dx}{\sqrt{x}}$$

have

$$kT = 2m\sqrt{\frac{a}{\pi}}\frac{1}{2\sqrt{a}}\int_0^\infty \sqrt{x}e^{-x}dx$$

Now,

$$\Gamma(z) = Gamma\ Function = \int_0^\infty x^{z-1}e^{-x}dx$$

with properties

$$\Gamma(1/2) = \sqrt{\pi}\ , \Gamma(1) = 1$$

$$\Gamma(z+1) = z\Gamma(z)$$

$$\Gamma(3/2) = (1/2)\Gamma(1/2) = \sqrt{\pi}/2, etc$$

Then have

$$kT = 2m\sqrt{\frac{a}{\pi}}\frac{1}{2\sqrt{a}}\Gamma(3/2) = \frac{m}{2a} \rightarrow a = \frac{m}{2kT}$$

and

$$f(v_i) = Ce^{av_i^2} = \sqrt{\frac{m}{2\pi kT}}e^{-\frac{mv_i^2}{2kT}} \tag{01.13}$$

$$f(\vec{v}) = C^3e^{a\vec{v}^2} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\vec{v}^2}{2kT}} \tag{01.14}$$

Thus, have determined velocity distribution function.

Example: If you poke a hole

1.3 Equipartition of Energy

Equation $$\langle \varepsilon_{kinetic} \rangle = \frac{3}{2}kT$$

is special case of more general result called **equipartition theorem.**

Relation involves **translational kinetic energy** – equipartition theorem involves **all forms of energy.**

Total translational kinetic energy contains three (because of three spatial dimensions) terms each a quadratic function of velocity.

Every energy term of this form represents **degree of freedom** of system.

Other degrees of freedom include rotational motion, vibrational motion, etc.

All of these forms are quadratic functions, that is,

$$\frac{1}{2}mv_x^2, \frac{1}{2}mv_y^2, \frac{1}{2}mv_z^2, \frac{1}{2}I\omega_x^2, \frac{1}{2}I\omega_y^2, \frac{1}{2}kx^2, etc$$

Equipartition theorem says that for each such degree of freedom contribution to average energy is $\frac{1}{2}kT$.

Therefore, if system contains N objects each with f degrees of freedom, then total thermal energy is

$$U_{thermal} = \frac{1}{2}NfkT \tag{01.15}$$

Note, as shall see in our discussions, that there are other forms of energy contributing to total energy of system.

Equipartition theorem applies **only** to forms of energy that change with temperature.

1.4 Heat and Work

Pressure, Work and Chemical Potential

Now want to discuss several other state quantities.

In general, measure **amounts of matter** in terms of particle number N.

Since N assumes very large value for macroscopic systems, will often use multiples of **Avogadro's number** $N_A = 6.0221367 \times 10^{23}$.

Atomic mass unit u is especially convenient for measuring masses of single particles (atoms and molecules).

Defined by

$$1\,u = \frac{1}{12} m_{^{12}C} \tag{01.16}$$

that is, in terms of mass of one atom of carbon isotope ^{12}C.

Avogadro's number is just number of particles each with mass $1\,u$ whose total mass is $1\,gm$ so that

$$N_A = \frac{1\,gm}{1\,u} = 6.0221367 \times 10^{23} \tag{01.17}$$

Quantity N_A particles is also called $1\,mole$ of particles.

If system consists of several kinds of particles, for instance N_1, N_2, ... , N_n particles of n different species, so-called **molar fraction** X is convenient quantity for measuring chemical constitution

$$X_i = \frac{N_i}{N_1 + N_2 + \ldots\ldots + N_n} \tag{01.18}$$

Clearly have $\sum_i X_i = 1$.

Molar fraction therefore denotes fractional makeup of a system.

It is an intensive variable and can assume different values in different phases.

Pressure can be understood in purely mechanical terms as force which acts perpendicular to known area A

$$p = \frac{F_{\perp A}}{A} \qquad (01.19)$$

Therefore have units $N \cdot m^{-2} = Pa = Pascal$.

Interestingly enough, pressure has same dimensions as energy density

$$N \cdot m^{-2} = kg \cdot m \cdot s^{-2} \cdot m^{-2} = J \cdot m^{-3}$$

For many systems will find that pressure related to energy density in very simple way.

For ideal gas pressure is the product of particle density and kinetic energy of particles, that is, temperature. Therefore, $p = \frac{2}{3}e$, where $e = \rho(E_{kinetic})$ is (kinetic)energy density of ideal gas.

Similar to temperature, pressure can be measured locally, that is, in a small part of system.

Central quantity in thermodynamics (and physics in general) is energy.

In thermodynamics, only total energy of system, which is macroscopic quantity, plays role.

Although, energy of single particle has no meaning, **mean** energy per particle E/N is very important.

Thermodynamics does not, however, tell us how total energy is distributed over individual particles.

As an example of forms of energy mentioned above use concept of work for our discussion in many thermodynamic systems.

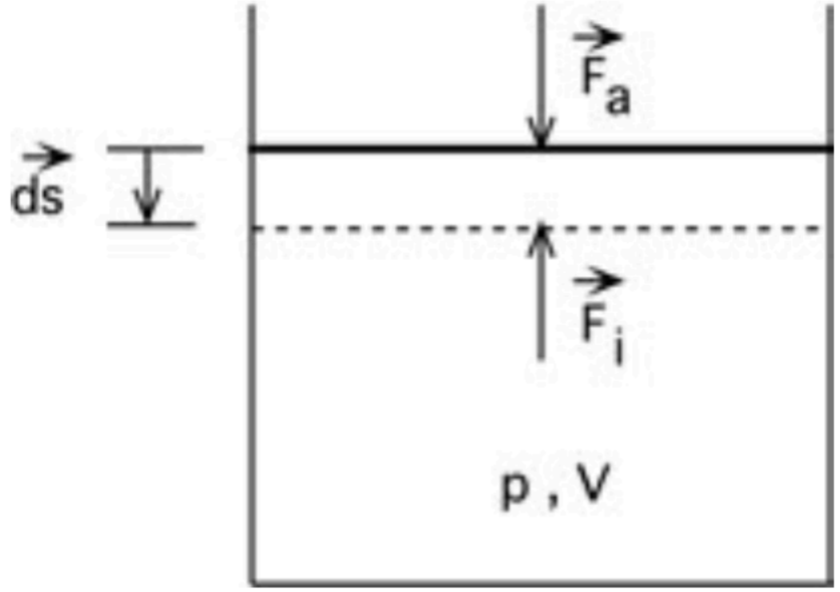
In particular, have

$$W = -\vec{F}_i \cdot d\vec{s} \tag{01.20}$$

where $\vec{F}_i$ is force exerted by system and $d\vec{s}$ is a small displacement.

Minus sign in eq (01.20) is purely a convention in thermodynamics - count energy which is added to system as positive and energy which is subtracted from system as negative.

For example, for work performed on a system consider compression of a gas against its internal pressure as in the figure below.



Concerning the compressional work

In equilibrium, external force $\vec{F}_a$ is just equal(and opposite) to force exerted by system $\vec{F}_i$, where $F_i = pA$, which is exerted by pressure p on a piston with area A.

If one pushes piston a distance $d\vec{s}$ further into volume against force exerted by system, amount of work is

$$W = pAds > 0 \tag{01.21}$$

since $d\vec{s}$ and $\vec{F}_i$ point in opposite directions.

Now $Ads = -dV$ is decrease in gas volume $dV < 0$ in container and therefore have

$$W = -pdV \tag{01.22}$$

Clearly, this equation also holds for an expansion.

Note that can only consider an infinitesimal amount of work since pressure changes during compression.

To calculate total compressional work need equation of state $p(V)$ and must integrate as shall see.

It is general property of energy added to or subtracted from a system that it is product of an intensive state quantity (pressure) and change of an extensive state quantity (volume).

Now consider work necessary to **add another particle** to a thermodynamic system.

One might think that this does not require any work at all, but this is not case.

System must maintain equilibrium after adding particle.

Therefore, cannot simply put particle at rest into system.

Rather, has to have certain energy that is comparable to mean energy of all other particles.

Define

$$W = \mu dN \tag{01.23}$$

as work necessary to change particle number by dN particles.

Intensive field quantity μ is called **chemical potential** and represents resistance of system to adding particles.

If system consists of several particle species, each species has own chemical potential μ_i,and dN_i is change in particle number of species i.

Will be valid as long as particle species do not interact with each other.

All different kinds of work have generic property that they can be converted into each other without restrictions.

For example, can lift weight with electrical energy or gain electrical energy from mechanical work with help of a generator.

No a priori reason that conversion cannot proceed completely, that is, with rate of 100%, although real energy converters always have losses.

Heat and Heat Capacity

Situation completely different with another kind of energy of principle importance in thermodynamics, namely, **heat**.

Heat is defined as any spontaneous flow of energy from one object to another caused by difference in temperature between objects.

Say that heat "flows" from hotter object to colder object.

All other forms of energy transfer between systems is included in some form of **work**.

Note that both heat and work refer to energy flow.

Can define total energy in system, but is meaningless to ask about amount of heat or work in system.

Can only talk about amount of heat or work that has entered or left a system.

Realized early in study of thermodynamics that heat is form of energy.

An experimental result that work(of mechanical or electrical origin) performed on system often increases temperature and can use this property to define amount of heat.

Therefore define

$$Q = CdT \tag{01.24}$$

Q = small amount of heat which causes temperature increase dT for system.

Constant of proportionality C called **total heat capacity** of system.

To fix unit for C have to define standard system.

Originally, had thermochemical **calorie** as unit of heat.

Amount of heat that warms 1 gram of water from $14.5°C$ to $15.5°C$.
This corresponds to the definition $C_{1gH_2O,15^oC} = 1\,cal/°C$.

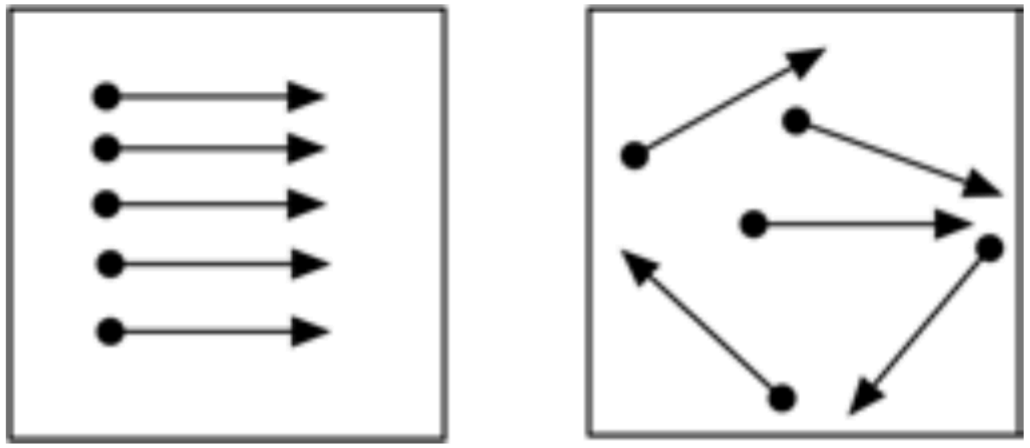
By precise measurements Joule determined the exact amount of mechanical work done on an isolated container of water and measured corresponding increase in temperature --> 1 cal of heat equivalent to 4.184 Joules of mechanical work.

Nowadays, one produces defined amount of heat using an electrical resistance heater. SI(MKS) unit for heat capacity is $J/K = Joule/K$.

Principle qualitative difference between work and heat is simply explained in microscopic picture.

According to picture, heat is energy which is statistically(or randomly) distributed over all particles.

For example, consider particles with parallel (ordered) momenta, as in figure, which move in one direction.



Particles with
(a) parallel and (b) statistically
distributed momenta

Kinetic energy of particles can be completely regained at any moment and can be converted into other forms of energy, for example, by decelerating particles using a force.

However, if particles move in completely disordered and statistical or random manner, not possible to extract all of kinetic energy by such a simple device.

For example, if exert force on particles like those in figure(b) above, some particles would be decelerated and others would be accelerated, so cannot extract total kinetic energy from system.

Simpler to change work into heat, which practically always happens by itself, than to gain useful work from heat.

Here again, exceedingly large number of particles in macroscopic systems plays an important role.

For example, possible to create, under certain circumstances, an appropriate (space-dependent) force field for few particles in figure(b), with property that it decelerates all of particles, while particles transfer their kinetic energy to creating mechanism of field.

However, for 10^{23} particles this is **unimaginable**, and in so-called thermodynamic limit $N \to \infty$ it is **impossible**.

At this point, return once more to heat capacity defined in connection with equation (01.24).

Clearly, amount of heat Q is an extensive quantity, therefore total heat capacity must also be an extensive quantity, since temperature is an intensive variable.

One can, however, define an intensive quantity, specific heat c as

$$C = mc \tag{01.25}$$

where m is mass of substance.

Possible to define specific heat on a molar basis, $C = nc_{mol}$ with $n = N / N_A$.

Quantity c_{mol} is **molar specific heat.**

Must take into account fact that heat capacity may depend on external conditions under which heat is transferred to system.

Matters whether measurement performed at constant pressure or at constant volume.

One writes c_V and c_p for specific heats at constant volume and constant pressure, respectively.

Note at this point that definition $c_{H_2O} = 4.184\ J/K \cdot g$ holds at constant atmospheric pressure.

Specific Heat

Now continue discussion of specific heat.

As said earlier, specific heat depends on external conditions under which amount of heat is transferred to system.

If happens at constant pressure(for example, atmospheric pressure) obtain c_p, while c_V is measured at constant volume.

Specific heats c_V as well as c_p considered functions of state variables T and p, which are easiest to control experimentally.

For most dilute gases $(where\ \rho \to 0)$, specific heats are approximately independent of pressure and for the rare gases also approximately independent of the temperature.

If interpret specific heat as ability of substance to absorb energy in statistically(randomly) distributed way, becomes clear that this ability increases with number of **degrees of freedom** of particle(or number of **coordinates** needed to describe particle), that is, there are more ways (places to put) to distribute energy.

For example, particles in monatomic rare gases only have possibility of translational motion, while particles in diatomic gases also able to rotate.

If add certain amount of heat Q to system at constant pressure, system will not only heat up, but, in general, also will expand, and, thus, will do work against external pressure (atmospheric pressure).

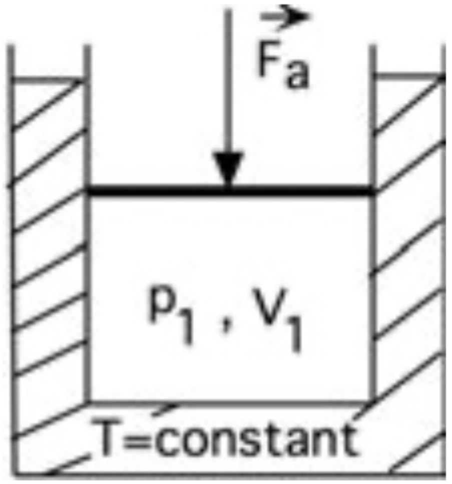
Amount of heat added is therefore not only stored in gas in form of statistically distributed kinetic and potential energy, but is also required to do work against external pressure.

Thus, system can, in general, store larger amount of heat at constant pressure than at constant volume (no work done) so that find, in general, $c_p > c_V$.

Specific heat is of great importance in thermodynamics since is easy to measure and can be used to calculate many other properties.

1.5 Isothermal Expansion

Consider expansion of gas at constant temperature (**isothermal expansion**) as shown in figure below.



Isothermal System

As shown, constant temperature is practically realized by **heat bath**, that is, by large vessel with water at temperature T, which is in contact with system and is in **thermal equilibrium** with system(have **same** temperature).

Can accomplish isothermal expansion of gas from volume V_1 to volume V_2 by removing external force which acts on piston and maintains equilibrium.

Thus, gas will rapidly expand up to volume V_2.

During rapid expansion process, local pressure differences, turbulence and temperature and density gradients will occur.

Process happens by itself and would never reverse itself.

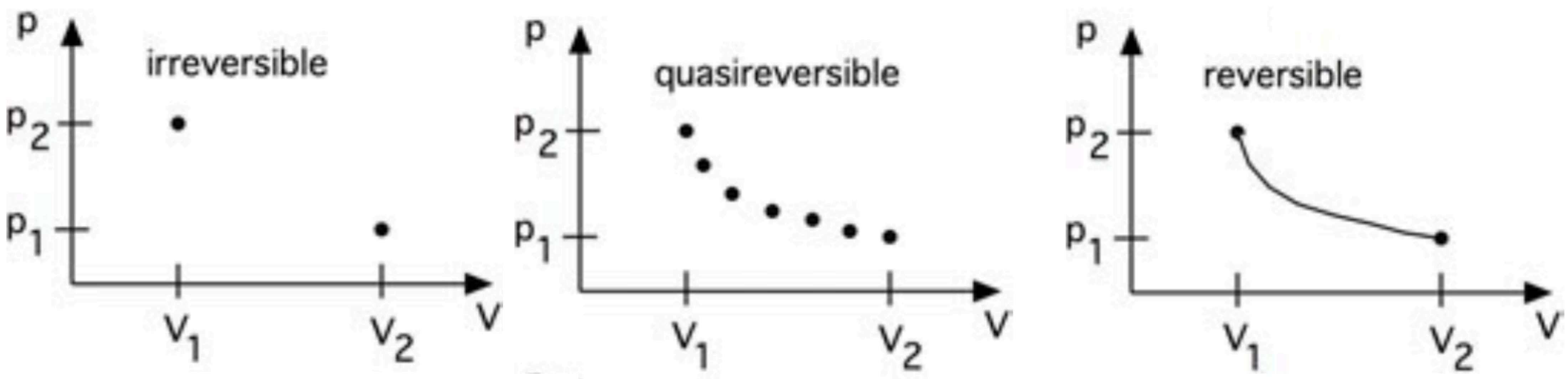
Therefore, it is irreversible.

During expansion, cannot assign values to macroscopic state quantities.

Can do this only after equilibrium state reestablished at volume V_2.

Work done by expansion of system is zero as long as one uses an ideal massless piston.

This process is illustrated in the left figure below.



Different ways to perform a process

Note only two points are labelled for irreversible process since these represent only states that are equilibrium states where can assign values to state variables.

Can also perform isothermal expansion reversibly, or at least quasi-reversibly, if decrease force at each step by only an infinitesimal amount and wait for system to come to a new equilibrium state (middle figure).

Length of waiting period depends on relaxation time of system.

Major differences from irreversible(isothermal) expansion are that in this case thermodynamic variables have definite values for each intermediate step (each intermediate equilibrium state) and that equation of state is applicable in each intermediate equilibrium state.

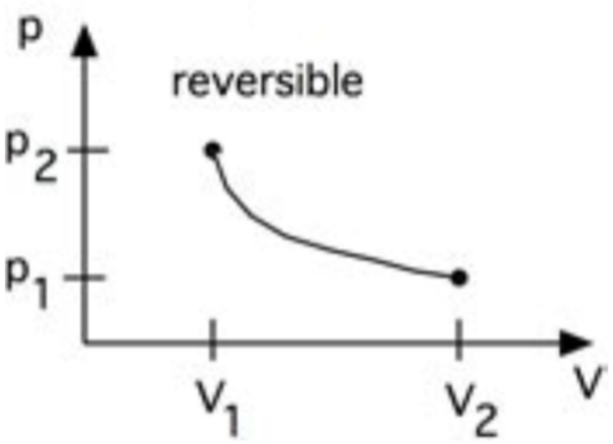
If consider an ideal gas for our system, have equation of state

$$p = \frac{NkT}{V} \qquad (01.26)$$

and can calculate total amount of work done in expansion of system,

$$W_{21} = -\int_{V_1}^{V_2} p\,dV = -NkT\int_{V_1}^{V_2} \frac{dV}{V} = -NkT\,\ell n\frac{V_2}{V_1} \qquad (01.27)$$

Since all intermediate states in reversible process are equilibrium state, all points on pV–isotherm representing process known and can draw continuous curve as shown in last part of figure.



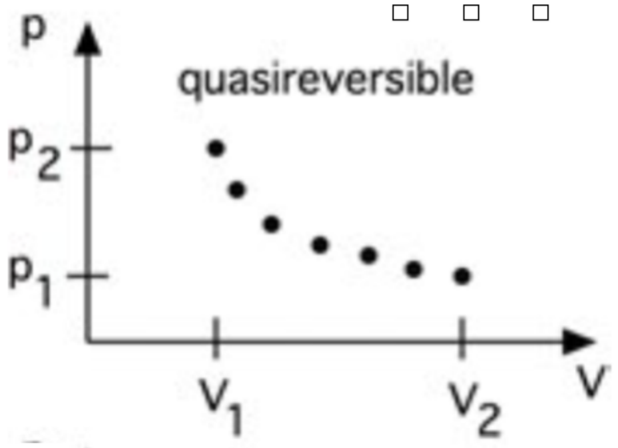
Contrary to irreversible expansion, system has now done work against external force $\vec{F}_a$.

Note that this reversible work of system is maximum work that can be extracted from system.

Real expansions, of course, lie between these two extreme cases of completely irreversible expansion $(W_{21} = 0)$ and completely reversible expansion

$$\left(W_{21} = -NkT \ell n \frac{V_2}{V_1} \right)$$

Illustrated by middle plot in figure where there exist intermediate equilibrium states but not a continuum.



Although initial and final states are identical for reversible and irreversible processes, work done(energy balance) is completely different.

Clearly, irreversible process wastes work.

Also case, however, if consider isothermal compression.

For reversible process need, in this case, the work

$$W_{12} = -\int_{V_2}^{V_1} pdV = -NkT\int_{V_2}^{V_1}\frac{dV}{V} = -NkT\ell n\frac{V_1}{V_2} = NkT\ell n\frac{V_2}{V_1} > 0 \qquad (01.28)$$

Here, assumed that in each step force on piston is only infinitesimally increased.

If instead push piston spontaneously with large effort, have to spend more work, which is consumed in turbulences and finally transferred to heat bath in form of heat.

First Law of Thermodynamics

In earlier discussion realized that heat is just another form of energy.

Heat is energy which is statistically (randomly) distributed among particles of system.

In physics, principle of conservation of energy is of fundamental importance and experiment supports assumption that this principle is correct in macroscopic as well as microscopic systems.

Therefore, in addition to work which is done by or on a system, have to also consider heat exchanged with surroundings.

Can assign an **internal energy** U to each macroscopic system.

For an isolated system which does not exchange work or heat with its surroundings, internal energy U is identical to total energy E of system, which is known from mechanics or electrodynamics.

However, if system able to exchange work or heat with its surroundings, an extended energy laws holds.

Change of internal energy for an arbitrary (reversible or irreversible) change of state is given by sum of the work W and the heat Q exchanged with surroundings.

Write **first law of thermodynamics** as:

$$dU = W + Q \tag{01.29}$$

Crucial to realize that work and heat exchanged with the surroundings in a small change of state may depend only on initial and final state of system.

Internal energy, however, is an exact differential.

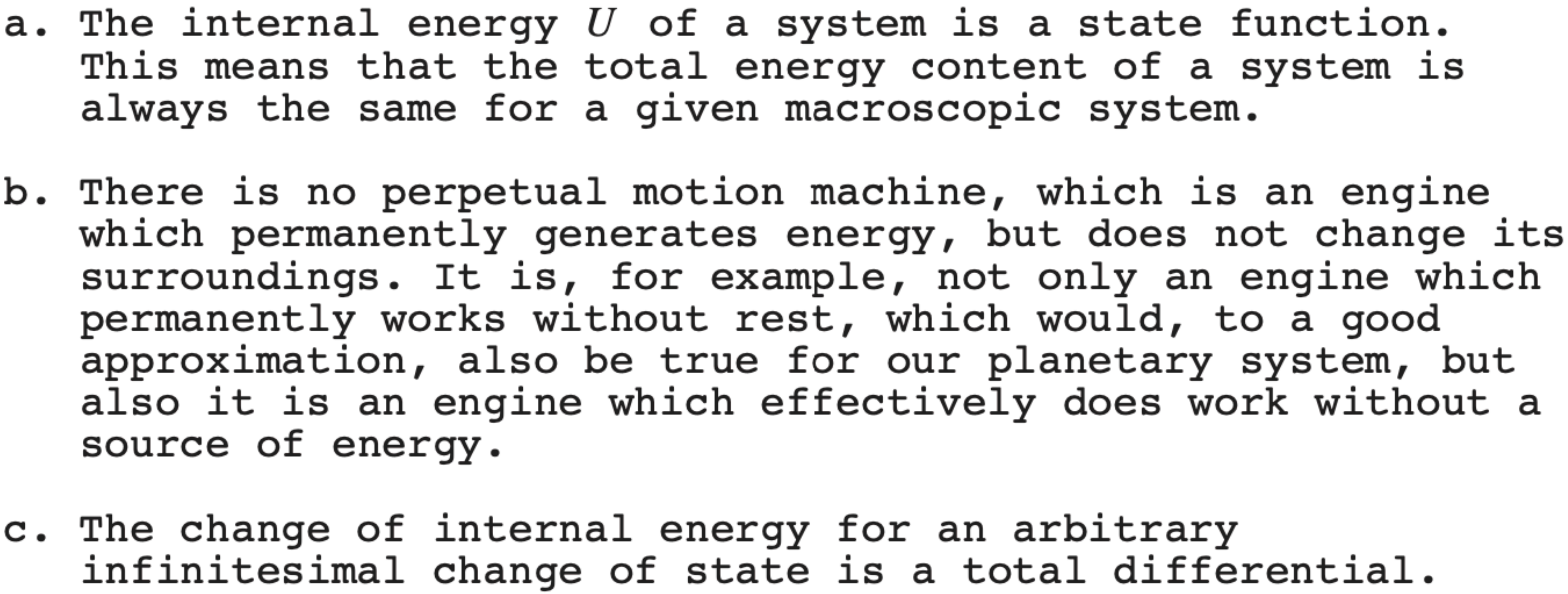
Note that work, for example, has form $W = -pdV$ only for reversible processes.

For irreversible processes it may be case that $W = 0$.

Same holds for exchanged heat, that is, $Q = C_V dT$ only valid for reversible processes, while equation (01.29) is **always true.**

Exist many formulations of first law of thermodynamics, which all have same meaning, namely, that in energy balance of system, exchanged work and heat together yield total change of energy of system.

Here are some of formulations of first law, which are all **equivalent:**



a. The internal energy *U* of a system is a state function. This means that the total energy content of a system is always the same for a given macroscopic system.

b. There is no perpetual motion machine, which is an engine which permanently generates energy, but does not change its surroundings. It is, for example, not only an engine which permanently works without rest, which would, to a good approximation, also be true for our planetary system, but also it is an engine which effectively does work without a source of energy.

c. The change of internal energy for an arbitrary infinitesimal change of state is a total differential.

Equivalence of the assertions (a) and (c) follows from our earlier discussions, that is, if dU is total differential, then exists state function U and vice versa.

Assertion (b) also equivalent to (c), that is, if (b) not true, then would be a working substance for a thermodynamic process where energy would always be generated, although after some time system return to its initial state.

This would contradict contour-independence of integrating a total differential.

Emphasize that energy law holds independently of procedure for reversible as well as for irreversible changes of state.

Internal Energy and Total Differential

As an example, calculate internal energy of ideal gas.

Already derived following results

$$pV = mN\frac{1}{3}\langle\vec{v}^2\rangle = \frac{2}{3}N\frac{1}{2}m\langle\vec{v}^2\rangle = \frac{2}{3}N\langle\varepsilon_{kinetic}\rangle$$

where $\langle\varepsilon_{kinetic}\rangle$ is mean kinetic energy per particle, and

$$\langle\varepsilon_{kinetic}\rangle = \frac{3}{2}kT \qquad \text{so that} \qquad pV = NkT$$

For ideal gas, particles possess only kinetic energy(no potential energy) and therefore $\langle \varepsilon_{kinetic} \rangle$ is total mean energy.

In statistical interpretation, however, internal energy is total mean energy of system, that is,

$$U = \langle E_{kin} \rangle = N \langle \varepsilon_{kin} \rangle = \frac{3}{2} NkT \tag{01.29}$$

Now determine specific heat of ideal gas.

Consider container with ideal gas at constant volume in heat bath of temperature T.

If temperature changed by dT, then have

$$dU = W + Q$$

Work exchanged with surroundings is

$$W = -pdV = 0$$

since $V=$ constant and thus $dV = 0$.

Note changes of state at constant volume called **isochoric** processes. Therefore, have

$$dU = Q = C_V(T)dT \tag{01.30}$$

where used heat capacity C_V at constant volume.

Note that Q can be integrated in this process.

For dilute gases, specific heat is approximately constant, so can easily do integral to get

$$U(T) - U_0(T_0) = C_V(T - T_0)$$

If consider that **total heat capacity** is proportional to particle number, that is, $C_V = Nc_v$, where c_v is constant **specific heat per particle of ideal gas**, get

$$U(T) - U_0(T_0) = Nc_V(T - T_0) \tag{01.31}$$

Comparing with (01.29) have

$$c_V = \frac{3}{2}k \Rightarrow C_V = \frac{3}{2}Nk$$

Results make clear real practical importance of specific heat.

With help of (01.30) can determine internal energy of real gases from their measured specific heat.

Quite generally, identify total heat capacity at constant volume with

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V$$

where have used standard definition of partial derivative.

This works out because (01.30) always holds for $V =$ constant.

Adiabatic Equations for Ideal Gas

Determine relationship between temperature and volume of ideal gas if there is no heat exchanged with surroundings in some process.

A process in which there is no heat exchange is called an **adiabatic** process.

According to first law, with $Q = 0$, and $W = -pdV$, have

$$dU = W = -pdV$$

for reversible adiabatic process.

If system is compressed by volume dV, that is, if work done on system, energy content of system increases by $dU = -pdV > 0$ since $dV < 0$.

From earlier

$$U = \frac{3}{2}NkT \qquad \text{and from} \qquad C_V = \left.\frac{\partial U}{\partial T}\right|_V$$

see that for ideal gas generally (for any process where $dV \neq 0$) holds that $dU = C_V(T)dT$.

Therefore, obtain relationship between dT and dV for adiabatic changes of volume of ideal gas

$$C_V(T)dT = -pdV$$

If use ideal gas law for $p(V,T)$ get

$$C_V(T)dT = -\frac{NkT}{V}dV \qquad (01.32)$$

This is a differential equation which describes the relationship between V and T for an adiabatic change of state.

Since $C_V =$ constant, we can integrate (01.32) by separation of variables from an initial state (T_0, V_0) to a final state (T,V),

$$\int_{T_0}^{T} \frac{C_V}{Nk} \frac{dT}{T} = -\int_{V_0}^{V} \frac{dV}{V} \Rightarrow \frac{C_V}{Nk} \ell n \frac{T}{T_0} = -\ell n \frac{V}{V_0}$$

If we use $C_V = \frac{3}{2} Nk$ and rearrange terms we get

$$\left(\frac{T}{T_0}\right)^{3/2} = \frac{V}{V_0} \qquad (01.33)$$

With the help of the ideal gas law we can also derive an equivalent relation between p and V or p and T, that is, for reversible adiabatic processes, we have

$$\left(\frac{T}{T_0}\right)^{5/2} = \frac{p}{p_0} \qquad \text{and} \qquad \left(\frac{V_0}{V}\right)^{5/3} = \frac{p}{p_0} \qquad (01.34)$$

Equations (01.33) and (01.34) are the adiabatic equations of an ideal gas.

Note that they differ logically from the ideal gas law, since here we have considered a specific process(an adiabatic process).

In the same way as for processes with constant temperature(isotherms), constant pressure(isobars), or constant volume(isochores) we can eliminate a variable of the ideal gas equation.

As we will see, for adiabatic, reversible processes another(new) state variable, the total entropy of the system, will be constant(**isoentropes**).

From (01.34) we have $pV^{5/3} =$ constant, the **adiabates**(or isoentropes) in a pV diagram are steeper (dp/dV) than the **isotherms** where the law of Boyle, $pV =$ constant holds.

Example: Put a few spoonfuls

Example: An ideal gas is made

Example: In the course of pumping

Example: In an earlier example we calculated

As we can see from this example, although the initial and final states are the same in both cases, the work done in the isothermal expansion depends on the way in which the process is carried out.

★

1.6 Some Mathematics

Next set of slides will be very mathematical for those of you that can follow - only results to be used later are important.

I present these mathematics to illustrate the power and encourage you to learn more mathematics.

Previous calculation is special case of general experimental result that work done in a process and heat transferred, not only depend on initial/final states of system,but also on way process is carried out.

Means that work and heat **cannot** describe a macroscopic state in a unique way.

They are **not** state quantities!

Mathematically, means work done and the heat transferred are not exact or total differentials.

Investigate this problem in detail shortly.

If consider state quantity as function of certain state variables (for example, T, p, etc), call state quantity a **state function.**

Experiment shows number of state variables which are necessary to uniquely determine state depends on possible **kinds** of energy which system can absorb or emit.

For many systems these are, for example, heat δQ and mechanical work δW_{mech}, as well as chemical energy δW_{chem}.

To any of these kinds of energy belongs a state variable, for example, T, V, and N, and sufficient to determine these three quantities to fix values of all other state quantities.

However, if system consists of various particle species, a separate particle number belongs to each particle species.

Discuss this problem in detail later when study thermodynamic laws and Gibbs' phase rule.

Now investigate some generic properties of state functions –- will restrict discussion to functions of two state variables, for example,

$$z = f(x,y) \tag{01.35}$$

Often impossible to solve an equation of state for a certain quantity and one has to be content with an implicit equation of form

$$f(x,y,z) = 0 \tag{01.36}$$

Characteristic of state quantities and hence of state functions that depend only on values of state variables, but not on way (on procedure) in which these values are assigned.

If change state variables by dx and dy with respect to initial values x and y, as done in reversible changes of state, then for change of z we have

$$dz = \left.\frac{\partial f(x,y)}{\partial x}\right|_y dx + \left.\frac{\partial f(x,y)}{\partial y}\right|_x dy \tag{01.37}$$

Common practice in thermodynamics to denote fixed variables in partial differentiation in form $|_x$ or $|_y$.

Always do this carefully since y and x are often not independent, but are related by laws of thermodynamics.

Exact and Inexact Differentials; Line Integrals

Start from function

$$z = f(x,y) \tag{01.38}$$

with differential

$$dz = \left.\frac{\partial f(x,y)}{\partial x}\right|_y dx + \left.\frac{\partial f(x,y)}{\partial y}\right|_x dy \tag{01.39}$$

Now introduce more general and mathematically convenient notation.

Equation (01.39) can be interpreted as **scalar product** of **gradient** of f with **vector**

$$\begin{pmatrix} dx \\ dy \end{pmatrix} = d\vec{x}$$

and can then be written in form

$$df(\vec{x}) = \nabla f(\vec{x}) \cdot d\vec{x} \qquad \nabla f = \frac{\partial f}{\partial x}\hat{\boldsymbol{i}} + \frac{\partial f}{\partial y}\hat{\boldsymbol{j}} + \frac{\partial f}{\partial z}\hat{\boldsymbol{k}} \tag{01.40}$$

Property of total differentials with importance in thermodynamics is that corresponding original function (state function) can be obtained, up to additive constant, via line integration along **arbitrary** curve.

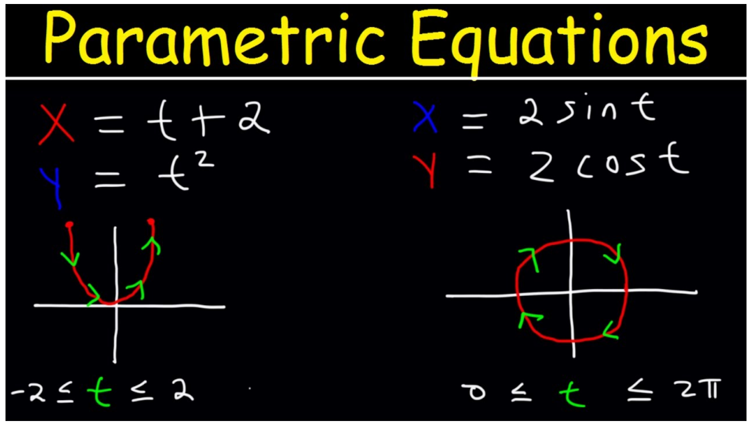
$$f(\vec{x}) - f_0(\vec{x}_0) = \int_C \nabla f(\vec{x}) \cdot d\vec{x} \tag{01.41}$$

Curve C leads from $\vec{x}_0 = \begin{pmatrix} x_0 \\ y_0 \end{pmatrix}$ to $\vec{x} = \begin{pmatrix} x \\ y \end{pmatrix}$.

If $\vec{x}(t)$ with $t \in [0,1]$ is parametric(t) representation of curve, explicit calculation done by

$$f(\vec{x}) - f_0(\vec{x}_0) = \int_0^1 dt \nabla f(\vec{x}(t)) \cdot \frac{d\vec{x}}{dt} \tag{01.42}$$

Here integrand only a function of parameter t.



$$\longrightarrow$$

$$y = (x-2)^2$$

$$x^2 + y^2 = 4$$

Now important question is following: when is given differential total?, or equivalently, under what conditions is integration in equation (01.41) or (01.42) **independent** of integration contour.

Problem connected with these equations already known from mechanics, where use same formalism to calculate work.

There, however, **if** force can be derived from **potential** by $\vec{F} = -\nabla V(\vec{r})$, work **is** total differential, in contrast to thermodynamics where work W is not a total differential.

Existence of a potential is (mathematical sense) necessary and sufficient for equation (01.41) to be independent of integration contour.

If an arbitrary differential $\vec{F}(\vec{x}) \cdot d\vec{x}$ is given, this differential is complete (or total) if $\vec{F}(\vec{x}) = \nabla f(\vec{x})$ for a potential $f(\vec{x})$.

Existence of a potential is still not a very practical criterion, however, on which to decide whether a given differential is complete.

Easy, however, to derive a necessary and sufficient condition whether a force possesses a potential.

If $\vec{F}(\vec{x}) = \nabla f(\vec{x})$, then

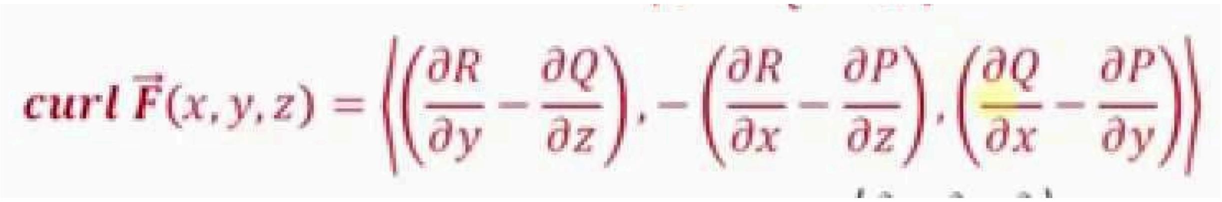
$$F_x = \frac{\partial f}{\partial x} \quad , \quad F_y = \frac{\partial f}{\partial y} \quad , \quad F_z = \frac{\partial f}{\partial z}$$

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} = 0$$

$$\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x} = \frac{\partial^2 f}{\partial z \partial x} - \frac{\partial^2 f}{\partial x \partial z} = 0$$

$$\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z} = \frac{\partial^2 f}{\partial y \partial z} - \frac{\partial^2 f}{\partial z \partial y} = 0$$

or



$$\mathbf{curl}\,\vec{\mathbf{F}}(x,y,z) = \left\langle \left(\frac{\partial R}{\partial y} - \frac{\partial Q}{\partial z}\right), -\left(\frac{\partial R}{\partial x} - \frac{\partial P}{\partial z}\right), \left(\frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y}\right) \right\rangle$$

$$\nabla \times \vec{F} = curl\vec{F} = 0 \qquad (01.43)$$

is necessary and sufficient condition.

Thus, if $\nabla \times \vec{F} = curl\vec{F} = 0$ then $\vec{F}(\vec{x}) \cdot d\vec{x}$ is a total or exact differential.

A Simple Differential

Consider the differential

$$\vec{F}(\vec{x})\cdot d\vec{x} = yxdx + x^2dy$$

It is not exact since

$$\vec{F} = F_x\hat{x} + F_y\hat{y} = yx\hat{x} + x^2\hat{y}$$

gives

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = \frac{\partial(x^2)}{\partial x} - \frac{\partial^2(yx)}{\partial y} = 2x - x = x \neq 0$$

On the other hand, the differential

$$\vec{F}(\vec{x})\cdot d\vec{x} = ydx + xdy$$

is exact since

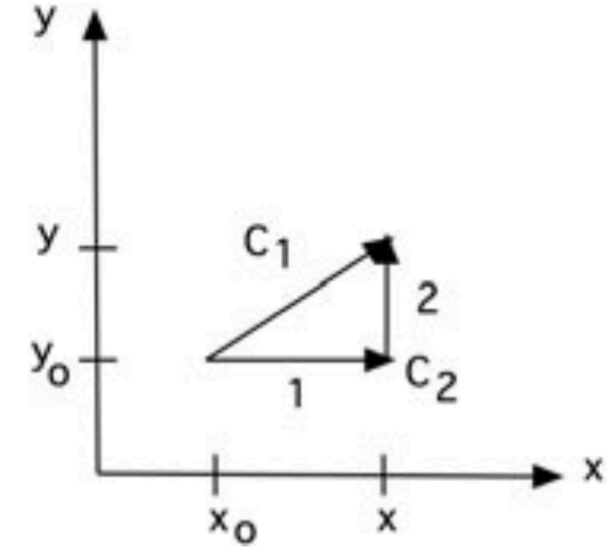
$$\vec{F} = F_x\hat{x} + F_y\hat{y} = y\hat{x} + x\hat{y}$$

gives

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = \frac{\partial(x)}{\partial x} - \frac{\partial^2(y)}{\partial y} = 1 - 1 = 0$$

In this last case, we can calculate the function whose total differential is given by $\vec{F}(\vec{x})\cdot d\vec{x} = ydx + xdy$. To do this we integrate along the contour

$$C_1 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} x_0 + t(x - x_0) \\ y_0 + t(y - y_0) \end{pmatrix} \quad , \quad t \in [0,1]$$



Representation of the Integration Contours

and we have using equation (01.36)

$$\begin{aligned} f(x,y) - f_0(x_0,y_0) &= \int_0^1 dt \nabla f(x(t),y(t)) \cdot \left(\frac{dx(t)}{dt}, \frac{dy(t)}{dt}\right) \\ &= \int_0^1 dt \left[F_x \frac{dx(t)}{dt} + F_y \frac{dy(t)}{dt} \right] \\ &= \int_0^1 dt \left[(y_0 + t(y - y_0))(x - x_0) + (x_0 + t(x - x_0))(y - y_0) \right] \\ &= y_0(x - x_0) + \frac{1}{2}(y - y_0)(x - x_0) + x_0(y - y_0) + \frac{1}{2}(x - x_0)(y - y_0) \\ &= xy - x_0 y_0 \end{aligned}$$

so that

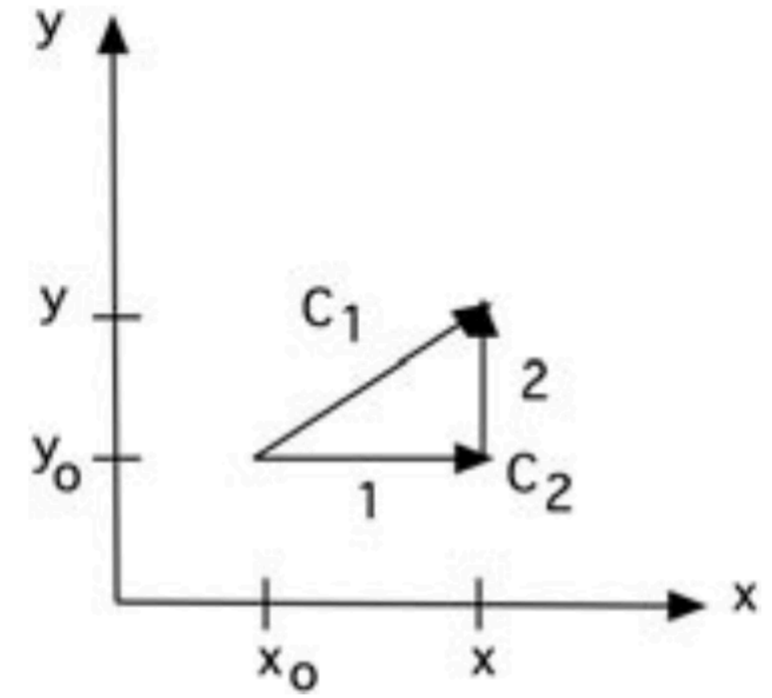
$$f(x,y) = xy$$

which clearly works since

$$\frac{\partial f}{\partial x} = y = F_x \quad , \quad \frac{\partial f}{\partial y} = x = F_y$$

as expected.

Now show the result is obtained via another curve C_2 as shown in figure below



Representation of the Integration Contours

Therefore,

$$C_2 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{cases} \begin{pmatrix} t \\ y_0 \end{pmatrix} & , \quad t \in [x_0, x] \\ \begin{pmatrix} x \\ t \end{pmatrix} & , \quad t \in [y_0, y] \end{cases}$$

where we have to add the integrals over both parts of the curve (the parameter t does not have to be normalized on $(0,1)$ in these cases):

$$
\begin{aligned}
f(x,y) - f_0(x_0,y_0) &= \int_{x_0}^{x} dt \nabla f(x(t),y(t)) \cdot \left(\frac{dx(t)}{dt}, \frac{dy(t)}{dt} \right) + \int_{y_0}^{y} dt \nabla f(x(t),y(t)) \cdot \left(\frac{dx(t)}{dt}, \frac{dy(t)}{dt} \right) \\
&= \int_{x_0}^{x} dt \left[F_x \frac{dx(t)}{dt} + F_y \frac{dy(t)}{dt} \right] + \int_{y_0}^{y} dt \left[F_x \frac{dx(t)}{dt} + F_y \frac{dy(t)}{dt} \right] \\
&= \int_{x_0}^{x} dt \left[y_0 \cdot 1 + t \cdot 0 \right] + \int_{y_0}^{y} dt \left[t \cdot 0 + x \cdot 1 \right] \\
&= y_0(x - x_0) + x(y - y_0) \\
&= xy - x_0 y_0
\end{aligned}
$$

where we have used

$$
\begin{aligned}
&\frac{dx(t)}{dt} = 1 \,,\, \frac{dy(t)}{dt} = 0 \quad \text{on Part 1} \\
&\frac{dx(t)}{dt} = 0 \,,\, \frac{dy(t)}{dt} = 1 \quad \text{on Part 2}
\end{aligned}
$$

The result is identical to that of the first contour integration. For many practical cases the curve C_2 will be the most convenient type to use as we shall see.

some variable always being held constant

Possible to construct an exact differential from nonexact differential $\vec{F}(\vec{x}) \cdot d\vec{x}$ by multiplication with an appropriate function $g(\vec{x})$.

Determination of $g(\vec{x})$ requires solution of a system of partial differential equations.

