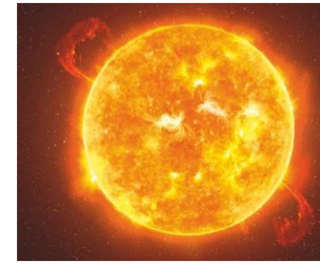
THERMODYNAMICS & STATISTICAL MECHANICS

It's all about TIME SCALES.....

Lots of different Timescales....

Slow Stream



Star

Fire

Piece of Wood

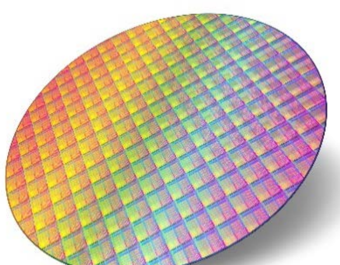
Fast Stream

Galaxies

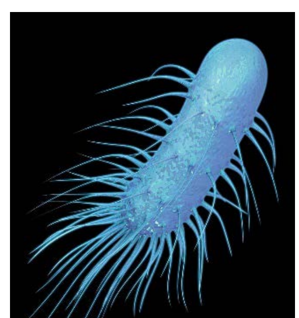
Piece of Glass

Bar Magnet

Litre of Air



Si wafer



Bacterium

Block of Ice in Water

THERMODYNAMICS – a SUMMARY

A. EMPIRICAL APPROACH: Based on empirical observation

1. Assume the system is near "Thermodynamic Equilibrium" (we will define this later)
2. Identify the "Thermodynamic Variables" and "state functions"

Intensive quantities: these are variables such as temperature T, pressure p and density ρ. They are, by definition, independent of the system size.

Extensive quantities: these are variables such as mass M, internal energy U, volume V, magnetization M, and entropy S. They scale with the system size.

State Functions: these are functions of the thermodynamic variables which define the thermodynamic state of the system (eg energy U, free energy F, etc.).

B. DEDUCTIVE APPROACH: Based on a kind of axiomatic framework

0th Law of thermodynamics: If 2 systems are each in thermal equilibrium with a 3rd system, they are in thermal equilibrium with each other – and have the same temperature (definition).

1st Law of thermodynamics: When energy passes between systems, then the total energy is conserved.

2nd Law of Thermodynamics: The sum of the entropies of interacting thermodynamic systems increases in time.

3rd Law of thermodynamics: The entropy of a system approaches a constant value as the temperature T approaches absolute zero.

SOME BASIC CONCEPTS in THERMODYNAMICS

KEY THING TO REMEMBER: The structure & many of the ideas you will find in thermodynamic theory depend to a large extent on the history of the subject – which began with a study of gases, later extended to more complex quasi-homogeneous systems. It is actually a miracle that these ideas can be applied to a much broader range of systems – BUT, often we have to be rather careful in realizing the limitations (or we need to generalize the ideas somewhat).

Absolute Temperature T: Defined so that its value represents the actual thermal energy in the system. The simplest way to do this is based on the pressure of a fixed volume of gas of very low density – then the ideal gas law is accurately obeyed, according to which