Can see this as follows.

Let $g(\vec{x})\vec{F}(\vec{x})\cdot d\vec{x}$ be corresponding total or exact differential.

Then have for n variables from conditions (01.43) that

$$\frac{\partial}{\partial x_i}\left(g(\vec{x})\vec{F}_k(\vec{x})\right)=\frac{\partial}{\partial x_k}\left(g(\vec{x})\vec{F}_i(\vec{x})\right) \quad i,k=1,2,\ldots,n \tag{01.44}$$

For a given $\vec{F}(\vec{x})$ these are determining equations for unknown function $g(\vec{x})$.

One calls $g(\vec{x})$ the **integrating factor.**

The Integrating Factor

Consider differential

$$\vec{F}(\vec{x})\cdot d\vec{x}=yxdx+x^2dy$$

Want to determine $g(x,y)$ such that

$$g(x,y)\vec{F}(\vec{x})\cdot d\vec{x}=g(x,y)yxdx+g(x,y)x^2dy$$

is an exact differential.

This means that have relation

$$\frac{\partial}{\partial x}\left(g(x,y)x^2\right)=\frac{\partial}{\partial y}\left(g(x,y)xy\right) \tag{01.45}$$

In this case the system of partial differential equations reduces to a single partial differential equation for $g(x,y)$. We try to solve this by the **product ansatz** or the **method of separation of variables**

$$g(x,y)=g_1(x)g_2(y)$$

If we insert this ansatz into equation (01.53) we have

$$2xg_1(x)g_2(y)+x^2g_2(y)\frac{dg_1(x)}{dx}=xg_1(x)g_2(y)+xyg_1(x)\frac{dg_2(y)}{dy}$$

If we now divide this equation by $xg(x,y)=xg_1(x)g_2(y)\neq 0$ and rearrange the terms we have

$$1+\frac{x}{g_1(x)}\frac{dg_1(x)}{dx}=\frac{y}{g_2(y)}\frac{dg_2(y)}{dy} \tag{01.46}$$

here we have a complete separation of the variables x and y. Since equation (01.60) must be valid for all x and y, we must have both sides of equation (01.60) equal to the same constant, say C Therefore,

$$1+\frac{x}{g_1(x)}\frac{dg_1(x)}{dx}=C=\frac{y}{g_2(y)}\frac{dg_2(y)}{dy}$$

Each of these equation is easily solved. We have

$$\frac{1}{g_1(x)}\frac{dg_1(x)}{dx}=\frac{C-1}{x} \quad and \quad \frac{1}{g_2(y)}\frac{dg_2(y)}{dy}=\frac{C}{y}$$

$$\frac{d\ell ng_1(x)}{dx}=\frac{C-1}{x} \quad and \quad \frac{d\ell ng_2(y)}{dy}=\frac{C}{y}$$

$$\ell ng_1(x)=(C-1)\ell nx+K_1 \quad and \quad \ell ng_2(y)=C\ell ny+K_2$$

or

$$g(x,y)=g_1(x)g_2(y)=Kx^{C-1}y^C \quad , \quad K=e^{K_1+K_2}$$

where C,K_1 and K_2 are arbitrary constants. Since we want to determine one special function $g(x,y)$, we may choose $C=0$, $K_1=-K_2$ so that

$$g(x,y)=\frac{1}{x}$$

Therefore, the new differential is

$$g(\vec{x})\vec{F}(\vec{x})\cdot d\vec{x}=ydx+xdy$$

which we showed earlier is an exact differential.

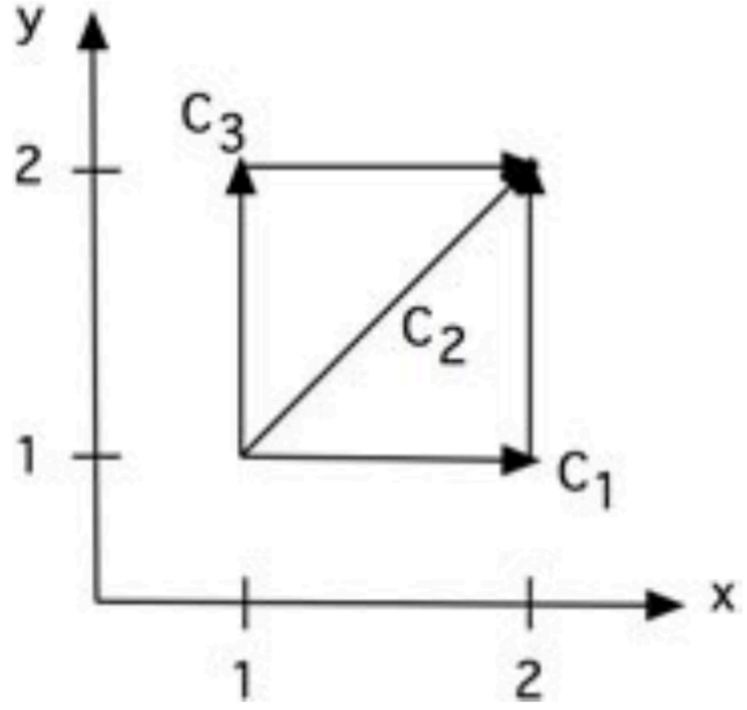
Exact and Inexact Differentials

Consider differential

$$\vec{F}(\vec{x}) \cdot d\vec{x} = (x^2 - y)dx + xdy \tag{01.47}$$

Is it exact?

Calculate $\int_{C_i} \vec{F}(\vec{x}) \cdot d\vec{x}$ where C_i are contours from $(1,1)$ to $(2,2)$ in figure below.



Representation of the Integration Contours

If not an exact differential, what is integrating factor?

Determine original function.

If differential (01.47) were exact

$$\frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = \frac{\partial (x^2 - y)}{\partial y} - \frac{\partial x}{\partial x} = -2$$

would necessarily vanish, which clearly is not case.

Therefore, it is not an exact differential.

Calculate integrals $\int_{C_i} \vec{F}(\vec{x}) \cdot d\vec{x}$ as line integrals with appropriate parameterization:

We use

$$C_1 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{cases} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2t+1 \\ t \end{pmatrix} & , \quad t \in \left[0, \frac{1}{2}\right] \\ \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2 \\ 2t \end{pmatrix} & , \quad t \in \left[\frac{1}{2}, 1\right] \end{cases} \tag{01.48}$$

The corresponding integral becomes

$$\int_{C_1} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_0^{1/2} dt\left((2t+1)^2 - 1\right) + \int_{1/2}^{1} dt(2 \cdot 2) = (1/3 + 1) + 2 = 10/3$$

Similarly for the curve C_2 we have

$$C_2 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} t+1 \\ t+1 \end{pmatrix} \quad , \quad t \in [0,1] \tag{01.49}$$

and the corresponding integral is

$$\int_{C_2} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_0^1 dt\left[\left((t+1)^2 - t - 1\right) \cdot 1 + (t+1) \cdot 1\right] = \int_0^1 dt(t+1)^2 = 7/3$$

Finally, the curve C_3 is given by

$$C_3 = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{cases} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 \\ 2t+1 \end{pmatrix} & , \quad t \in \left[0, \frac{1}{2}\right] \\ \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2t \\ 2 \end{pmatrix} & , \quad t \in \left[\frac{1}{2}, 1\right] \end{cases} \tag{01.50}$$

and the integral along the curve is

$$\int_{C_3} \vec{F}(\vec{x}) \cdot d\vec{x} = \int_0^{1/2} dt 2 \cdot 1 + \int_{1/2}^{1} dt\left(((2t)^2 - 2) \cdot 2\right) = -1 + 8 \int_{1/2}^{1} t^2 dt = 4/3$$

All three curves yield, as expected, different values for the integral, since the differential is not exact.

Let us now determine the integrating factor. If we denote it by $g(x,y)$, we must have

$$\vec{F}(\vec{x}) = ((x^2 - y), x)$$

and

$$\frac{\partial}{\partial y}\left(F_x g(x,y)\right) - \frac{\partial}{\partial x}\left(F_y g(x,y)\right) = \frac{\partial}{\partial y}\left((x^2 - y) g(x,y)\right) - \frac{\partial}{\partial x}\left(x g(x,y)\right) = 0$$

We use the product ansatz $g(x,y) = g_1(x) g_2(y)$. This gives after division by $g(x,y) = g_1(x) g_2(y) \neq 0$

$$(x^2 - y)\frac{d\ell n g_2(y)}{dy} - x\frac{d\ell n g_1(x)}{dx} = 2$$

The derivative $\frac{d\ell n g_2(y)}{dy}$ must equal zero since otherwise there is no possibility to choose functions $g_1(x)$ and $g_2(y)$ so that the left hand side equals the right hand side for arbitrary x and y. The second term depends only on x and the right hand side is a constant. We then obtain

$$\frac{d\ell n g_1(x)}{dx} = -\frac{2}{x} \rightarrow g_1(x) = \frac{1}{x^2}$$

while $g_2(y) = 1$ so that $\ell n g_2(y) = 0$. Therefore we get $g(x,y) = x^{-2}$. In fact

$$g(x,y)\vec{F}(\vec{x}) \cdot d\vec{x} = \left(1 - \frac{y}{x^2}\right)dx + \frac{1}{x}dy \tag{01.51}$$

which is an exact differential since

$$\frac{\partial}{\partial y}\left(1 - \frac{y}{x^2}\right) = -\frac{1}{x^2} = \frac{\partial}{\partial x}\left(\frac{1}{x}\right)$$

We can also show that the integrals $\int\limits_C g(\vec{x})\vec{F}(\vec{x}) \cdot d\vec{x}$ have the same value for all integration contours. With same parameterizations as earlier (equations ((01.42-44) we have

$$\int\limits_{C_1} g(\vec{x})\vec{F}(\vec{x}) \cdot d\vec{x} = \int\limits_0^{1/2} \left(1 - \frac{1}{(2t+1)^2}\right) 2dt + \int\limits_{1/2}^{1} \frac{1}{2} 2dt$$

$$= \frac{3}{2} - \int\limits_0^{1/2} \frac{2}{(2t+1)^2} dt = \frac{3}{2} - \frac{1}{2} = 1$$

and

$$\int_{C_2} g(\vec{x})\vec{F}(\vec{x})\cdot d\vec{x} = \int_0^1 \left[\left(1-\frac{1}{t+1}\right)+\frac{1}{t+1}\right]dt = 1$$

and

$$\int_{C_3} g(\vec{x})\vec{F}(\vec{x})\cdot d\vec{x} = \int_0^{1/2} 1\cdot 2dt + \int_{1/2}^{1}\left(1-\frac{2}{(2t)^2}\right)2dt$$

$$= 2 - \int_{1/.2}^{1}\frac{dt}{t^2} = 2+1-2 = 1$$

Thus, along the contours C_1, C_2 and C_3 (and along all others) one obtains the same value.

There exists a primitive function, which we now determine. We integrate starting from any initial point (x_0,y_0) to the final point (x,y) along the most convenient path:

$$C = \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} t \\ \dfrac{y-y_0}{x-x_0}(t-x_0)+y_0 \end{pmatrix} \quad , \quad t\in[x_0,x]$$

and we obtain for the primitive function

$$
\begin{aligned}
f(x,y) - f_0(x_0,y_0) &= \int_C g(\vec{x})\nabla f(\vec{x})\cdot d\vec{x} \\
&= \int_{x_0}^{x} dt\left[1 - \frac{1}{t^2}\left(\frac{y-y_0}{x-x_0}(t-x_0)+y_0\right) + \frac{1}{t}\left(\frac{y-y_0}{x-x_0}\right)\right] \\
&= \int_{x_0}^{x} dt\left[1 + \frac{1}{t^2}\left(\frac{y-y_0}{x-x_0}x_0 - y_0\right)\right] = x - x_0 + \left(\frac{y}{x} - \frac{y_0}{x_0}\right)
\end{aligned}
$$

By differentiation, one immediately shows that this is the correct primitive function for equation (01.47).

Cyclic thermodynamic processes will be of special interest.

They form basis for all thermodynamic engines, which we will discuss in detail later.

Some fundamental statements, however, can be made now with help of first law.

For example, for a **cycle**, where working substance of system returns to its initial state after a series of changes of state, equation

$$\oint dU = 0 \qquad (01.52)$$

has to be fulfilled, since dU is a total differential and thus contour-independent.

If such a cycle nevertheless does utilizable work, obviously a corresponding amount of heat (extracted from the surroundings) has been converted to this work.

Now study such a cycle with an ideal gas in more detail.

Example: As an illustration of why

1.7 Latent Heat

When heat enters system without increasing its temperature, then say that a **phase transformation** is occurring.

Technically heat capacity is infinite since

$$C = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty \text{ during the phase transformation}$$

Still of interest, however, to know amount of heat required to melt or boil a substance completely.

This amount divided by mass is called **latent heat** of transformation

$$L = \frac{Q}{m} \text{ to accomplish the transformation} \qquad (01.53)$$

By convention, one assumes that pressure is constant and no work (besides usual constant-pressure expansion or compression) is done during process.

1.8 Enthalpy

Many processes take place at constant pressure, for example, system is contained in an open container in contact with atmosphere.

Keeping track of compression-expansion work during these processes can be tedious and time consuming.

Ask following question: what is total energy would have to expend to create a given system out of nothing and put it into environment (all under constant pressure)?

Answer is another thermodynamic state variable called **enthalpy**, namely,

$$H = U + PV \tag{01.54}$$

where PV, pressure of environment times total volume of system (that is, total space would need to clear out to make room for system), is work needed to make room for system.

In other words, if you could annihilate system, energy you could expect to extract is not just U, but also work PV done by atmosphere as it collapses to fill vacuum left behind.

Why is enthalpy useful?

Suppose that change takes place in system - you add some heat or some chemicals react or whatever - while pressure is held constant.

Energy, volume and enthalpy can all change ($\Delta U, \Delta V, \Delta H$).

New enthalpy is

$$H + \Delta H = (U + \Delta U) + P(V + \Delta V) = H + (\Delta U + P\Delta V)$$

or

$$\Delta H = \Delta U + P\Delta V \quad \text{at constant pressure} \tag{01.55}$$

This says that enthalpy can increase for two reasons

(1) because the energy increases
(2) because the system expands and
work is done on the surroundings

Now first law of thermodynamics says that

$$\Delta U = Q + (-P\Delta V) + W_{other}$$

so that

$$\Delta H = Q + W_{other} \qquad \text{at constant pressure} \tag{01.56}$$

that is, change of enthalpy is caused **only** by heat and other forms of work and **not** by expansion-compression work.

For simple case of raising an object's temperature, change in enthalpy per degree, a constant pressure, is the same as heat capacity at constant pressure, that is,

$$C_P = \left(\frac{Q}{\Delta T}\right)_P = \left(\frac{\Delta U - W}{\Delta T}\right)_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\Delta H}{\Delta T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{01.57}$$

Example: Consider the combustion

1.9 Rates of Processes

Make a quick pass through some ideas about how systems relax towards equilibrium states.

Will only state some definitions and ideas, which will be sufficient for our purposes at this level.

Heat Conduction

The law of heat conduction is due to Fourier

$$\frac{Q}{\Delta t} = -k_t A \frac{dT}{dx}$$

where k_t is the thermal conductivity. The minus sign indicates that if T increases from left to right, then Q flows from right to left.

Let us use this result to derive the **heat equation.**

We consider a uniform rod of material whose temperature varies along its length, in the x direction.

We consider a small segment of the rod of length Δx. Assume the center of the segment is located at x and the two ends at $x \pm \Delta/2$.

Assume the Q_1 flows in the left end at $x - \Delta/2$ and Q_2 flows in the right end at $x + \Delta/2$.

We consider a uniform rod of material whose temperature varies along its length, in the x direction.

We consider a small segment of the rod of length Δx. Assume the center of the segment is located at x and the two ends at $x \pm \Delta / 2$.

Assume the Q_1 flows in the left end at $x - \Delta / 2$ and Q_2 flows in the right end at $x + \Delta / 2$.

The rate of heat flow into the segment from the left is

$$\frac{Q_1}{\Delta t} = -k_t A \left.\frac{dT}{dx}\right|_{x-\Delta x/2}$$

where the – sign indicates Q_1 is positive when heat flows into the segment (left to right).

The rate of heat flow into the segment from the right is

$$\frac{Q_2}{\Delta t} = +k_t A \left.\frac{dT}{dx}\right|_{x+\Delta x/2}$$

where the + sign indicates Q_2 is positive when heat flows into the segment (right to left).

Therefore, the total rate of heat flow into the segment is

$$\frac{Q}{\Delta t} = +k_t A \frac{dT}{dx}\bigg|_{x+\Delta x/2} - k_t A \frac{dT}{dx}\bigg|_{x-\Delta x/2} = k_t A \Delta x \frac{d^2T}{dx^2}$$

On the other hand, the heat input Q can be written as $C\Delta T = mc\Delta T$ where C is the heat capacity and m is the mass of the segment. Remember that c is then the specific heat. The equation then becomes

$$\frac{Q}{\Delta t} = \frac{mc\Delta T}{\Delta t} = k_t A \Delta x \frac{d^2T}{dx^2}$$

the heat equation

But $m/(A\Delta x)$ is the density ρ of the rod, while $\frac{\Delta T}{\Delta t} \to \frac{\partial T}{\partial t}$ and we have

$$\frac{\partial T}{\partial t} = \frac{k_t}{c\rho}\frac{\partial^2 T}{\partial x^2} = K\frac{\partial^2 T}{\partial x^2}$$

where we are now using partial derivatives to recognize the fact that T depends on both x and t.

Conductivity of an Ideal Gas

In a gas the rate of heat conduction is limited by how far a molecule can travel before it collides with another molecule. The average distance traveled between collisions is called the **mean free path.**

We now make an estimate of the mean free path for an ideal gas.

For simplicity, imagine that all of the molecules in the gas except one are frozen in place. How far does the remaining molecule travel between collisions?

A collision occurs when the center of one molecule comes within one molecular diameter ($2r$, where r is the radius of the molecule) of the center of some other molecule. The collision rate would be the same if all the frozen molecules were points and the moving molecule had a radius $2r$, so we will assume that is true.

As the molecule travels along, it sweeps out an imaginary cylinder of space whose radius is $2r$. When the volume of this cylinder equals the average volume per molecule in the gas, we are likely to get a collision. The mean free path ℓ is roughly the length of this cylinder when this condition is met:

volume of cylinder = average volume per molecule

$$\pi(2r)^2\ell \approx \frac{V}{N} \Rightarrow \ell \approx \frac{1}{4\pi r^2}\frac{V}{N}$$

The average time between collisions is given by

$$\overline{\Delta t} \approx \frac{\ell}{\bar{v}} \approx \frac{\ell}{v_{rms}}$$

where

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

Example: A frying pan is quickly

2 - Second Law

We now must answer some outstanding important questions.

What is temperature?

Why does heat flow spontaneously from a hotter object to a cooler object and never the other way?

More generally, why do so many thermodynamic processes happen in one direction but never the reverse (irreversible processes)?

The short answer to the last question is that irreversible processes are **not inevitable**, they are just **overwhelmingly probable.**

Certain states of macroscopic systems must be overwhelmingly more probable than all others and therefore systems will spontaneously move to these most probable states with little likelihood of the reverse process occurring.

Statistical considerations are of enormous importance for gaining deeper insight into the purely phenomenological relationships of thermodynamics.

As we will see, it is just the second law of thermodynamics which establishes a very close connection between the statistical and phenomenological points of view. The second law, as we shall see, formulates the well-known fact that all isolated systems evolve towards an equilibrium state, where the state quantities remain constant after a characteristic relaxation time.

Furthermore, the second law, as we shall see, asserts that this process never reverses itself.

A good example of this fact is a gas which always expands to homogeneously fill spontaneously available volume after a certain time period. However, a spontaneous gathering of the gas in one corner of the volume has never been observed, although this would not contradict the law of conservation of energy.

The entropy will be the state quantity that uniquely characterizes this tendency. Processes which happen spontaneously and lead to equilibrium will be connected with an increase in entropy. In equilibrium, the entropy will assume its maximum value and does not change anymore.

2.1 Two-State Systems

Let us start our investigations in this area with a simple system.

Consider a system with three coins: a penny, a nickel and a dime (three **distinguishable** coins).

Suppose we now flip the three coins. How many possible outcomes are there? In this system, the number is small enough that we can list all the possibilities below:

Penny	*Nickel*	*Dime*
H	*H*	*H*
H	*H*	*T*
H	*T*	*H*
T	*H*	*H*
H	*T*	*T*
T	*H*	*T*
T	*T*	*H*
T	*T*	*T*

A list of all possible "microstates"
of a set of 3 coins

Clearly there are $2^3 = 8$ possibilities or outcomes. We assume that the coins are fair so that each of each outcome is the same. Therefore, the probability of each outcome is 1/8.

There is only 1 way to get exactly 3 heads or exactly 3 tails, so that the probability of getting exactly 3 heads is 1/8 and the probability of getting exactly 3 tails is 1/8.

Now there are 3 different ways to get 2 heads and 1 tails, so that the probability of getting exactly 2 heads is 3/8 and similarly the probability of getting exactly 2 tails is also 3/8.

Note that the probability of getting an outcome = sum over all the probability of the individual outcomes = 1 as it must be.

Some definitions:

Each of the 8 different outcomes is called a **microstate**, where we must specify the state of each individual coin (in this case).

If we only specify that the state has exactly 2 heads, we are describing a **macrostate**, that is, a state which can be represented by 1 or more microstates. The number of microstates corresponding to a given macrostate is called the **multiplicity.** For the macrostate of exactly 2 heads the multiplicity is 3. We use the symbol Ω for the multiplicity.

Another example from classical mechanics is the state of motion of N particles which is uniquely determined by $3N$ coordinates and $3N$ momenta $\left(q_j, p_j\right)$ of the N particles at a certain time. The set $\left(q_j, p_j\right)$ is called the **microstate** of the system, which of course varies with time. Each microstate $\left(q_j, p_j\right)$ corresponds to one point in a $6N$-dimensional space, **the phase space.**

A typical macrostate might be a state of the system with a given **total energy**, which is a condition that can generally be satisfied by many different microstates.

In the simple 3 coin example above we have

$$\Omega(0\ heads) = 1, \Omega(1\ heads) = 3, \Omega(2\ heads) = 3, \Omega(3\ heads) = 1$$

so that

$$\Omega(all) = 1 + 3 + 3 + 1 = 8 = 2^3 \text{ = total number of microstates}$$

Then we define the probability of any macrostate as

$$\Pr(n\ heads \mid 3\ coins) = \frac{\Omega(n\ heads)}{\Omega(all)} \tag{2.01}$$

These results rely on the assumption that all microstates are equally probable.

Another example: Suppose that we have $n = 100$ coins. The total number of microstates is now very large, namely, $2^n = 2^{100}$ since each of the 100 coins has 2 possible states. The number of macrostates, however, is only $101 = n + 1$, namely,

$$0\ heads, 1\ heads, 2\ heads, \ldots\ldots\ldots\ldots, 99\ heads, 100\ heads$$

What are the multiplicities of these macrostates?

For n heads and therefore $100 - n$ tails, we are asking for the number of ways we can arrange 100 objects such that we have n heads and $100 - n$ tails. The number of ways we can arrange 100 "different" objects is $100!$. If some of these objects are identical, then switching identical objects does not change an arrangement and we have overcounted. Therefore, the number of ways we can arrange 100 objects such that we have n heads and $100 - n$ tails is given by

$$\Omega(100, n) = \frac{100!}{n!(100 - n)!} \tag{2.02}$$

Let us see that this agrees with our example of 3 coins. We have

$$\Omega(3,0) = \frac{3!}{0!(3)!} = 1\,,\ \Omega(3,1) = \frac{3!}{1!(2)!} = 3$$

$$\Omega(3,2) = \frac{3!}{2!(1)!} = 3\,,\ \Omega(3,3) = \frac{3!}{3!(0)!} = 1$$

which agrees with our earlier results. The general formula for N coins is

$$\Omega(N,n) = \frac{N!}{n!(N-n)!} = \binom{N}{n} \qquad \textbf{Binomial coefficient} \qquad (2.03)$$

The corresponding probability is given by

$$\Pr(n \mid N) = \frac{\Omega(N,n)}{\Omega(all)} = \frac{N!}{n!(N-n)!}\frac{1}{2^N} \qquad (2.04)$$

where we have assumed fair coins so that the

probability of heads = $p = 1/2$

probability of tails = $q = 1 - p = 1/2$

and the probability result above really should be written

$$\Pr(n \mid N, 1/2) = \frac{\Omega(N,n)}{\Omega(all)} = \frac{N!}{n!(N-n)!}\left(\frac{1}{2}\right)^{n}\left(\frac{1}{2}\right)^{N-n} \qquad (2.05)$$

or

$$\Pr(n \mid N,p) = \frac{\Omega(N,n)}{\Omega(all)} = \frac{N!}{n!(N-n)!}(p)^n(1-p)^{N-n} \tag{2.06}$$

We note that

$$(p+q)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!}(p)^n(q)^{N-n} = \sum_{n=0}^{N} \Pr(n \mid N,p) = 1$$

for $p+q=1$ as expected.

Example: Suppose you flip 50 fair coins

(a) How many possible outcomes(microstates) are there?
(b) How many ways are there of getting exactly 25 heads and 25 tails?
(c) What is the probability of getting exactly 25 heads and 25 tails?
(d) What is the probability of getting exactly 30 heads and 20 tails?
(e) What is the probability of getting exactly 40 heads and 10 tails?
(f) What is the probability of getting 50 heads and no tails?
(g) Plot a graph of the probability of getting n heads versus n.

Solution:

(a) There are two possible states for the first coin, and for each of these, two for the second, and for each of these, two for the third, and so on. So the total number of microstates is

$$\Omega = 2^{50} = 1.13 \times 10^{15}$$

(b) The number of ways of getting exactly 25 heads is

$$\Omega(25) = \binom{50}{25} = \frac{50!}{(25!)^2} = 1.26 \times 10^{14}$$

(c) The probability of getting exactly 25 heads is

$$P(25) = \frac{\Omega(25)}{\Omega} = 0.112$$

(d) The probability of getting 30 heads is

$$P(30) = \frac{\Omega(30)}{\Omega} = \frac{1}{2^{50}} \frac{50!}{30!20!} = 0.042$$

(e) The probability of getting 40 heads is

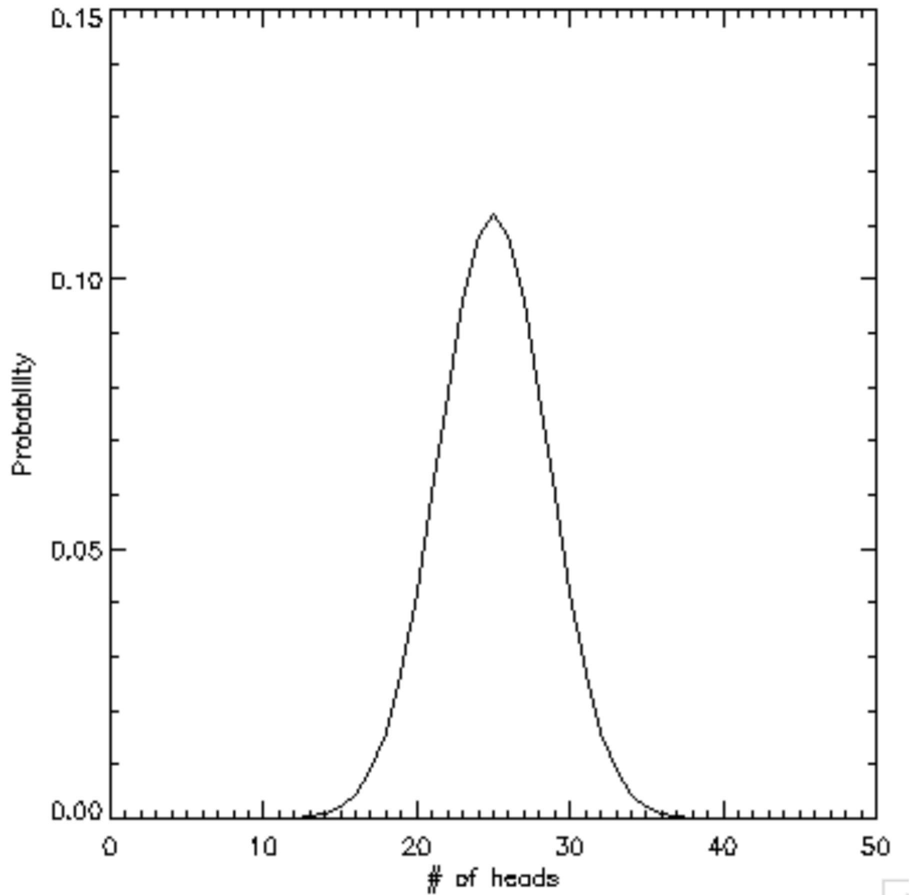
$$P(40) = \frac{\Omega(40)}{\Omega} = \frac{1}{2^{50}} \frac{50!}{40!10!} = 0.0000091$$

(f) The probability of getting 50 heads is

$$P(50) = \frac{\Omega(50)}{\Omega} = \frac{1}{2^{50}} \frac{50!}{50!0!} = \frac{1}{2^{50}} = 8.88 \times 10^{-16}$$

since there is only one way to do it.

(g)



You might ask what all this coin tossing stuff has to with real physical systems?

The Two-State Paramagnet

Quantum mechanically the electron spin (its intrinsic angular momentum) has only two possible orientations (up or down - parallel or anti-parallel) with respect to the direction of an applied magnetic field.

The lowest energy configuration corresponds to the electrons aligning themselves antiparallel to the magnetic field.

The effect is called **paramagnetism** and the material is said to be a paramagnet.

This real system is then identical to the coin tossing system if we identify spin parallel to field with heads and spin anti-parallel to field with tails.

If we let $N_\uparrow$ be the number of spins pointing "up" at some particular time and $N_\downarrow$ be the number of spins pointing "down". The total number of spins is then $N = N_\uparrow + N_\downarrow$, which is fixed. The system has one microstate for each possible value of $N_\uparrow$ from 0 to N. The multiplicity is given by the same formula as before:

$$\Omega(N_\uparrow,N) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!N_\downarrow!} = \frac{N!}{N_\uparrow!(N-N_\uparrow)!} \qquad (2.07)$$

(getting ahead of ourselves)

Digression

The fundamental assumption of statistical mechanics is that all microstates which have the same total energy can be found with equal probability.

Although the microstate of the system drastically changes with time, in macroscopic equilibrium we nevertheless always observe the same macroscopic state quantities such as pressure, temperature, volume, etc.

This means that many microstates lead to the same macroscopic state quantities.

We denote by Ω the number of these microstates “**compatible**" with a given macrostate.

Easy to convince ourselves that number of available microstates for a gas which homogeneously occupies volume V is overwhelmingly larger than number of available microstates compatible with smaller volume.

If characterize macrostate by volume V available to our N particles, number of microstates $\Omega(V)$ available to **1** particle proportional to V.

In fact, a single particle may assume all possible momenta $-\infty < p < \infty$ and all coordinates q in the volume V.

For N particles which are **independent** of each other, the numbers of microstates available to each particle have to be multiplied so that $\Omega(V) \alpha V^N$.

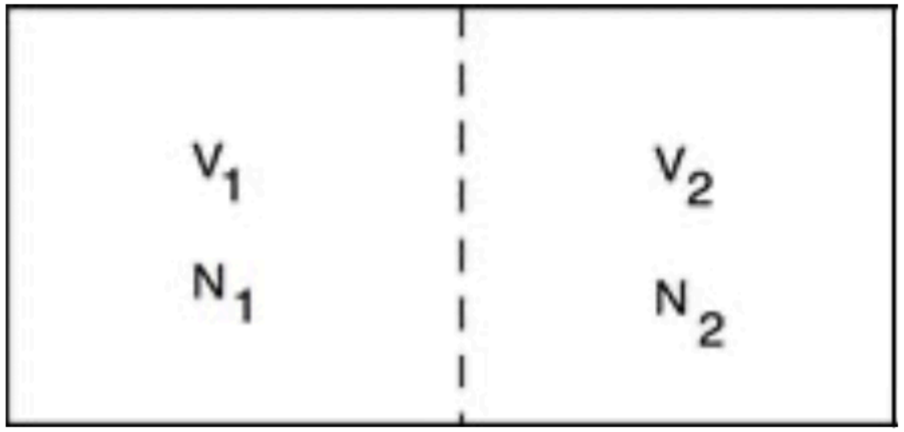
If we now compare $\Omega(V)$ with the number of microstates in a volume half the size, then $\Omega(V/2) \alpha (V/2)^N$.

Thus, this case is less probable by a factor $(1/2)^N$ than the case where the gas would homogeneously occupy the whole volume.

However, for a macroscopic number of particles, for example, of the order of Avogadro's number $N_A \approx 10^{23}$, this is an incredibly small number, namely, $(1/2)^{10^{23}}$.

Microstates in a Simple System

We consider a container with volume V, which is homogeneously filled with N particles of a gas in equilibrium. We now **imagine** the container to be divided into two compartments with volumes V_1 and V_2 where $V = V_1 + V_2$ and with N_1 and N_2 particles($N = N_1 + N_2$), respectively, as shown in the figure below.



Model System

We set $V_1 = pV$ and $V_2 = qV$. For the fractions p and q of the total volume we must have $p + q = 1$.

The total number of microstates compatible with N particles and the total volume V has to be proportional to V^N, as we saw earlier. According to the binomial theorem we then have

$$\Omega_{tot}(N,V) \propto V^N = \left(V_1 + V_2\right)^N = \sum_{N_1=0}^{N} \binom{N}{N_1} V_1^{N_1} V_2^{N-N_1} \qquad (2.08)$$

where $N - N_1 = N_2$ and

$$\binom{N}{N_1} = \frac{N!}{N_1!(N-N_1)!}$$

is the standard binomial coefficient. On the other hand,

$$\Omega_1(N_1,V_1) \propto V_1^N \qquad \text{and} \qquad \Omega_2(N_2,V_2) \propto V_2^N$$

are just numbers of microstates compatible with volumes (called **partial** volumes) V_1 and V_2 and the particle numbers N_1 and N_2, respectively.

Equation (02.08) therefore has a very illustrative meaning.

Consider a macrostate with N_1 particles in partial volume V_1.

Obviously, there are exactly N_1 possibilities of selecting these particles from a total of N **chosen** particles.

Number of corresponding microstates is proportional to V_1^N, while for the remaining $N - N_1 = N_2$ in volume V_2 there are still V_2^N microstates which can be assumed.

Each term in sum is therefore the total number of microstates, if there are N_1 particles in partial volume V_1.

Now obtain total number of **all** possible microstates by summing over all possible particle numbers in V_1.

Therefore, we may interpret the expression

$$\Omega(V_1,V_2,K,N) = \binom{N}{K} V_1^K V_2^{N-K}$$

as the number of microstates of the situation where K particles are in V_1 and $N-K$ particles are in V_2. Finally, we can then interpret

$$p_K = \frac{\Omega(V_1,V_2,K,N)}{\Omega_{tot}(N,V)} = \frac{1}{V^N}\binom{N}{K}(pV)^K(qV)^{N-K} = \binom{N}{K} p^K q^{N-K} \tag{2.09}$$

as the probability that there are just K particles in the fictitious volume V_1 and $N-K$ particles are in V_2. With (02.09) we can now find the average number of particles in volume V_1. This number is by definition

$$\overline{K} = \langle K \rangle = \sum_{K=0}^{N} p_K K = \sum_{K=0}^{N} K \binom{N}{K} p^K q^{N-K} \tag{2.10}$$

We now apply a trick often used in the calculation of such average values and write

$$Kp^K = p\frac{\partial}{\partial p}p^K$$

so that

$$\bar{K} = \sum_{K=0}^{N}\binom{N}{K}p\frac{\partial}{\partial p}p^K q^{N-K} = p\frac{\partial}{\partial p}\sum_{K=0}^{N}\binom{N}{K}p^K q^{N-K}$$

$$= p\frac{\partial}{\partial p}(p+q)^N = Np(p+q)^{N-1}$$

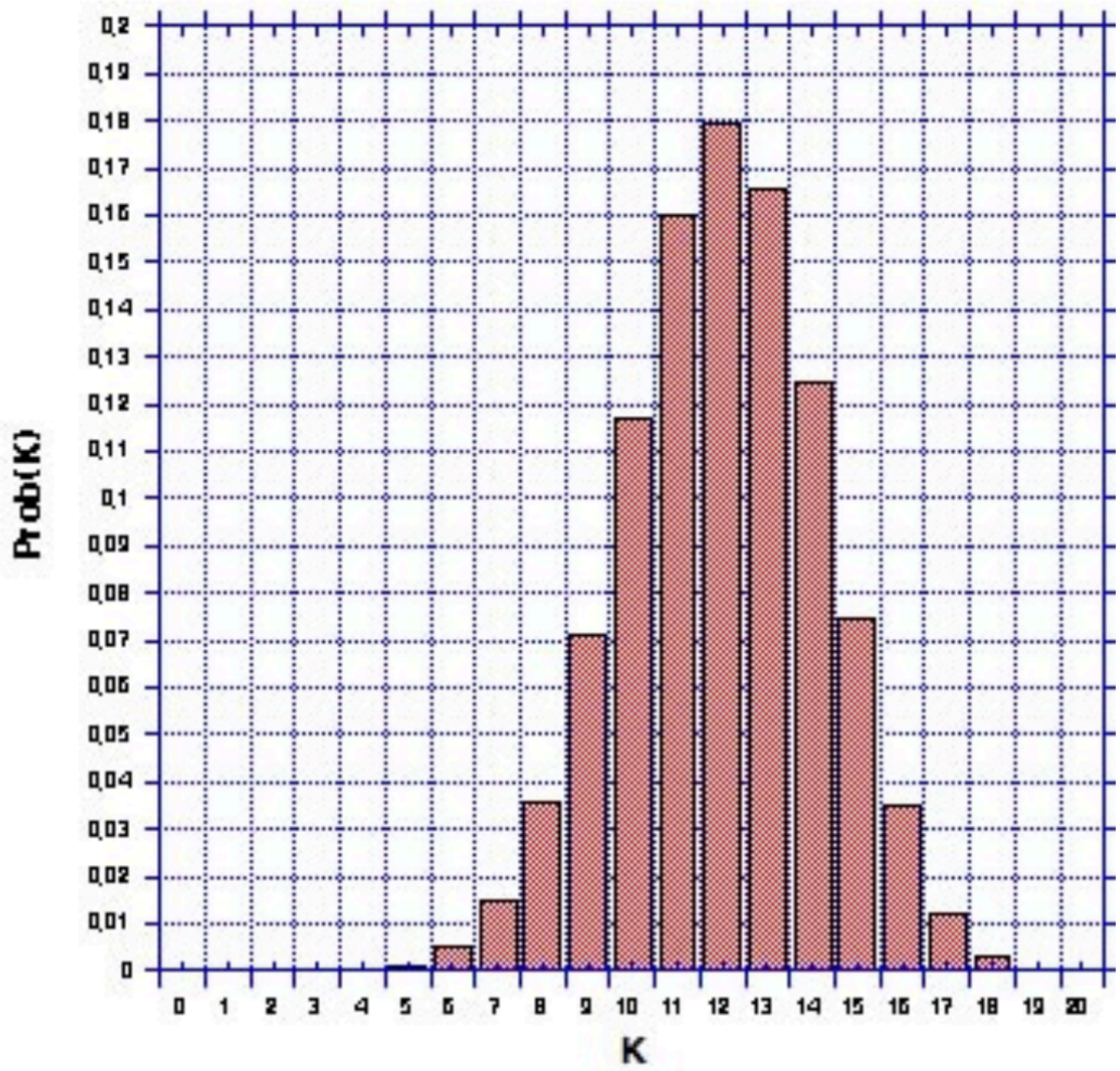
Since $p+q=1$, have $\bar{K} = Np$ or $\bar{K}/N = V_1/V$.

On average, there will be just as many particles in fictitious volume V_1 as corresponds to fraction V_1/V.

This is, of course, obvious, since equilibrium corresponds to a homogeneous(uniform) distribution of particles.

Furthermore, can calculate **fluctuations around this value** and ask for probability of finding value that deviates from $\bar{K} = Np$.

To this end, simply plot probabilities p_K as function of K as shown in figure below.



The maximum in the figure just corresponds to the average $K_{\max} = \overline{K}$.

For this example, with total of $N = 20$ particles and a volume $V_1 = 0.6V$ it is therefore still quite probable to find 11 or 13 particles in V_1 instead of $K = 12$ particles.

A definite measure of these deviations from average value is mean square deviation. This is defined

$$
\begin{aligned}
\overline{(\Delta K)^2} &\equiv \overline{\left(K-\overline{K}\right)^2} = \sum_{K=0}^{N} p_K\left(K-\overline{K}\right)^2 \\
&= \sum_{K=0}^{N} p_K(K)^2 - 2\sum_{K=0}^{N} p_K\left(K\overline{K}\right) + \sum_{K=0}^{N} p_K\left(\overline{K}\right)^2 = \sum_{K=0}^{N} p_K(K)^2 - 2\overline{K}\sum_{K=0}^{N} K p_K + \overline{K}^2 \sum_{K=0}^{N} p_K \\
&= \sum_{K=0}^{N} p_K(K)^2 - 2\overline{K}\,\overline{K} + \overline{K}^2 = \overline{K^2} - \overline{K}^2
\end{aligned}
\tag{2.11}
$$

where we have used $\sum_{K=0}^{N} p_K = 1$. Now

$$
\begin{aligned}
\overline{K^2} &= \sum_{K=0}^{N} K^2 p_K = \sum_{K=0}^{N} K^2 \binom{N}{K} p^K q^{N-K} = \sum_{K=0}^{N} \left(p\frac{\partial}{\partial p}\right)^2 p^K \binom{N}{K} q^{N-K} = \left(p\frac{\partial}{\partial p}\right)^2 \sum_{K=0}^{N} \binom{N}{K} p^K q^{N-K} \\
&= \left(p\frac{\partial}{\partial p}\right)^2 (p+q)^N = p\left[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}\right] = p\left[N + pN(N-1)\right]
\end{aligned}
$$

so that

$$
\overline{(\Delta K)^2} = \overline{K^2} - \overline{K}^2 = p\left[N + pN(N-1)\right] - (Np)^2 = Np(1-p) = Npq
$$

This means that the width or spread of the distribution, measured by

$$\Delta^* K = \sqrt{\overline{(\Delta K)^2}}$$

increases as $\sqrt{N}$. The **relative width or spread**, that is, the width $\Delta^* K$ with respect to the average particle number in volume V_1 is then

$$\frac{\Delta^* K}{\overline{K}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{N}} \tag{2.12}$$

This represents the fluctuation relative to mean particle number.

Here can clearly see that relative deviation from equilibrium decreases as $N^{-1/2}$ and is very small for macroscopic particle numbers, that is, $N_A = 10^{24} \Rightarrow N_A^{-1/2} = 10^{-12}$.

Hence, macroscopic fluctuations (for example, all particles suddenly in V_1) are extremely improbable.

On the other hand, small deviations in small spatial regions are quite normal.

If choose a very small partial volume ($p \rightarrow 0$), fluctuations can nevertheless be quite large.

This corresponds, for example, to local density fluctuations in gases, which are of appreciable size only on a microscopic scale (10^{-8} - $10^{-10}\ m$).

These fluctuations can become observable in some experiments.

For example, density fluctuations of a gas in vicinity of critical point(to be discussed later) are especially large.

Can be observed by change in scattering of light in gas (critical opalescence).

Very difficult to understand this phenomenon without using statistical point of view.

The Einstein Model of a Solid

We now consider a collection of microscopic systems that can each store any number of energy "quanta", all of the same size. As we will see later in the course the quantum mechanical harmonic oscillator system has this property, that is, the energy levels of a single oscillator are given by

$$E_n = \hbar\omega(n + 1/2) \qquad\qquad n = 0,1,2,......$$

The ground state energy (lowest) is $E_0 = \hbar\omega/2$ (called the zero-point energy for reasons we derive later in the course). If we measure the energy of the oscillator relative to the ground state the allowed energies are given by

$$E_n = n\hbar\omega \qquad\qquad n = 0,1,2,......$$

Einstein's model of a solid is a collection of identical oscillators each with quantized allowed energy values as given above.

We first consider a very small system to see how things work. We assume we have 3 oscillators, $N = 3$.

Oscillator :	#1	#2	#3
Energy :	0	0	0
	1	0	0
	0	1	0
	0	0	1
	2	0	0
	0	2	0
	0	0	2
	1	1	0
	1	0	1
	0	1	1
	3	0	0
	0	3	0
	0	0	3
	2	1	0
	2	0	1
	1	2	0
	0	2	1
	1	0	2
	0	1	2
	1	1	1

Let us enumerate the microstates directly. We must specify the individual energy value of each of the oscillators. We will use total energy to characterize macrostates.

From the table we have

$$\Omega(E=0) = 1\,,\, \Omega(E=1) = 3\,,\, \Omega(E=2) = 6\,,\, \Omega(E=3) = 10$$

The general formula for the multiplicity of an Einstein solid with N oscillators and q quanta of energy is

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \tag{2.13}$$

Clearly, this works for the table above

$$\Omega(E=0)=\Omega(3,0)=\binom{2}{0}=\frac{(2)!}{0!(2)!}=1 \quad , \quad \Omega(E=1)=\Omega(3,1)=\binom{3}{1}=\frac{(3)!}{1!(2)!}=3$$

$$\Omega(E=2)=\Omega(3,2)=\binom{4}{2}=\frac{(4)!}{2!(2)!}=6 \quad , \quad \Omega(E=3)=\Omega(3,3)=\binom{5}{3}=\frac{(5)!}{3!(2)!}=10$$

General Proof:

Graphical representation of a microstate with N oscillators and q quanta of energy:

•|•••||••••

represents the microstate with 1 quantum in the first oscillator, 3 quanta in the second oscillator, 0 quanta in the third oscillator and 4 quanta in the fourth oscillator.

This is a unique representation of the microstate. Every possible sequence of dots and lines corresponds to a microstate. There are always q dots and $N-1$ lines for a total of $q+N-1$ symbols.

Given q and N, the number of possible arrangements is the number of ways of choosing q of the symbols to be dots, that is,

$$\binom{q+N-1}{q}$$

Interacting Systems

In the preceding discussions we figured out how to count microstates.

To understand heat flow and irreversible processes we must now consider two Einstein solids that can share energy (interact).

Assume that we have two solids:

$$A: N_A, q_A \quad \text{and} \quad B: N_B, q_B$$

which are isolated from their environment but can exchange energy with each other.

We know how to describe the macrostates of each separate system. How do we describe the macrostate of the composite system.

Assumptions:

Two solids are weakly interacting, which means that rate of energy exchange between systems is much smaller than rate of energy exchange within each separate system. Means that for short time scales can assume that separate system energies U_A and U_B are essentially constant.

Macrostate of composite system can then be specified by instantaneous values of U_A and U_B . Can calculate composite system multiplicity in this case.

On longer time scales values of U_A and U_B will change so that also need to calculate total multiplicity for all allowed values of U_A and U_B under constraint that $U = U_A + U_B$ is constant (always true).

We first consider a small system (so we can explicitly show all the relevant steps). We choose

$$N_A = 3 = N_B , N = N_A + N_B \quad , \quad q = q_A + q_B = 6 \rightarrow U = 6\hbar\omega$$

There are 7 possible macrostates corresponding to $q_A = 0,1,2,3,4,5,6$. We then have

$$\Omega_A = \binom{q_A + N_A - 1}{q_A} = \frac{(q_A + N_A - 1)!}{q_A!(N_A - 1)!}$$

$$\Omega_B = \binom{q_B + N_B - 1}{q_B} = \frac{(q_B + N_B - 1)!}{q_B!(N_B - 1)!}$$

and

$$\Omega(N,q) = \Omega_A(N_A,q_A)\Omega_B(N_B,q_B)$$

that is, the total multiplicity of any macrostate of the composite system is the product of the multiplicities of the individual systems.

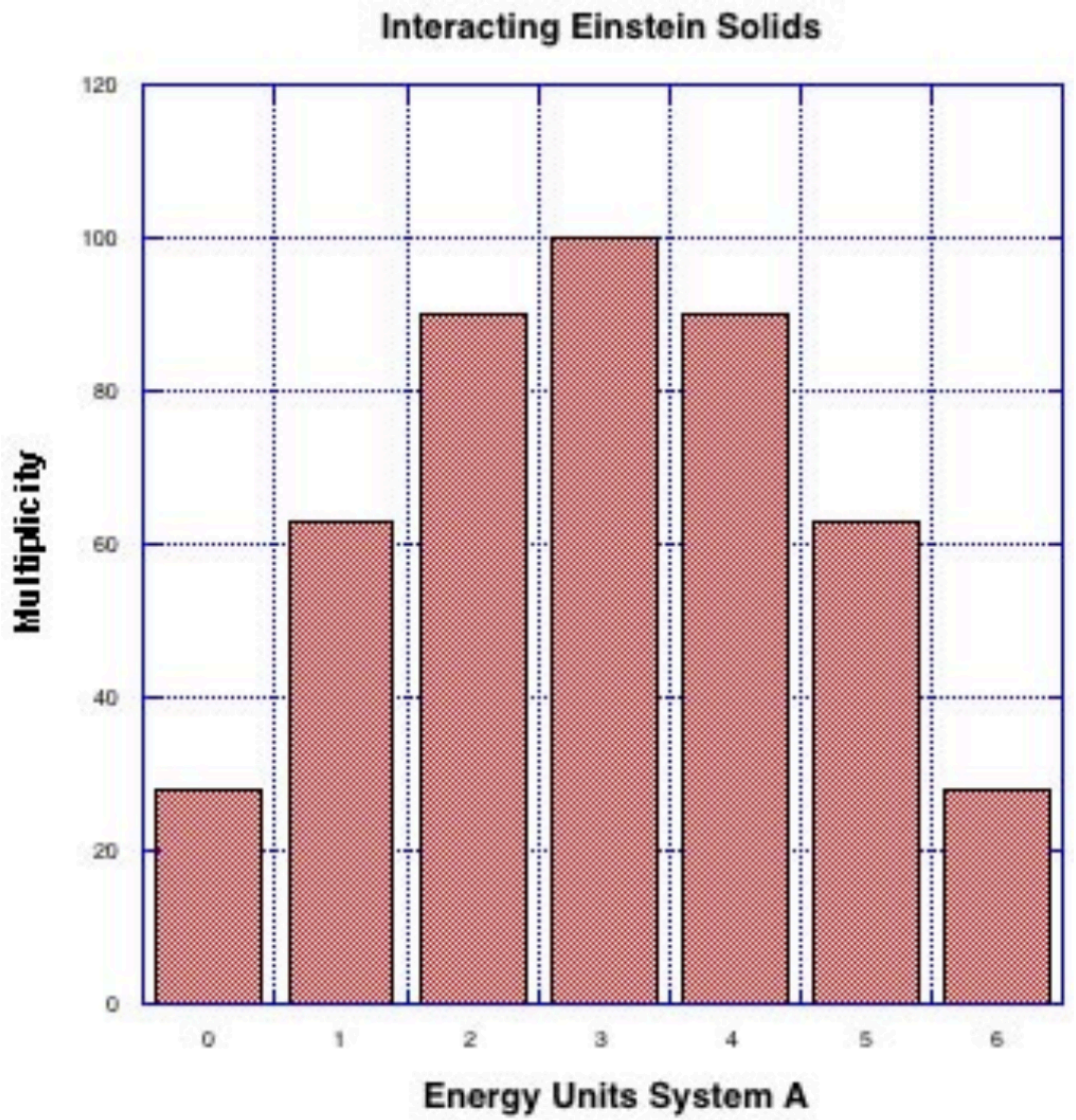
A table of these values is shown below

q_A	Ω_A	q_B	Ω_B	$\Omega = \Omega_A\Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

The total number of macrostates for the composite system is the sum of the last column

$$462 = \binom{q+N-1}{q} = \binom{13}{6} = \frac{13!}{6!7!}$$

A bar graph of the last column looks like:



As the system evolves in time all 462 microstates are accessible to the system since no conservation laws are violated.

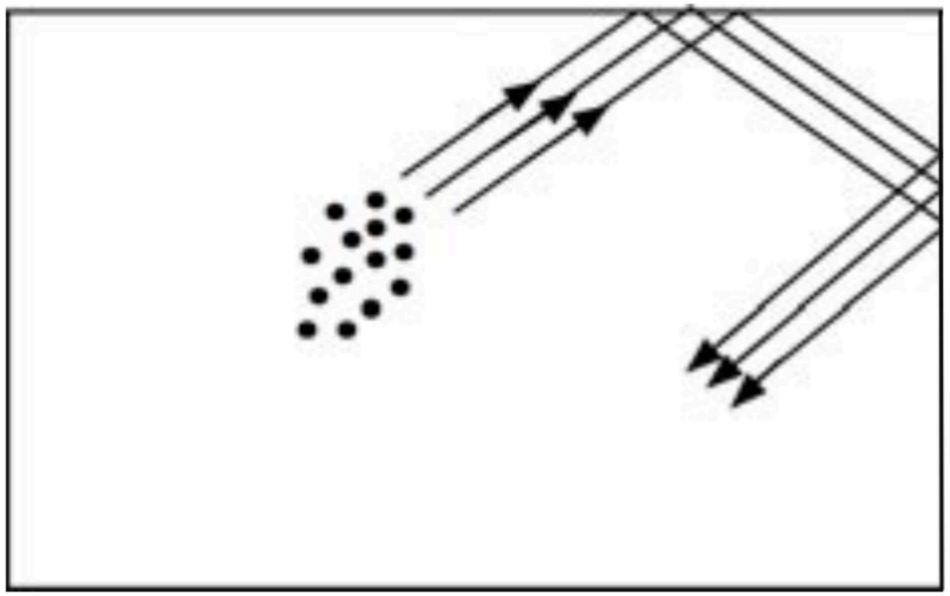
Now let us return to the very important assumption I mentioned earlier.

We assume that over very long time scales, energy exchanges are such that **all 462 microstates are equally probable**, that is, the composite system is equally likely to be in any of the 462 microstates. As I said earlier, this is the **fundamental assumption of statistical mechanics.**

> **In an isolated system in thermal equilibrium,**
> **all accessible microstates are equally probable.**

Concerning the Equal Probability of all Microstates

We imagine a box-shaped container and initialize all gas particles at time t_0 in the vicinity of the point P with **parallel** momenta as in the figure below.



Model System

Obviously, this is a microstate which is far from equilibrium. However, if our system behaves **ideally**, it will **never** reach equilibrium! For if each particle is reflected at the walls in an ideal way(equal angles), then the trajectories will forever stay parallel, and certain regions of coordinate space will never be reached.

In addition, the velocities of the particles will change (for pointlike particles with no mutual interactions) only with respect to direction, but not with respect to their magnitude. Thus, the equilibrium distribution will never be reached. This however, means that we may not assume that all microstates for this system have equal probability.

A more detailed consideration, however, shows that this system is too idealized. The fundamental objection is that, because of the quantum mechanical uncertainty relation $\Delta x \Delta p > \hbar$, we **cannot in principle** construct such an initial state, so that the particles will move randomly in all directions even after a short period of time.

Even in the framework of classical mechanics, where such an initial state is possible, there are actually no ideally reflecting walls and pointlike particles with no mutual interactions. Even the microscopic structure of a real wall is sufficient to distribute the particles, after a short time, homogeneously over the whole container. In addition, we would have to consider the thermal motion of the particles of the wall and the mutual collisions of the gas particles.

Finally, even the initial conditions can only be determined up to a certain measurement uncertainty, which also leads to randomization of the motion. Thus, even in this case the equilibrium distribution will be reached as the equilibrium state and the equal probability assumptions remains valid.

In the end, the equal probability of all compatible microstates is an assumption which can only be justified by experiments that check predictions based on the assumption. Up to now, no one has invented an experiment which disproves this assumption.

Many other things we have assumed so far or implicitly assumed to be true have also been questioned by physicists over the years. They have all also withstood this test of time and remain valid in the face of extensive experimentation.

The fundamental assumptions leads us to conclude that, while all 462 microstates are equally probable, some macrostates are more probable than others. For example, the probability of finding the composite system in the fourth macrostate where each system has 3 quanta of energy is 100/462, while the probability of finding the composite system in the first macrostate with all of the energy in system B is 28/462.

If we started off in the first state with all the energy in system B, then after a period of time the probability is large that we would find the energy more evenly distributed.

We may therefore say:

We may therefore say:

Since for every macrostate there exists a large number of microstates, the fact that an isolated system assumes an equilibrium state after a sufficiently long period of time can be traced back to the fact that **more microstates** belong to the equilibrium state than to any nonequilibrium state. Therefore we may understand the effort of the system to reach a maximum in of the multiplicity also as a transition to the most probable state, that is, the one with the largest number of microstates.

Let us now look at larger systems.

The table and graph below are for the case

$$N_A = 300 \,, N_B = 200 \,, N = N_A + N_B = 500 \quad , \quad q = q_A + q_B = 100 \rightarrow U = 100\hbar\omega$$

$$\Omega_A = \frac{(q_A + 299)!}{q_A!(299)!} \quad , \quad \Omega_B = \frac{(q_B + 199)!}{q_B!(199)!}$$

This composite system has 101 macrostates given by $q_A = 0,1,2,....,100$.

q_A	Ω_A	Ω_B	$\Omega = \Omega_A \Omega_B$	$\Pr ob = \Omega / \Omega(all)$
0	1	2.7721676e+81	2.7721676e+81	2.9931326e-35
1	300	9.2714637e+80	2.7814391e+83	3.0031431e-33
2	45150	3.0801171e+80	1.3906729e+85	1.5015212e-31
3	4545100	1.0163349e+80	4.6193440e+86	4.9875444e-30
4	3.4429132e+08	3.3305571e+79	1.1466819e+88	1.2380821e-28
5	2.0932913e+10	1.0838423e+79	2.2687976e+89	2.4496398e-27
6	1.0640897e+12	3.5022115e+78	3.7266673e+90	4.0237139e-26
7	4.6515922e+13	1.1235764e+78	5.2264192e+91	5.6430086e-25
8	1.7850485e+15	3.5785139e+77	6.3878208e+92	6.8969837e-24
9	6.1088327e+16	1.1313515e+77	6.9112368e+93	7.4621202e-23
10	1.8876293e+18	3.5501029e+76	6.7012782e+94	7.2354262e-22
11	5.3196826e+19	1.1055684e+76	5.8812728e+95	6.3500595e-21
12	1.3786844e+21	3.4165134e+75	4.7102937e+96	5.0857435e-20
13	3.3088426e+22	1.0475720e+75	3.4662509e+97	3.7425402e-19
14	7.3976266e+23	3.1866702e+74	2.3573796e+98	2.5452825e-18
15	1.5485698e+25	9.6159171e+73	1.4890919e+99	1.6077850e-17
16	3.0487469e+26	2.8780033e+73	8.7743036e+99	9.4736891e-17
17	5.6670824e+27	8.5424834e+72	4.8410957e+100	5.2269716e-16
18	9.9803618e+28	2.5142770e+72	2.5093394e+101	2.7093548e-15
19	1.6703974e+30	7.3370362e+71	1.2255766e+102	1.3232653e-14
20	2.6642838e+31	2.1224998e+71	5.6549418e+102	6.1056880e-14
21	4.0598611e+32	6.0860208e+70	2.4708399e+103	2.6677865e-13
22	5.9237064e+33	1.7294807e+70	1.0244936e+104	1.1061543e-12
23	8.2931890e+34	4.8700179e+69	4.0387979e+104	4.3607239e-12
24	1.1161250e+36	1.3586644e+69	1.5164394e+105	1.6373123e-11
25	1.4464980e+37	3.7548544e+68	5.4313895e+105	5.8643167e-11
26	1.8081225e+38	1.0277886e+68	1.8583677e+106	2.0064952e-10
27	2.1831405e+39	2.7859472e+67	6.0821142e+106	6.5669096e-10
28	2.5495963e+40	7.4769906e+66	1.9063307e+107	2.0582812e-09
29	2.8836813e+41	1.9865067e+66	5.7284522e+107	6.1850579e-09
30	3.1624371e+42	5.2237769e+65	1.6519866e+108	1.7836638e-08

```
31   3.3664653e+43   1.3593472e+65  4.5761951e+108   4.9409562e-08
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33   3.5032918e+45   8.9133781e+63  3.1226164e+109   3.3715151e-07
34   3.4311652e+46   2.2450990e+63  7.7033055e+109   8.3173234e-07
35   3.2743119e+47   5.5915673e+62  1.8308535e+110   1.9767879e-06
36   3.0469291e+48   1.3767117e+62  4.1947428e+110   4.5290990e-06
37   2.7669410e+49   3.3501728e+61  9.2697307e+110   1.0008606e-05
38   2.4538398e+50   8.0557591e+60  1.9767543e+111   2.1343181e-05
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42   1.2134955e+54   2.3784714e+58  2.8862643e+112   0.00031163237
43   9.6515221e+54   5.3677565e+57  5.1807020e+112   0.00055936473
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45   5.7515273e+56   2.6246750e+56  1.5095890e+113   0.0016299159
46   4.3136454e+57   5.6833514e+55  2.4515963e+113   0.0026470091
47   3.1755773e+58   1.2130473e+55  3.8521256e+113   0.0041591723
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53   3.5012083e+63   8.3132762e+50  2.9106511e+114   0.031426544
54   2.2887528e+64   1.5883089e+50  3.6352464e+114   0.039250060
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59   2.1783425e+68   3.0837640e+46  6.7174943e+114   0.072529348
60   1.3033749e+69   5.2680969e+45  6.8663054e+114   0.074136075
```

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62   4.4787575e+70   1.4447859e+44  6.4708456e+114   0.069866262
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81   1.5960483e+84   9.8821054e+26  1.5772318e+111   1.7029503e-05
82   7.4157854e+84   8.6128441e+25  6.3871004e+110   6.8962058e-06
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84   1.5561875e+86   5.6228245e+23  8.7501691e+109   9.4476308e-07
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86   3.1472880e+87   2.9330100e+21  9.2310272e+108   9.9668174e-08
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90   1.1571287e+90   3.5216131e+16  4.0749594e+106   4.3997678e-10
91   4.9591228e+90   1.6849824e+15  8.3560344e+105   9.0220803e-11
```

```
 92  2.11e+91    210.3     8   7.29e+13    31.9  1.54e+105  242.2
 93  8.88e+91    211.7     7   2.82e+12    28.7  2.50e+104  240.4
 94  3.71e+92    213.1     6   9.57e+10    25.3  3.56e+103  238.4
 95  1.54e+93    214.6     5   2.80e+09    21.8  4.32e+102  236.3
 96  6.34e+93    215.9     4   68685050    18.0  4.35e+101  234.0
 97  2.59e+94    217.4     3    1353400    14.1  3.50e+100  231.5
 98  1.05e+95    218.8     2      20100     9.9  2.11e+99   228.7
 99  4.21e+95    220.2     1        200     5.3  8.43e+97   225.5
100  1.68e+96    221.6     0          1     0.0  1.68e+96   221.6
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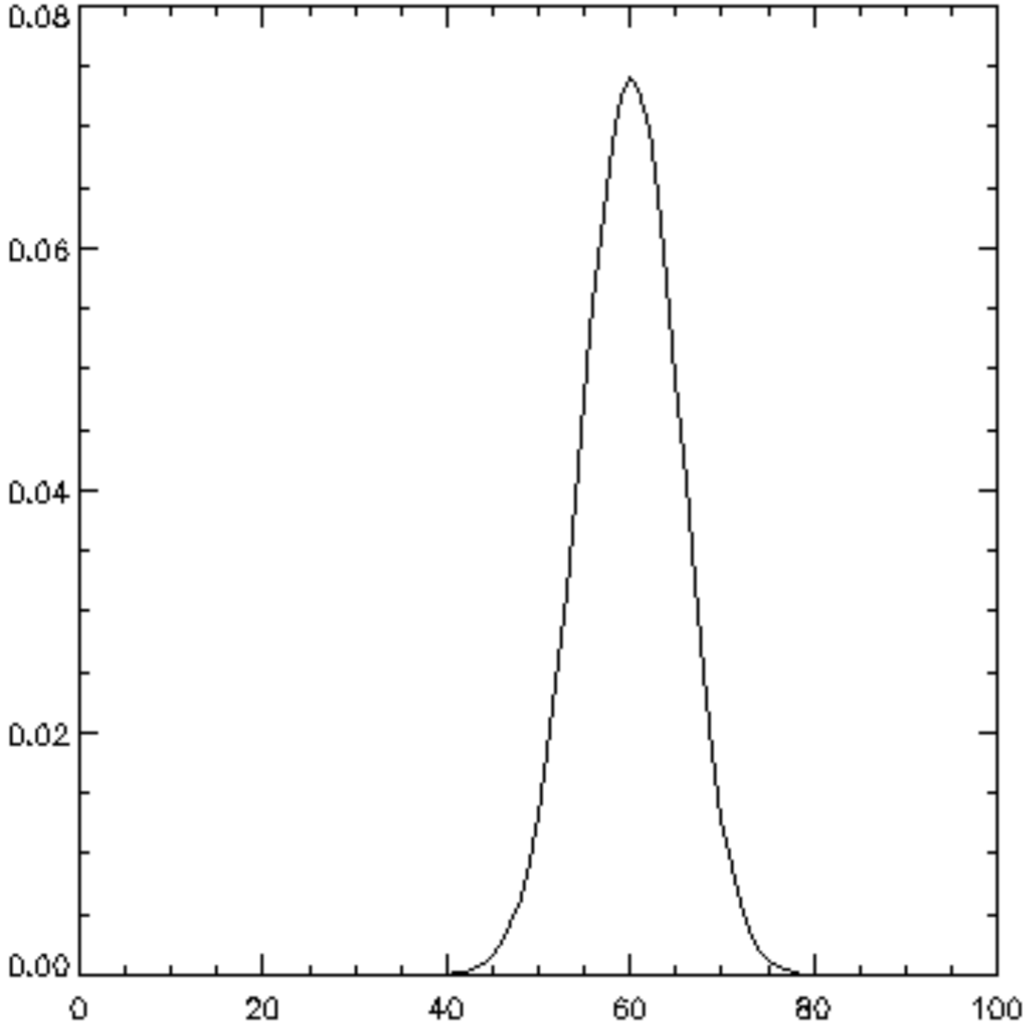


Plot of $\Pr ob = \Omega / \Omega(all)$ versus q_A

As can be seen from the data run even the least likely macrostate with all the energy in system B of the composite system ($q_A = 0$) has a multiplicity of 2.77×10^{81}. The most likely macrostate with $q_A = 60$ has a multiplicity of 6.87×10^{114}.

The important feature of these numbers is not that they are large, but that their ratio is large. The most likely macrostate is more than 10^{33} time more probable than the least likely macrostate.

The total number of microstates (sum of 4th column) is about 9×10^{115}. The probabilities of the microstates are listed in the last column.

The probability of finding the system in the most likely macrostate is 7.41%. There are several other macrostates with q_A near 60 whose probabilities are about the same value. Clearly, however, as q_A gets farther away from 60 on either side, the probability drops off very sharply.

The probability of finding $q_A < 30$ or $q_A > 90$ is less than 10^{-6}. The probability of finding $q_A < 10$ is less than 10^{-20}, which is small enough that you are not likely to see this happen in a time interval equal to the age of the universe.

Suppose, however, the system is initially prepared in a state with q_A very different than 60 (say much less than 60 so that most of the energy is in system B). If we now wait for the system to evolve in time, we almost certainly find that the energy rearranges itself (energy flows from B to A) and that the q_A tends towards 60.

The system exhibits **irreversible** behavior: energy flows spontaneously between systems(B to A) so that q_A tends towards 60. We never observe energy flow from A to B (the reverse process) except for small fluctuation around $q_A = 60$.

The system spontaneously(irreversibly) tends towards the most probable macrostate.

This is the physical explanation of **heat**(flow): it is a **probabilistic** phenomenon, not absolutely certain, but extremely likely.

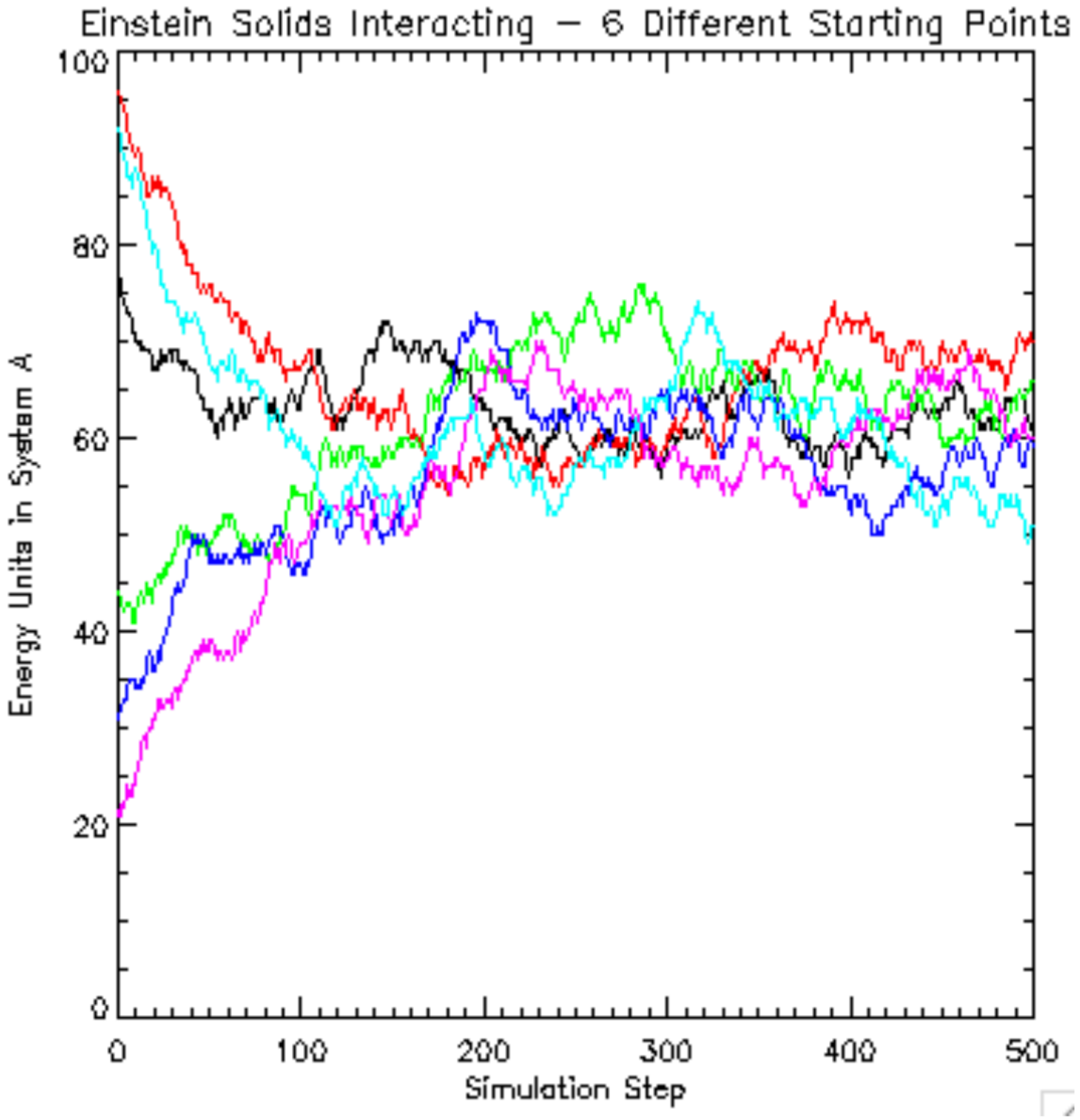
We have found a new law of physics:

> The spontaneous flow of energy **stops** when a system is at, or very near, its **most likely macrostate**, that is, the macrostate with the greatest multiplicity.

The "law of increase of multiplicity" is one version of the **second law of thermodynamics**.

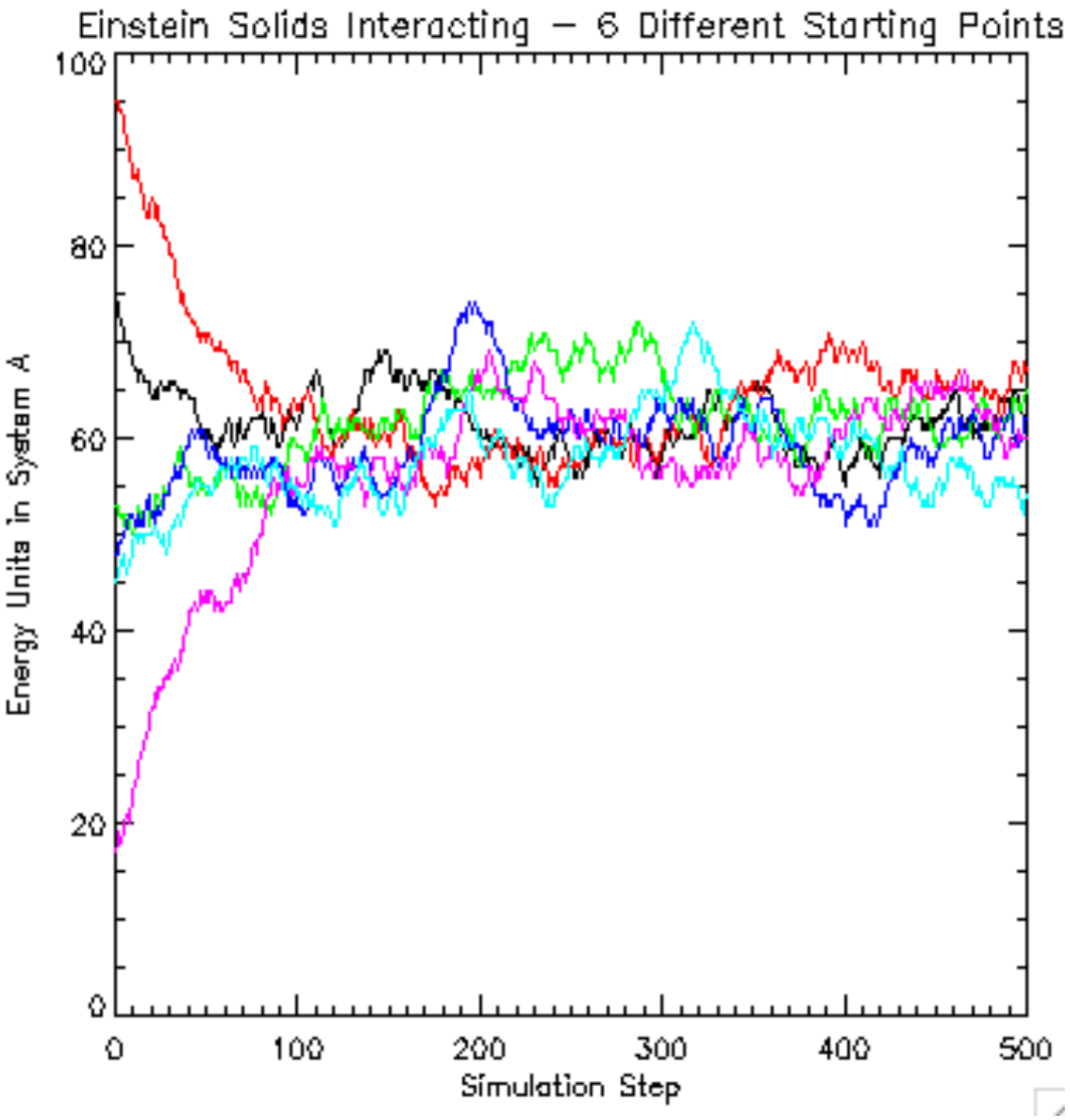
It is not, however, a **fundamental** law at all - it is just a very strong statement about probabilities.

The graphs below show the results of the simulation runs.

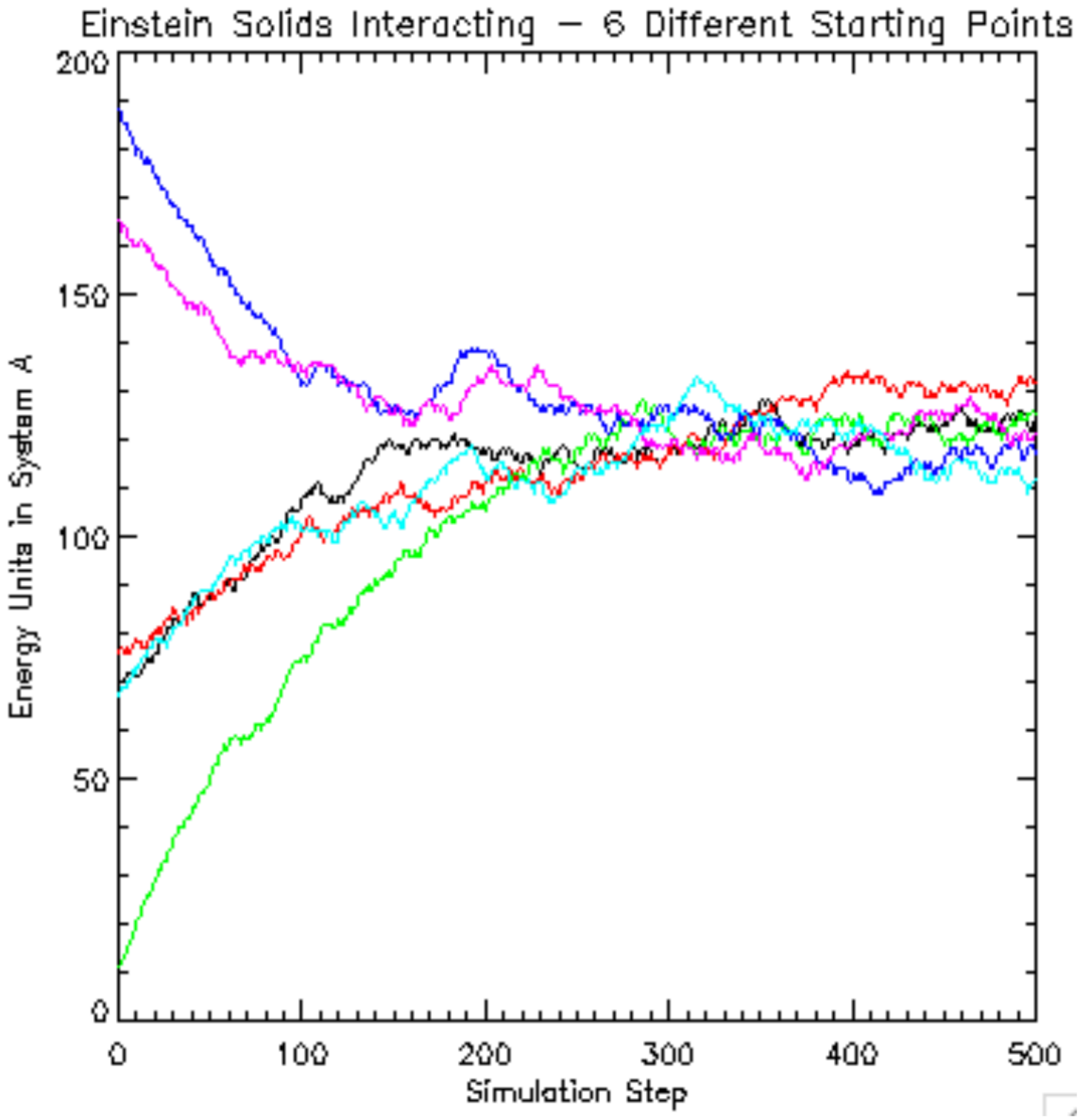


Parameters: $N_A = 60$, $N_B = 40$, $q = 100$

The simulation of the interacting Einstein solids and clearly shows the system moving to the most likely macrostate independent of the starting configuration or arrangement of the energy.



Parameters: $N_A = 300$, $N_B = 200$, $q = 100$



Parameters: $N_A = 600$, $N_B = 400$, $q = 200$

We clearly see the systems move towards the most like macrostate independent of starting configurations.

We also notice that as the number of oscillators gets larger the fluctuations decrease when we are near the most likely macrostate.

This result agrees with the ideas presented earlier.

Large Systems

What happens when the number of oscillators gets very large? First, we have to decide what we mean by large numbers.

Small numbers are number like 6, 23, and 42. These are straightforward to manipulate.

Large numbers are such that we can add a small number to it and not change it. For example, we can write (for all practical purposes)

$$10^{23} + 23 = 10^{23}$$

The only times this rule does not work is in the following type of situation

$$\frac{10^{23} + 50 - 10^{23}}{25} = \frac{50}{25} = 2$$

Very large numbers are even larger than large numbers, for example, $10^{10^{23}}$. Very large number can be multiplied by large numbers without changing them, for example

$$10^{10^{23}} \times 10^{23} = 10^{10^{23}+23} = 10^{10^{23}}$$

Again there are exceptions, for example

$$\frac{10^{10^{23}} \times 10^{23}}{10^{10^{23}}} = 10^{23}$$

A common trick for manipulating large numbers is to use then logarithm function since

$$\log(10^{23}) = 23$$

$$\log(10^{10^{23}}) = 10^{23}$$

and so on.

We, however, need to be able to deal with the factorial function of a large number. This is handled by Stirling's approximation.

Derivation of Stirling's Formula

We start with the definition of the Gamma Function:

$$\Gamma(p+1) = p! = \int_0^\infty x^p e^{-x} dx = \int_0^\infty e^{p\ell nx - x} dx$$

Substitute a new variable y such that

$$x = p + y\sqrt{p} \rightarrow dx = \sqrt{p}dy$$

Note that $x = 0 \rightarrow y = -\sqrt{p}$. We then have

$$p! = \int_0^\infty e^{p\ell nx - x} dx = \int_{-\sqrt{p}}^\infty e^{p\ell n\left(p + y\sqrt{p}\right) - p - y\sqrt{p}} \sqrt{p}dy$$

For large p, the logarithm can be expanded in the following power series

$$\ell n p\left(1+\frac{y}{\sqrt{p}}\right)=\ell n p+\ell n\left(1+\frac{y}{\sqrt{p}}\right)=\ell n p+\frac{y}{\sqrt{p}}-\frac{y^2}{2p}+\ldots\ldots$$

Substituting back into the original equation we get

$$p!\approx\int_{-\sqrt{p}}^{\infty}e^{p\ell n p+y\sqrt{p}-y^2/2-p-y\sqrt{p}}\sqrt{p}dy=e^{p\ell n p-p}\sqrt{p}\int_{-\sqrt{p}}^{\infty}e^{-y^2/2}dy$$

$$\approx e^{p\ell n p-p}\sqrt{p}\left[\int_{-\infty}^{\infty}e^{-y^2/2}dy-\int_{-\infty}^{-\sqrt{p}}e^{-y^2/2}dy\right]=e^{p\ell n p-p}\sqrt{p}\left[\sqrt{2\pi}-\int_{-\infty}^{-\sqrt{p}}e^{-y^2/2}dy\right]$$

The remaining integral tends to zero as $p\rightarrow\infty$. Therefore,

$$p!\approx e^{p\ell n p-p}\sqrt{2\pi p}=p^p e^{-p}\sqrt{2\pi p} \tag{2.14}$$

With a little more effort one can find

$$p!\approx e^{p\ell n p-p}\sqrt{2\pi p}=p^p e^{-p}\sqrt{2\pi p}\left(1+\frac{1}{12p}+\frac{1}{288p^2}+\ldots.\right)$$

If all we care about is the logarithm of $n!$, then we can use

$$\ell n(n!)\approx n\ell n(n)-n \tag{2.15}$$

Example: Suppose that you flip 1000 coins.

(a) What is the probability of getting exactly 500 heads and 500 tails?
(b) What is the probability of getting exactly 600 heads and 400 tails?

Solution: First note that for 1000 coins the total number of possible outcomes (microstates) is 2^{1000}.

(a) The number of ways of getting exactly 500 heads and 500 tails is

$$\Omega(500)=\binom{1000}{500}=\frac{1000!}{(500!)^2}=\frac{1000^{1000}e^{-1000}\sqrt{2\pi\cdot 1000}}{\left(500^{500}e^{-500}\sqrt{2\pi\cdot 500}\right)^2}=\frac{2^{1000}}{\sqrt{500\pi}}$$

The probability is this divided by 2^{1000} or $P(500)=\dfrac{1}{\sqrt{500\pi}}=0.025$ or the chance of getting exactly 500 heads is about 2.5% or 1 in 40.

(b) The number of ways of getting exactly 600 heads and 400 tails is

$$\Omega(600)=\binom{1000}{600}=\frac{1000!}{600!400!}=\frac{1000^{1000}e^{-1000}\sqrt{2\pi\cdot 1000}}{\left(600^{600}e^{-600}\sqrt{2\pi\cdot 600}\right)\left(400^{400}e^{-400}\sqrt{2\pi\cdot 400}\right)}=\frac{1000^{1000}}{600^{600}400^{400}\sqrt{480\pi}}$$

The probability is this divided by 2^{1000} or

$$P(600)=\frac{1000^{1000}}{2^{1000}600^{600}400^{400}\sqrt{480\pi}}=\frac{500^{1000}}{600^{600}400^{400}\sqrt{480\pi}}=\frac{500^{600}500^{400}}{600^{600}400^{400}\sqrt{480\pi}}=\left(\frac{5}{6}\right)^{600}\left(\frac{5}{4}\right)^{400}\frac{1}{\sqrt{480\pi}}$$

or 4.6×10^{-11} which is much smaller than $P(500)$.

Multiplicity of a Large Einstein Solid

The multiplicity formula is, in general,

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$

We only consider the case when $q >> N >>> 1$ which corresponds to many more energy quanta than oscillators (called the "high-temperature" limit as we shall see). Therefore,

$$\Omega(N,q) = \frac{(q+N)!}{q!N!} \tag{2.16}$$

We now take the logarithm and apply Stirling's formula:

$$\begin{aligned}\ell n\Omega &= \ell n\left(\frac{(q+N)!}{q!N!}\right) = \ell n\big((q+N)!\big) - \ell n\big(q!\big) - \ell n\big(N!\big) \\ &= (q+N)\ell n\big(q+N\big) - (q+N) - q\ell n\big(q\big) + q - N\ell n\big(N\big) + N \\ &= (q+N)\ell n\big(q+N\big) - q\ell n\big(q\big) - N\ell n\big(N\big)\end{aligned}$$

Now since $q >> N$ we have

$$\ell n(q+N) = \ell n\left(q\left(1+\frac{N}{q}\right)\right) = \ell n\big(q\big) + \ell n\left(1+\frac{N}{q}\right) = \ell n\big(q\big) + \frac{N}{q}$$

where we have used

$$\ell n(1+x) = x \quad , \quad x << 1$$

We then have

$$\ell n\Omega = (q+N)\left(\ell n(q) + \frac{N}{q}\right) - q\ell n(q) - N\ell n(N)$$

$$= N\ell n\frac{q}{N} + N + \frac{N^2}{q} \approx N\ell n\frac{q}{N} + N$$

Thus,

$$\Omega(N,q) = e^{N\ell n\frac{q}{N}+N} = e^N\left(\frac{q}{N}\right)^N = \left(\frac{eq}{N}\right)^N \qquad (2.17)$$

This result says(since N is a large number) that if we increase either N or q by a small amount, then Ω will increase by a very large amount because of the large exponent N.

Example: Derive a formula similar to eq (2.17) for the multiplicity of and Einstein solid in the "low temperature" limit $q << N$.

Solution: To simplify Ω in the limit $q << N$ (with both q and N large), we can start by repeating the steps above to obtain

$$\ell n\Omega = \ell n\left(\frac{(q+N)!}{q!N!}\right) = \ell n((q+N)!) - \ell n(q!) - \ell n(N!)$$

$$= (q+N)\ell n(q+N) - (q+N) - q\ell n(q) + q - N\ell n(N) + N$$

$$= (q+N)\ell n(q+N) - q\ell n(q) - N\ell n(N)$$

Now expand the first logarithm in the limit $q << N$:

$$\ell n(q+N) \approx \ell n\left[N\left(1+\frac{q}{N}\right)\right] = \ell nN + \ell n\left(1+\frac{q}{N}\right) \approx \ell nN + \frac{q}{N}$$

Therefore we have

$$\ell n\Omega = q\ell nN + q + \frac{q^2}{N} - q\ell nq \approx q\ell n\frac{N}{q} + q$$

where we have dropped the term $\frac{q^2}{N}$ since it is smaller than the others. We then have

$$\Omega = e^{q\ell n\frac{N}{q}+q} = \left(\frac{N}{q}\right)^q e^q = \left(\frac{eN}{q}\right)^q$$

We now ask the question: what is the spread of macrostates with appreciable probability for two interacting Einstein solids? or how skinny is the peak of the multiplicity function?

For simplicity we assume that each solid has N oscillators and we have a total of q energy quanta and that $q >> N >>> 1$. The multiplicity of the composite system is then

$$\Omega(2N,q) = \Omega(N,q_A)\Omega(N,q_B) = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \qquad (2.18)$$

where q_A and q_B are the number of energy quanta in systems A and B and $q = q_A + q_B$.

If we graph this as a function of q_A, it will have a very sharp peak at $q_A = q/2$, where the energy is distributed equally between the solids. The height of the peak is a very large number

$$\Omega_{\max} = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N}$$

What does this graph look like near the peak? We set

$$q_A = q/2 + x \rightarrow q_B = q/2 - x$$

where $1 << x <<< q$. We then get

$$\Omega = \left(\frac{e}{N}\right)^{2N}\left(\left(\frac{q}{2}\right)^2 - x^2\right)^N$$

We can simplify the second factor as follows:

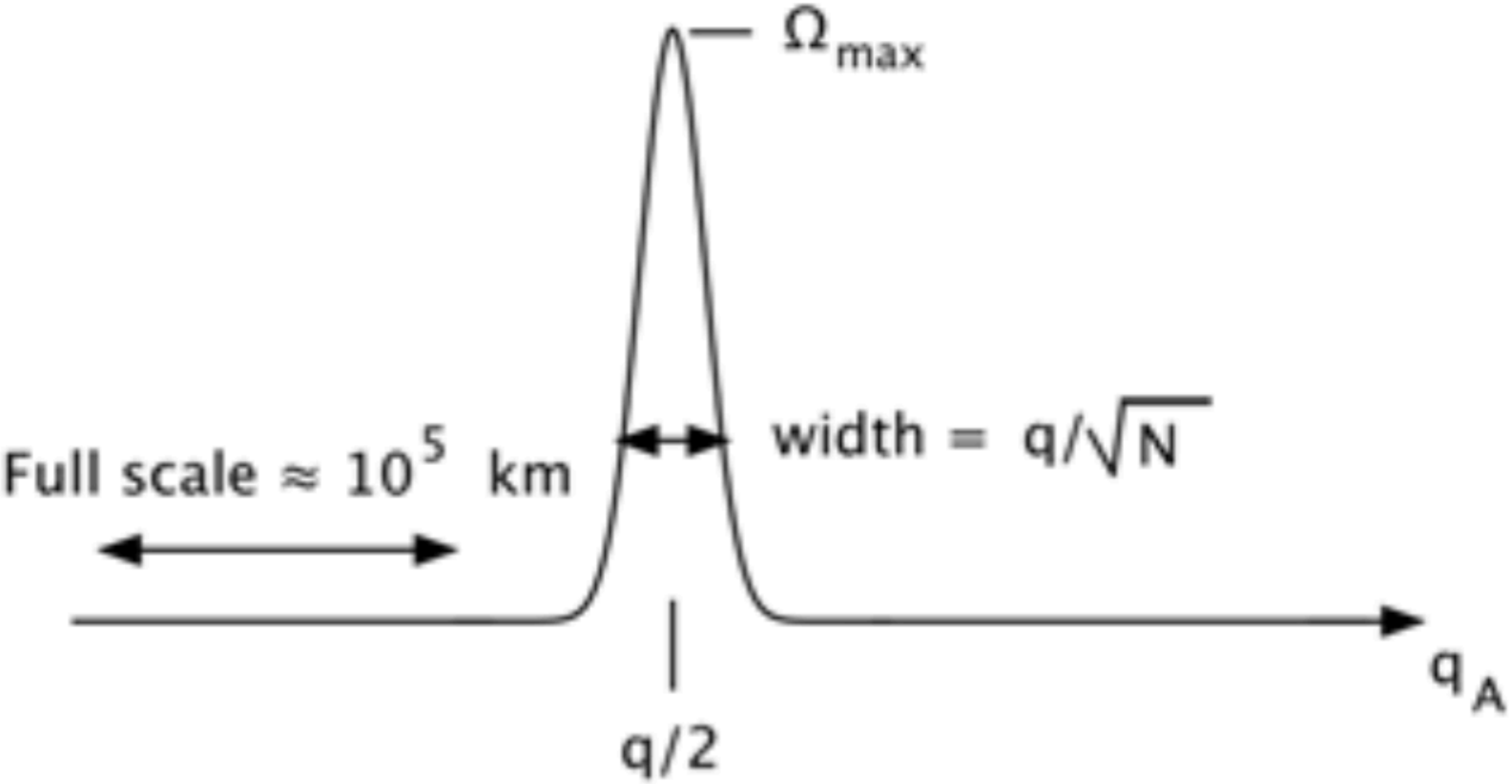
$$\ell n\left(\left(\frac{q}{2}\right)^2 - x^2\right)^N = N\ell n\left(\left(\frac{q}{2}\right)^2 - x^2\right) = N\ell n\left(\left(\frac{q}{2}\right)^2\left(1 - \left(\frac{2x}{q}\right)^2\right)\right)$$

$$= N\left[\ell n\left(\frac{q}{2}\right)^2 + \ell n\left(1 - \left(\frac{2x}{q}\right)^2\right)\right] = N\left[\ell n\left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2\right]$$

Thus,

$$\Omega = \left(\frac{e}{N}\right)^{2N} e^{N\left[\ell n\left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2\right]} = \Omega_{\max} e^{-N\left(\frac{2x}{q}\right)^2}$$

A function of this form is called a **Gaussian.** It has a peak at $x = 0$ and a sharp fall-off on either side as shown in the figure below:



The multiplicity falls to $1/e$ of its maximum value when

$$N\left(\frac{2x}{q}\right)^2 = 1 \rightarrow x = \frac{q}{2\sqrt{N}}$$

This is a very large number.

However, if $N = 10^{20}$ it is one part in 10 billion of the entire scale of the graph or on the scale of the graph with the width of the peak on the order of 1 cm, the full scale of the graph would be 10^{10} cm or 100,000 km (twice around the earth). The multiplicity drops to 10^{-44} of the maximum within 10 cm of the peak!!

This result tell us that for two interacting Einstein solid in thermal equilibrium with each (the final state after a long time), any random fluctuations away from the most likely macrostate will be **completely unmeasurable**!

Once the system has come to thermal equilibrium so that all the microstates are equally probable, we can assume that it is in the most likely macrostate.

The limit where a system becomes infinitely large so that measurable fluctuations away from then most likely macrostate never occur, is called the **thermodynamic limit.**

Example: For a single large, two-state paramagnet, the multiplicity function is very sharply peaked about $N_{\uparrow} = N/2$.

(a) Use Stirling's approximation to estimate the height of the peak in the multiplicity function.
(b) Derive a formula for the multiplicity function in the vicinity of the peak.
(c) How wide is the peak in the multiplicity function?
(d) Suppose you flip 1,000,000 coins. Would you be surprised to obtain 501,000 heads and 499,000 tails? Would you be surprised to obtain 510,000 heads and 490,000 tails?

Solution:

(a) The most likely macrostate is $N_\uparrow = N_\downarrow = N/2$. At this point the multiplicity is

$$\Omega_{\max} = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{((N/2)!)^2} \approx \frac{N^N e^{-N}\sqrt{2\pi N}}{((N/2)^{N/2} e^{-N/2}\sqrt{2\pi N/2})^2} = 2^N\sqrt{\frac{2}{\pi N}}$$

(b) By Stirling's approximation, the multiplicity is

$$\Omega = \frac{N!}{N_\uparrow! N_\downarrow!} \approx \frac{N^N e^{-N}\sqrt{2\pi N}}{(N_\uparrow^{N_\uparrow} e^{-N_\uparrow}\sqrt{2\pi N_\uparrow})\left(N_\downarrow^{N_\downarrow} e^{-N_\downarrow}\sqrt{2\pi N_\downarrow}\right)} = \frac{N^N}{N_\uparrow^{N_\uparrow} N_\downarrow^{N_\downarrow}}\sqrt{\frac{N}{2\pi N_\uparrow N_\downarrow}}$$

If we set $N_\uparrow = N/2 + x$, then $N_\downarrow = N/2 - x$ and the multiplicity becomes

$$\Omega = \frac{N^N}{(N/2+x)^{N_\uparrow}(N/2-x)^{N_\downarrow}}\sqrt{\frac{N}{2\pi(N/2+x)(N/2-x)}}$$

$$= \frac{N^N}{\left(\left(\frac{N}{2}\right)^2 - x^2\right)(N/2+x)^x (N/2-x)^{-x}}\sqrt{\frac{N}{2\pi\left(\left(\frac{N}{2}\right)^2 - x^2\right)}}$$

At this point it becomes simpler to work with logarithms:

$$\ell n\Omega = N\ell nN - \frac{N}{2}\ell n\left[\left(\frac{N}{2}\right)^2 - x^2\right] - x\ell n\left(\frac{N}{2}+x\right) + x\ell n\left(\frac{N}{2}-x\right)$$

$$+ \ell n\sqrt{\frac{N}{2\pi}} - \frac{1}{2}\ell n\left[\left(\frac{N}{2}\right)^2 - x^2\right]$$

So far we have not assumed anything about the size of x relative to N. But if $x << N$, we can expand each of the logarithms containing two terms. For example

$$\ell n\left[\left(\frac{N}{2}\right)^2 - x^2\right] = \ell n\left(\frac{N}{2}\right)^2 + \ell n\left[1-\left(\frac{2x}{N}\right)^2\right] \approx 2\ell n\left(\frac{N}{2}\right) - \frac{2x^2}{N}$$

Similarly,

$$\ell n\left(\frac{N}{2} \pm x\right) = \ell n\left(\frac{N}{2}\right) + \ell n\left(1 \pm \frac{2x}{N}\right) \approx \ell n\left(\frac{N}{2}\right) \pm \frac{2x}{N}$$

With these approximations, the logarithm of the multiplicity becomes

$$\begin{aligned}\ell n\Omega = N\ell nN - \frac{N}{2}\left(2\ell n\left(\frac{N}{2}\right) - \frac{2x^2}{N}\right) - x\left(\ell n\left(\frac{N}{2}\right) + \frac{2x}{N}\right) \\ + x\left(\ell n\left(\frac{N}{2}\right) - \frac{2x}{N}\right) + \ell n\sqrt{\frac{N}{2\pi}} - \frac{1}{2}\ell n\left[\left(\frac{N}{2}\right)^2 - x^2\right] \\ = N\ell n2 - \frac{2x^2}{N} + \ell n\sqrt{\frac{N}{2\pi}} - \frac{2x^2}{N^2}\end{aligned}$$

The last term is much smaller than the others and can be neglected. Exponentiating the remaining terms gives

$$\Omega = 2^N\sqrt{\frac{2}{\pi N}}e^{-2x^2/N}$$

This is a Gaussian function, peaked at $x = 0$ where its value $2^N\sqrt{\frac{2}{\pi N}}$ agrees with part (a).

(c) The Gaussian falls off to $1/e$ of its peak value when $\frac{2x^2}{N} = 1$ or $x = \sqrt{\frac{N}{2}}$. So the full width of the peak would be twice this or $\sqrt{2N}$.

(d) For $N = 10^6$, the half-width of the peak in the multiplicity function would be $\sqrt{500000}$ or about 700. So an excess of 1000 heads puts us only a little beyond the point where the Gaussian has fallen off to $1/e$ of its maximum value. I would not be surprised to get this many heads, although I might be surprised to get an excess of exactly 1000. On the other hand and excess of 10000 heads lies far outside of the peak in the multiplicity function. At this point the Gaussian has fallen off to $e^{-200} \approx 10^{-87}$ of its maximum value. If I got a result anywhere close to this, I would be quite certain that the coins were not fair.

Now let us return to the ideal gas we discussed earlier.

In eq (02.08) I made some assumption about multiplicities in order to discuss a simple example. Let us expand that discussion to see the correct result.

For simplicity we consider a monatomic ideal gas.

Multiplicity of a Monatomic Ideal Gas

We start with only one molecule and work our way to N molecules.

Suppose we have a single gas atom with kinetic energy U in a container of volume V. How many microstates are there for fixed U and V?

Since a container with twice the volume allows twice as many states (particle locations) to the molecule, the multiplicity must be linear in V. In addition, since the more different momentum vectors the particle can have allows it the have more microstates, the multiplicity should also be proportional to the "volume" available in **momentum space**, V_p, where momentum space is an imaginary "space" in which the axes are p_x, p_y, and p_z. Each "point" in momentum space corresponds to a possible momentum vector for the particle.

Therefore we might write as the multiplicity for one particle

$$\Omega_1 \propto VV_p. \tag{2.19}$$

In order to make use of this result (eq (02.17) we must determine the available volume in momentum space. The molecule's kinetic energy must equal U, we have a constraint

$$U = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

or

$$p_x^2 + p_y^2 + p_z^2 = 2mU$$

which defines the surface of a sphere in momentum space with radius $\sqrt{2mU}$. If a molecule has energy U, then its momentum vector must lie somewhere on the surface of such a sphere in momentum space. Therefore, the "volume" of momentum space is really the surface area of this sphere - actually it is multiplied by a small thickness to give a spherical shell as the "volume", because U will not be precisely known (see below).

The other problem with eq (02.19) is determining the proportionality constant. While the result seems to make sense, we still do not know how to count the microstates and get a finite number for the multiplicity, that is, the allowed number of states seems to be infinite even for only one particle.

To count the actual number of microstates we must invoke a result from quantum mechanics (we will derive this result later). If the single molecule is treated as a quantum system, then it must satisfy the **Heisenberg Uncertainty Principle (HUP):**

$$(\Delta x)(\Delta p_x) \approx \hbar \qquad (02.20)$$

where Δx is a measure of the spread of x values in a large set of measurements and Δp_x is a measure of the spread of p_x values in a large set of measurements.

We choose approximate equality in the HUP relation (it is actually ≥) because we are interested in situations where we are specifying the position and momentum as precisely as possible. The same limitation hold for y and z.

The total number of distinct states is then

$$\Omega_1 = \frac{VV_p}{\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z} = \frac{VV_p}{\hbar^3} \qquad (02.21)$$

What happens if we add a second molecule? We need a factor of the form in eq (02.19) for each molecule and it seems as if they must be multiplied because for each state of molecule 1 there are Ω_1 states for molecule 2. However, this is not exactly true. The V factors work that way, but the V_p factors do not since only the total energy for the two molecules is constrained. The constraint equation now becomes

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = 2mU$$

This equation describes the surface of a 6-dimensional "hypersphere in momentum space. Thus the multiplicity function becomes

$$\Omega_2 = \frac{V^2}{\hbar^6}\left(\text{area of momentum hypersphere}\right)$$

The formula is correct only if the 2 molecules are distinguishable from each other. If they are indistinguishable we have over counted the microstates by a factor of 2 (interchange of the particles does not count as a new microstate). Therefore,

$$\Omega_2 = \frac{1}{2}\frac{V^2}{\hbar^6}\left(\text{area of momentum hypersphere}\right)$$

This process generalizes to N molecules so that

$$\Omega_N = \frac{1}{N!}\frac{V^N}{\hbar^{3N}}\left(\text{area of momentum hypersphere}\right)$$

where the hypersphere(still with radius $2mU$) is $3N$-dimensional.

The area of a d-dimensional hypersphere is (

$$"area" = \frac{2\pi^{d/2}}{(d/2-1)!} r^{d-1}$$

For $d = 3N$ we get

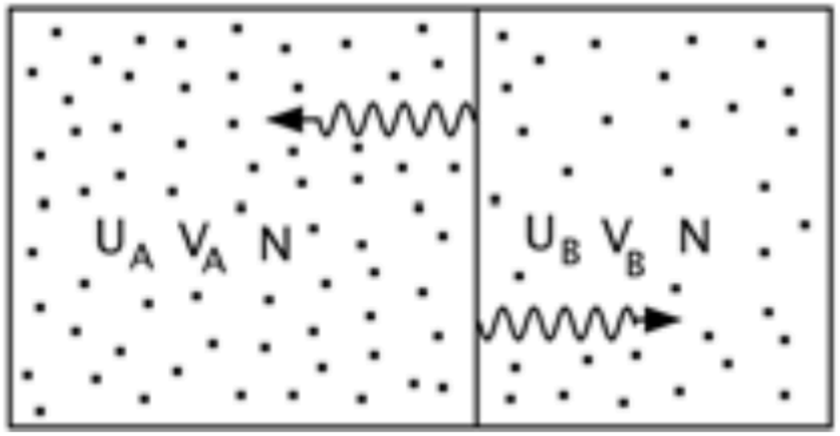
$$\Omega_N = \frac{1}{N!}\frac{V^N}{\hbar^{3N}}\frac{2\pi^{3N/2}}{(3N/2-1)!}(\sqrt{2mU})^{3N-1} \approx \frac{1}{N!}\frac{V^N}{\hbar^{3N}}\frac{2\pi^{3N/2}}{(3N/2)!}(\sqrt{2mU})^{3N}$$

or

$$\Omega_N = f(N)V^N U^{3N/2}$$

Interacting Ideal Gases

We now consider a system with two ideal gases each confined to a fixed volume, separated by a partition that allows transfer of energy as shown below:



The total energy of the two gases is fixed. The total multiplicity of this system is

$$\Omega_{total} = \Omega_{N,A}\Omega_{N,B} = (f(N))^2(V_A V_B)^N(U_A U_B)^{3N/2}$$

Since this multiplicity function is similar to the cases we have already discussed, if we use the same reasoning we find that, for the cases where the systems can exchange energy,

(1) The multiplicity function plotted as a function of U_A (or U_B) has a very sharp peak:

$$\text{width of peak} = \frac{V_{total}}{\sqrt{N}}$$

which says that, for large N, only a very small fraction of the microstates have an appreciable probability of occurring (for a system in equilibrium).

If, on the other hand, the partition is movable and thus the systems can exchange volume, similar arguments lead to the conclusion that

(1) The multiplicity function plotted as a function of V_A (or V_B) has a very sharp peak:

$$\text{width of peak} = \frac{U_{total}}{\sqrt{3N/2}}$$

which says that, for large N, only a very small fraction of the microstates have an appreciable probability of occurring (for a system in equilibrium).

In either case, the equilibrium macrostate is essentially determined to within a tiny fraction of the energy (or volume) available (if N is large).

Finally, if the partition is fixed, but we poke holes in it to let the molecules move between systems, then we want to look at the behavior of as a function of U_A (or U_B) and N_A (or N_B).

The analysis is very difficult (statistical mechanics), but once again we would find a sharp peak indicating that the equilibrium macrostate is fixed to very high precision (the equilibrium state is the one where the density is the same on both sides).

Entropy

As we have already realized with the help of these examples, the larger Ω , the more probable is the corresponding macrostate, and **the macrostate with the largest number $\Omega_{\max}$ of possible microscopic realizations corresponds to thermodynamic equilibrium.**

Hence, if the particles of a system have arbitrary given coordinates and momenta in the beginning(for example, a gas which gathers in one corner of a box), (q_j , p_j) assume some other values in the course of time, that is, another possible microstate.

All of the many possible microstates correspond to only one macrostate, namely, the equilibrium state.

Thus, after a long period of time, one observes only the equilibrium state, with a probability that is very near to unity.

In particular,in this statistical point of view deviations from the equilibrium state are, for a finite number of particles, not impossible but only extremely improbable.

Especially for very small systems in extreme situations (for example, gases near a critical point) one may indeed observe deviations from the equilibrium state in the form of **fluctuations** which will have appreciable size only under certain conditions.

We state this result as follows:

> Any large system in equilibrium will be found in the macrostate with the greatest multiplicity.

The is just a more general statement of the **second law of thermodynamics.**

Another way to say it is simply:

> Multiplicity tends to increase.

We will treat this rule (learning from looking at probabilities) as a fundamental law from now on.

For two statistically independent systems the total number of compatible microstates Ω_{tot} is the product of the numbers for the individual systems, namely, $\Omega_{tot} = \Omega_1\Omega_2$.

The multiplicities tend to be very large numbers and thus are very difficult to work with. We thus introduce a new quantity called the entropy by the relation

$$S = k\ell n\Omega \tag{2.22}$$

where k is Boltzmann's constant. We will see later that there is a natural thermodynamic quantity that has all the same properties as that of the entropy defined by eq (02.20) and we set the two quantities equal to each other.

Since $\Omega_{tot} = \Omega_1\Omega_2$, we then have

$$S = k\ell n\Omega = k\ell n\Omega_1\Omega_2 = k\ell n\Omega_1 + k\ell n\Omega_2 = S_1 + S_2$$

so that the entropy is an extensive state quantity, which is simply added for both systems making up the larger system, $S_{tot} = S_1 + S_2$.

Furthermore, according to our discussion, the entropy S has to assume a maximum in equilibrium.

Eq (02.20) represents the fundamental relationship between thermodynamics and statistical mechanics. With this relationship, we recognize that the equilibrium state of thermodynamics with a maximum of the entropy is the state with the largest number of microscopic possibilities of realizing this state.

We can then restate the second law:

> Any large system in equilibrium will be found in the macrostate with the greatest entropy.

or

> Entropy tends to increase.

□

The peak in the entropy distribution as function of macrostates is not as sharp as that of the multiplicity since the logarithm function tends to smooth out such sharp peaks. The conclusions are the same however.

Although "spontaneous" processes always occur because of a net increase in entropy, is it possible that human intervention could bring about a net decrease in entropy?

The answer is certainly yes. You can easily turn all coins to heads or sort a shuffled deck of cards or clean up a messy room.

Although each of these processes represents a decrease in entropy (very small decrease) the effort required by us to carry out the rearrangements always represents a larger increase of entropy so that there is a net increase for the combined systems.

Example: How many possible arrangements are there for a deck of 52 playing cards? Suppose you start with a sorted deck and shuffle it repeatedly so that all the arrangements become "accessible". How much entropy do you create in the process? Is this entropy significant compared to the entropy associated with arranging thermal energy among the molecules in the cards?

Solution: There are 52 possible cards that could be on top and for each of these choices there are 51 possibilities for the next card, then 50 for the next, and so on down to 1 choice for the bottom card. So the total number of arrangements is $52! = 8.06 \times 10^{67}$. If all arrangements are accessible, then the entropy is

$$\frac{S}{k} = \ell n 52! = 156 \rightarrow S = 156k = 2.16 \times 10^{-21}\ J/K$$

This is then the amount of entropy created by shuffling the cards and its tiny compared to the entropy associated with the thermal motions, which is typically a large number (proportional to the number of particles) in fundamental units and a number of order 1 when multiplied by Boltzmann's constant.

Entropy of an Ideal Gas

We have an ideal monatomic gas the result

$$\Omega = \frac{1}{N!}\frac{V^N}{\hbar^{3N}}\frac{2\pi^{3N/2}}{(3N/2)!}(\sqrt{2mU})^{3N}$$

Therefore the corresponding entropy is given by

$$S = k\ell n\Omega = k\ell n\left[\frac{1}{N!}\frac{V^N}{\hbar^{3N}}\frac{2\pi^{3N/2}}{(3N/2)!}(\sqrt{2mU})^{3N}\right]$$
$$= -k\ell nN! + kN\ell nV - 3kN\ell n\hbar + k\ell n2 + \frac{3Nk}{2}\ell n\pi - k\ell n(3N/2)! + \frac{3Nk}{2}\ell n(2m$$

Now $\ell n(n!) \approx n\ell n(n) - n$ so that

$$\ell nN! = N\ell nN - N \quad \text{and} \quad \ell n(3N/2)! = \frac{3N}{2}\ell n\frac{3N}{2} - \frac{3N}{2}$$

so that

$$\begin{aligned} S &= -k(N\ell nN - N) + kN\ell nV - 3kN\ell n\hbar + k\ell n2 \\ &\qquad + \frac{3Nk}{2}\ell n\pi - k\left(\frac{3N}{2}\ell n\frac{3N}{2} - \frac{3N}{2}\right) + \frac{3Nk}{2}\ell n(2mU) \\ &= Nk\left(-\ell nN + 1 + \ell nV - 3\ell n\hbar + \frac{3}{2}\ell n\pi - \frac{3}{2}\ell n\frac{3N}{2} + \frac{3}{2} + \frac{3}{2}\ell n(2mU)\right) \qquad (02.23) \\ &= Nk\left(\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right) \end{aligned}$$

which is the **Sackur-Tetrode** equation.

This equation says that the entropy change when the volume changes from V_i to V_f with U and N fixed is

$$\Delta S = Nk\ell n\frac{V_f}{V_i} \tag{02.24}$$

This corresponds to a quasistatic isothermal (U fixed) expansion where the gas pushes on a piston, doing mechanical work, while we simultaneously supply heat from the outside to keep the gas at constant temperature or internal energy. We can think of the entropy increase being caused by the heat input. Putting heat into a system always increases the entropy as we shall see in the next chapter.

A very different way of letting a gas expand is the following:

(1) Initially the gas is separated by a partition from an evacuated chamber.

(2) We then puncture the partition letting the gas freely expand to fill the whole available space.

This process is called **free expansion.**

The amount of work done in this process is zero! The gas is not pushing on anything so it cannot do any work.

The amount of heat in this process is zero! No heat flows into or out of the gas.

Therefore, by the first law we have

$$\Delta U = Q + W = 0$$

The energy content of the gas does not change during free expansion! Therefore we have

$$\Delta S = Nk\ell n\frac{V_f}{V_i}$$

and the entropy increases!

This entropy increase was not caused by the input of heat. Instead, we have manufactured new entropy (increase of volume or phase space) right on the spot.

Example: Show that during the quasistatic isothermal expansion of a monatomic ideal gas, the change in entropy is related to the heat input Q by the simple formula

$$\Delta S = \frac{Q}{T}$$

We will show later that this result is true for **any** quasistatic process. Show, however, that it is not valid for the free expansion process.

Solution: The increase in entropy during quasistatic isothermal expansion of an ideal gas is given by

$$\Delta S = Nk\ell n\frac{V_f}{V_i}$$

where V_i and V_f are the initial and final volumes. But the heat input during this process is given by

$$Q = -W = +\int_{V_i}^{V_f} PdV = +\int_{V_i}^{V_f} \frac{NkT}{V}dV = NkT\ell n\frac{V_f}{V_i}$$

Therefore, we have $\Delta S = Q/T$.

For free expansion, however, we still have $\Delta S = Nk\ell n\frac{V_f}{V_i}$ but $Q = 0$, therefore, $\Delta S \neq Q/T$.

Entropy of Mixing

Suppose that we start with two different monatomic ideal gases, A and B, each with the same energy,volume and number of particles. Suppose also that they occupy two halves of a divided chamber, separated by a partition. If we now remove the partition, the entropy increases. To calculate how much we treat each gas as a separate system even after they mix. Since gas A expands to fill twice its original volume, it entropy increases by

$$\Delta S_A = Nk\ell n\frac{V_f}{V_i} = Nk\ell n2$$

The entropy of gas B increases by the same amount giving a total increase of

$$\Delta S = \Delta S_A + \Delta S_B = 2Nk\ell n2$$

which is called the **entropy of mixing.** This only occurs if the two gases are different. If the gases are the same, there is no increase of entropy since we cannot tell if anything happened.

Example: Calculate the entropy of mixing for a system of two monatomic ideal gases, A and B, whose relative proportion is arbitrary. Let N be the total number of molecules and let x be the fraction of these that are species B.

Solution: The number of B molecules is xN. When the partition is removed, these molecules expand to fill a volume that is greater by a factor of $1/x$ so their entropy increases by

$$\Delta S_B = (xN)k\ell n\frac{1}{x} = -Nkx\ell nx$$

according to the **Sackur-Tetrode** equation. Similarly, the number of A molecules is $(1-x)N$ and these expand in volume by a factor of $1/(1-x)$ so that

$$\Delta S_A = ((1-x)N)k\ell n\frac{1}{1-x} = -Nk(1-x)\ell n(1-x)$$

The total entropy increase upon mixing is their sum,

$$\Delta S_{mixing} = \Delta S_A + \Delta S_B = -Nk\left[x\ell nx + (1-x)\ell n(1-x)\right]$$

When $x = 1/2$, this expression reduces to

$$\Delta S_{mixing} = -Nk\left[\tfrac{1}{2}\ell n\tfrac{1}{2} + \tfrac{1}{2}\ell n\tfrac{1}{2}\right] = Nk\ell n2$$

Since N is the total number of molecules, which was $2N$ above the results agree.

3 - Interactions and Implications

We now know that whenever two large systems interact, they will evolve toward whatever macrostate has the highest possible entropy (multiplicity). This is the statement of the second law of thermodynamics. Most important results of thermodynamics, as we shall see, are consequences of the second law.

Although we have hinted at various relationships, we now want to carefully work out the relations between entropy and other thermodynamic variables like temperature, pressure, etc.

Temperature

The second law says that when two objects are in thermal equilibrium, their total entropy is a maximum.

We earlier defined the temperature to be some quantity which is the same for both objects when they are in thermal equilibrium, that is, we said that they were at the same temperature. We have seen that the temperature appears in the internal energy of an ideal gas, that is, $U = 3NkT/2$ and in the equation of state of the ideal gas, that is, $PV = NkT$. This two results are the result of the laws of mechanics and/or the equipartition theorem and experiment.

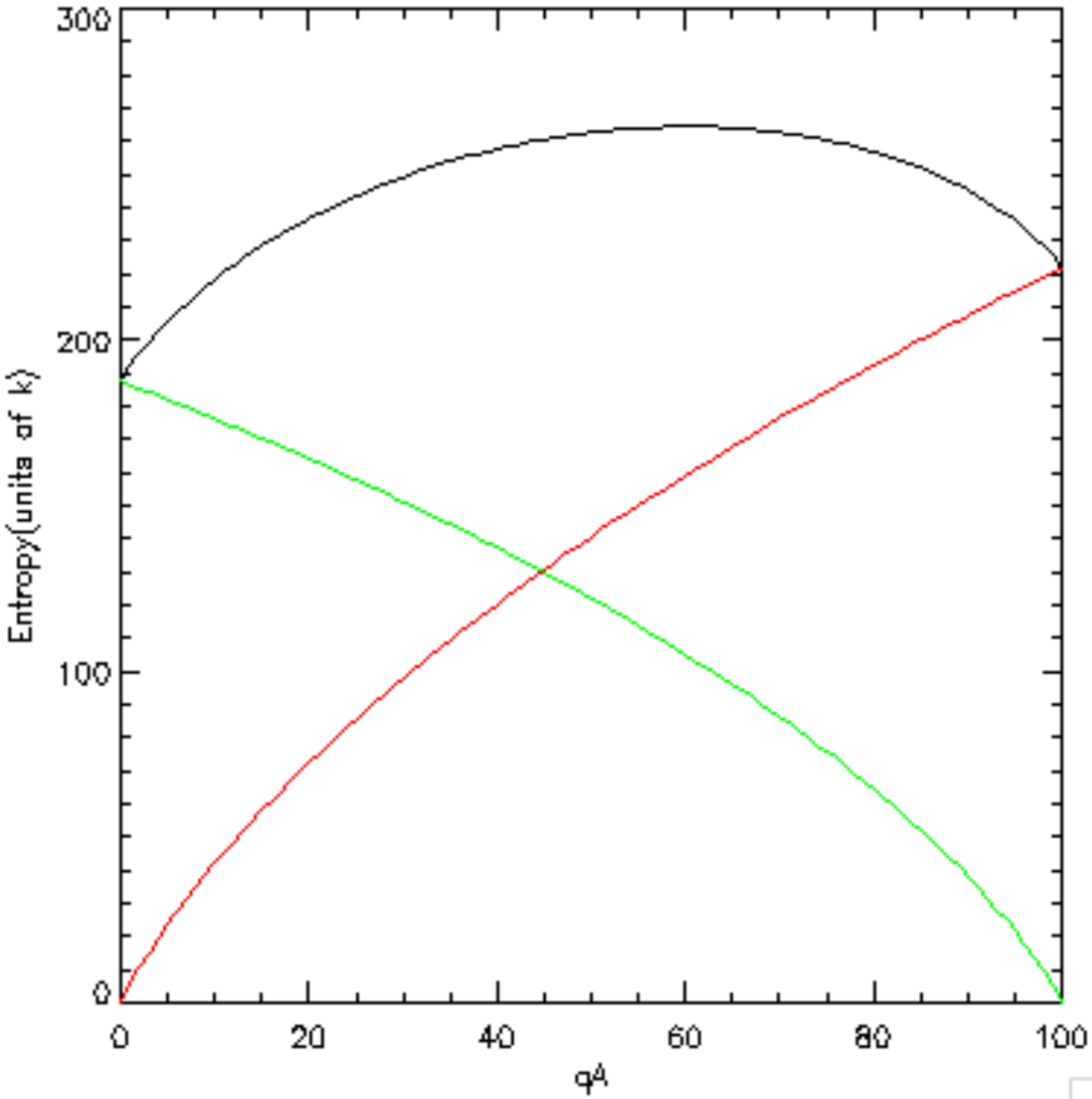
Let us attempt now to find some mathematical relation for the temperature. We consider a specific example of two Einstein solids, A and B that are weakly interacting, that is, they can exchange energy but their total energy is fixed. We use the model we considered earlier where the number of oscillators in the two solids are $N_A = 300$ and $N_B = 200$ and that they are sharing 100 quanta of energy ($q = 100$). We now list all the microstates and multiplicities as before and add columns for the entropies.

q_A	Ω_A	S_A/k	q_B	Ω_B	S_B/k	Ω_{total}	S_{total}/k
0	1	0	100	2.77e+81	187.5	2.77e+81	187.5
1	300	5.7	99	9.27e+80	186.4	2.78e+83	192.1
2	45150	10.7	98	3.08e+80	185.4	1.39e+85	196.0
3	4545100	15.3	97	1.02e+80	184.2	4.62e+86	199.6
4	3.44e+08	19.7	96	3.33e+79	183.1	1.15e+88	202.8
5	2.09e+10	23.8	95	1.08e+79	182.0	2.29e+89	205.7
6	1.06e+12	27.7	94	3.50e+78	180.9	3.73e+90	208.5
7	4.65e+13	31.5	93	1.12e+78	179.7	5.23e+91	211.2
8	1.79e+15	35.1	92	3.58e+77	178.6	6.39e+92	213.7
9	6.11e+16	38.7	91	1.13e+77	177.4	6.91e+93	216.1
10	1.89e+18	42.1	90	3.55e+76	176.3	6.70e+94	218.3
11	5.32e+19	45.4	89	1.11e+76	175.1	5.88e+95	220.5
12	1.38e+21	48.7	88	3.42e+75	173.9	4.71e+96	222.6
13	3.31e+22	51.9	87	1.05e+75	172.7	3.47e+97	224.6
14	7.40e+23	55.0	86	3.19e+74	171.6	2.36e+98	226.5
15	1.55e+25	58.0	85	9.62e+73	170.4	1.49e+99	228.4
16	3.05e+26	61.0	84	2.88e+73	169.1	8.77e+99	230.1
17	5.67e+27	63.9	83	8.54e+72	167.9	4.84e+100	231.8
18	9.98e+28	66.8	82	2.51e+72	166.7	2.51e+101	233.5
19	1.67e+30	69.6	81	7.34e+71	165.5	1.23e+102	235.1
20	2.66e+31	72.4	80	2.12e+71	164.2	5.65e+102	236.6
21	4.06e+32	75.1	79	6.09e+70	163.0	2.47e+103	238.1
22	5.92e+33	77.8	78	1.73e+70	161.7	1.02e+104	239.5
23	8.29e+34	80.4	77	4.87e+69	160.5	4.04e+104	240.9
24	1.12e+36	83.0	76	1.36e+69	159.2	1.52e+105	242.2
25	1.45e+37	85.6	75	3.75e+68	157.9	5.43e+105	243.5
26	1.81e+38	88.1	74	1.03e+68	156.6	1.86e+106	244.7
27	2.18e+39	90.6	73	2.79e+67	155.3	6.08e+106	245.9
28	2.55e+40	93.0	72	7.48e+66	154.0	1.91e+107	247.0
29	2.88e+41	95.5	71	1.99e+66	152.7	5.73e+107	248.1
30	3.16e+42	97.9	70	5.22e+65	151.3	1.65e+108	249.2

q_A	Ω_A	S_A / k	q_B	Ω_B	S_B / k	Ω_{total}	S_{total} / k
31	3.37e+43	100.2	69	1.36e+65	149.0	4.58e+108	250.2
32	3.48e+44	102.6	68	3.50e+64	148.6	1.22e+109	251.2
33	3.50e+45	104.9	67	8.91e+63	147.3	3.12e+109	252.1
34	3.43e+46	107.2	66	2.25e+63	145.9	7.70e+109	253.0
35	3.27e+47	109.4	65	5.59e+62	144.5	1.83e+110	253.9
36	3.05e+48	111.6	64	1.38e+62	143.1	4.19e+110	254.7
37	2.77e+49	113.8	63	3.35e+61	141.7	9.27e+110	255.5
38	2.45e+50	116.0	62	8.06e+60	140.2	1.98e+111	256.3
39	2.13e+51	118.2	61	1.91e+60	138.8	4.07e+111	257.0
40	1.80e+52	120.3	60	4.49e+59	137.4	8.09e+111	257.7
41	1.49e+53	122.4	59	1.04e+59	135.9	1.55e+112	258.3
42	1.21e+54	124.5	58	2.38e+58	134.4	2.89e+112	258.9
43	9.65e+54	126.6	57	5.37e+57	132.9	5.18e+112	259.5
44	7.52e+55	128.7	56	1.20e+57	131.4	8.99e+112	260.1
45	5.75e+56	130.7	55	2.62e+56	129.9	1.51e+113	260.6
46	4.31e+57	132.7	54	5.68e+55	128.4	2.45e+113	261.1
47	3.18e+58	134.7	53	1.21e+55	126.8	3.85e+113	261.5
48	2.30e+59	136.7	52	2.55e+54	125.3	5.86e+113	262.0
49	1.63e+60	138.6	51	5.29e+53	123.7	8.62e+113	262.3
50	1.14e+61	141.0	50	1.08e+53	122.1	1.23e+114	262.7
51	7.81e+61	142.5	49	2.17e+52	120.5	1.69e+114	263.0
52	5.27e+62	144.4	48	4.28e+51	118.9	2.26e+114	263.3
53	3.50e+63	146.3	47	8.31e+50	117.2	2.91e+114	263.6
54	2.29e+64	148.2	46	1.59e+50	115.6	3.64e+114	263.8
55	1.47e+65	150.1	45	2.98e+49	113.9	4.39e+114	264.0
56	9.34e+65	151.9	44	5.50e+48	112.2	5.14e+114	264.13
57	5.83e+66	153.7	43	9.96e+47	110.5	5.81e+114	264.25
58	3.59e+67	155.6	42	1.77e+47	108.8	6.35e+114	264.34
59	2.18e+68	157.4	41	3.08e+46	107.0	6.72e+114	264.40
60	1.30e+69	159.1	40	5.27e+45	105.3	6.87e+114	264.42

q_A	Ω_A	S_A/k	q_B	Ω_B	S_B/k	Ω_{total}	S_{total}/k
61	7.69+69	160.9	39	8.82e+44	103.5	6.78e+114	264.41
62	4.48e+70	162.9	38	1.44e+44	101.7	6.47e+114	264.36
63	2.57e+71	164.4	37	2.32e+43	99.9	5.96e+114	264.28
64	1.46e+72	166.1	36	3.63e+42	98.0	5.30e+114	264.1
65	8.17e+72	167.9	35	5.56e+41	96.1	4.55e+114	264.0
66	4.52e+73	169.6	34	8.32e+40	94.2	3.76e+114	263.8
67	2.47e+74	171.3	33	1.21e+40	92.3	3.00e+114	263.6
68	1.33e+75	172.9	32	1.73e+39	90.3	2.30e+114	263.3
69	7.11e+75	174.7	31	2.39e+38	88.4	1.70e+114	263.0
70	3.75e+76	176.3	30	3.23e+37	86.4	1.21e+114	262.7
71	1.95e+77	178.0	29	4.22e+36	84.3	8.25e+113	262.3
72	1.01e+78	179.6	28	5.37e+35	82.3	5.41e+113	261.9
73	5.13e+78	181.2	27	6.63e+34	80.2	3.40e+113	261.4
74	2.58e+79	182.9	26	7.92e+33	78.1	2.05e+113	260.9
75	1.29e+80	184.5	25	9.15e+32	75.9	1.18e+113	260.4
76	6.36e+80	186.1	24	1.02e+32	73.7	6.49e+112	259.8
77	3.11e+81	187.6	23	1.10e+31	71.5	3.41e+112	259.1
78	1.50e+82	189.2	22	1.14e+30	69.2	1.71e+112	258.4
79	7.18e+82	190.8	21	1.13e+29	66.9	8.14e+111	257.7
80	3.40e+83	192.3	20	1.08e+28	64.6	3.68e+111	256.9
81	1.60e+84	193.9	19	9.88e+26	62.2	1.58e+111	256.0
82	7.42e+84	195.4	18	8.61e+25	59.7	6.39e+110	255.1
83	3.41e+85	196.9	17	7.14e+24	57.2	2.44e+110	254.2
84	1.56e+86	198.5	16	5.62e+23	54.7	8.75e+109	253.2
85	7.03e+86	200.0	15	4.18e+22	52.1	2.94e+109	252.1
86	3.15e+87	201.5	14	2.93e+21	49.4	9.23e+108	250.9
87	1.40e+88	203.0	13	1.93e+20	46.7	2.69e+108	249.7
88	6.14e+88	204.4	12	1.18e+19	43.9	7.26e+107	248.4
89	2.68e+89	205.9	11	6.72e+17	41.0	1.80e+107	247.0
90	1.16e+90	207.4	10	3.52e+16	38.1	4.07e+106	245.5

q_A	Ω_A	S_A/k	q_B	Ω_B	S_B/k	Ω_{total}	S_{total}/k
91	4.96e+90	208.8	9	1.68e+15	35.1	8.36e+105	243.9
92	2.11e+91	210.3	8	7.29e+13	31.9	1.54e+105	242.2
93	8.88e+91	211.7	7	2.82e+12	28.7	2.50e+104	240.4
94	3.71e+92	213.1	6	9.57e+10	25.3	3.56e+103	238.4
95	1.54e+93	214.6	5	2.80e+09	21.8	4.32e+102	236.3
96	6.34e+93	215.9	4	68685050	18.0	4.35e+101	234.0
97	2.59e+94	217.4	3	1353400	14.1	3.50e+100	231.5
98	1.05e+95	218.8	2	20100	9.9	2.11e+99	228.7
99	4.21e+95	220.2	1	200	5.3	8.43e+97	225.5
100	1.68e+96	221.6	0	1	0.0	1.68e+96	221.6



S_A= red S_B= green S= black

A plot of the entropies from the table above.

At equilibrium ($q_A = 60$) the total entropy is a maximum so its graph has a horizontal tangent, that is,

$$\frac{\partial S_{total}}{\partial q_A} = 0 \quad \text{or} \quad \frac{\partial S_{total}}{\partial U_A} = 0 \quad \text{at equilibrium}$$

It is a partial derivative because the number of oscillators in each solid is being held fixed (note that $U_A = \text{constant} \times q_A$). The slope of the S_{total} graph is the sum of the slopes of the S_A and S_B graphs so that

$$\frac{\partial S_{total}}{\partial U_A} = 0 = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A}$$

Since $dU_A + dU_B = dU_{total} = 0 \rightarrow dU_A = -dU_B$ we then have

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad \text{at equilibrium}$$

This says that the quantity that is the same for two systems in thermal equilibrium is the slope of their entropy versus energy graphs. This quantity must be related to the temperature.

Let us investigate this idea further. This result says that the slopes of the tangents to the graphs of S_A and S_B are equal in magnitude at thermal equilibrium. Away from equilibrium (say $q_A = 20$) the solid whose graph has a steeper tangent line tends to gain energy spontaneously, that is, if energy passes from the solid with a small slope to the solid with a steeper slope (B to A in this case), then the entropy gain by A will be greater than the entropy lost by B

$$\Delta S_A = \frac{\partial S_A}{\partial U_A}\Delta U > \Delta S_B = \frac{\partial S_B}{\partial U_B}\Delta U \quad \text{at} \quad q_A = 20$$

and the total entropy will increase (that is why the process happens spontaneously) as required by the second law. The system is just moving towards maximum entropy or thermal equilibrium.

Thus, the second law says that energy will always flow from the system with smaller slope to the system with larger slope. The latter system increases its entropy rapidly if it gains energy and the former system does not lose too much entropy if it loses energy.

Since we know experimentally that heat flows from high temperature to low temperature system, the steep slope must correspond to a low temperature and the smaller slope to a lower temperature.

Dimensional analysis gives us a hint at what to do. We have

$$\frac{\partial S}{\partial U} \rightarrow \frac{J/K}{J} = \frac{1}{K}$$

Therefore, the reciprocal of the slope has units of temperature (kelvin) and we propose

$$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}$$

or the temperature of the system is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

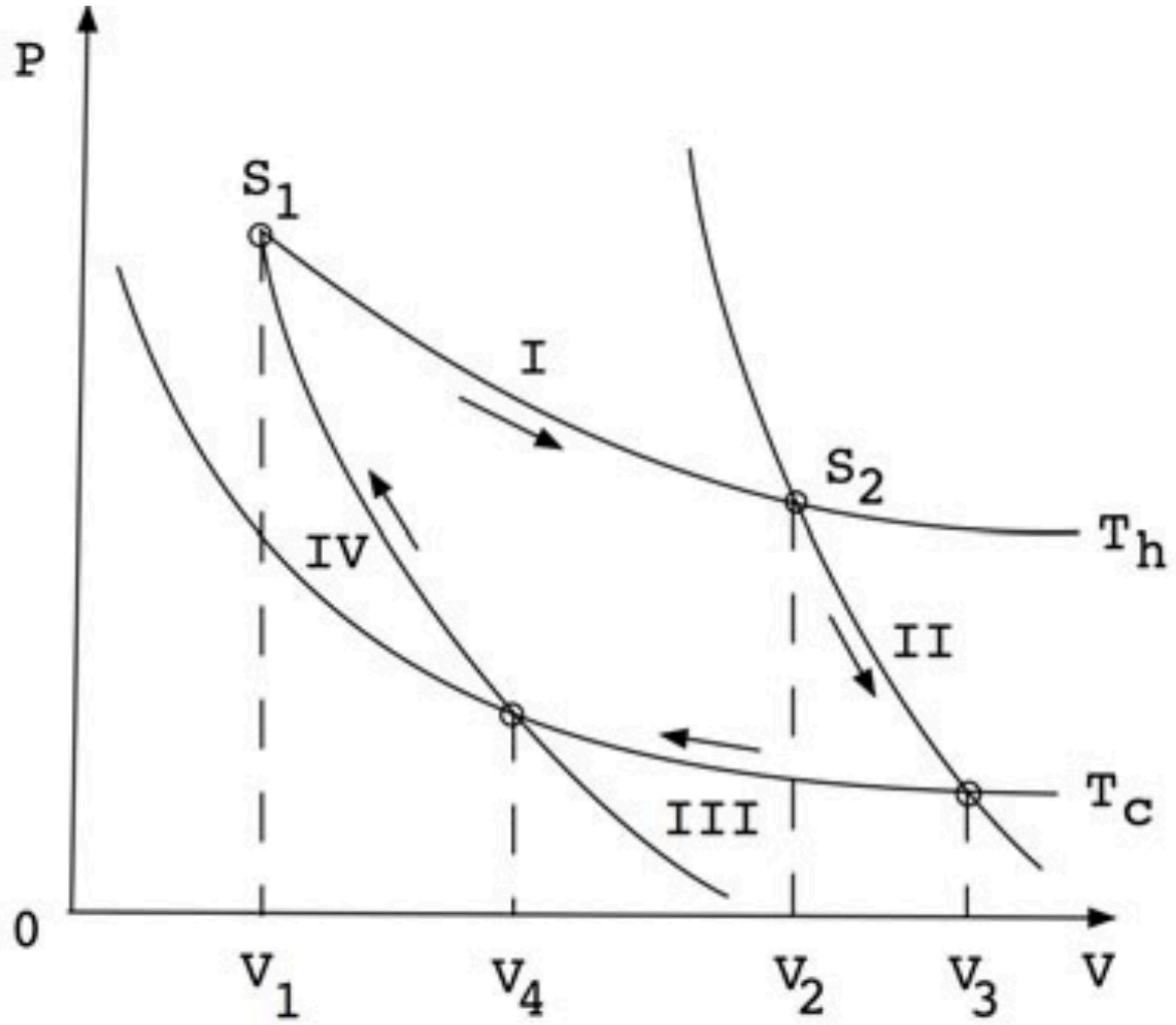
Let us look at this another way.

Cyclic thermodynamic processes are of great importance. They form the basis for all thermodynamic engines, which we will discuss in detail later.

Some fundamental statements, however, can be made now with the help of the first law. For example, for a **cycle**, where the working substance of the system returns to its initial state after a series of changes of state, the equation $\oint dU = 0$ has to be fulfilled, since dU is a total differential and thus contour-independent. If such a cycle nevertheless does useful work, obviously a corresponding amount of heat (extracted from the surroundings) has been converted to this work. We now study such a cycle with an ideal gas in more detail.

Carnot's Process and Connection to Entropy

This cycle, with an ideal gas as the working substance, was developed by Carnot in 1824. Its importance originates from the fact that it is not only to be interpreted as an idealized limiting case of real cycles, but also that it will make some important ideas clear to us. The Carnot process is performed in four successive reversible steps, which are illustrated in a *pV* diagram in the figure below.



Step 1. Isothermal expansion from volume V_1 to volume V_2 at constant temperature T_h. For the isotherm we have

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}$$

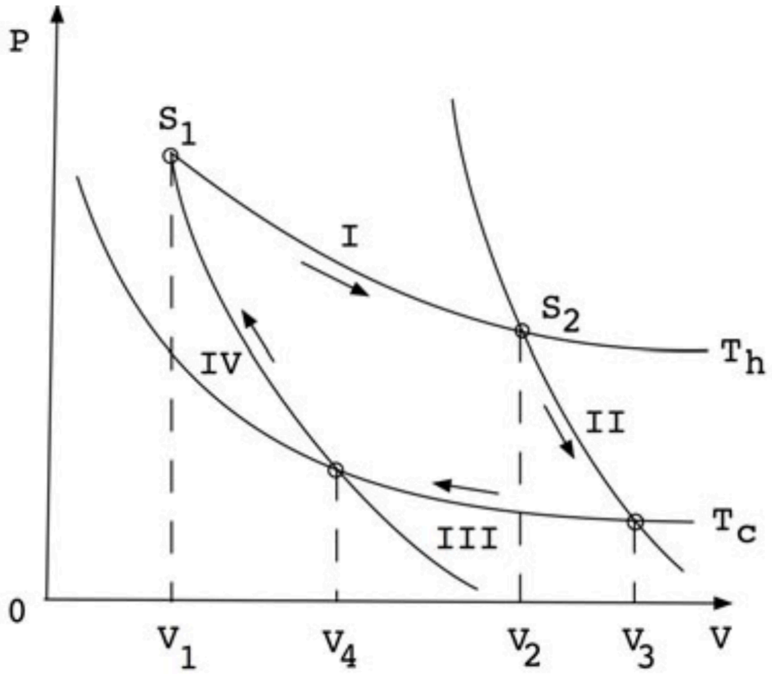
Since $U = 3NkT/2$ for an ideal gas, we know that the energy of an ideal gas, the working substance, cannot be changed at constant temperature. Consequently, we have that (from the first law)

$$\Delta U_I = W_I + Q_I = 0$$

From this we can calculate Q_I, with the help of eq (01.34)

$$Q_I = -W_I = NkT_h \ell n \frac{V_2}{V_1}$$

This is the amount of heat exchanged with the heat bath in the first step. Since $V_2 > V_1$, $Q_I > 0$, that is, the amount of heat Q_I is **added** to the gas as the expense of the heat bath.



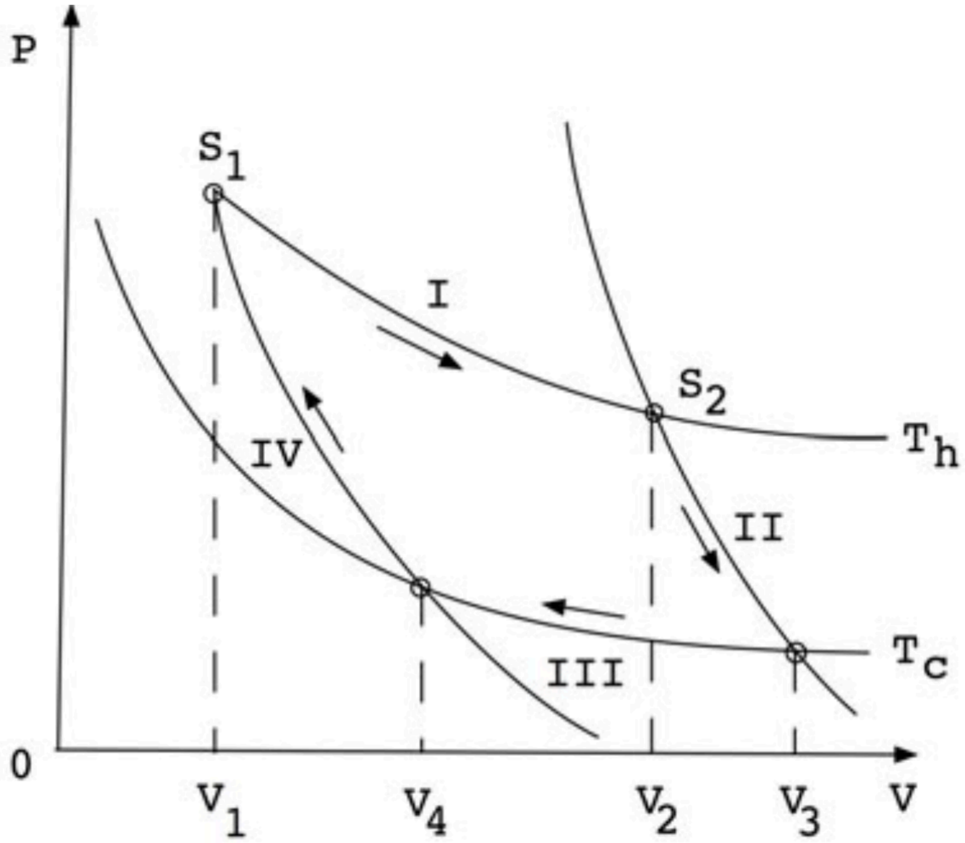
Step 2. Adiabatic expansion of the isolated working substance from V_2 to V_3. Here the temperature changes from T_h to T_c. The indices h and c denote *hot* and *cold*, that is, $T_h > T_c$. We get using (01.47)

$$\left(\frac{T_h}{T_c}\right)^{3/2} = \frac{V_3}{V_2}$$

Since $Q_{II} = 0$ (for an adiabatic process) the work done in the expansion is taken from the internal energy,

$$W_{II} = \Delta U_{II} = C_V(T_c - T_h)$$

where the sign of the above term corresponds to the direction $T_h \to T_c$. For an ideal gas, $C_V = 3Nk/2$, that is, C_V is a constant independent of temperature and volume. The difference of the internal energies for this part of the process is given by this equation even though the volume changes.



Step 3. We now compress the system isothermally from V_3 to V_4 at the (constant) smaller temperature T_c. In analogy with Step 1, we have

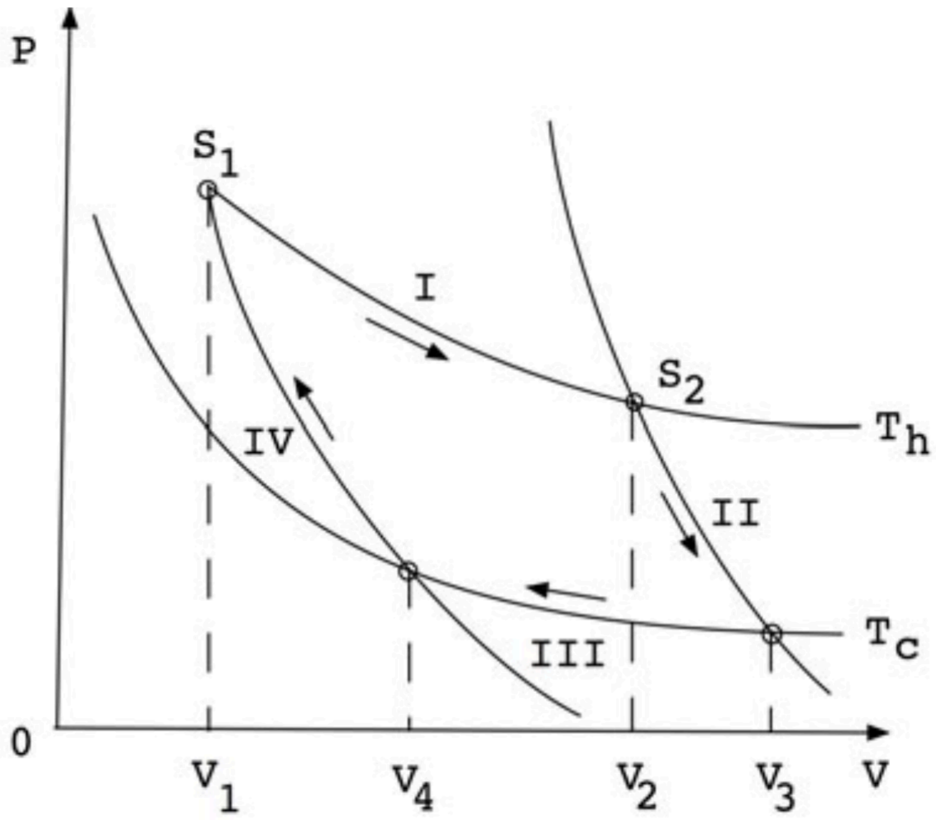
$$\frac{V_4}{V_3} = \frac{p_3}{p_4}$$

The work done during the compression is, because $\Delta U_{III} = 0$ at $T =$ constant, given to the heat bath in the form of heat

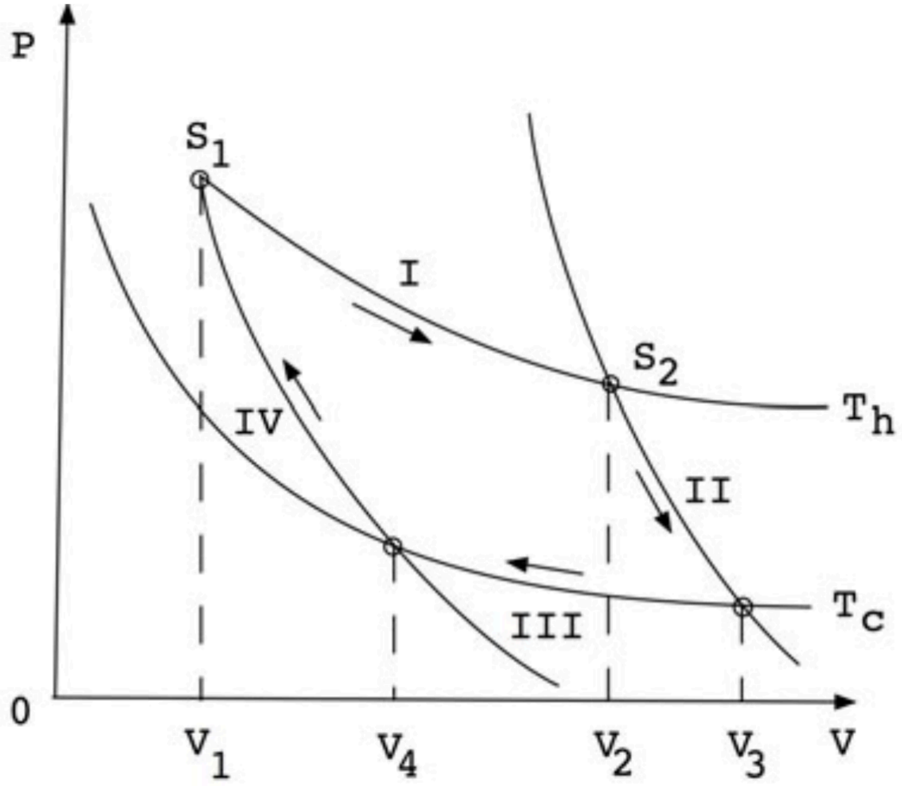
$$\Delta U_{III} = 0 = W_{III} + Q_{III}$$

$$-W_{III} = Q_{III} = NkT_c \ell n \frac{V_4}{V_3}$$

This is the amount of heat absorbed by the heat bath in this step. Since $V_4 < V_3$, it follows that $Q_{III} < 0$, that is, the gas **loses** this amount of heat.



Step 4. Finally, we restore the system to the initial state via an adiabatic compression from V_4 to V_1. The temperature increases again from T_c to T_h such that



$$\left(\frac{T_c}{T_h}\right)^{3/2} = \frac{V_1}{V_4}$$

Since $Q_{IV} = 0$ it follows that

$$W_{IV} = \Delta U_{IV} = C_V(T_h - T_c)$$

Let us first check the total energy balance of the process. We have

$$\Delta U_{total} = \underbrace{Q_I + W_I}_{I} + \underbrace{W_{II}}_{II} + \underbrace{Q_{III} + W_{III}}_{III} + \underbrace{W_{IV}}_{IV}$$

If we insert the above results, we immediately find that $\Delta U_{total} = 0$, as it should be for a cycle. We have $Q_I + W_I = 0$ and similarly, $Q_{III} + W_{III} = 0$ and furthermore, $W_{II} = -W_{IV}$. In addition, we have the following equations for the amount of heat exchanged with the heat bath:

$$Q_I = NkT_h \ell n \frac{V_2}{V_1} \qquad Q_{III} = NkT_c \ell n \frac{V_4}{V_3}$$

On the other hand, we also have that

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

so that

$$\frac{Q_I}{T_h} = Nk\ell n\frac{V_2}{V_1} = Nk\ell n\frac{V_3}{V_4} = -\frac{Q_{III}}{T_c} \Rightarrow \frac{Q_I}{T_h} + \frac{Q_{III}}{T_c} = 0$$

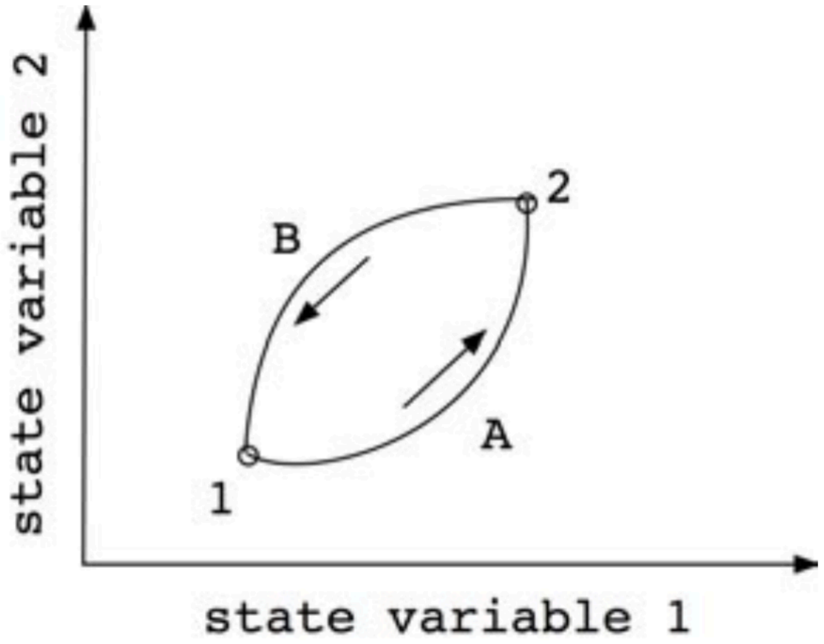
This equation is of great importance, for it is valid not only for this special Carnot process, but according to all experimental evidence, for **any reversible cyclic process.**

If we decompose the Carnot process into infinitesimal parts, we can replace this result with the equation

$$\oint \frac{Q}{T} = 0$$

If we are able to prove the validity of this equation for arbitrary closed contours and not only for Carnot processes, then we will have shown according to our earlier discussions about exact differentials that the quantity Q/T is contour-independent and thus an exact differential. In other words, $1/T$ is the integrating factor for the nonexact differential Q.

We can deduce the equivalence of $\oint \frac{Q}{T} = 0$ and the statement that Q/T is an exact differential in the following manner. If one integrates from state 1 to state 2 and back again as shown in the figure below



then it follows that

$$\oint \frac{Q}{T} = \int_{C_A(1\to 2)} \frac{Q}{T} + \int_{C_B(2\to 1)} \frac{Q}{T} = 0$$

If we reverse the direction of integration on the curve C_B (the integral changes sign), then we have

$$\int_{C_A(1\to 2)} \frac{Q}{T} - \int_{C_B(1\to 2)} \frac{Q}{T} = 0 \Rightarrow \int_{C_A(1\to 2)} \frac{Q}{T} = \int_{C_B(1\to 2)} \frac{Q}{T}$$

and it is clear that the integral $\int_1^2 \frac{Q}{T}$ is contour-independent.

As can be experimentally confirmed Q/T is an exact differential not only for ideal gases, but for any other reversible thermodynamic process. In other words, there has to exist a **state function**, the total differential of which is Q/T. This extensive state function is the **entropy** S, which is defined via

$$dS = \frac{Q}{T} \quad , \quad S_1 - S_0 = \int_0^1 \frac{Q}{T}$$

This result can also serve as a measuring instruction. To this end, one has to measure the amount of heat reversibly exchanged by the system at a given temperature T. This method(the above equation) then determines the entropy difference. The absolute value of the entropy cannot be determined.

Since the entropy is constant when $Q = 0$ in an adiabatic process, the Carnot process is just a rectangle in the TS plane, that is, T = constant in steps I and III and S = constant in steps II and IV.

The Carnot process effectively does a work ΔW, as can be seen from the corresponding equations, since the compressional work to be done in steps III and IV is smaller than the expansion work set free in steps I and II, namely,

$$W = W_I + W_{II} + W_{III} + W_{IV} = -NkT_h \ell n \frac{V_2}{V_1} - NkT_c \ell n \frac{V_4}{V_3}$$

so that we have

$$W = -Nk(T_h - T_c) \ell n \frac{V_2}{V} = -(Q_I + Q_{III})$$

Since $T_h > T_c$ and $V_2 > V_1$, this is a negative quantity. Therefore, W is work done by the gas. Clearly, a Carnot cycle can represent an "engine" which transforms heat in to work. The work done by the engine increases with the temperature difference $T_h - T_c$ and with the compression ratio V_2 / V_1.

We will say more about this Carnot process later.

Some More Real World Examples

The entropy for an Einstein solid is

$$S = k\ell n\left(\frac{eq}{N}\right)^N = Nk\left[\ell n\frac{q}{N} + 1\right]$$

If we write $U = q\varepsilon$, then

$$S = Nk\left[\ell n\frac{U}{\varepsilon N} + 1\right] = Nk\ell nU - Nk\ell n\varepsilon N + Nk$$

Therefore the temperature should be

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{Nk}{U} \Rightarrow U = NkT$$

The equipartition theorem implies that $U = \frac{1}{2}kTf$. An Einstein solid has 2 degrees of freedom for each oscillator so that $f = 2N$ and therefore

$$U = \frac{1}{2}kTf = NkT$$

as above.

This means that the result

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

no constants are missing from the definition of temperature.

Earlier we derived the entropy of a monatomic ideal gas. We found

$$S = Nk\left(\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right) = Nk\ell nV + Nk\ell nU^{3/2} + g(N)$$

Therefore the temperature is given by

$$T = \left(\frac{3Nk/2}{U}\right)^{-1} \rightarrow U = \frac{3}{2}NkT$$

as expected.

Entropy of the Ideal Gas (another way)

We want to determine the entropy of an ideal gas at constant particle number as a function of T and V.

For a reversible change of state, the first law now reads

$$dU = TdS - pdV$$

where we have used $Q = TdS$ (will say more about this later). With the equations of state

$$U = \frac{3}{2}NkT \quad , \quad pV = NkT$$

for an ideal gas, we can solve the above equation for dS:

$$dS = \frac{3}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V}$$

Starting from a state T_0, V_0 with entropy S_0, we integrate this equation,

$$S(T,V) - S_0(T_0,V) = \frac{3}{2} Nk\ell n \frac{T}{T_0} + Nk\ell n \frac{V}{V_0} = Nk\ell n \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \right]$$

and if we substitute $V \propto T/p$ we get

$$S(T,p) - S_0(T_0,p_0) = Nk\ell n \left[\left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right]$$

Thus, the entropy of an ideal gas increases with temperature and volume.

Since the entropy is an extensive quantity, it has to be proportional to the particle number N, that is,

$$S(N,T,p) = Nk \left(s_0(T_0,p_0) + \ell n \left[\left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right] \right)$$

where $s_0(T_0,p_0)$ is an arbitrary dimensionless function of the reference state (T_0, V_0). In a statistical treatment values of $s_0(T_0,p_0)$ can be directly calculated!

Entropy and Heat

Earlier we defined the heat capacity at constant volume (energy capacity) as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

For an Einstein solid with $q >> N$, the heat capacity is

$$C_V = \left(\frac{\partial NkT}{\partial T} \right)_{N,V} = Nk$$

while for a monatomic ideal gas

$$C_V = \left(\frac{\partial 3NkT/2}{\partial T} \right)_{N,V} = 3Nk/2$$

In both cases the heat capacity is independent of the temperature.

Steps to Predict Heat Capacity

(1) Use quantum mechanics and some combinatorics to find an expression for the multiplicity Ω in terms of U, V, N and any other relevant variables.

(2) Take the logarithm to find the entropy S

(3) Differentiate S with respect to U and take the reciprocal to find the temperature T as a function of U and other variables.

(4) Solve for U as a function of T (and other variables).

(5) Differentiate $U(T)$ to obtain a prediction for the heat capacity (with other variables held fixed).

There are only a few simple systems for which this process be actually carried out (step (1) is the hard step), namely, the Einstein solid, the ideal gas, the two-state paramagnet, etc. Statistical mechanics gives us better ways to find U with out finding the multiplicity.

Example: Starting with the result of the previous example $U = N\varepsilon e^{-\frac{\varepsilon}{kT}}$ calculate the heat capacity of an Einstein solid in the low-temperature limit.

Solution: We have for an Einstein solid in the low-temperature limit

$$U = N\varepsilon e^{-\frac{\varepsilon}{kT}}$$

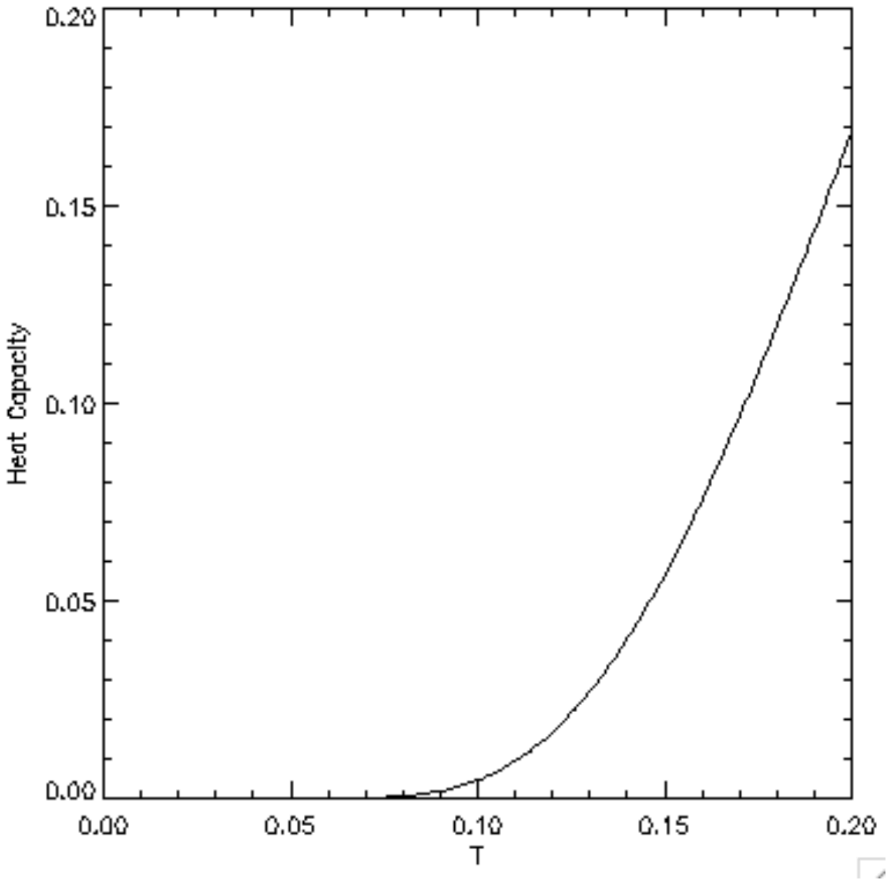
Therefore,

$$C_V = N\varepsilon \frac{d}{dT} e^{-\frac{\varepsilon}{kT}} = N\varepsilon\left(\frac{\varepsilon}{kT^2}\right)e^{-\frac{\varepsilon}{kT}} = Nk\left(\frac{\varepsilon}{kT}\right)^2 e^{-\frac{\varepsilon}{kT}}$$

Even though the factor $\frac{\varepsilon}{kT}$ blows up as $T \to 0$, the whole expression goes to zero because of the exponential factor, that is,

$$\lim_{T\to 0}\frac{e^{-\frac{\varepsilon}{kT}}}{T^2} = 0$$

A graph is shown



Measuring Entropies

I indicated earlier how we would measure the entropy. Let us review that idea so that we can find the entropy even if we cannot calculate it theoretically. The procedure is shown below.

If we add some heat to a system while holding its volume constant and doing no other forms of work, the entropy changes by

$$dS = \frac{dU}{T} = \frac{Q}{T} \quad \text{(constant volume, no work)}$$

Heat and temperature are easy to measure and thus we can easily find the entropy change.

If the temperature remains constant during the process, then the above relation holds even for large values, that is,

$$\Delta S = \frac{\Delta U}{T} = \frac{Q}{T}$$

When the temperature is changing we must use

$$dS = \frac{C_V(T)dT}{T}$$

so that

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V(T)dT}{T}$$

Example: In order to take

Example: Experimental measurements

Example: A bit of computer memory is some physical object that can be in two different states, often interpreted as 0 and 1. A byte is eight bits, a kilobyte (kb) is 1024 ($=2^{10}$) bytes, a megabyte (mb) is 1024 kb and a gigabyte (gb) is 1024 mb.

(a) Suppose that your computer erases or overwrites one gb of memory keeping no record of the information that was stored. Explain why this must create a certain minimum amount of entropy, and calculate how much.

(b) If this entropy is dumped into an environment at room temperature, how much heat must come along with it? Is this amount of heat significant?

Solution: Thermodynamics of Computing

(a) Since $1\,gb = (1024)^3\ bytes = 8\times(1024)^3\ bits = 2^{33}\ bits$, before the memory was erased, it could have been in any one of $2^{2^{33}}$ different states (at least). After it is erased, its new microstate is completely specified and unrelated to the previous one, but somehow the whole system, including the hardware that did the erasing, must still have $2^{2^{33}}$ possible states, corresponding to the number of possible initial conditions. The multiplicity of possible states gives the system an entropy equal to

$$S = k\ell n 2^{2^{33}} = k\cdot 2^{33}\ell n 2 = k(6.0\times10^{9}) = 8.2\times10^{-14}\ J/K$$

(b) To dump this entropy into an environment at $300\,K$ would require a heat transfer of at least

$$Q = T\Delta S = (300\ K)\left(8.2\times10^{-14}\ J/K\right) = 2.5\times10^{-11}\ J$$

or 25 picojoules. Not a very significant amount. Of course, today's computers are much less thermodynamically efficient, expelling a good deal more waste heat than this lower limit. Will the thermodynamic limit ever become a significant constraint?

Paramagnetism

We now reconsider the two-state paramagnet introduced earlier. This is an example where the equipartition theorem does not apply. It turns out to be a very interesting mathematical exercise and paradoxical from a physics standpoint.

Review of the Model

System = N spin-1/2 particles in a constant magnetic field $\vec{B}$ pointing in the $+z$ direction as shown below:

↑

$\vec{B}$ ⇑⇓⇓⇓⇓⇑⇑⇑⇑⇑⇓⇑⇑⇓⇑⇑⇓⇓⇑⇓

↑

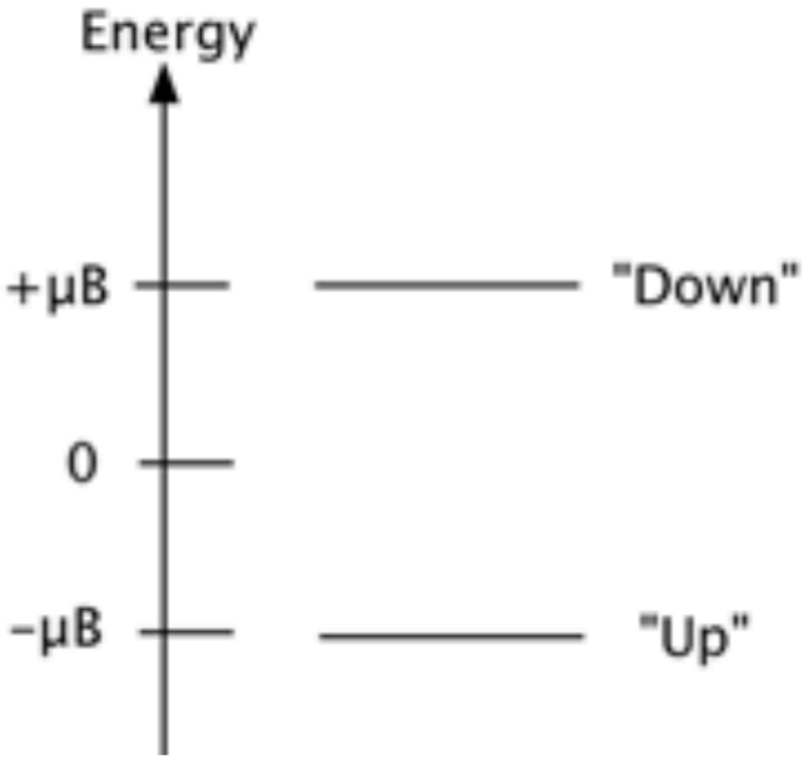
Quantum mechanics says that the component of the particle's spin angular momentum along the direction of the magnetic field is **quantized**, that is, it takes on only certain discrete values.

If the spin is J, then there are $2J+1$ allowed values of the component. For $J=1/2$ (electrons), there are 2 values which we call "up" and "down" along the z-axis.

The magnetic field interacts with the spin(actually dipoles) and changes the energy of the electron according to

$$U = -2\vec{\mu}\vec{J}\cdot\vec{B} = \begin{cases} +\mu B \text{ for spin "down" or anti - parallel to field direction} \\ -\mu B \text{ for spin "up" or parallel to field direction} \end{cases}$$

The energy level diagram for a single electron in the magnetic field looks like:



The total energy of the system is

$$U = \mu B(N_{\downarrow} - N_{\uparrow}) = \mu B(N - 2N_{\uparrow})$$

where $N_{\uparrow}$ and $N_{\downarrow}$ are the numbers up and down respectively, and $N = N_{\downarrow} + N_{\uparrow}$. We define the magnetization M as

$$M = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B}$$

Let us determine the entropy as a function of the energy and the

temperature dependence of these quantities and the heat capacity.

As we saw earlier the multiplicity is given by

$$\Omega(N_{\uparrow}, N) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$$

Numerical Solution

For $N = 100$ the table of data values is given below.

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
100	-100	1.00	1.00E+00	0.00	0.00	0.000
99	-98	0.98	1.00E+02	4.61	0.47	0.074
98	-96	0.96	4.95E+03	8.51	0.54	0.310
97	-94	0.94	1.62E+05	11.99	0.60	0.365
96	-92	0.92	3.92E+06	15.18	0.65	0.398
95	-90	0.90	7.53E+07	18.14	0.70	0.420
94	-88	0.88	1.19E+09	20.90	0.75	0.433
93	-86	0.86	1.60E+10	23.50	0.79	0.440
92	-84	0.84	1.86E+11	25.95	0.84	0.442
91	-82	0.82	1.90E+12	28.27	0.88	0.440
90	-80	0.80	1.73E+13	30.48	0.93	0.436
89	-78	0.78	1.42E+14	32.58	0.97	0.428
88	-76	0.76	1.05E+15	34.59	1.02	0.419
87	-74	0.74	7.11E+15	36.50	1.07	0.408
86	-72	0.72	4.42E+16	38.33	1.12	0.396
85	-70	0.70	2.53E+17	40.07	1.17	0.382
84	-68	0.68	1.35E+18	41.74	1.22	0.368
83	-66	0.66	6.65E+18	43.34	1.28	0.353
82	-64	0.64	3.07E+19	44.87	1.34	0.337
81	-62	0.62	1.32E+20	46.33	1.40	0.322
80	-60	0.60	5.36E+20	47.73	1.46	0.305
79	-58	0.58	2.04E+21	49.07	1.53	0.289
78	-56	0.56	7.33E+21	50.35	1.60	0.273
77	-54	0.54	2.49E+22	51.57	1.68	0.256
76	-52	0.52	7.98E+22	52.73	1.76	0.240
75	-50	0.50	2.43E+23	53.85	1.84	0.224
74	-48	0.48	7.00E+23	54.90	1.93	0.209
73	-46	0.46	1.92E+24	55.91	2.03	0.193
72	-44	0.44	5.00E+24	56.87	2.14	0.178

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
71	−42	0.42	1.24E+25	57.78	2.26	0.163
70	−40	0.40	2.94E+25	58.64	2.39	0.149
69	−38	0.38	6.63E+25	59.46	2.53	0.135
68	−36	0.36	1.43E+26	60.22	2.68	0.122
67	−34	0.34	2.95E+26	60.95	2.85	0.110
66	−32	0.32	5.81E+26	61.63	3.05	0.097
65	−30	0.30	1.10E+27	62.26	3.26	0.086
64	−28	0.28	1.98E+27	62.85	3.51	0.075
63	−26	0.26	3.42E+27	63.40	3.80	0.065
62	−24	0.24	5.67E+27	63.90	4.13	0.056
61	−22	0.22	9.01E+27	64.37	4.52	0.047
60	−20	0.20	1.37E+28	64.79	4.98	0.039
59	−18	0.18	2.01E+28	65.17	5.55	0.031
58	−16	0.16	2.83E+28	65.51	6.26	0.025
57	−14	0.14	3.81E+28	65.81	7.17	0.019
56	−12	0.12	4.94E+28	66.07	8.38	0.014
55	−10	0.10	6.14E+28	66.29	10.07	0.009
54	−8	0.08	7.35E+28	66.47	12.60	0.006
53	−6	0.06	8.44E+28	66.61	16.81	0.003
52	−4	0.04	9.32E+28	66.70	25.23	0.001
51	−2	0.02	9.89E+28	66.76	50.49	0.000
50	0	0.00	1.01E+29	66.78	∞	0.000
49	2	−0.02	9.89E+28	66.76	−50.49	0.000
48	4	−0.04	9.32E+28	66.70	−25.23	0.001
47	6	−0.06	8.44E+28	66.61	−16.81	0.003
46	8	−0.08	7.35E+28	66.47	−12.60	0.006
45	10	−0.10	6.14E+28	66.29	−10.07	0.009
44	12	−0.12	4.94E+28	66.07	−8.38	0.014
43	14	−0.14	3.81E+28	65.81	−7.17	0.019
42	16	−0.16	2.83E+28	65.51	−6.26	0.025
41	18	−0.18	2.01E+28	65.17	−5.55	0.031
40	20	−0.20	1.37E+28	64.79	−4.98	0.039

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
40	20	−0.20	1.37E+28	64.79	−4.98	0.039
39	22	−0.22	9.01E+27	64.37	−4.52	0.047
38	24	−0.24	5.67E+27	63.90	−4.13	0.056
37	26	−0.26	3.42E+27	63.40	−3.80	0.065
36	28	−0.28	1.98E+27	62.85	−3.51	0.075
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21	58	−0.58	2.04E+21	49.07	−1.53	0.289
20	60	−0.60	5.36E+20	47.73	−1.46	0.305
19	62	−0.62	1.32E+20	46.33	−1.40	0.322
18	64	−0.64	3.07E+19	44.87	−1.34	0.337
17	66	−0.66	6.65E+18	43.34	−1.28	0.353
16	68	−0.68	1.35E+18	41.74	−1.22	0.368
15	70	−0.70	2.53E+17	40.07	−1.17	0.382
14	72	−0.72	4.42E+16	38.33	−1.12	0.396

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
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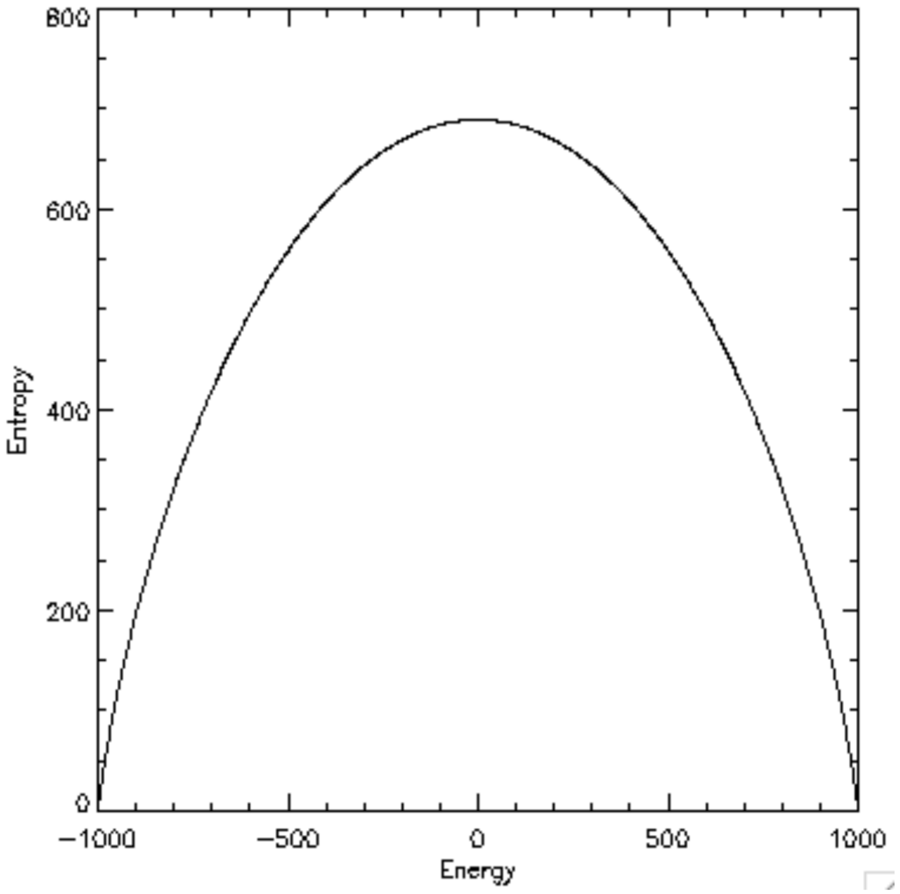
12	76	-0.76	1.05E+15	34.59	-1.02	0.419
11	78	-0.78	1.42E+14	32.58	-0.97	0.428
10	80	-0.80	1.73E+13	30.48	-0.93	0.436
9	82	-0.82	1.90E+12	28.27	-0.88	0.440
8	84	-0.84	1.86E+11	25.95	-0.84	0.442
7	86	-0.86	1.60E+10	23.50	-0.79	0.440
6	88	-0.88	1.19E+09	20.90	-0.75	0.433
5	90	-0.90	7.53E+07	18.14	-0.70	0.420
4	92	-0.92	3.92E+06	15.18	-0.65	0.398
3	94	-0.94	1.62E+05	11.99	-0.60	0.365
2	96	-0.96	4.95E+03	8.51	-0.54	0.310
1	98	-0.98	1.00E+02	4.61	-0.47	0.074
0	100	-1.00	1.00E+00	0.00	0.00	0.000

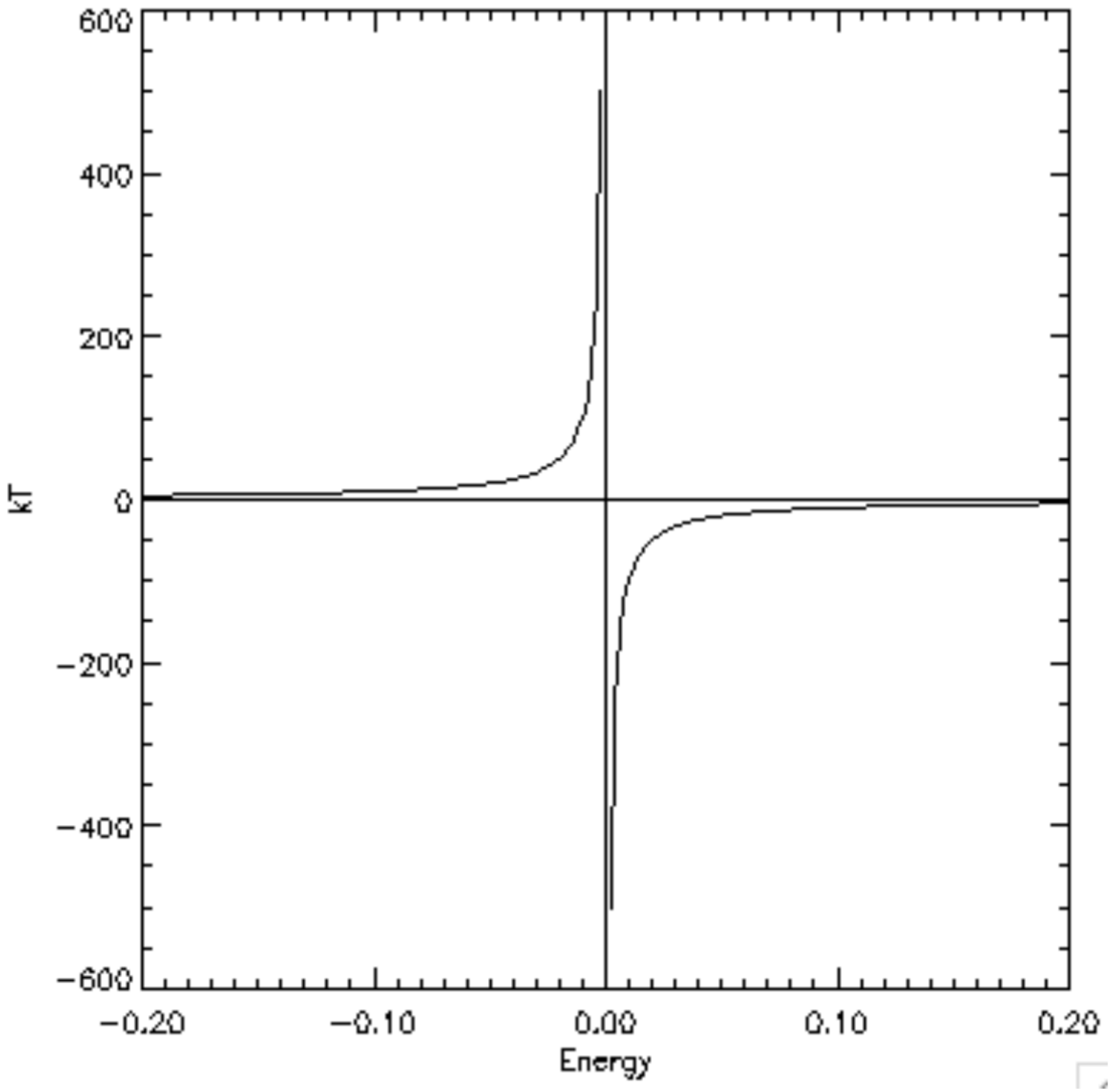
The following graphs are the results for the case $N = 1000$.

The behavior of the entropy as a function of the energy is shown below. The maximum multiplicity and entropy occur at $U = 0$ where one-half of the spins point down (see figure below). If we add energy from this value, the multiplicity and entropy decrease since there are fewer ways to arrange the energy. Let us look at this in more detail.



Suppose the system starts out in the state with all spins pointing up which is the minimum energy state. This corresponds to the point (-1000,0) on the graph. Notice that the entropy-energy graph has a large slope which means that the system has a strong tendency to absorb energy from its surroundings. As the energy increase (still negative), the entropy-energy curve slope becomes smaller which means that the tendency to absorb energy decreases. As the slope goes to zero its tendency to absorb energy goes to zero also. At this point one-half the spins point up, the entropy is a maximum and the system is equally probable to lose or gain energy (fluctuate about equilibrium). If we now add more energy the slope becomes negative which means that the system spontaneously gives up energy to any nearby object whose slope is positive, that is, any allowed process that increases entropy happens spontaneously.

During this sequence of steps what is happening to the temperature? As can be seen from the graph below, initially(all spins point up) the temperature, which is the reciprocal of the slope of the first graph, is very small. As we add energy the temperature rises (like a normal system). In fact, the temperature (in this simple model) goes to infinity at equilibrium, which means that the system will easily give up energy to any other system (at finite temperature). As we add more energy, the temperature goes negative(the slope is negative), but the system will behave as if the temperature were getting "higher". Negative temperature only occur for systems with limited energy which means that the multiplicity decreases as the maximum allowed energy is approached.



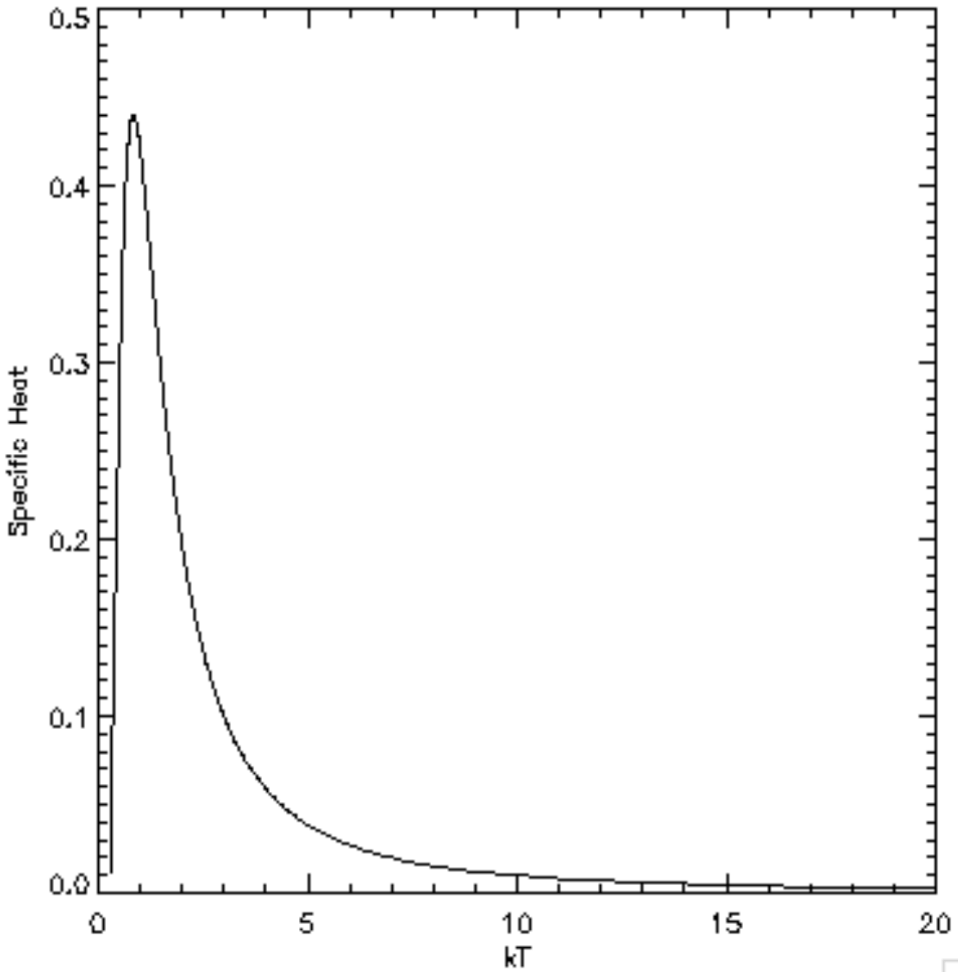
This all illustrates an important point. Entropy is the more fundamental quantity governed by the second law - entropy will be maximized. Temperature is less fundamental (it is just the slop of the entropy curve) and represents the willingness of the system to absorb or give off energy.

The table also gives the magnetization (formula above) and the specific heat (slope of energy versus temperature graph).

The graph below indicates that the specific heat depends strongly on the temperature (not a constant as we saw for the Einstein solid and the ideal gas).

At zero temperature the specific heat goes to zero (this is the **third law of thermodynamics**).

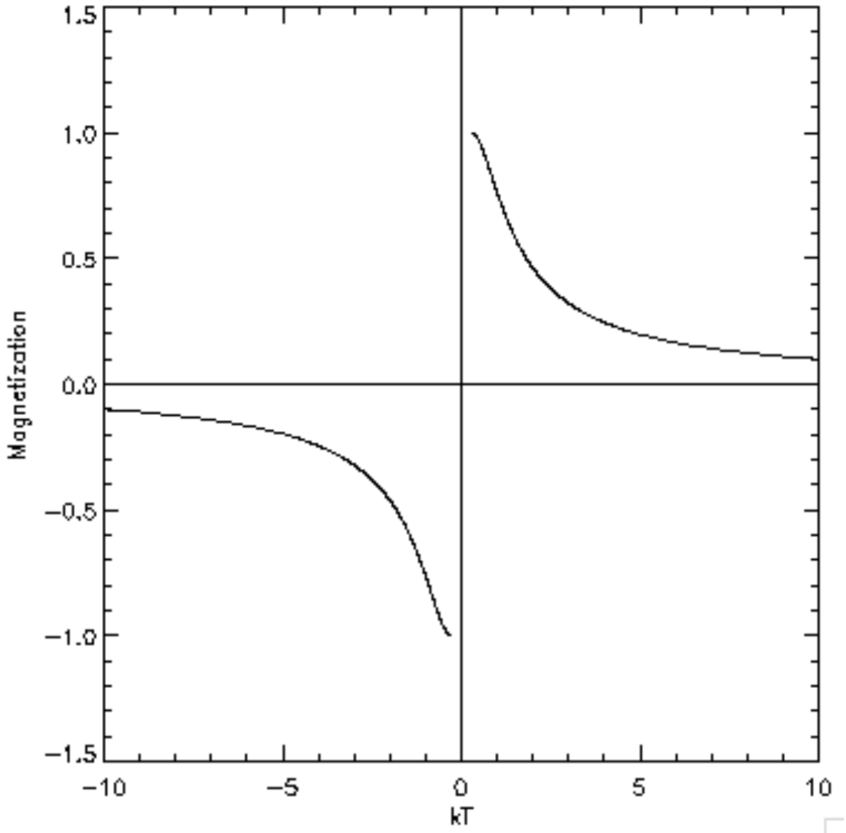
It also goes to zero as the temperature approaches infinity since at that point only a small amount of energy is required to produce a very large change in temperature.



Finally, the behavior of the magnetization is shown in the graph below.

At zero temperature, the system is "saturated" with all dipole pointing up (maximum magnetization).

As the temperature approaches infinity we move to the state of maximum "randomness" with exactly half of the spins pointing up.



Analytic Solution

This system can also be solved analytically. We assume that N is very large and also that $N_\uparrow$ and $N_\downarrow$ are large. The entropy is then

$$\frac{S}{k} = \ell n\Omega(N_\uparrow, N) = \ell n\frac{N!}{N_\uparrow!(N-N_\uparrow)!} = \ell nN! - \ell nN_\uparrow! - \ell n(N-N_\uparrow)!$$

$$\approx N\ell nN - N - N_\uparrow\ell nN_\uparrow + N_\uparrow - (N-N_\uparrow)\ell n(N-N_\uparrow) + (N-N_\uparrow)$$

$$= N\ell nN - N_\uparrow\ell nN_\uparrow - (N-N_\uparrow)\ell n(N-N_\uparrow)$$

The temperature is given by

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{N,B}=\frac{\partial N_\uparrow}{\partial U}\frac{\partial S}{\partial N_\uparrow}=-\frac{1}{2\mu B}\frac{\partial S}{\partial N_\uparrow}$$

$$=-\frac{1}{2\mu B}k\frac{\partial}{\partial N_\uparrow}\left[N\ell nN-N_\uparrow\ell nN_\uparrow-(N-N_\uparrow)\ell n(N-N_\uparrow)\right]$$

$$=-\frac{1}{2\mu B}\left[-\ell nN_\uparrow-1+\ell n(N-N_\uparrow)+1\right]=\frac{k}{2\mu B}\ell n\frac{N_\uparrow}{N-N_\uparrow}$$

However,

$$U=\mu B(N_\downarrow-N_\uparrow)=\mu B(N-2N_\uparrow)$$

so that

$$N_\uparrow=\frac{N}{2}-\frac{U}{2\mu B}\Rightarrow\frac{1}{T}=\frac{k}{2\mu B}\ell n\frac{N-\frac{U}{\mu B}}{N+\frac{U}{\mu B}}$$

We can now solve for the energy U as follows:

$$\frac{N-\frac{U}{\mu B}}{N+\frac{U}{\mu B}}=e^{\frac{2\mu B}{kT}}\rightarrow N-\frac{U}{\mu B}=\left(N+\frac{U}{\mu B}\right)e^{\frac{2\mu B}{kT}}$$

$$U\left(1+e^{\frac{2\mu B}{kT}}\right)=\mu BN\left(1-e^{\frac{2\mu B}{kT}}\right)\rightarrow U=N\mu B\frac{1-e^{\frac{2\mu B}{kT}}}{1+e^{\frac{2\mu B}{kT}}}$$

Now

$$\frac{1-e^{\frac{2\mu B}{kT}}}{1+e^{\frac{2\mu B}{kT}}} = \frac{e^{-\frac{\mu B}{kT}} - e^{\frac{\mu B}{kT}}}{e^{-\frac{\mu B}{kT}} + e^{\frac{\mu B}{kT}}} = -\frac{\sinh\frac{\mu B}{kT}}{\cosh\frac{\mu B}{kT}}$$

so that

$$U = -N\mu B \tanh\frac{\mu B}{kT}$$

The heat capacity is then given by

$$C_B = \frac{\partial U}{\partial T} = -N\mu B\frac{\partial}{\partial T}\tanh\frac{\mu B}{kT} = -N\mu B\frac{\mu B}{k}\frac{dx}{dT}\frac{d}{dx}\tanh x$$

where $x = \frac{\mu B}{kT}$.

Now

$$\frac{d}{dx}\tanh x = \frac{d}{dx}\frac{\sinh x}{\cosh x} = \frac{\cosh^2 x - \sinh^2 x}{\cosh^2 x} = \frac{1}{\cosh^2 x}$$

so that

$$C_B = Nk\frac{1}{\cosh^2\frac{\mu B}{kT}}\left(\frac{\mu B}{kT}\right)^2$$

Finally,

$$M = -\frac{U}{B} = N\mu\tanh\frac{\mu B}{kT}$$

and

$$\begin{aligned}
S &= N\ell nN - N_{\uparrow}\ell nN_{\uparrow} - (N-N_{\uparrow})\ell n(N-N_{\uparrow}) \\
&= N\ell nN - \left(\frac{N}{2}-\frac{U}{2\mu B}\right)\ell n\left(\frac{N}{2}-\frac{U}{2\mu B}\right) - \left(\frac{N}{2}+\frac{U}{2\mu B}\right)\ell n\left(\frac{N}{2}+\frac{U}{2\mu B}\right) \\
&= N\ell nN - \left(\frac{N}{2}-\frac{U}{2\mu B}\right)\ell n\left(\frac{N}{2}-\frac{U}{2\mu B}\right) - \left(\frac{N}{2}+\frac{U}{2\mu B}\right)\ell n\left(\frac{N}{2}+\frac{U}{2\mu B}\right)
\end{aligned}$$

Physical Properties:

Magnetization:

For $T \to \infty$, $x \to 0$ and $\tanh x \to 0$ so that the magnetization goes to zero.
For $T \to 0$, $x \to \infty$ and $\tanh x \to 1$ so that the magnetization saturates.

Specific Heat:

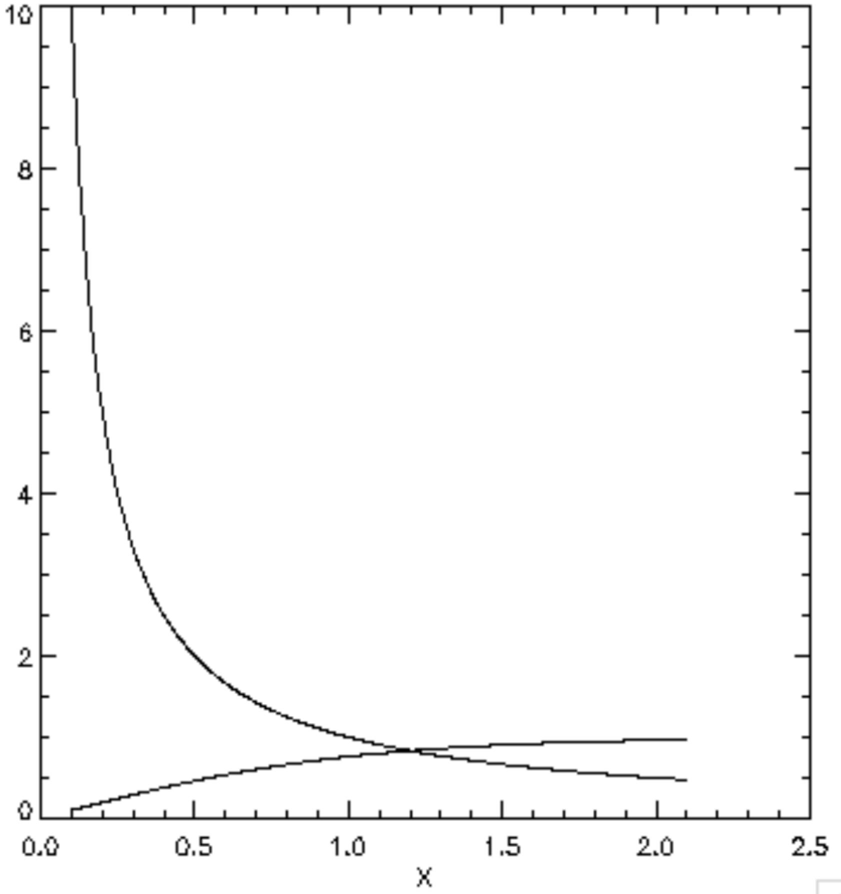
For $T \to \infty$, $x \to 0$ and $\frac{x^2}{\cosh^2 x} \to 0$ so that the specific heat goes to zero.

For $T \to 0$, $x \to \infty$ and $\frac{x^2}{\cosh^2 x} \to 0$ so that the specific heat goes to zero.

The specific heat has a maximum when

$$\frac{dC_B}{dx} = 0 = \frac{2x}{\cosh^2 x} - 2\frac{x^2 \sinh x}{\cosh^3 x} \Rightarrow \cosh x - x \sinh x = 0 \Rightarrow \tanh x = \frac{1}{x}$$

A graphical solution of the last equation is found by plotting $\tanh x$ versus x and $2/x$ versus x and finding the intersection



which says that the maximum is approximately $x = 1.2$ or at $kT/\mu B = 0.84$.

Mechanical Equilibrium and Pressure

Up to this point we have been discussing systems that were in thermal equilibrium and we found that the equilibrium state was characterized by the temperature when the systems could spontaneously exchange energy.

Suppose now we consider the two interacting systems A and B, each characterized by the variables U, V and S, where the total energy $U = U_A + U_B$ and the total volume $V = V_A + V_B$ are held fixed. The system can, however, exchange energy and volume now.

The entropy is now a function of two variables, namely, $S = S(U,V)$. The entropy must still be a maximum in the final equilibrium state. In this case the maximum of the entropy function is given by

$$\frac{\partial S_{total}}{\partial U_A} = 0 \quad \text{and} \quad \frac{\partial S_{total}}{\partial V_A} = 0$$

The first condition was the subject of the earlier work and we found that the two systems must have

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \Rightarrow T_A = T_B$$

The volume is now held fixed in these derivatives (particle number also).

In a similar manner if the systems exchange volume (a movable partition), then we must have

$$\frac{\partial S_{total}}{\partial V_A} = 0 = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}$$

since $dV = dV_A + dV_B = 0$. We therefore conclude that

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad \text{at equilibrium (mechanical)}$$

The energy is held fixed in these derivatives (particle number also).

When two system are in mechanical equilibrium, experiment says that their pressures are equal. Using dimensional analysis we find that $\frac{\partial S_A}{\partial V_A}$ has dimensions of pressure/Kelvin. Since we already know that $T_A = T_B$, the new equilibrium condition can also be written

$$T_A \frac{\partial S_A}{\partial V_A} = T_B \frac{\partial S_B}{\partial V_B} \quad \text{(dimensions of pressure)}$$

We thus choose

$$T\left(\frac{\partial S}{\partial V}\right)_{U,N} = P$$

and the equilibrium condition becomes $P_A = P_B$.

Does the definition make sense? Let us apply it to an ideal gas. Our earlier work gave the results

$$\Omega = f(N)V^N U^{3N/2} \quad \text{and} \quad S = Nk\ell nV + \frac{3}{2}Nk\ell nU + k\ell nf(N)$$

Using the definition we have

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N} = T\frac{\partial(Nk\ell nV)}{\partial V} = \frac{NkT}{V} \Rightarrow PV = NkT$$

which is the correct equation of state.

The Thermodynamic Identity

Since the entropy is a function of two variables, namely, $S = S(U,V)$, we can always write (just mathematics)

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = \frac{1}{T}dU + \frac{P}{T}dV$$

or

$$dU = TdS - PdV$$

This relation is the fundamental thermodynamic identity. It is true for any infinitesimal change in any system, provided no other variables(such as the system particle numbers) are changing.

Entropy and Heat Revisited

The thermodynamic identity looks suspiciously like the first law. In fact, in my earlier derivation of the entropy of an ideal gas, we equated the quantities,

$$Q = TdS \quad , \quad W = -PdV$$

so that the equation was equivalent to the first law $dU = Q + W$.

The associations are not valid for all processes however.

They are valid if any change in volume is quasistatic (this allows the pressure to be uniform throughout the system at all times), if no other forms of work are done and if not other relevant variables are changing. In these cases we know that $W = -PdV$ and we then have

$$dU = Q + W = Q - PdV \Rightarrow Q = TdS \qquad \text{(quasistatic)}$$

This says that under constrained conditions $S = Q/T$ even if work is being done.

Example: Polymers, like rubber

Diffusive Equilibrium and the Chemical Potential

Let us now consider two interacting systems A and B, each characterized by the variables U, N and S, where the total energy $U = U_A + U_B$, the total volume $V = V_A + V_B$ and the total number of particles $N = N_A + N_B$ are held fixed. The system can, however, exchange energy and particle number; we assume each system volume remains fixed for simplicity. We also assume that both systems contain the same type of particle (or species).

As in earlier discussions, if the systems exchange particle (holes in the partition), then we must have

$$\frac{\partial S_{total}}{\partial N_A} = 0 = \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_A} = \frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}$$

since $dN = dN_A + dN_B = 0$. We therefore conclude that

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad \text{at equilibrium (diffusive)}$$

The energy and volume are held fixed in these derivatives. Since we already know that $T_A = T_B$, the new equilibrium condition can also be written

$$-T_A \frac{\partial S_A}{\partial N_A} = -T_B \frac{\partial S_B}{\partial N_B} \quad \text{(for diffusive equilibrium)}$$

We define $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$ = chemical potential and then in diffusive equilibrium

$$\mu_A = \mu_B$$

If the systems are not in equilibrium, then the system with the larger value of $\frac{\partial S}{\partial N}$ will tend to gain particles since it can gain more entropy than the other system loses. Because of the minus sign in the definition of μ, however, this system has the smaller value of μ. Thus, particles flow from the system with higher μ into the system with lower μ.

This means we need to generalize the thermodynamic identity when the system is in general equilibrium. In particular, we now have $S = S(U,V,N)$, so that we can always write (just mathematics)

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

or

$$dU = TdS - PdV + \mu dN$$

The term μdN is called "chemical work".

There is one further modification we must introduce.

Suppose that each system contains several types of particles (that is, air is a mixture of nitrogen and oxygen), then each species has its own chemical potential

$$\mu_1 = -T\left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2} \quad , \quad \mu_2 = -T\left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1} \quad \text{and so on}$$

The thermodynamics identity then becomes

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

Now consider the relation

$$dU = TdS - PdV + \mu dN$$

which says that $U = U(S,V,N)$ and therefore

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N} \quad , \quad -P = \left.\frac{\partial U}{\partial V}\right|_{S,N} \quad , \quad \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}$$

These are the equations of state of the system.

Now rearranging we have

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

which says that $S = S(U,V,N)$ and therefore

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} \quad , \quad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \quad , \quad -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{U,V}$$

Again, these are the equations of state of the system.

Let us demonstrate all of this with the help of an example. Let us consider the entropy of the ideal gas as derived earlier

$$S(N,T,p) = Nk\left[s_0(T_0,p_0) + \ell n\left\{\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)\right\}\right]$$

If we rewrite this in terms of the independent variables U, N and V using $U = 3NkT/2$ and $pV = NkT$ ($U_0 = 3N_0kT_0/2$ and $p_0V_0 = N_0kT_0$, respectively) we get

$$S(N,V,U) = Nk\left[s_0(N_0,V_0,U_0) + \ell n\left\{\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\}\right]$$

All equations of state of the ideal gas can now be obtained by partial differentiation

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N,\ldots} = \frac{3}{2}Nk\frac{1}{U} \Rightarrow U = \frac{3}{2}NkT$$

$$\frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N,\ldots} = Nk\frac{1}{V} \Rightarrow pV = NkT$$

$$-\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{U,V,\ldots} = k\left[s_0 + \ell n\left\{\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\right\}\right] - \frac{5}{2}k$$

One then gets for the chemical potential of an ideal gas

$$\mu(p,T) = kT\left(\frac{5}{2} - s_0\right) - kT\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{p_0}{p}\right)$$

However, the knowledge of the state function (fundamental relation) $S(U,V,N,\ldots.)$ yields even more information.

If the entropy can be increased by a change in the variables $U,V,N,\ldots.$, the corresponding process happens spontaneously and irreversibly.

The equilibrium state of the system is finally given by a maximum of the entropy as a function of the variables $U,V,N,\ldots$.

Because of these properties, the entropy is a so-called **thermodynamic potential.**

Just like the potential energy of mechanics, the entropy gives information about the most stable (equilibrium) position of the system.

And just as with differences in potential energy, entropy differences are the reason why a process happens in an isolated system.

Finally, the knowledge of the state function $S(U,V,N,\ldots)$ or equivalently $U(U,V,N,\ldots)$ contains also knowledge of the main equations of a system.

The extensive state variables $U,S,V,N,\ldots$ are very useful for isolated systems, where they assume constant values in equilibrium, but in practice, for example, in a heat bath, these state variables are often not appropriate.

It is, for example, experimentally far easier to control, instead of the entropy, the corresponding(conjugate) intensive variable, the temperature.

Quite analogously, in many cases, one might prefer the pressure, for example, atmospheric pressure, as the variable instead of the volume, etc.

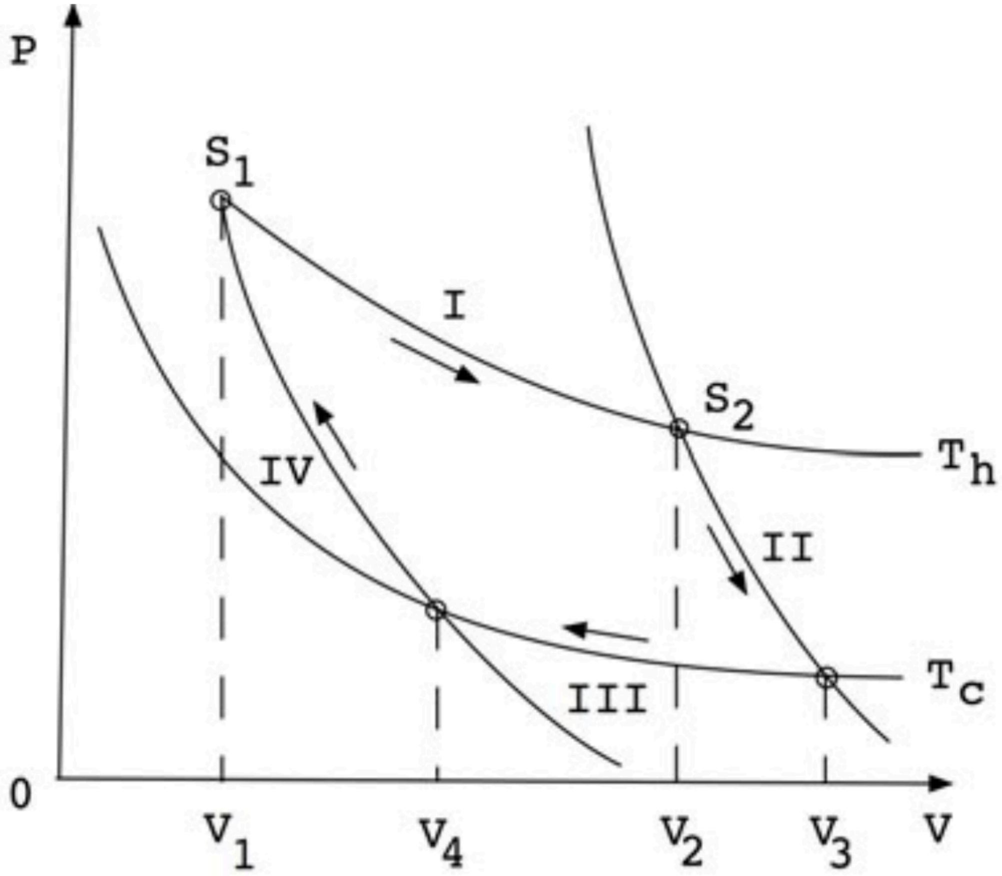
Therefore, it is reasonable to look for other thermodynamic potentials which have quite analogous properties to the entropy or the energy, but which depend on the conjugate intensive variables.

We will do this later.

Example: Consider an Einstein

4 - Engines and Refrigerators

Earlier we discussed the so-called Carnot cycle. The Carnot process is performed in four successive reversible steps, which are illustrated in a *pV* diagram in the figure below.



Step 1. Isothermal expansion from volume V_1 to volume V_2 at constant temperature T_h. For the isotherm we have

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}$$

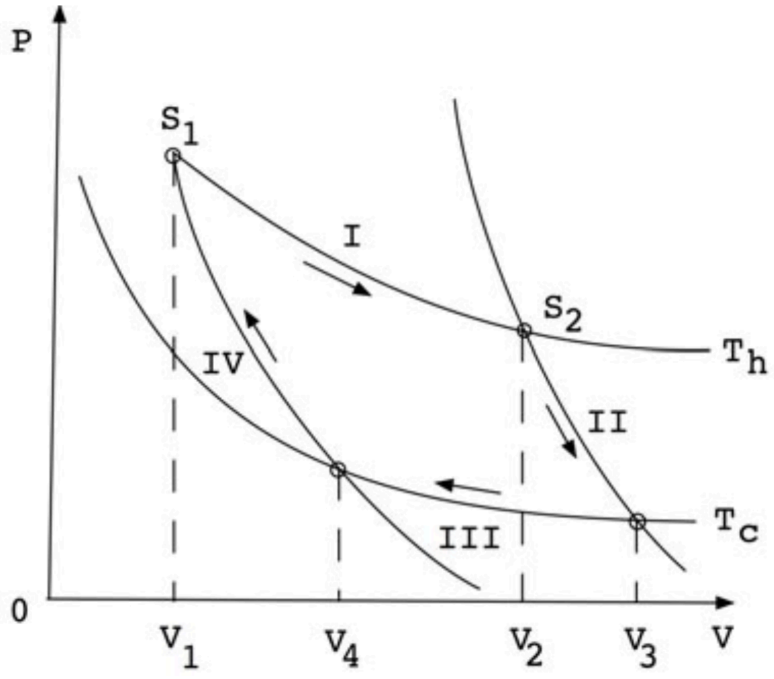
Since $U = 3NkT/2$ for an ideal gas, we know that the energy of an ideal gas, the working substance, cannot be changed at constant temperature. Consequently, we have that (from the first law)

$$\Delta U_I = W_I + Q_I = 0$$

From this we can calculate Q_I, with the help of eq (01.34)

$$Q_I = -W_I = NkT_h \ell n \frac{V_2}{V_1}$$

This is the amount of heat exchanged with the heat bath in the first step. Since $V_2 > V_1$, $Q_I > 0$, that is, the amount of heat Q_I is **added** to the gas as the expense of the heat bath.



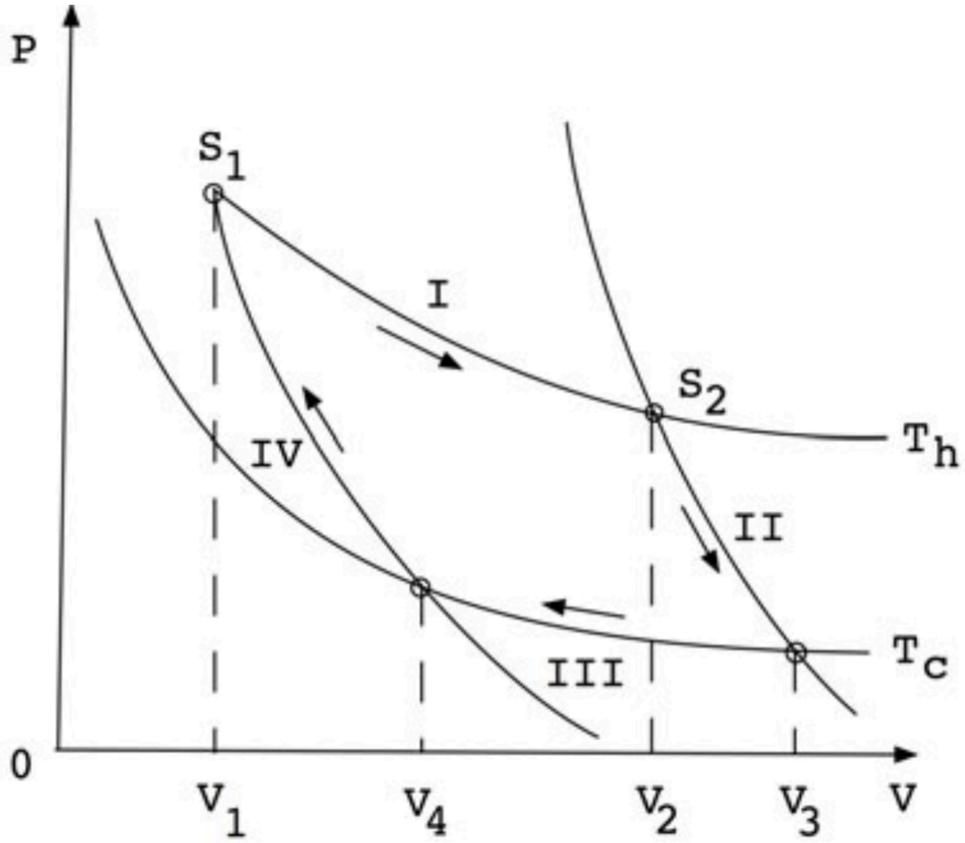
Step 2. Adiabatic expansion of the isolated working substance from V_2 to V_3. Here the temperature changes from T_h to T_c. The indices h and c denote *hot* and *cold*, that is, $T_h > T_c$. We get using (01.47)

$$\left(\frac{T_h}{T_c}\right)^{3/2} = \frac{V_3}{V_2}$$

Since $Q_{II} = 0$ (for an adiabatic process) the work done in the expansion is taken from the internal energy,

$$W_{II} = \Delta U_{II} = C_V(T_c - T_h)$$

where the sign of the above term corresponds to the direction $T_h \to T_c$. For an ideal gas, $C_V = 3Nk/2$, that is, C_V is a constant independent of temperature and volume. The difference of the internal energies for this part of the process is given by this equation even though the volume changes.



Step 3. We now compress the system isothermally from V_3 to V_4 at the (constant) smaller temperature T_c. In analogy with Step 1, we have

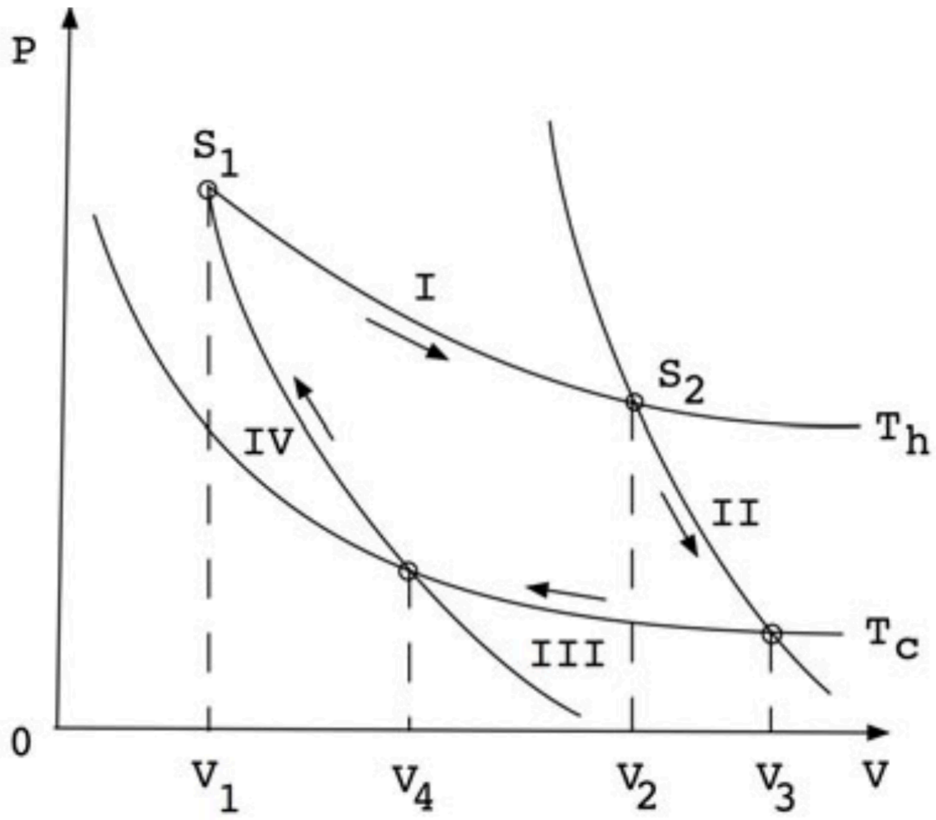
$$\frac{V_4}{V_3} = \frac{p_3}{p_4}$$

The work done during the compression is, because $\Delta U_{III} = 0$ at $T =$ constant, given to the heat bath in the form of heat

$$\Delta U_{III} = 0 = W_{III} + Q_{III}$$

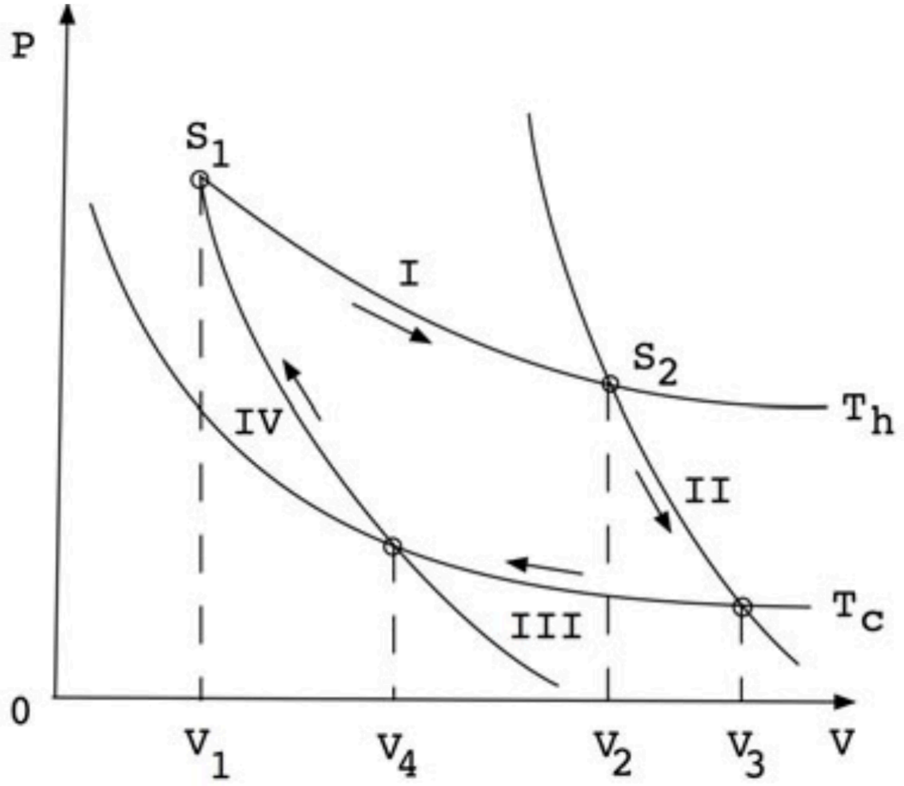
$$-W_{III} = Q_{III} = NkT_c \ell n \frac{V_4}{V_3}$$

This is the amount of heat absorbed by the heat bath in this step. Since $V_4 < V_3$, it follows that $Q_{III} < 0$, that is, the gas **loses** this amount of heat.



Step 4. Finally, we restore the system to the initial state via an adiabatic compression from V_4 to V_1. The temperature increases again from T_c to T_h such that

$$\left(\frac{T_c}{T_h}\right)^{3/2} = \frac{V_1}{V_4}$$



Since $Q_{IV} = 0$ it follows that

$$W_{IV} = \Delta U_{IV} = C_V(T_h - T_c)$$

Let us first check the total energy balance of the process. We have

$$\Delta U_{total} = \underbrace{Q_I + W_I}_{I} + \underbrace{W_{II}}_{II} + \underbrace{Q_{III} + W_{III}}_{III} + \underbrace{W_{IV}}_{IV}$$

If we insert the above results, we immediately find that $\Delta U_{total} = 0$, as it should be for a cycle. We have $Q_I + W_I = 0$ and similarly, $Q_{III} + W_{III} = 0$ and furthermore, $W_{II} = -W_{IV}$. In addition, we have the following equations for the amount of heat exchanged with the heat bath:

$$Q_I = NkT_h \ell n \frac{V_2}{V_1} \qquad Q_{III} = NkT_c \ell n \frac{V_4}{V_3}$$

On the other hand, we also have that

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

so that

$$\frac{Q_I}{T_h} = Nk\ell n\frac{V_2}{V_1} = Nk\ell n\frac{V_3}{V_4} = -\frac{Q_{III}}{T_c} \Rightarrow \frac{Q_I}{T_h} + \frac{Q_{III}}{T_c} = 0$$

This equation is of great importance, for it is valid not only for this special Carnot process, but according to all experimental evidence, for **any reversible cyclic process.**

Since the entropy is constant when $Q = 0$ in an adiabatic process, the Carnot process is just a rectangle in the TS plane, that is, T = constant in steps I and III and S = constant in steps II and IV.

The Carnot process effectively does a work ΔW, as can be seen from the corresponding equations, since the compressional work to be done in steps III and IV is smaller than the expansion work set free in steps I and II, namely,

$$W = W_I + W_{II} + W_{III} + W_{IV} = -NkT_h\ell n\frac{V_2}{V_1} - NkT_c\ell n\frac{V_4}{V_3}$$

so that we have

$$W = -Nk(T_h - T_c)\ell n\frac{V_2}{V_1} = -(Q_I + Q_{III})$$

Since $T_h > T_c$ and $V_2 > V_1$, this is a negative quantity. Therefore, W is work done by the gas. Clearly, a Carnot cycle can represent an "engine" which transforms heat in to work. The work done by the engine increases with the temperature difference $T_h - T_c$ and with the compression ratio V_2 / V_1.

Let us now calculate the efficiency of this engine. As efficiency η we define the ratio between the heat transformed into work and the total heat absorbed,

$$\eta = \frac{|\Delta W|}{\Delta Q_I} = \frac{\Delta Q_I + \Delta Q_{III}}{\Delta Q_I} = 1 + \frac{\Delta Q_{III}}{\Delta Q_I}$$

Using the result $\frac{Q_I}{T_h} + \frac{Q_{III}}{T_c} = 0$ we have

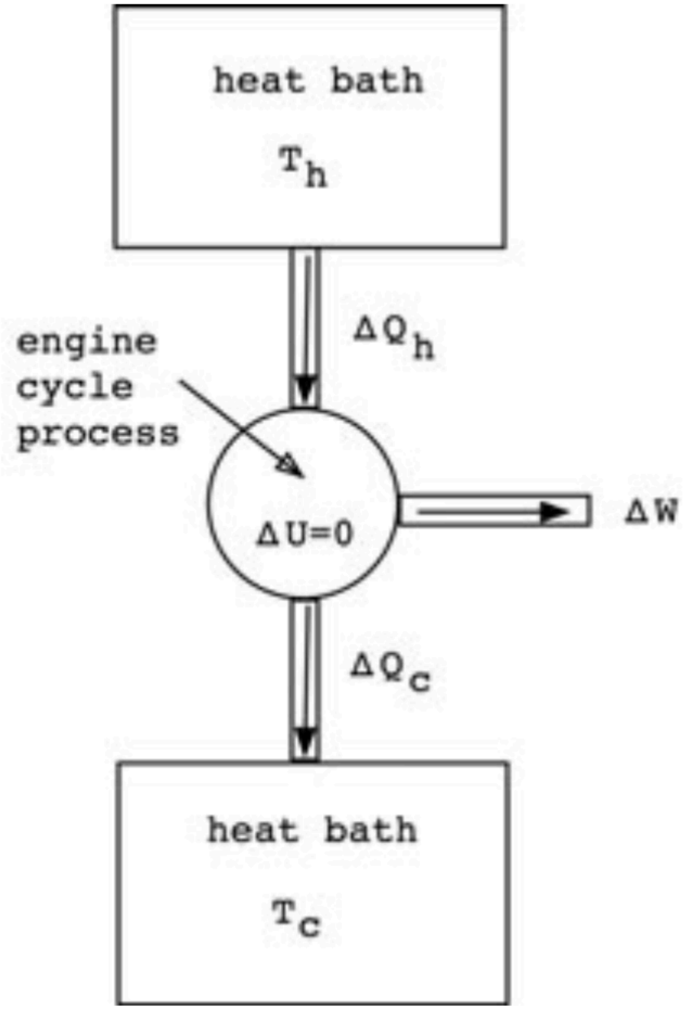
$$\eta = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h}$$

Therefore, the efficiency increases with the temperature difference $T_h - T_c$ as we stated earlier. However, since one cannot avoid losing a certain amount of heat ΔQ_{III}, which is radiated away into the cooler heat bath (at T_c), the efficiency is appreciably smaller than 1. Thus, even with this idealized engine it is not possible to transform the heat ΔQ_I (at T_h) completely into work, except for the case where the cooler heat bath has the temperature $T_c = 0$ (or the hotter heat bath the temperature $T_h \to \infty$). It can be shown that there is no heat engine with a better efficiency than the Carnot cycle.

Thermodynamic Engines

Cyclic heat engines play an extraordinarily large role in technology. A large part of the energy used in daily life is produced in such engines, for example, power plants and internal combustion engines. The reason is that heat can most easily be produced in various chemical or nuclear processes. The direct generation of utilizable forms of work out of natural sources is, in comparison, far more difficult, for example, hydroelectric power plants, tidal power plants, wind energy and direct transformation of solar energy into electric energy. This also confirms the experience that heat as statistically distributed energy is nearly always produced.

Now we want to calculate the efficiency of a general reversible cyclic process. To this end we schematize the substantial parts of a heat engine as shown in the figure below.



Each engine needs a heat reservoir ($T = T_h$) from which to extract heat energy and a second reservoir ($T = T_c$) to absorb the waste heat of the process, that is, to cool the engine. An engine which works with only one reservoir cannot perform utilizable work in a **cyclic process.**

According to the first law it holds that

$$0 = \Delta W + \Delta Q_h + \Delta Q_c$$

We have already defined the efficiency η as the fraction $|\Delta W| / \Delta Q_h$, which tells us how much heat energy ΔQ_h is transformed into work, where

$$\begin{aligned} &\Delta W < 0 \quad \text{work done by engine} \\ &\Delta Q_h > 0 \quad \text{heat added to engine} \\ &\Delta Q_c < 0 \quad \text{heat taken away from engine} \end{aligned}$$

as

$$\eta_{irr} < \eta_{rev} = -\frac{\Delta W}{\Delta Q_h} = \frac{\Delta Q_h + \Delta Q_c}{\Delta Q_h}$$

Since the engine will work reversibly, it holds that

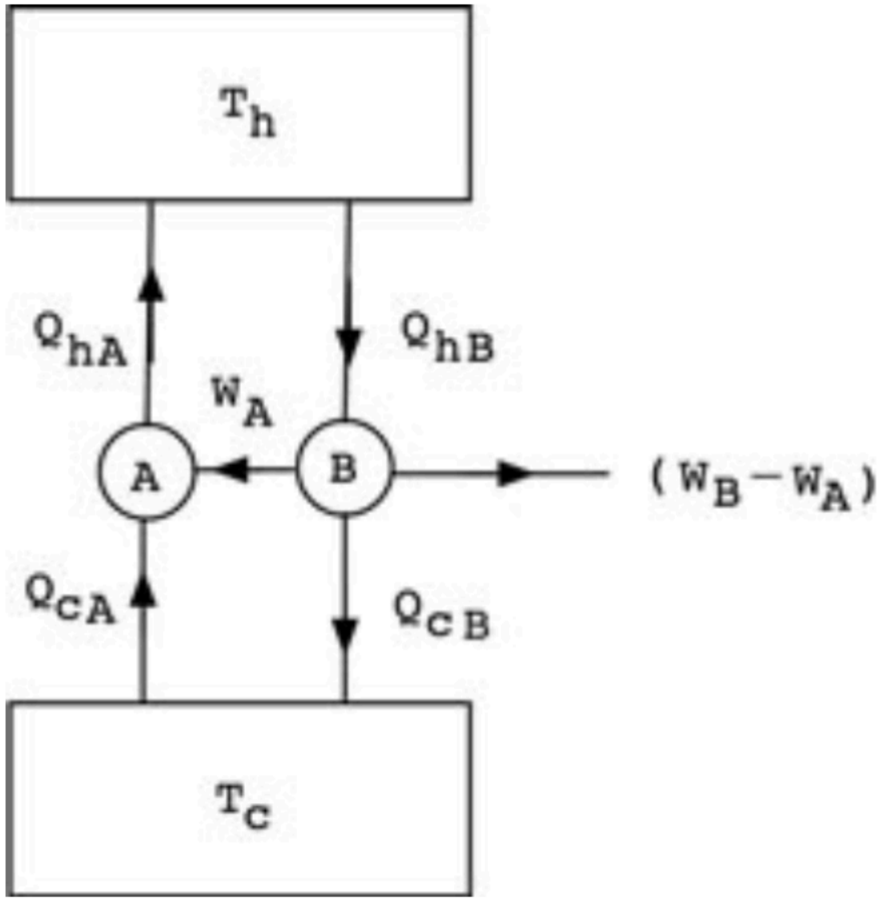
$$\delta Q_h = T_h dS \quad \text{and} \quad \delta Q_c = -T_c dS$$

Here dS is the well-defined change in entropy (state function) in a small partial step of the cycle. Note here that $dS \neq 0$, although only equilibrium states occur. The reason is that the engine (working material) is not an isolated system! The signs in the last equation correspond to the directions given in the figure. Since $\Delta W < 0$ (performed work) we have

$$\eta = \frac{T_h - T_c}{T_h}$$

For the efficiency it is always true that $\eta \leq 1$. The transformation of heat into work would only be complete if one could avoid heat loss (waste heat). This, however, is only possible if the cold reservoir has the temperature $T_c = 0$. On the other hand from the efficiency equation it is obvious that not only the temperature of the hot reservoir, that is, the temperature of the flame of a burner, is important, but also the temperature at which the waste heat is radiated off (the temperature of the exhaust gases). To gain high efficiency, the latter temperature should be as small as possible. An important point of our consideration is that the efficiency equation always holds, independent of the working material and the specific technical realization of the engine, for if there were two reversible cycles with different efficiencies, one could construct a perpetual motion engine.

In particular, one would then be able to connect two processes as shown in the figure below.



Engine A works here in the reverse direction, that is, as a heat pump expelling the energy W_A and the heat Q_{cA} from the cold reservoir as heat Q_{hA} into the hot reservoir. The energy W_A is here generated by the process B, which we will suppose works at a higher efficiency, so that there remains an amount of work $W_B - W_A$. If η_A and η_B denote the efficiencies of the engines (with $\eta_B > \eta_A$), then if we only consider absolute values and choose signs according to the figure, we have

$$W_A = \eta_A Q_{hA} \quad , \quad W_B = \eta_B Q_{hB}$$
$$Q_{cA} = Q_{hA} - W_A \quad , \quad Q_{cB} = Q_{hB} - W_B$$

If we now adjust the engine in such a way that $Q_{hA} = Q_{hB} = Q_h$, then there will be no change in the hot reservoir on a long time scale, since the same amount of heat is taken out as is pumped back. Then

$$Q_{cA} = (1 - \eta_A) Q_h > Q_{cB} = (1 - \eta_B) Q_h$$

since $\eta_B > \eta_A$. Thus, the heat

$$\Delta Q_c = Q_{cA} - Q_{cB} = (\eta_B - \eta_A) Q_h$$

is effectively drawn out of the cold reservoir. Hence the engine performs work

$$W_B - W_A = (\eta_B - \eta_A) Q_h$$

while cooling the cold reservoir. This is exactly a perpetual motion engine, which performs work and merely cools a heat reservoir. The vain efforts lasting for centuries to construct such and engine, which does not contradict the energy law but rather the entropy law, resulted in the recognition that $\Delta Q_c = W_B - W_A = 0$ or that

$$\eta_A = \eta_B = \frac{T_h - T_c}{T_h}$$

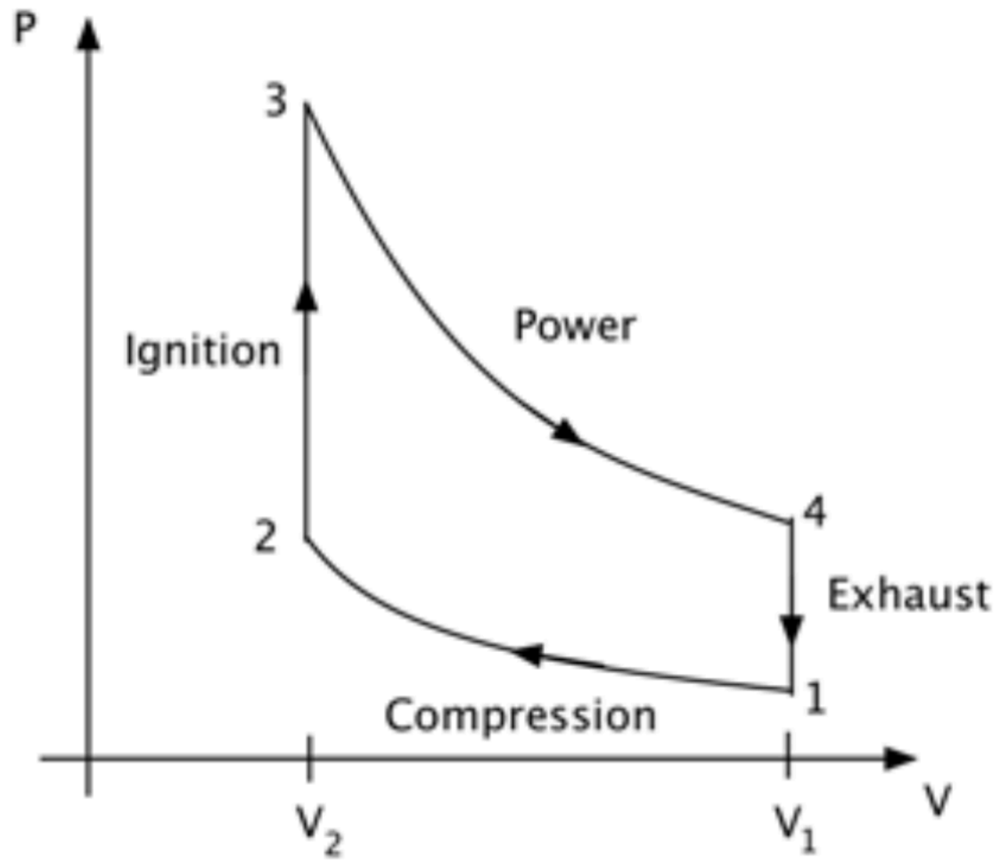
for all reversible processes at given T_h and T_c.

Real Heat Engines

The Carnot engine is a theoretical system that sets limits on the maximum possible efficiency of a thermodynamic heat engine and is a standard against which to compare real engines.

Internal Combustion Engines - Otto Cycle

This is the familiar gasoline engine found in automobiles. The working material is initially a mixture of vaporized gasoline and air. The mixture is subjected to the cycle shown in the figure below.



The mixture is first injected into a cylinder and compressed adiabatically by a piston. A spark plug then ignites the mixture raising its temperature and pressure while the volume remains constant. Next the high-pressure gas pushes the piston outward, expanding adiabatically and producing mechanical work. Finally the hot gases are expelled and replaced by a new mixture at lower temperature and pressure. The cycle (slightly idealized above) is called the **Otto cycle.**

The efficiency of the engine can be written as

$$e = 1 - \frac{Q_c}{Q_h}$$

so that we need to calculate the ratio Q_c / Q_h. Note that Q_h is the heat added in step 2-3 and Q_c is the heat expelled during step 4-1. There is no work performed during either of these steps, so by the first law, equipartition and the ideal gas law we have

$$Q_h = U_3 - U_2 = \frac{f}{2} Nk(T_3 - T_2) = \frac{f}{2} V_2(P_3 - P_2)$$
$$Q_c = U_4 - U_1 = \frac{f}{2} Nk(T_4 - T_1) = \frac{f}{2} V_1(P_4 - P_1)$$

The ratio Q_c / Q_h is therefore

$$\frac{Q_c}{Q_h} = \frac{V_1}{V_2} \frac{(P_4 - P_1)}{(P_3 - P_2)}$$

To eliminate the pressures from this equation we use the fact that 2-4 and 1-2 are adiabats to get

$$P_4 V_1^{\gamma} = P_3 V_2^{\gamma} \quad , \quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

so that

$$P_4 - P_1 = P_3 \left(\frac{V_2}{V_1} \right)^{\gamma} - P_2 \left(\frac{V_2}{V_1} \right)^{\gamma} = (P_3 - P_2) \left(\frac{V_2}{V_1} \right)^{\gamma}$$

or the ratio of the heats is

$$\frac{Q_c}{Q_h} = \frac{V_1}{V_2}\left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

and the efficiency is

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

where V_1/V_2 is the compression ratio and γ is the adiabatic exponent. For air $\gamma = 7/5$ and a typical compression ratio might be 8 so that we get a theoretical efficiency of $e = 1 - (1/8)^{2/5} = 0.56$.

If we eliminate the volumes in favor of the temperatures at the ends of each adiabatic step we have

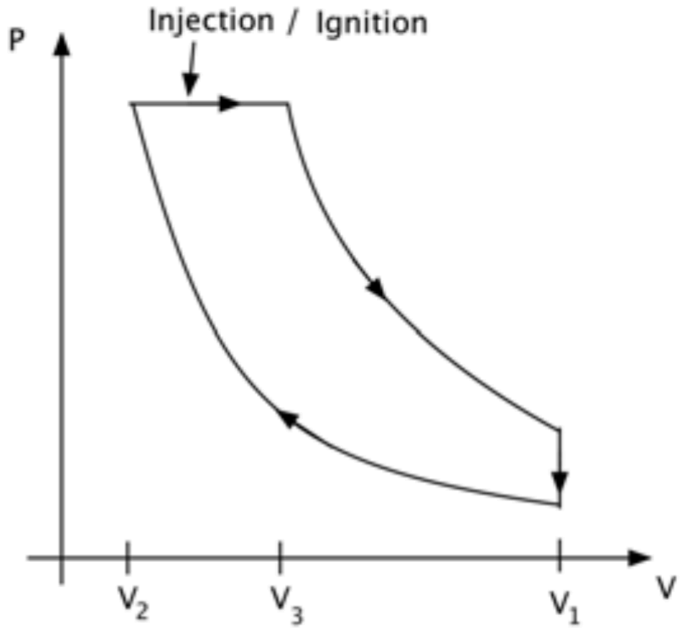
$$e = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3}$$

Both of these temperature ratios are greater than the ratio of the extreme temperatures T_1/T_3 that appears in the Carnot efficiency. The Otto engine is therefore less efficient than the Carnot engine. Other real world effects actually lower the efficiency of a real gasoline engine to about 20-30% instead of the theoretical 56%.

Diesel Engines

The obvious way to increase the efficiency of a gasoline engine is to increase the compression ratio. The problem is, however, that if the fuel mixture gets too hot it preignites spontaneously before point 2 is reached.

Preignition is avoided in a diesel engine by compressing only air, then spraying/ignition is done as the piston begins to move outward at a rate adjusted to maintain approximately constant pressure as shown in the figure below.



Example: Derive a formula for the efficiency of the diesel cycle in terms of the compression ratio V_1/V_2 and the cutoff ratio V_3/V_2

Solution: Following the same method as for the gasoline engine the heat input during step 2-3 is

$$Q_h = (U_3 - U_2) + P_2(V_3 - V_2) = \frac{f}{2}Nk(T_3 - T_2) + P_2(V_3 - V_2) = \frac{f+2}{2}P_2(V_3 - V_2)$$

while the waste heat output is

$$Q_c = (U_4 - U_1) = \frac{f}{2}V_1(P_4 - P_1)$$

Therefore the ratio of heats (which is 1 minus the efficiency) is

$$\frac{Q_c}{Q_h} = \frac{\frac{f}{2}V_1(P_4 - P_1)}{\frac{f+2}{2}P_2(V_3 - V_2)} = \frac{1}{\gamma}\frac{V_1(P_4 - P_1)}{P_2(V_3 - V_2)}$$

Since steps 3-4 and 1-2 are adiabatic, we have the relations

$$P_4V_1^\gamma = P_2V_3^\gamma \quad , \quad P_1V_1^\gamma = P_2V_2^\gamma$$

so that

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma}\frac{V_1}{(V_3 - V_2)}\left[\left(\frac{V_3}{V_1}\right)^\gamma - \left(\frac{V_2}{V_1}\right)^\gamma\right]$$

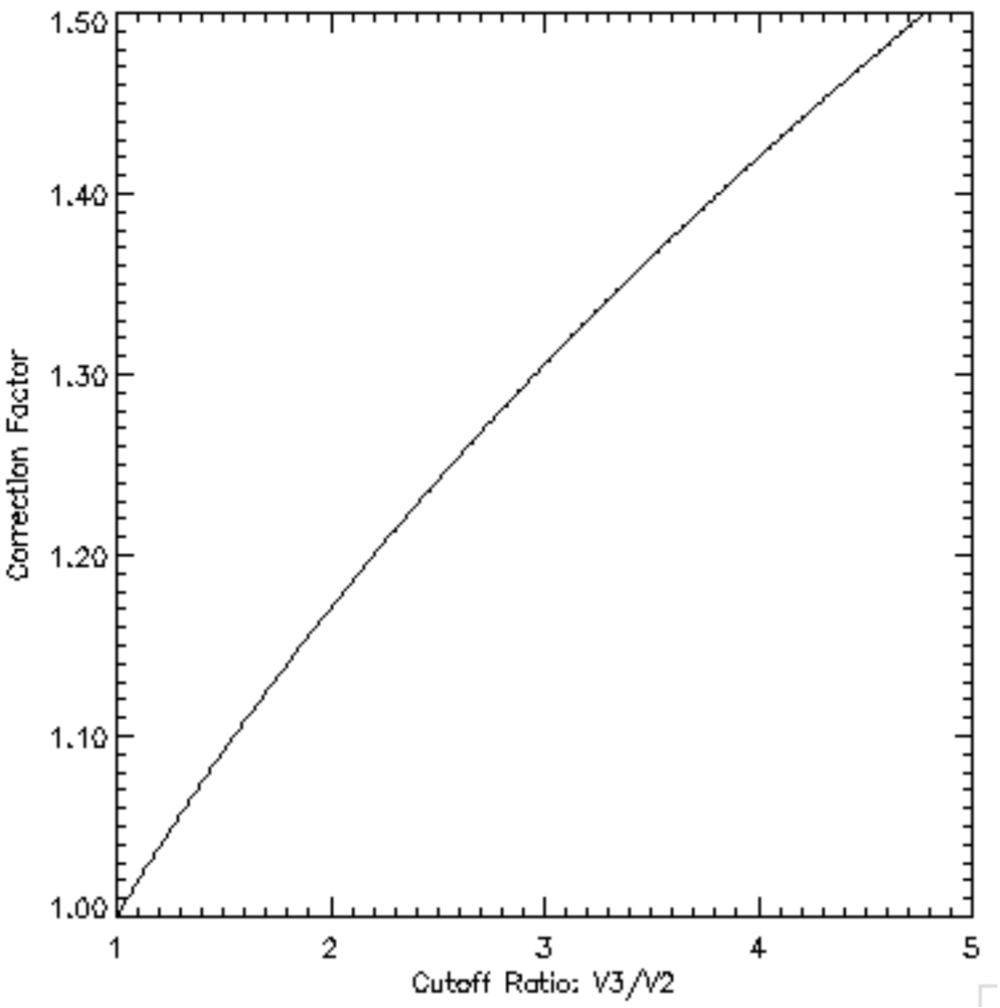
We can better understand this result by dividing numerator and denominator by V_2 and factoring out the compression ratio to get

$$\frac{Q_c}{Q_h} = \frac{1}{\gamma}\frac{V_1/V_2}{(V_3/V_2 - 1)}\left[\left(\frac{V_3}{V_2}\right)^\gamma\left(\frac{V_2}{V_1}\right)^\gamma - \left(\frac{V_2}{V_1}\right)^\gamma\right] = \left(\frac{V_2}{V_1}\right)^{\gamma-1}\frac{1}{\gamma}\frac{\left(V_3/V_2\right)^\gamma - 1}{V_3/V_2 - 1}$$

so that the efficiency is

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\left[\frac{1}{\gamma}\frac{\left(V_3/V_2\right)^\gamma - 1}{V_3/V_2 - 1}\right]$$

If we ignore the factor in [....] this expression is then the same as for the Otto cycle. The correction factor in the [...] depends only on γ and the cutoff ratio V_3/V_2. This factor is always greater than one as can be seen from the plot below for $\gamma = 7/5$.



The efficiency of the diesel engine is therefore always less than that of the Otto cycle for a given compression ratio V_2/V_1. Diesel engine can, however, have compression ratios as high as 20 and therefore have higher efficiencies than the Otto cycle theoretically). In practice the diesel engine efficiency can be as high as 40%.

Example: The ingenious Stirling engine is a true heat engine that absorbs heat from an external source. The working material can be air of any other gas. The engine consists of two cylinders with pistons, one in thermal contact with a hot reservoir and the other in thermal contact with a cold reservoir. The pistons are connected by a crankshaft in a complicated way that we will ignore and let the engineers worry about. Between the two cylinders is a passageway where the gas flows past a regenerator - a temporary heat reservoir, typically made of wire mesh, whose temperature varies gradually from the hot side to the cold side. The heat capacity of the regenerator is very large so its temperature is affected very little by the gas flowing past. The four steps in the engine's (idealized) cycle are as follows:

(1) **Power stroke:** while in the hot cylinder at temperature T_h, the gas absorbs heat and expands isothermally, pushing the hot piston outward. The piston in the cold cylinder remains at rest (all the way inward).

(2) **Transfer to the cold cylinder:** the hot piston moves in while the cold piston moves out, transferring the gas to the cold cylinder at constant volume. While on its way, the gas flows past the regenerator giving up heat and cooling to T_c.

(3) **Compression stroke:** The cold piston moves in, isothermally compressing the gas back to its original volume as the gas gives up heat to the cold reservoir. The hot piston remains at rest, all the way in.

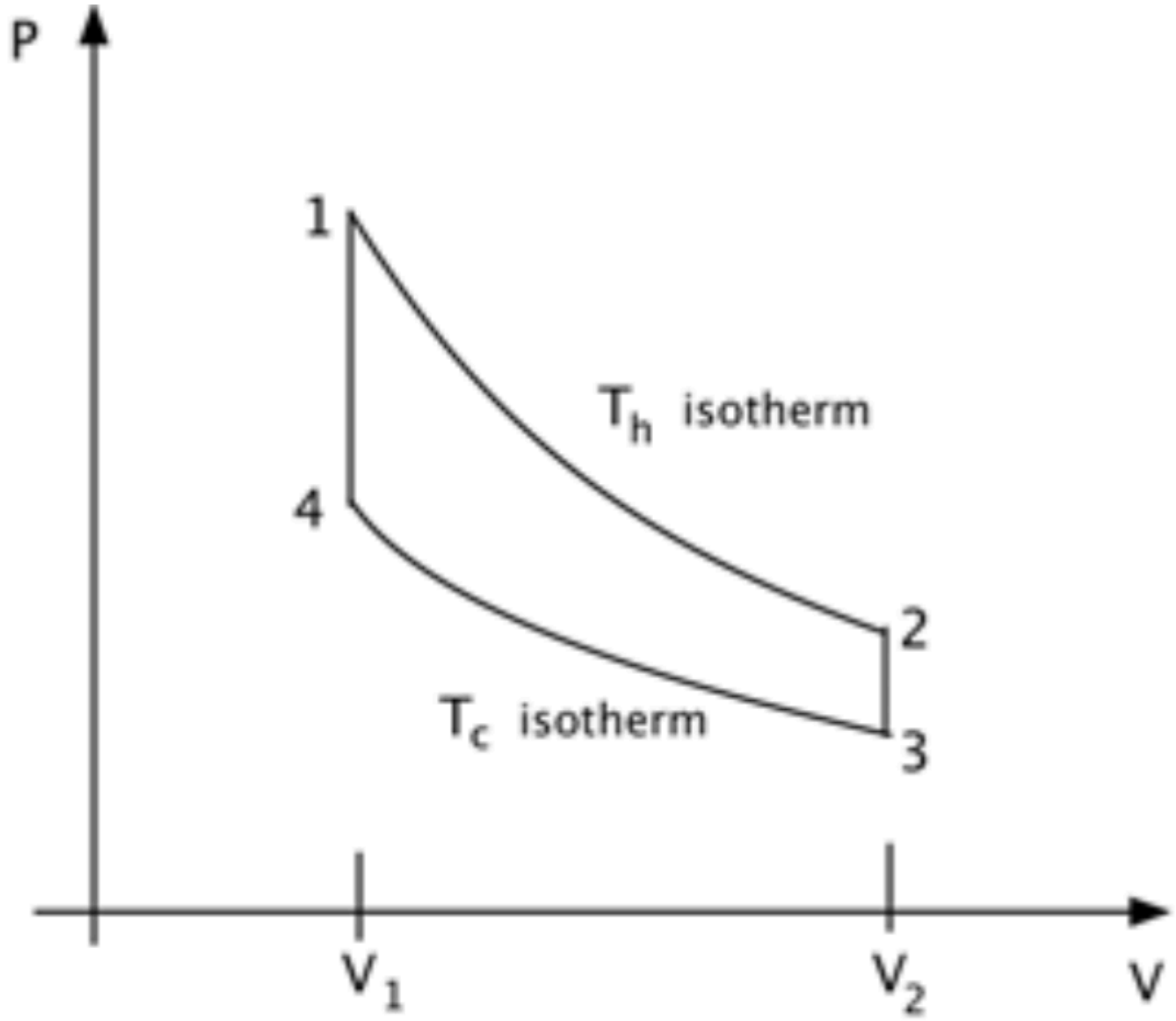
(4) **Transfer to the hot cylinder:** The cold piston moves the rest of the way in while the hot piston moves out, transferring the gas back to the hot cylinder at constant volume. While on its way, the gas flows past the regenerator, absorbing heat until it is again at T_h.

(A) Draw a *PV* diagram for this idealized Stirling engine.

(B) For get about the regenerator for the moment. Then, during step 2, the gas will give up heat to the cold reservoir instead of to the regenerator; during step 4, the gas will absorb heat from the hot reservoir. Calculate the efficiency of the engine in this case, assuming that the gas is ideal. Express the answer in terms of the temperature ratio T_c/T_h and the compression ratio (the ratio of the maximum and minimum volumes). Show that the efficiency is less than that of a Carnot engine operating between the same temperatures. Work out a numerical example.

(C) Now put the regenerator back. Argue that, if it works perfectly, the efficiency of the Stirling engine is the same as that of a Carnot engine.

(A) The cycle consists of two isothermal processes (at T_h and T_c) connected by constant volume processes:



(b) To calculate the efficiency, we need to know the net work done and the total heat input for one cycle. The work done by the gas during the power stroke is

$$W_{12} = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{NkT_h}{V}\,dV = NkT_h \ell n \frac{V_2}{V_1}$$

and the work done by the gas in the compression stroke is similarly

$$W_{34} = \int_{V_2}^{V_1} P\,dV = \int_{V_2}^{V_1} \frac{NkT_c}{V}\,dV = -NkT_c \ell n \frac{V_2}{V_1}$$

so the net work done per cycle is

$$W = W_{12} + W_{34} = Nk(T_h - T_c)\ell n \frac{V_2}{V_1}$$

Meanwhile, the heat input occurs during the power stroke and during the transfer to the hot cylinder. Because the power stroke is isothermal, the energy of the gas does not change during this step and therefore, by the first law

$$Q_{12} = W_{12} = NkT_h \ell n \frac{V_2}{V_1}$$

During the transfer to the hot cylinder there is no work done, so by the first law and the equipartition theorem, the heat input is

$$Q_{41} = U_1 - U_4 = \frac{f}{2} Nk(T_h - T_c)$$

Thus, the total heat input is

$$Q_h = Q_{12} + Q_{41} = NkT_h \ell n \frac{V_2}{V_1} + \frac{f}{2} Nk(T_h - T_c)$$

Now the efficiency is defined as $e = W / Q_h$. It is algebraically simpler to compute the reciprocal

$$\frac{1}{e} = \frac{Q_h}{W} = \frac{NkT_h \ell n \frac{V_2}{V_1} + \frac{f}{2} Nk(T_h - T_c)}{Nk(T_h - T_c) \ell n \frac{V_2}{V_1}} = \frac{T_h}{T_h - T_c} + \frac{f}{2 \ell n \frac{V_2}{V_1}}$$

The second term is always positive, but smaller for large compression ratios. Therefore $1/e$ is always greater than $1/e_C$ (the first term), that is, e less than e_C by an amount that is smaller when the compression ratio is large.

For example, if T_h is twice as large as T_c (say 600 K compared to 300 K), so that $e_C = 1/2$, and if the compression ration is 10 and the gas has 5 degrees of freedom per molecule, then

$$\frac{1}{e} = \frac{1}{2} + \frac{5}{2 \ell n 10} = 3.1 \Rightarrow e = 32\%$$

(c) With an ideal regenerator, the heat input during step 4-1 comes for free, because it is exactly the same $\frac{f}{2} Nk(T_h - T_c)$ as the heat output during step 2-3. Therefore only Q_{12} should be counted as part of Q_h, when computing the efficiency. Following the steps of the calculation in part (b), this means that the second term in the expression for $1/e$ is no longer present and therefore $e = e_C$.

The Stirling engine is easier to build than the Carnot engine.

5 - Free Energy, Phases and the van der Waals Gas

We will now attempt to apply thermodynamics to transformations of matter. We will need to extend our tools to handle constant-temperature and constant-pressure processes in different ways.

Free Energy

We earlier defined the enthalpy of a system as its energy plus the work needed to make room for it when the environment is held at constant pressure P:

$$H = U + PV$$

This is simply the total energy you would need to create the system out of nothing and put it into the environment ($\Delta V = V_f - V_i = V - 0 = V$).

If we could completely annihilate the system, then H is the energy available for other processes.

On the other hand, if we are in a constant-temperature environment, the system is able to extract heat from the environment for "free". Thus, we only need to provide whatever work is needed to create the system from nothing. We cannot recover all the energy as work since the constant-temperature environment means that we have to dispose of entropy by giving off heat into the environment.

We introduce to new quantities related to U and H. First,

$$\text{Helmholtz Free Energy} = F = U - TS$$

which is the total energy needed to create the system minus the heat you get for free from the environment at temperature T. The heat is

$$Q = T\Delta S = T(S_f - S_i) = T(S - 0) = TS$$

which says that the more entropy the system has, the more its energy can enter as heat. Thus F is the energy that comes from work. As before, if one annihilates the system F is the energy that one gets back as work; an amount of heat TS must be given to the environment to get rid of the system's entropy.

Similarly, if we are in a constant-pressure and constant-temperature environment, then the work that needs to be done to create the system (or the work that can be recovered by destroying the system) is the Gibbs Free Energy or

$$G = U - TS + PV$$

or the total energy minus the heat term in F plus the atmospheric work term in H.

The Principle of Maximum Entropy

The assertion of the second law of thermodynamics is that isolated systems strive for an equilibrium state which is characterized by a maximum in entropy. As we have seen this is, from the microscopic point of view, the most probable state, that is, the state with the largest number of microscopic realization possibilities.

All spontaneous (irreversible) processes in an isolated system increase the entropy, until the maximum is reached for the equilibrium state:

$$dS = 0 \quad , \quad S = S_{\max}$$

On the other hand, we know from mechanics, electrodynamics, and quantum mechanics that systems which are not isolated want to minimize their energy. For example, mechanical systems want to assume a state with a minimum of potential energy. A raindrop falls onto the earth, where its kinetic energy, gained from its initial potential energy, is transformed into heat. Similar arguments apply to a pendulum which finally reaches its rest position (equilibrium) due to the influence of friction, that is, it assumes a state with a minimum of potential energy. However, if in both cases, one keeps track of the heat created,then the total energy is not changed. It has merely been statistically (randomly) re-distributed in the form of heat among a larger number of particles (earth, support, etc). During this process, the entropy of the isolated total system (earth+air+raindrop or pendulum+air+support) has increased.

This leads us to the presumption that the striving for minimum energy can be traced to the striving for maximum entropy.

This can be understood with the help of the laws of thermodynamics. We consider and isolated system containing two subsystems (figure below).

$dU_1 = W_1$	$dU_2 = W_2 + Q_2$
$Q_1 = 0$	
S_1	S_2

We remove a certain work $W_1 < 0$ from system 1, for example a difference in potential energy.

The subsystem 1 will not exchange any heat with the surroundings during this process. For this reversible process we have

$$Q_1 = TdS_1 = 0$$

hence the entropy S_1 stays constant. If we now hand over a fraction ε of the work W_1 as heat and a fraction $(1-\varepsilon)$ as work to subsystem 2, we have

$$dU_2 = Q_2 + W_2 = -dU_1 = -W_1 > 0$$

$$Q_2 = -\varepsilon W_1 > 0 \qquad , \qquad W_2 = (1-\varepsilon)W_1$$

If heat is passed over to subsystem 2 while the temperature stays constant, we then have

$$Q_2 = TdS_2 > 0$$

Since S_1 = constant and $dS_2 > 0$, the total entropy of the isolated system has obviously increased through the transformation of work from subsystem 1 into heat in subsystem 2, and the internal energy of subsystem 1 has decreased.

One also notices that this process proceeds spontaneously as long as subsystem 1 can perform work, or in other words, until the total system reaches the state of maximum entropy. The transformation of work into heat is always an irreversible process and happens only until no more work can be performed (pendulum comes to rest!).

This conclusion can be expressed in very general terms:

> a nonisolated system at constant entropy ($Q=0$) heads for a state of minimum energy. Here one has to assume that at least part of the work W_1 is transformed into heat. However, if on the contrary $\varepsilon=0$ and $W_1=-W_2$, then S_1 = constant and S_2 = constant (because $Q_2=0$). The process is reversible and cannot happen spontaneously. Thus, the principle of minimum energy can be derived from the principle of maximum entropy.

Entropy and Energy as Thermodynamic Potentials

In many examples we have already seen that the entropy or the internal energy, respectively, are the central state quantities. If they are known as functions of the natural variables (U,S,V,N) of an isolated system, it is also guaranteed that all other thermodynamic quantities are completely known.

For example, if we know $U(S,V,N)$, we have that

$$dU = TdS - pdV + \mu dN$$

and thus

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N,\ldots} \quad , \quad -p = \left.\frac{\partial U}{\partial V}\right|_{S,N,\ldots} \quad , \quad \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V,\ldots}$$

so that temperature, pressure, and chemical potential are known functions of the natural variables.

A similar assertion holds for the entropy $S(U,V,N)$, if we rearrange $dU = TdS - pdV + \mu dN$ as

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

so that

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N,\ldots} \quad , \quad \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N,\ldots} \quad , \quad -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{U,V,\ldots}$$

The partial derivative equations are the equations of state of the system. We could, of course, reverse the process so that knowing all equations of state, we can calculate the entropy and the internal energy, respectively, as functions of the natural variables by integration.

The entropy of the ideal gas

We want to demonstrate this with the help of an example. Let us consider the entropy of the ideal gas, as given earlier.

$$S = Nk\left(\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right)$$

Knowing this equation, all equations of state of the ideal gas can be obtained by partial differentiation,

$$\begin{aligned}
\frac{1}{T} &= \left.\frac{\partial S}{\partial U}\right|_{V,N} = \frac{3}{2}Nk\frac{1}{U} \Rightarrow U = \frac{3}{2}NkT \\
\frac{P}{T} &= \left.\frac{\partial S}{\partial V}\right|_{U,N} = Nk\frac{1}{V} \Rightarrow PV = NkT \\
-\frac{\mu}{T} &= \left.\frac{\partial S}{\partial N}\right|_{U,V} = k\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right]
\end{aligned}$$

We then get for the chemical potential

$$\mu(P,T) = -kT\ell n\left[\left(\frac{2m\pi}{\hbar^2}\right)^{3/2}\frac{(kT)^{5/2}}{P}\right]$$

However, the knowledge of the state function (fundamental relation) $S(U,V,N)$ yields even more information. If the entropy can be increased by a change in the variables U,V,N, the corresponding process happens spontaneously and irreversibly. The equilibrium state of the system is finally given by a maximum of the entropy as a function of the variables U,V,N. Because of these properties, the entropy is a so-called **thermodynamic potential.** Just like the potential energy of mechanics, the entropy gives information about the most stable (equilibrium) position of the system and just as is the case for differences in potential energy, entropy differences are the reason why a process happens in an isolated system.

Finally, the knowledge of the state function $S(U,V,N)$ or equivalently $U(S,V,N)$ contains also knowledge of the main equations of a system. The extensive state variables U,S,V,N are very useful for isolated systems, where they assume constant values in equilibrium, but in practice, for example, in a heat bath, these state variables are often not appropriate. It is, for example, experimentally far easier to control, instead of the entropy, the corresponding(or conjugate) intensive variable, the temperature. Quite analogously, in many cases, one might prefer the pressure, for example, atmospheric pressure, as the variable instead of the corresponding extensive variable volume, etc. Therefore, it is reasonable to look for other thermodynamic potentials which have quite analogous properties to the entropy or the energy, but which depend on the conjugated intensive variables. Our aim is, therefore, for example, in the case of the internal energy $U(S,V,N)$, to perform a transformation from the entropy to the corresponding intensive variable

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

The transformation we need is the **Legendre transformation** as we will see shortly.

The four functions U, H, F and G, as defined earlier, are all called **thermodynamic potentials.**

Some Properties

Change at constant temperature T

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

$Q =$ heat added
$W =$ work done on system

If no new entropy is created, then
$Q = T\Delta S$ and $\Delta F = W$ = work done on system

If new entropy is created, then
$Q < T\Delta S$ and $\Delta F \leq W$ at constant T

Change at constant temperature P

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V$$

$Q =$ heat added
$W =$ work done on system = $-P\Delta V + W_{other}$

If no new entropy is created, then
$Q = T\Delta S$ and $\Delta F = W_{other}$ = work done on system

If new entropy is created, then
$Q < T\Delta S$ and $\Delta F \leq W_{other}$ at constant T,P

Euler's Equation and the Gibbs-Duhem Relation

To see how to transform between variables, we start from the first law for reversible changes of states for a system which is as general as possible. We assume that the system contains only 1 particle species for simplicity. Then we have

$$dU = TdS - PdV + \mu dN$$

Thus, the extensive internal energy U has to be interpreted as a function of the extensive state variables S,V,N in this case. Now, in general, an extensive state variable is proportional to the absolute size of the system. In other words, if one doubles all independent extensive state variables, all other dependent extensive quantities also become twice as large. For the internal energy, this means that

$$U(\alpha S,\alpha V,\alpha N) = \alpha U(S,V,N)$$

if α is the enlargement factor. One calls functions which have this property **homogeneous functions of first order.** All extensive variables are homogeneous functions of first order of the other extensive variables.

On the other hand, intensive variables are homogeneous functions of zeroth order of the extensive variables where

$$T(\alpha S,\alpha V,\alpha N) = T(S,V,N)$$

that is, they do not change if we divide or duplicate the system.

The equation $U(\alpha S,\alpha V,\alpha N) = \alpha U(S,V,N)$ has far-reaching consequences. If we consider an infinitesimal increase of the system ($\alpha = 1+\varepsilon$ with $\varepsilon << 1$), we can expand the left-hand side in a Taylor series:

$$U((1+\varepsilon)S,.......) = U + \frac{\partial U}{\partial S}\varepsilon S + \frac{\partial U}{\partial V}\varepsilon V + \frac{\partial U}{\partial N}\varepsilon N$$

If we insert this into the above equation and use the fact that

$$\frac{\partial U}{\partial S} = T \quad , \quad \frac{\partial U}{\partial V} = -P \quad , \quad \frac{\partial U}{\partial N} = \mu$$

it follows that

$$U((1+\varepsilon)S,.......) = U + \varepsilon U = U + \varepsilon\left(TS - PV + \mu N\right)$$

that is, we obtain **Euler's equation,**

$$U = TS - PV + \mu N$$

If we calculate the total differential of Euler's equation, we find that

$$dU = TdS - PdV + \mu dN + SdT - VdP + Nd\mu$$

so that (using the first law)

$$SdT - VdP + Nd\mu = 0$$

must always be valid. This is the **Gibbs-Duhem relation.**

It means that the intensive variables T,P and μ which are conjugate to the extensive variables S,V and N are not all independent of each other. In principle this can be readily understood, since from three extensive state variables, for example S,V and N one can derive only two independent intensive state variables, for example, S/N and V/N. All other combinations can be expressed in terms of these two.

Thermodynamic Identities

The idea of the Legendre transformation follows from the process discussed below.

Because of the thermodynamic identity for U

$$dU = TdS - PdV + \mu dN$$

it is natural to think of U as a function of the variables S, V and N.

We can replace the variable S, the entropy, by the temperature $T = \left.\frac{\partial U}{\partial S}\right|_{V,N}$ using the following operation

$$F = U - TS = (TS - PV + \mu N) - TS = -PV + \mu N$$

where we have used Euler's equation. The total differential of F is then

$$dF = dU - SdT - TdS = dU = TdS - PdV + \mu dN - SdT - TdS = -SdT - PdV + \mu dN$$

Hence the free energy F is a function of T,V,N, which contains exactly the same information as the internal energy U, but which now depends on the temperature instead of the entropy. In particular one obtains the equations of state

$$-S = \left.\frac{\partial F}{\partial T}\right|_{V,N} \quad , \quad -P = \left.\frac{\partial F}{\partial V}\right|_{T,N} \quad , \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$$

Subtracting TS to change the independent variable from S to T is called a **Legendre transformation.**

We can now do the same thing for the enthalpy.

We want to transform the internal energy $U(S,V,N)$ from the extensive variable V to the new intensive variable P. Since the term $-PdV$ in the differential of U occurs with a negative sign, we also have to change the sign in the Legendre transformation:

$$H = U + PV = TS + \mu N$$

where we have used Euler's equation.

This equation defines the **enthalpy**, which is also a thermodynamic potential, in variables S, P and N. The total differential of the enthalpy reads

$$dH = dU + PdV + VdP = TdS + VdP + \mu dN$$

If the enthalpy $H(S,P,N)$ is known, all other state quantities may be obtained by partial differentiation, as for U and F, that is,

$$T = \left.\frac{\partial H}{\partial S}\right|_{P,N} \quad , \quad V = \left.\frac{\partial F}{\partial P}\right|_{S,N} \quad , \quad \mu = \left.\frac{\partial H}{\partial N}\right|_{S,P}$$

For systems with given temperature and pressure we have to perform the Legendre transformation of the internal energy $U(S,V,N)$ with respect to two variables, namely, S and V in the following way:

$$G = U - TS + PV$$

The corresponding thermodynamic potential is the **free enthalpy** or **Gibbs' free energy.** The total differential of the free enthalpy reads

$$dG = dU - TdS - SdT + PdV + VdP = -SdT + VdP + \mu dN$$

Consequently, G indeed depends only on T, P and N. If the function $G(T,P,N)$ is known, we can obtain all further quantities (equations of state) by partial differentiation,

$$-S = \left.\frac{\partial G}{\partial T}\right|_{P,N} \quad , \quad V = \left.\frac{\partial G}{\partial P}\right|_{T,N} \quad , \quad \mu = \left.\frac{\partial G}{\partial N}\right|_{T,P}$$

These yield the equations of state of the system. User Euler's equation, which must be fulfilled in any case, we can identify the Gibbs' free enthalpy somewhat more explicitly. Euler's equation reads

$$U = TS - PV + \mu N$$

From this it immediately follows that

$$G = U - TS + PV = TS - PV + \mu N - TS + PV = \mu N$$

The third of the equations of state is thus trivially fulfilled for the free enthalpy, that is, $\mu = \left.\frac{\partial G}{\partial N}\right|_{T,P.} = \frac{G}{N}$. Hence, G is directly proportional to the particle number and **the free enthalpy per particle is identical with the chemical potential.**

Free energy of the ideal gas

We want to calculate the free energy of the ideal gas. From our earlier result

$$S = Nk\left(\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right)$$

we have

$$U(S,V,N) = \frac{3\hbar^2}{4m\pi} N^{5/3}\left(\frac{1}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - \frac{5}{2}\right)\right\}$$

Now we form

$$F = U - TS$$

To obtain $F(T,V,N)$ we have to replace S by T

$$T = \left.\frac{\partial U}{\partial S}\right|_{N,V} = \frac{\hbar^2}{2m\pi k}\left(\frac{N}{V}\right)^{2/3}\exp\left\{\frac{2}{3}\left(\frac{S}{Nk}-\frac{5}{2}\right)\right\}$$

This equation has to be solved for $S(T,V,N)$:

$$S(T,V,N) = Nk\left[\frac{5}{2} + \ell n\left\{\left(\frac{2m\pi kT}{\hbar^2}\right)^{3/2}\left(\frac{V}{N}\right)\right\}\right]$$

It then follows that

$$F(T,V,N) = \frac{3}{2}NkT - NkT\left[\frac{5}{2} + \ell n\left\{\left(\frac{2m\pi kT}{\hbar^2}\right)^{3/2}\left(\frac{V}{N}\right)\right\}\right]$$

Now we show that $F(T,V,N)$ as well as $U(S,V,N)$ or $S(U,V,N)$ contain all equations of state. To this end we just have to calculate the partial derivatives of $F(T,V,N)$ with respect to the variables:

$$S(T,V,N) = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left(\ell n\left[\frac{V}{N}\left(\frac{4m\pi U}{3N\hbar^2}\right)^{3/2}\right] + \frac{5}{2}\right)$$

$$p(T,V,N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V}$$

$$\mu(T,V,N) = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -kT\ell n\left\{\left(\frac{2m\pi kT}{\hbar^2}\right)^{3/2}\left(\frac{V}{N}\right)\right\}$$

Together with the reverse transformation,

$$U(T,V,N) = F(T,V,N) + TS = \frac{3}{2}NkT$$

the free energy is completely equivalent to $S(U,V,N)$ or $U(S,V,N)$.

Enthalpy of the Ideal Gas

We start again from

$$H = U + PV$$

To calculate $H(S,P,N)$ explicitly we have to eliminate V.

$$-P = \left.\frac{\partial U}{\partial V}\right|_{S,N} = -\frac{\hbar^2}{2m\pi}\left(\frac{N}{V}\right)^{5/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - \frac{5}{2}\right)\right\}$$

This equation has to be solved for V and inserted into $H = U + pV$. First, we have

$$V = \left(\frac{\hbar^2}{3m\pi}\frac{1}{P}\right)^{3/5} N \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - \frac{5}{2}\right)\right\}$$

If one inserts this into $H = U + pV$ one gets

$$H(S,P,N) = \frac{3\hbar^2}{4m\pi}N^{5/3}\left(\frac{1}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - \frac{5}{2}\right)\right\}$$
$$+ P\left(\frac{\hbar^2}{3m\pi}\frac{1}{P}\right)^{3/5} N \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - \frac{5}{2}\right)\right\}$$

Now with the help of the enthalpy we can to demonstrate the usefulness of various thermodynamic potentials for special systems. If we add an amount of heat Q to the system at constant volume, we have, with $W=0$,

$$dU = Q|_V$$

so that the amount of heat directly increases the internal energy. For the specific heat at constant volume it holds that

$$C_V = \left.\frac{Q}{dT}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V$$

However, if the heat Q is added under constant pressure, generally the volume of the system will change and a certain volume work will be performed and we have

$$dU = Q|_P - PdV$$

The internal energy is not very appropriate for describing this process since not only the temperature, but also the volume of the system changes. At constant pressure, however, this equation can be put in the form

$$dH = d(U+PV) = Q|_P$$

The specific heat at constant pressure therefore is

$$C_p = \left.\frac{Q}{dT}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P$$

If we rewrite the enthalpy as $H(T,P,N)$, that is changing appropriate variables, we have for an ideal gas

$$H(T,P,N) = \frac{5}{2}NkT$$

which also follows directly from $H = U + PV = \frac{3}{2}NkT + NkT$. Thus, we obtain for an ideal gas $C_P = \frac{5}{2} Nk$ while $C_V = \frac{3}{2} Nk$.

The specific heat at constant pressure is larger than that at constant volume by Nk, since a part of the heat $Q|_P$ is transformed into volume work against the external pressure P.

The Maxwell Relations

A variety of relations between the thermodynamic state variables can be derived from the fact that the thermodynamic potentials U, F, H, G are state functions, that is, they have exact differentials.

Then total differential of the internal energy reads (we now consider only systems which are completely characterized by three state variables),

$$dU = TdS - PdV + \mu dN = \left.\frac{\partial U}{\partial S}\right|_{V,N} dS + \left.\frac{\partial U}{\partial V}\right|_{S,N} dV + \left.\frac{\partial U}{\partial N}\right|_{S,V} dN$$

Since

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

it immediately follows for example that

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

In this manner many relations emerge that may allow for the calculation of unknown quantities from known quantities and which we now want to present in a systematic way. At first it follows from the equation for dU that

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

Corresponding relations exist for the free energy $F(T,V,N)$:

$$dF = -SdT - PdV + \mu dN = \left.\frac{\partial F}{\partial T}\right|_{V,N} dT + \left.\frac{\partial F}{\partial V}\right|_{T,N} dV + \left.\frac{\partial F}{\partial N}\right|_{T,V} dN$$

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

Analogously, it holds for the enthalpy $H(S,P,N)$ that

$$dH = TdS + VdP + \mu dN = \left.\frac{\partial H}{\partial S}\right|_{P,N} dS + \left.\frac{\partial H}{\partial P}\right|_{S,N} dP + \left.\frac{\partial H}{\partial N}\right|_{S,P} dN$$

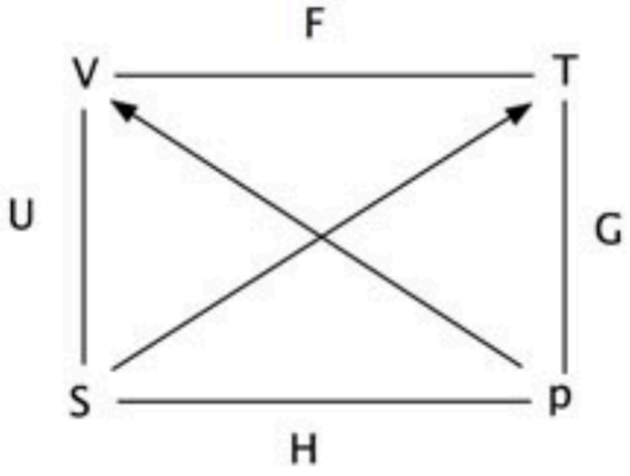
$$-\left.\frac{\partial S}{\partial V}\right|_{T,N} = -\left.\frac{\partial P}{\partial T}\right|_{V,N} \quad , \quad \left.\frac{\partial T}{\partial N}\right|_{S,P} = \left.\frac{\partial \mu}{\partial S}\right|_{P,N} \quad , \quad \left.\frac{\partial V}{\partial N}\right|_{S,P} = \left.\frac{\partial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

For the free enthalpy one has

$$dG = -SdT + VdP + \mu dN = \left.\frac{\partial G}{\partial T}\right|_{P,N} dT + \left.\frac{\partial G}{\partial P}\right|_{T,N} dP + \left.\frac{\partial G}{\partial N}\right|_{T,P} dN$$

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

These elations are called **Maxwell relations.** In the literature, one often considers systems with constant particle number ($dN = 0$). Thus, the number of relations is considerably reduced. There exists a simple device which allows for a quick overlook of the potentials and their variables and which yields the maxwell relations. This device is the thermodynamic rectangle which is shown below in the figure below.



Thermodynamic rectangle for N = constant

The thermodynamic rectangle was conceived especially for systems with constant particle number and without any extra variables. The variables V,T,P,S which are the only possible quantities at constant particle number, form the corners of the rectangle. Along the edges we denote the potentials, which depend on the variables at the corresponding corners, for example, $F(V,T)$. With this way of presentation, partial derivatives are easily read off. The derivative of a potential with respect to a variable (corner) is just given by the variable at the diagonally opposite corner. The arrows in the diagonals determine the sign.

For example, we have $\partial F/\partial V = -P$. The minus sign occurs because the direction $V \to P$ is opposite to the direction of the arrow. Analogously, we have, for example, $\partial G/\partial P = +V$. Even the Maxwell relations (now without N) are easy to read off the figure. Derivatives of variables along an edge of the rectangle, for example, $\partial V/\partial S$, at constant variable in the diagonally opposite corners, P, are just equal to the corresponding derivative along the other side, that is, $\partial T/\partial P$ at constant S. The signs have to be chosen according to the direction in which one follows the diagonals, for example, going from $V \to P$ yields a minus sign, as does the path $T \to S$.

Heat Capacities

Let us now establish a general relationship between the heat capacities C_V and C_p, which should, if possible, contain only quantities that are easy to measure.

The definitions of C_V and C_P read (N = constant):

$$C_V = \left.\frac{Q}{dT}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V$$

$$C_P = \left.\frac{Q}{dT}\right|_v = T\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P$$

In the first equation T and V are supposed to be independent variables, while in the second equation T and P are independent. One can write both equations with $S(T,V)$ or $S(T,P)$ respectively, as follows:

$$Q = TdS = C_V dT + T\left.\frac{\partial S}{\partial T}\right|_V dV$$

$$Q = TdS = C_P dT + T\left.\frac{\partial S}{\partial P}\right|_V dP$$

The pressure above can as well be regarded as a function of the variables T and V, which are sufficient to determine the state of the system (N = constant). With $P(T,V)$ we can eliminate dP in the last equation and obtain

$$Q = TdS = C_P dT + T\left.\frac{\partial S}{\partial P}\right|_V \left(\left.\frac{\partial P}{\partial T}\right|_V dT + \left.\frac{\partial P}{\partial V}\right|_T dV\right)$$

Since dS is a complete differential, the coefficients of dT

$$Q = TdS = C_V dT + T\left.\frac{\partial S}{\partial T}\right|_V dV \quad \text{and} \quad Q = C_P dT + T\left.\frac{\partial S}{\partial P}\right|_V \left(\left.\frac{\partial P}{\partial T}\right|_V dT + \left.\frac{\partial P}{\partial V}\right|_T dV\right)$$

have to be equal, that is,

$$C_V = C_P + T\left.\frac{\partial S}{\partial P}\right|_T \left.\frac{\partial P}{\partial T}\right|_V$$

By the way this relation is also the case for the coefficient of dV. This is proved via the chain rule $\left.\frac{\partial S}{\partial P}\right|_T \left.\frac{\partial P}{\partial V}\right|_T = \left.\frac{\partial S}{\partial V}\right|_T$. The above relationship between C_V and C_p is, however, still not very useful in practice, since, for example, $\left.\frac{\partial S}{\partial P}\right|_T$ is difficult to measure. The quantity $\left.\frac{\partial P}{\partial T}\right|_V$ is conveniently measurable for gases, but in fluids or solids processes at constant volume are connected with extreme pressure. Thus, if possible, we want to express both quantities in terms of easily measurable quantities. An earlier Maxwell relation reads

$$\left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$$

The right-hand side is the isobaric expansion coefficient α

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

Also, the factor $\left.\frac{\partial P}{\partial T}\right|_V$ can be rewritten with an often used trick in terms of other quantities. To this end, we consider the volume as a function of P and T, since these variables determine the state of the system as well as V and T. Then we have

$$dV = \left.\frac{\partial V}{\partial T}\right|_P dT + \left.\frac{\partial V}{\partial P}\right|_T dP$$

For processes at constant volume ($dV = 0$) it thus holds that

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

In the numerator we have the expansion coefficient αV, while in the denominator the isothermal compressibility κV appears:

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

Finally it follows that

$$C_V = C_P + TV\frac{\alpha^2}{\kappa}$$

In this relations, only quantities which are easy to measure appear.

Example: (Homework problem 1.46) Example: Use the thermodynamic Example: Functions encountered

Example: The partial derivative Example: The formula for Example: A formula analogous

Example: 5.23 By substracting

The Equation of State for a Real Gas

Generally, it is sufficient to fix a few state variables for a system. Then all other quantities assume values that depend on these state variables. We have already seen some examples:

$$pV = p_0V_0 \quad , \quad T = \text{constant}$$

or

$$V = \frac{T}{T_0}V_0 \quad , \quad p = \text{constant}$$

As a standard example for a general equation of state which connects all relevant variables, we have the ideal gas law

$$pV = NkT$$

which is, however, valid only for dilute gases (low pressure and density). The constant $N_Ak = R$ is called the **gas constant**.

An equation of state that is a better description of real gases over a wider range of the state variables is the equation of van der Waals. The ideal gas equation neglects the "volume" of a single particle which causes $V \to 0$ for $T \to 0$. We can fix this if we substitute for V the quantity $V - Nb$, where b is a measure of the volume of a single particle. Furthermore, the ideal gas equation neglects the interaction between the particles, which is mainly attractive.

Consider a sphere containing a gas with a particle density N/V. Inside the sphere, the force on any particle will be zero on the average. On the surface of the sphere, however,the particles feel an effective force in the direction of the inside of the sphere. This means that the pressure of a real gas has to be smaller than that of an ideal gas. We can account for this effect if we substitute $p_{ideal} = p_{real} + p_0$, where p_0 is the so-called inner pressure. Clearly, this says that the real pressure is smaller than the ideal pressure by an amount equal to the inner pressure. The inner pressure, however, is not a constant, but depends on the mean distance between particles and on how many particles are on the surface. Both dependences are in crude approximation proportional to the particle density N/V, so that $p_0 = a(N/V)^2$, where a is a constant.

Van der Waals' equation is then given by

$$\left(P + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT$$

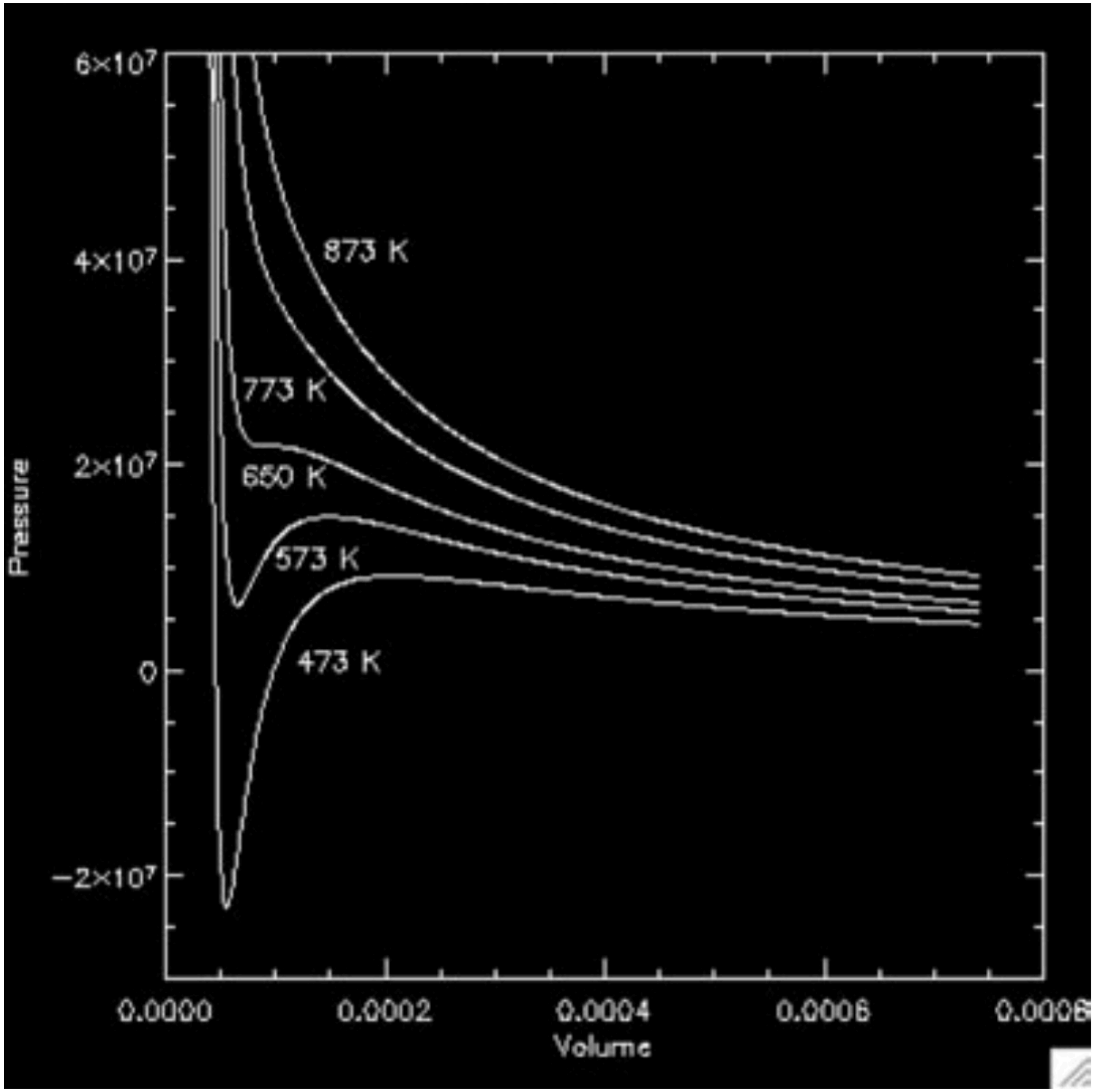
where the constants a and b depend on the particular substance.

We note that even though we attempted some justification for this equation of state for real gases, equations of state do not require any justification in thermodynamics. The only validity criterion for an assumed equation of state in thermodynamics is whether it accurately describes the experimental behavior of the system.

If we use experimental values appropriate for water

$$a = 0.56539\, Pa \cdot m^6 \cdot mol^{-2} \quad , \quad b = 0.031 \times 10^{-3}\, m^3 \cdot mol^{-1}$$

we get the isotherms (T=constant) curves for the van der Waals' equation of state shown in the figure below.



Selected isotherms for water

Clearly, there are **errors**.

For small temperatures and certain volumes the pressure becomes **negative.** This means that the inner pressure is too large in these regions. Furthermore, for positive pressure there are regions where the pressure decreases with decreasing volume, that is, where the system cannot be stable, but wants to compress spontaneously to a smaller volume. As we will see later, however, van der Waals is nevertheless much better than it seems at first sight. Note that for high temperatures and low densities, van der Waals' equation becomes the equation for the ideal gas. Some important approximations that we will use for van der Waals' equation are obtained as follows:

If we set N/V in the inner pressure equal to that of an ideal gas $N/V \approx P/kT$, we then get

$$\left(P+\left(\frac{P}{kT}\right)^{2} a\right)(V-Nb)=NkT$$

or

$$PV=NkT+N\left(b-\frac{a}{kT}\right)P+....$$

This type of expansion is called a **virial expansion** and the coefficient of P, $B(T)=N\left(b-\frac{a}{kT}\right)$, is the **first virial coefficient.**

Application of the Laws of Thermodynamics

We want to calculate the internal energy $U(T,V)$ of a real gas. The exact differential of U reads

$$dU=\left.\frac{\partial U}{\partial T}\right|_{V} dT+\left.\frac{\partial U}{\partial V}\right|_{T} dV$$

We have already identified the expression

$$\left.\frac{\partial U}{\partial T}\right|_{V}=C_{V}(T,V)$$

as the **heat capacity** because $Q = dU = C_V dT$ at V = constant. Thus, we can determine the temperature dependence of U at constant volume provided $C_V(T,V)$ is known. The dependence of the internal energy on the volume can be expressed by state quantities which are easier to determine. In most cases, one has an equation of state $f(T,p,V,N) = 0$, and we want to replace $\left.\frac{\partial U}{\partial V}\right|_T$ by these quantities (a typical application for thermodynamics), that is, to express $\left.\frac{\partial U}{\partial V}\right|_T$ in terms of T and p and derivatives of these intensive variables.

To this end we denote the exact differential of the entropy $S(V,T)$,

$$dS(V,T) = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV$$

for which, on the other hand,

$$dS = \frac{Q}{T} = \frac{dU + PdV}{T} = \frac{1}{T} C_V dT + \left(\frac{1}{T} \left.\frac{\partial U}{\partial V}\right|_T + \frac{P}{T} \right) dV$$

also is valid. By comparing coefficients we find

$$\left.\frac{\partial S}{\partial T}\right|_V = \frac{1}{T} C_V = \frac{1}{T} \left.\frac{\partial U}{\partial T}\right|_V \quad \text{and} \quad \left.\frac{\partial S}{\partial V}\right|_T = \frac{1}{T} \left.\frac{\partial U}{\partial V}\right|_T + \frac{P}{T}$$

Since S is an exact differential it must hold that

$$\frac{\partial^2 S}{\partial V \partial T} = \left.\frac{\partial}{\partial V} \left(\frac{1}{T} \left.\frac{\partial U}{\partial T}\right|_V \right)\right|_T = \frac{\partial^2 S}{\partial T \partial V} = \left.\frac{\partial}{\partial T} \left(\left.\frac{\partial U}{\partial V}\right|_T + \frac{P}{T} \right)\right|_V$$

Performing the differentiation yields, using

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

the result that

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left.\frac{\partial U}{\partial T}\right|_V + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{P}{T^2} + \frac{1}{T}\left.\frac{\partial P}{\partial T}\right|_V$$

$$\left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_V - p$$

Thus, we have reached our aim to express $\left.\frac{\partial U}{\partial V}\right|_T$ by the derivatives of the equation of state, since we can readily determine $P = P(N,T,V)$ also for real gases. We then have

$$dU = C_V(V,T)dT + \left(T\left.\frac{\partial P}{\partial T}\right|_V - P\right)dV$$

We will see shortly that such relations are easily derived using the theory of transformations of variables for functions of more than one variable. Here we were forced to explicitly perform all of the individual steps. It is not even necessary to know $C_V(V,T)$, rather it is sufficient to know $C_V(V = \text{constant}, T)$. Since dU is an exact differential one has

$$\left.\frac{\partial C_V}{\partial V}\right|_T = \frac{\partial}{\partial T}\left(T\left.\frac{\partial p}{\partial T}\right|_V - P\right)\Bigg|_V$$

However, the right-hand side can be as well determined from the equation of state, so that we can calculate the volume dependence of the heat capacity. For an ideal gas one has, for example,

$$P = P(N,T,V) = \frac{NkT}{V}$$

and thus

$$T\left.\frac{\partial P}{\partial T}\right|_V - P = 0 \Rightarrow \left.\frac{\partial C_V}{\partial V}\right|_T = 0$$

Therefore, the heat capacity of an ideal gas cannot depend on the volume. As we already know, it is even absolutely constant.

Internal Energy of the van der Waals Gas

The equation of state of the van der Waals gas reads

$$\left(P + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT$$

We now evaluate $\left(T\left.\frac{\partial p}{\partial T}\right|_V - P\right)$:

$$P = P(N,T,V) = \frac{NkT}{V - Nb} - \left(\frac{N}{V}\right)^2 a$$

$$\left.\frac{\partial P}{\partial T}\right|_V = \frac{Nk}{V - Nb}$$

$$T\left.\frac{\partial P}{\partial T}\right|_V - P = \left(\frac{N}{V}\right)^2 a$$

Hence, as for the ideal gas, the heat capacity of a van der Waals gas cannot depend on the volume because

$$\left.\frac{\partial C_V}{\partial V}\right|_T = \left.\frac{\partial}{\partial T}\left(T\left.\frac{\partial P}{\partial T}\right|_V - P\right)\right|_V = 0$$

Thus, we have

$$dU = C_V(V,T)dT + \left(\frac{N}{V}\right)^2 a dV$$

We can integrate this starting from an initial state (T_0,P_0) with internal energy U_0,

$$U(V,T) - U_0(V_0,T_0) = \int_{T_0}^{T} C_V(T)dT - N^2 a\left(\frac{1}{V} - \frac{1}{V_0}\right)$$

For temperature differences which are not too large $C_V(T)$ is approximately constant and thus

$$U(V,T) = U_0(V_0,T_0) + C_V(T - T_0) - N^2 a\left(\frac{1}{V} - \frac{1}{V_0}\right)$$

The internal energy increases with volume. This is quite obvious from a microscopic point of view since the particles are on the average further away from each other, but the interaction is attractive. For large volumes, that is small particle densities, this equation becomes the result for the ideal gas, that is, the larger V, the smaller is the increase of U with V.

Entropy of the van der Waals Gas

We have

$$dS = \left.\frac{\partial S}{\partial T}\right|_V dT + \left.\frac{\partial S}{\partial V}\right|_T dV = \frac{1}{T}C_V dT + \left(\frac{1}{T}\left.\frac{\partial U}{\partial V}\right|_T + \frac{P}{T}\right)dV$$

$$= \frac{1}{T}C_V dT + \left.\frac{\partial P}{\partial T}\right|_V dV$$

The quantity $\left.\frac{\partial P}{\partial T}\right|_V$ for the van der Waals gas can be calculated and we get

$$dS = \frac{1}{T}C_V dT + \frac{Nk}{V - Nb}dV$$

Starting from an initial state (T_0,V_0) with internal energy S_0 we can integrate this equation

$$S(V,T) - S_0(V_0,T_0) = \int_{T_0}^{T} C_V(T)dT + Nk\ell n\frac{V - Nb}{V_0 - Nb}$$

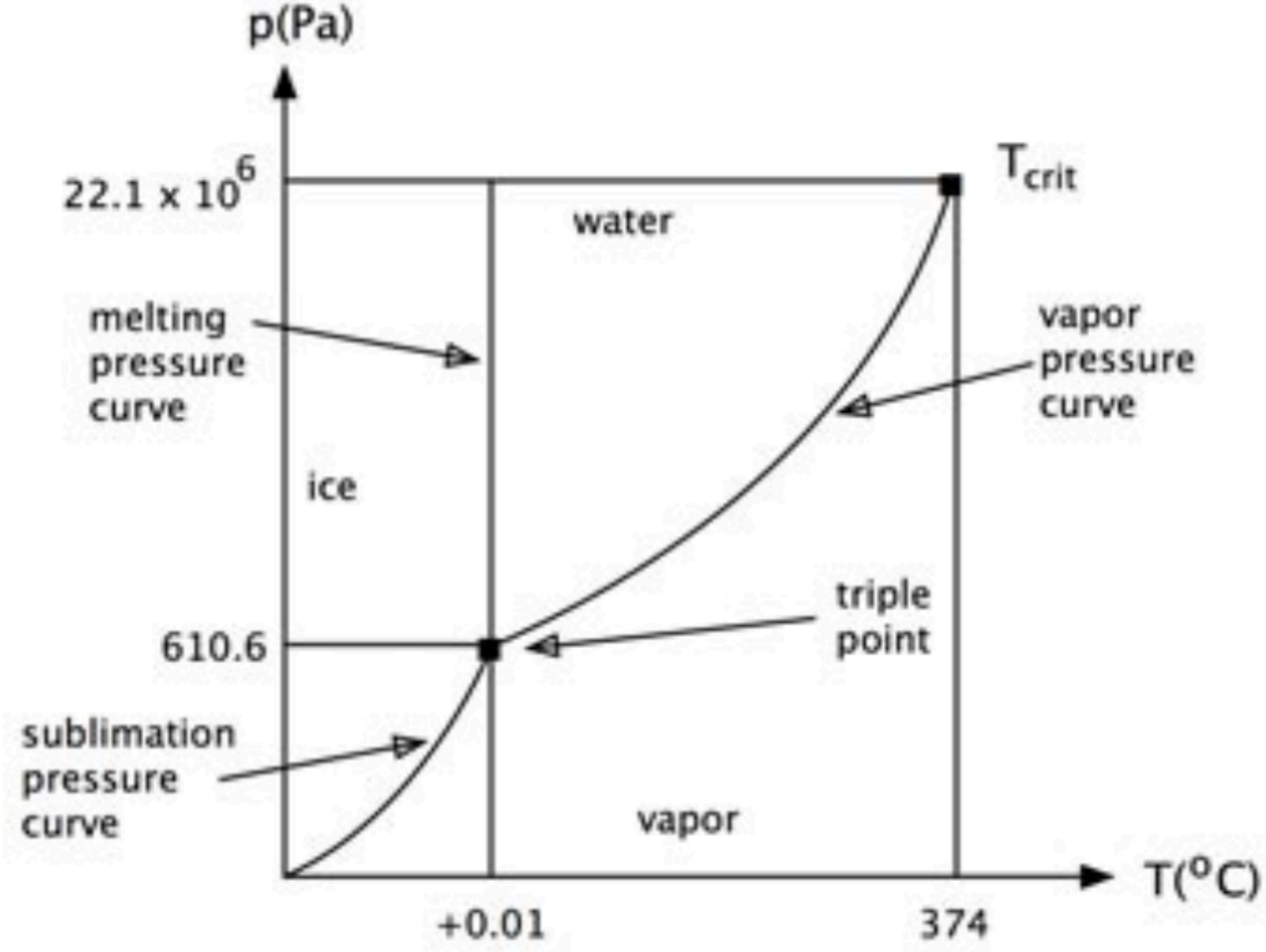
For temperature differences that are not too large ($\approx 100K$) we have $C_V(T)$ is approximately constant and thus

$$S(V,T) = S_0(V_0,T_0) + C_V\ell n\frac{T}{T_0} + Nk\ell n\frac{V - Nb}{V_0 - Nb}$$

The entropy of a van der Waals gas is nearly identical to that of an ideal gas; one only has to reduce the volume by the proper volume Nb of the particles.

Phase Transformations of Pure Substances

A **phase transformation** is a discontinuous change in the properties of a substance when its environment is basically unchanged. Examples are melting ice and boiling water, both of which occur with essentially no change in temperature. The different forms of the substance, that is like ice, water and steam, are called **phases.** In many cases there is more than one variable that can affect the phase of a substance. For example, one can condense steam either by lowering the temperature or raising the pressure. A graph showing the equilibrium phases as a function of temperature and pressure is called a **phase diagram.** A phase diagram for water is shown below.



Phase diagram of water

Clearly the diagram is divided into three regions, indicating the conditions under which ice, water or steam is the most stable phase.

The lines on the phase diagram represent conditions under which two different phases can coexist in equilibrium. For example, ice and water coexist stably at $0°C$ and 1 atm (~1 bar). The pressure at which a gas can coexist with its solid or liquid phase is called the **vapor pressure;** thus, the vapor pressure of water at room temperature is approximately 0.03 bar. At $T = 0°C$ and $P = 0.006\,bar$ all three phases coexist; this point is called the **triple point**.

Clausius-Clapeyron Equation

We want to derive a general equation to determine the vapor pressure of a liquid in equilibrium with its vapor. We have the following equilibrium conditions for two subsystems which can exchange energy, volume and particles:

$$T_{liq} = T_{vap} \quad , \quad P_{liq} = P_{vap} \quad , \quad \mu_{liq} = \mu_{vap}$$

Because of the Gibbs-Duhem relation these conditions are not independent from each other. If the equation of state is known and if we assume T and P to be given, we can calculate μ_{liq} and μ_{vap}. The equation

$$\mu_{liq}(p,T) = \mu_{vap}(p,T)$$

yields a dependence between P and T, that is, we can calculate the vapor pressure for a given temperature. If we change the temperature by dT in this equation, the vapor pressure also has to change by a certain amount dP to maintain equilibrium. For the corresponding changes $d\mu_{liq}$ and $d\mu_{vap}$ it must hold that

$$d\mu_{liq}(P,T) = d\mu_{vap}(P,T)$$

This can be expressed with the Gibbs-Duhem relation $SdT - Vdp + Nd\mu = 0$ in the following way

$$d\mu_{liq}(P,T) = -\frac{S_{liq}}{N_{liq}}dT + \frac{V_{liq}}{N_{liq}}dP$$

$$d\mu_{vap}(P,T) = -\frac{S_{vap}}{N_{vap}}dT + \frac{V_{vap}}{N_{vap}}dP$$

or with $s_{liq} = \dfrac{S_{liq}}{N_{liq}}$, $v_{liq} = \dfrac{V_{liq}}{N_{liq}}$ and analogous relations for the vapor we have

$$dP(v_{liq} - v_{vap}) = dT(s_{liq} - s_{vap}) \Rightarrow \frac{dP}{dT} = \frac{s_{liq} - s_{vap}}{v_{liq} - v_{vap}}$$

This is the **Clausius-Clapeyron equation.** It is a differential equation for the vapor pressure $P(T)$, if the entropy and volume per particle are known as functions of T and P. Now $S_{vap} - S_{liq} = \dfrac{Q_{liq \to vap}}{T}$ is the entropy difference between the liquid and vapor phases. At a given evaporation temperature, this entropy difference corresponds to an amount of heat $Q_{liq \to vap}$ which has to be added to evaporate **all** particles from the liquid into the vapor phase. This quantity depends at first also on the amount of liquid to be evaporated. However, changing to the corresponding intensive variables and referring to a certain amount of material, for example, per particle or per mole,

$$s_{vap} - s_{liq} = \frac{S_{vap}}{N_{vap}} - \frac{S_{liq}}{N_{liq}} = \frac{Q'_{liq \to vap}}{T}$$

The sign was chosen according to the direction liquid → vapor. Now $Q'_{liq \to vap} = \dfrac{Q_{vap}}{N_{vap}} - \dfrac{Q_{liq}}{N_{liq}}$ is the amount of heat required to evaporate **one** particle. This quantity can again be a function of pressure(vapor pressure) and temperature. However, in many cases and for not too large temperature differences, this evaporation heat may be considered to be constant. Analogously, the intensive variables v_{vap} and v_{liq}, the volume per particle in the vapor and liquid phases, respectively, are also in general functions of the vapor pressure and the temperature. With the **evaporation heat per particle** $Q'_{liq \to vap}$ we thus obtain

$$\frac{dp}{dT} = \frac{1}{T} \frac{Q'_{liq \to vap}}{v_{vap} - v_{liq}}$$

Since the right-hand side can in general be a complicated function of the vapor pressure P and the evaporation temperature T, one has a differential equation of the type $\frac{dP}{dT} = f(P,T)$ for the vapor pressure as a function of temperature, $P(T)$.

For an ideal gas the volume attained by N_A particles at room temperature and a pressure of one atmosphere is $22{,}400\,cm^3$, while a liquid like H_2O attains only a volume of $18cm^3$ under these conditions, this means that in many cases $v_{vap} >> v_{liq}$ and we get

$$\frac{dp}{dT} = \frac{Q'_{liq\to vap}}{Tv_{vap}}$$

The intensive quantities Q' and v_{vap} can, of course, be inserted as measured per mole instead of measure per particle. However, the approximation $v_{vap} >> v_{liq}$ becomes very bad if one approaches the critical point. Then $v_{vap} \approx v_{liq}$ and $Q'_{liq\to vap} \approx 0$. The quotient $\frac{Q'_{liq\to vap}}{v_{vap} - v_{liq}}$ nevertheless stays constant.

Vapor Pressure of a Liquid

Let us determine the vapor pressure of a liquid in equilibrium with its vapor under the assumption that the evaporation heat per particle does not depend on pressure or temperature and that the vapor behaves as an ideal gas.

The best starting point is the equation

$$\frac{dP}{dT} = \frac{Q'_{liq\to vap}}{Tv_{vap}}$$

With $v_{vap} = \frac{V_{vap}}{N_{vap}} = \frac{kT}{P}$ we get

$$\frac{dP}{dT} = \frac{P}{kT^2} Q'_{liq \to vap}$$

We may integrate this after separating variables, for example, from an initial temperature T_0 with vapor pressure P_0 to a final temperature T with vapor pressure P.

$$\frac{dP}{P} = \frac{dT}{kT^2} Q'_{liq \to vap}$$

$$\ell n \frac{P}{P_0} = -\frac{Q'_{liq \to vap}}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

$$P(T) = P_0(T_0) \exp\left\{ -\frac{Q'_{liq \to vap}}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}$$

Thus, the vapor pressure increases strongly with temperature ($Q'_{liq \to vap} > 0$). Note that these same equations hold under the same conditions also for the sublimation pressure of a solid: $v_{solid} << v_{vap}$ is correct but the sublimation heat is larger. Thus the pressure curve for sublimation is steeper than the vapor pressure curve. Both curves cross at the triple point. See a typical phase diagram earlier.

Now we have understood the essential properties of the phase diagram of a material. Besides the vapor pressure and sublimation pressure curves, the melting pressure curve also meets at the triple point, since at this point solid, liquid, and vapor phases are simultaneously present (coexist). The melting pressure curve, however, has to be calculated since now $v_{solid} \approx v_{liq}$. Therefore, the melting pressure curves are very steep in the PT diagram (for $v_{solid} = v_{liq}$ they are vertical). For water, the solid phase is less dense than the liquid, $v_{solid} > v_{liq}$, but the heat of liquefaction $Q'_{solid \to liq} > 0$. Thus, the melting pressure curve has positive slope in these cases. One calls the deviating behavior of water the "water anomaly"

Example: An inventor proposes to make a heat engine using water/ice as the working material, taking advantage of the fact that water expands as it freezes. A weight to be lifted is place on top of a piston over a cylinder of water at $1°C$. The system is then placed in thermal contact with a low-temperature reservoir at $-1°C$ until the water freezes into ice, lifting the weight. The weight is then removed and the ice is melted by putting it in contact with a high-temperature reservoir at $1°C$. The inventor is pleased with this device because it can seemingly perform an unlimited amount of work while absorbing only a finite amount of heat. Explain the flaw in the inventor's reasoning and use the Clausius-Clapeyron relation to prove that the maximum efficiency of this engine is still given by the Carnot formula.

Solution: The flaw in the inventor's reasoning is that the weight that can be lifted by the water as it freezes into ice is limited, because too much weight would apply enough pressure to lower the freezing point of the water below $-1°C$ and then the water would not freeze at all. Let the water in the cylinder have height h_w and cross-sectional area A. When it freezes into ice, its height increases to h_i. If the mass it lifts is m, then the work performed upon freezing is $mg(h_i - h_w)$. If L is the heat needed to remelt the ice, then the efficiency of the engine is

$$e = \frac{W}{Q_h} = \frac{mg(h_i - h_w)}{L}$$

If the pressure on the system with the weight absent is atmospheric pressure, then there is really no need for the high-temperature reservoir to be hotter than $T_h = 0°C$; higher T_h would just lead to wasted heat as the system is cooled back to $0°C$. If T_c is the temperature of the cold reservoir, then according to the Clausius-Clapeyron relation, the maximum pressure we can add to the system without shifting the freezing point below T_c is

$$dP = \frac{L}{T_h(V_i - V_w)}(T_h - T_c)$$

where $V_i = h_i A$ and $V_w = h_w A$ are the volumes of the two phases and we have used T_h in the denominator because L refers to the heat input from the hot reservoir. Setting this quantity equal to the pressure exerted by the lifted mass gives

$$\frac{mg}{A} = \frac{L}{T_h(V_i - V_w)}(T_h - T_c) \Rightarrow \frac{mg(h_i - h_w)}{L} = \frac{T_h - T_c}{T_h}$$

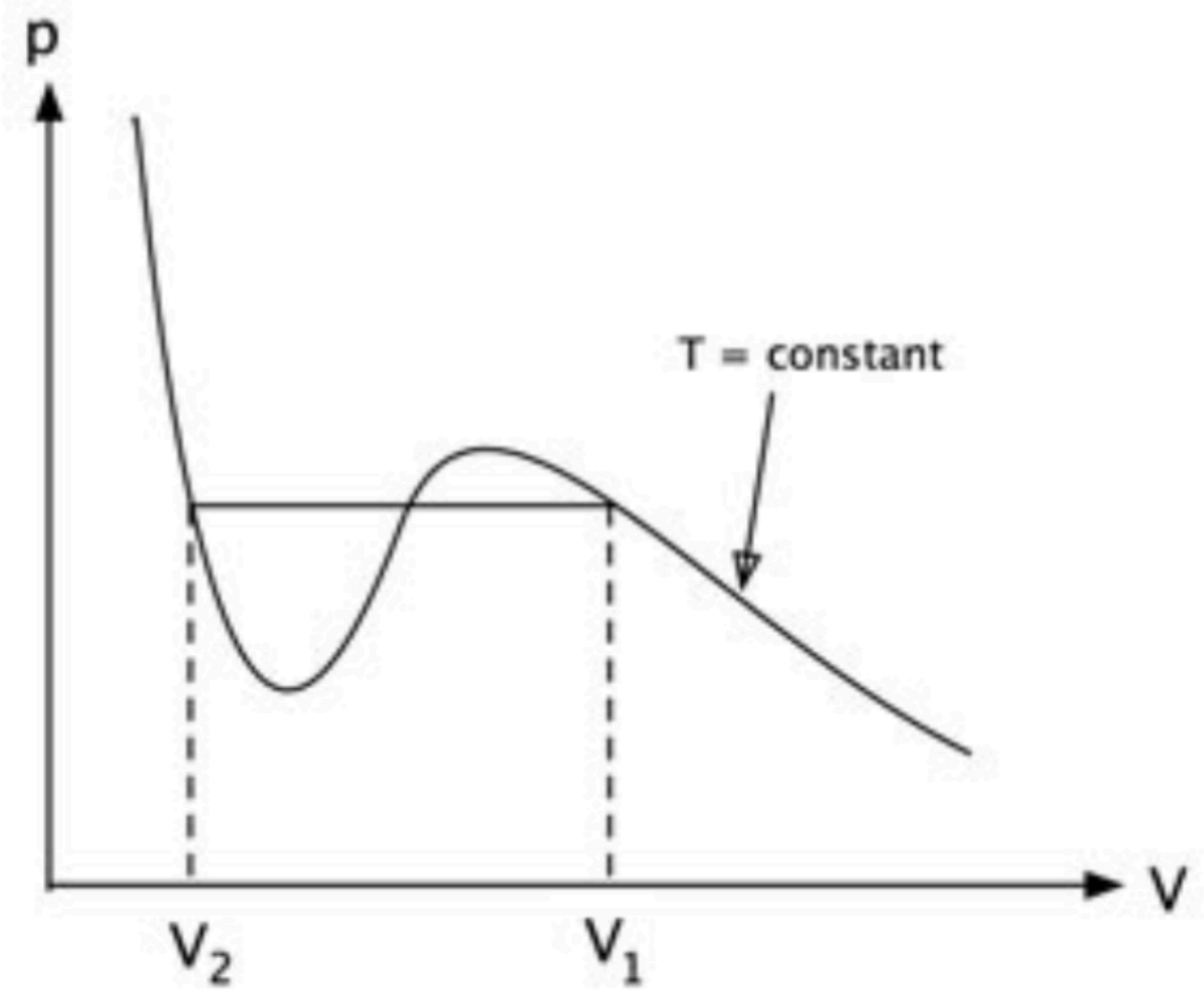
In other words, the maximum efficiency of the engine is $1-(T_c/T_h)$.

Phase Equilibrium and the Maxwell Construction

When we introduced van der Waals equation of state we already mentioned some inconsistencies of this equation. The isotherms of van der Waals equation (figure below)

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = NkT$$

show regions of negative pressure as well as mechanically unstable regions having $\frac{\partial P}{\partial V} > 0$, where a gas wants to compress itself.



Isotherms of the van der Waals gas

We now want to show that these contradictions can be resolved by considering the phase transition from gas to liquid. Most gases, if we compress them at constant temperature, start to liquefy below a critical temperature at a certain volume V_1.

In equilibrium between vapor and liquid, however, a certain vapor pressure $P_{vap}(T)$ is established, which we have already calculated for an ideal gas from the equilibrium conditions:

$$P_{liq} = P_{vap} \quad , \quad T_{liq} = T_{vap} \quad , \quad \mu_{liq}(P,T) = \mu_{vap}(P,T)$$

The vapor pressure $P_{vap}(T)$ is solely a function of temperature and does not depend on the vapor volume V, so that one obtains a horizontal isotherm in the PV diagram. An isothermal compression beyond the point of liquefaction V_1 has the effect that more and more vapor is converted into liquid, until at point V_2 the whole amount of gas is liquefied. If we further compress the system the pressure increases strongly because of the small compressibility of the fluid.

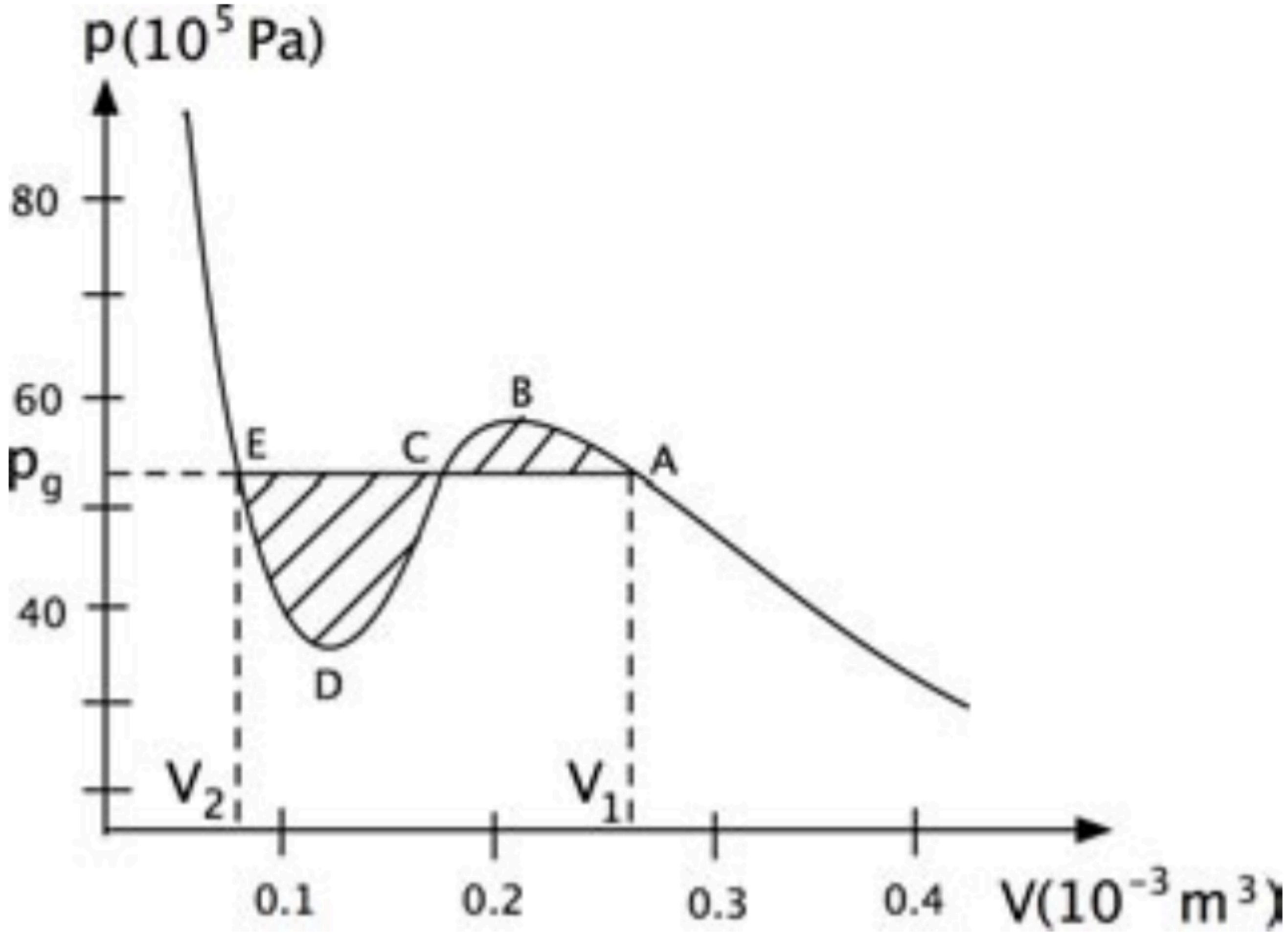
It is remarkable that **neither the density of the liquid (given by N/V_2) nor the density of the vapor (given by N/V_1) changes during this phase transition.** The increase of the average density, which is enforced by the transition from V_1 to V_2 is solely caused by the creation of more and more liquid and the simultaneous reduction of the partial volume of the vapor phase.

The pressure P_{vap} can be calculated from our earlier derivation, if the temperature and chemical potentials of the vapor and liquid are known. Now, however, we want to present a method known as the **Maxwell construction.** The internal energy $U(V,T)$ at fixed particle number is a state function which depends only on the volume for a given temperature. For constant temperature we therefore have the energy difference (integrating the first law for $dN = 0$)

$$\Delta U = T(S_2 - S_1) - \int_{V_1}^{V_2} p(V)dV$$

between two volumes V_1 and V_2 with the entropies S_1 and S_2 for the purely gaseous and purely liquid phases, respectively. Since U is an exact differential, it does not matter whether ΔU is calculated along the direct path of constant vapor pressure ($P(V) = P_{liq} = P_{vap} = \text{constant}$) or along the van der Waals isotherm (see figure below), for which the following holds ($T = \text{constant}$):

$$P(V) = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2}$$



Maxwell construction

In the first case, we simply have ($Q = T(S_2 - S_1)$ is the latent heat of the phase transition)

$$\Delta U_1 = Q - P_{vap}(V_2 - V_1)$$

and in the case of the van der Waals isotherm we have

$$\Delta U_2 = Q - NkT\ell n\frac{V_2 - Nb}{V_1 - Nb} - N^2 a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

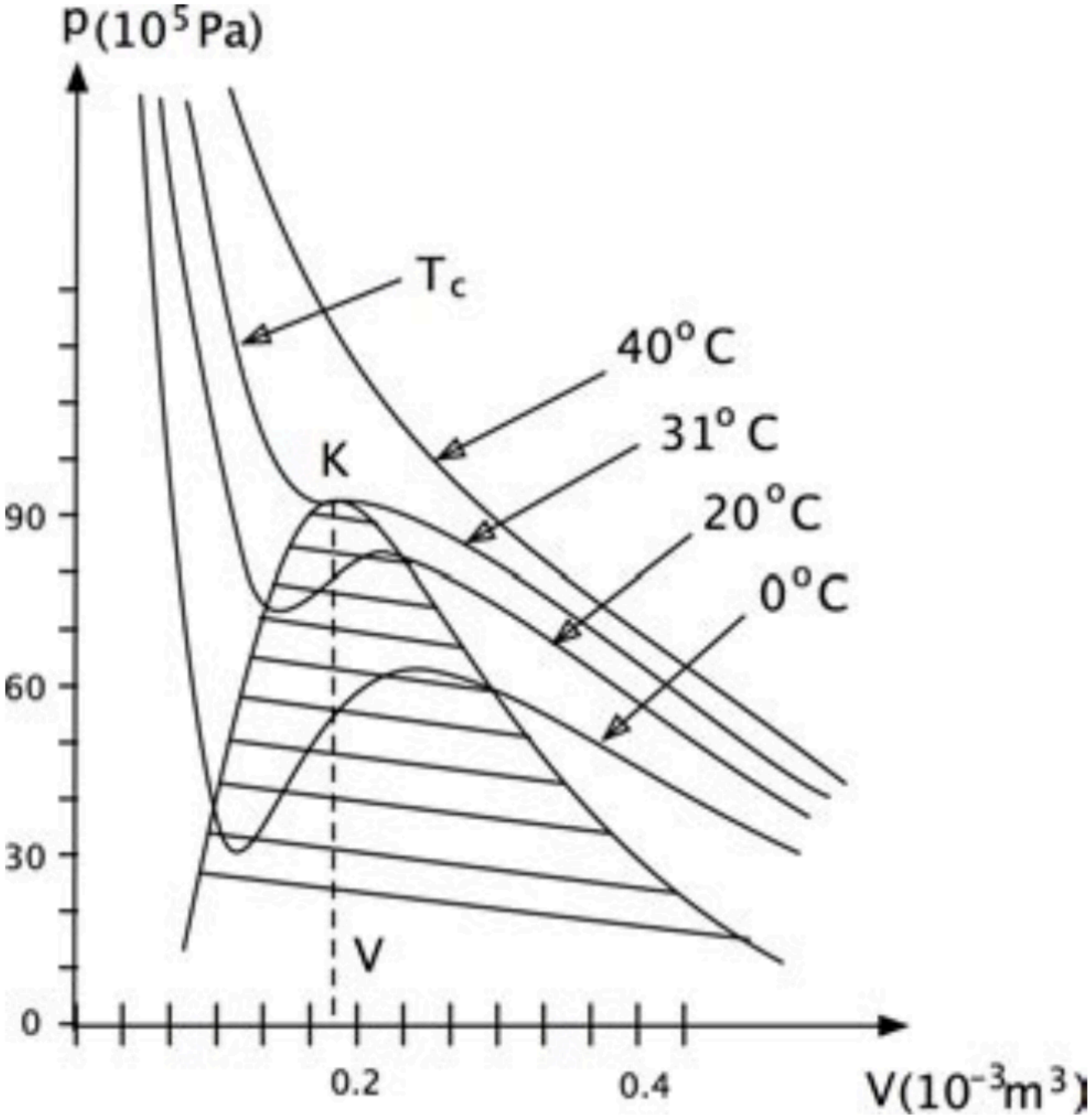
From the independence of path condition $\Delta U_1 = \Delta U_2$ we get

$$-P_{vap}(V_2 - V_1) = -NkT\ell n\frac{V_2 - Nb}{V_1 - Nb} - N^2 a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

One can, in principle, determine the unknown pressure P_{vap} as well as the also unknown volumes V_1 and V_2, if one solves van der Waals equation for $V_1(P_{vap},T)$ and $V_2(P_{vap},T)$ (points A and E). Note that for a given P_{vap} and T the van der Waals isotherm also has a third (unstable) solution at C.

However, the last equation can be understood far more easily.

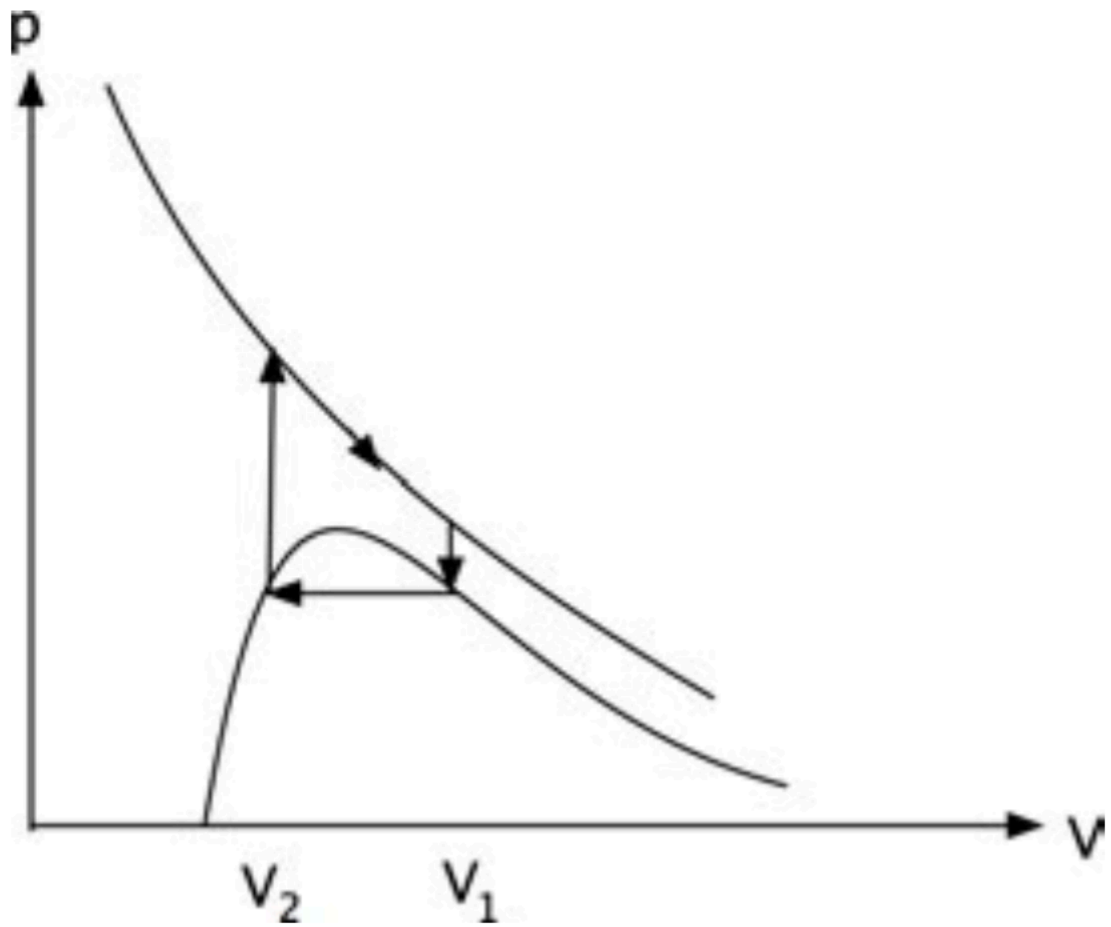
It tells us that the area $P_{vap}(V_2 - V_1)$ of the rectangle between V_1 and V_2 below the unknown vapor pressure equals the area below the van der Waals isotherm, or, in other words, the area between the straight line of the vapor pressure and the van der Waals isotherm ABC has to equal the analogous area CDE. This is the well-known **Maxwell construction.** The explicit calculation following last equation is equivalent to the Maxwell construction. If one draws points A and E for a couple of isotherms in a diagram, one obtains the boundary (shaded area) of the phase coexistence region as shown in the figure below.



Critical point and critical isotherm

In this region the van der Waals isotherms have to be replaced by straight lines for the vapor pressure. The maximum of the coexistence curve, the so-called **critical point** K lies on the isotherm, which only has a saddle point (instead of extrema D and B in the figure above). Above the critical temperature the Maxwell construction is no longer possible; the liquid and the gas are no longer distinguishable.

With the help of the figure below one can also understand another phenomenon. If one isothermally compresses a real gas below the the critical temperature until all of the gas is liquefied, then increases the temperature at constant volume V_2 to a point above the critical temperature and then expands the gas to the initial volume V_1 at constant temperature one can again regain the initial (gaseous) state without a noticeable second phase transition (by a temperature decrease at constant volume).



Scheme of the process

This means that above the critical temperature (the critical isotherm) a distinction between the gaseous and liquid states is no longer reasonable! This distinction is only possible below the critical temperature since liquids and gases have very different densities and thus a **phase boundary surface** exists between the phases. At the critical point, however, the density of the liquid and the gas assume equal values and a distinction between the phases is no longer possible above the critical temperature.

Because of the importance of the critical point we want to calculate the critical state quantities T_{cr}, P_{cr} and V_{cr} from the van der Waals equation. The critical point is characterized by the fact that both derivatives vanish (a saddle point):

$$\left.\frac{\partial P}{\partial V}\right|_{T_{cr},V_{cr}} = 0 \quad , \quad \left.\frac{\partial^2 P}{\partial V^2}\right|_{T_{cr},V_{cr}} = 0$$

or

$$-\frac{NkT_{cr}}{(V_{cr}-Nb)^2} + \frac{2aN^2}{V_{cr}^3} = 0 \text{ and } 2\frac{NkT_{cr}}{(V_{cr}-Nb)^3} - \frac{6aN^2}{V_{cr}^4} = 0$$

We then have

$$\frac{\dfrac{6aN^2}{V_{cr}^4}}{\dfrac{2aN^2}{V_{cr}^3}} = \frac{2\dfrac{NkT_{cr}}{(V_{cr}-Nb)^3}}{\dfrac{NkT_{cr}}{(V_{cr}-Nb)^2}} \Rightarrow \frac{3}{V_{cr}} = \frac{2}{V_{cr}-Nb} \Rightarrow V_{cr} = 3Nb$$

One then gets

$$T_{cr} = \frac{2aN}{kV_{cr}^3}(V_{cr}-Nb)^2 = \frac{2aN}{kV_{cr}^3}\frac{4}{9}V_{cr}^2 = \frac{8a}{27kb}$$

From V_{cr} and T_{cr} it finally follows with van der Waals equation that

$$P_{cr} = \frac{8Nka}{54Nkb^2} - \frac{aN^2}{9Nb^2} = \frac{a}{27b^2}$$

The critical state quantities are therefore uniquely determined by the parameters a and b. Hence for all gases one should have

$$\frac{P_{cr}V_{cr}}{NkT_{cr}} = \frac{3}{8} = 0.375$$

Experimentally, one finds for this last equation numbers between 0.25 and 0.35, which once again confirms the qualitative usefulness of van der Waals equation.

On the other hand, a measurement of the critical data of a gas yields a comfortable method for determining the parameters a and b.

Along the way, one can also experimentally find the (metastable) parts AB and DE of the van der Waals isotherm in nonequilibrium situations.

If a gas is very carefully compressed at constant temperature (avoiding concussions and condensation nuclei), one can follow the isotherm beyond point A nearly up to point B.

The same holds for the other side for isothermal expansion beyond point E to point D.

One speaks of delayed condensation or delayed boiling, respectively.

The system is metastable in this region and switches over to the stable phase coexistence state even under small perturbations.

The same phenomena can be observed for isochoric temperature changes.

Here one speaks of superheated liquid or supercooled vapor, respectively. Analogous phenomena occur for the solid-liquid phase transition.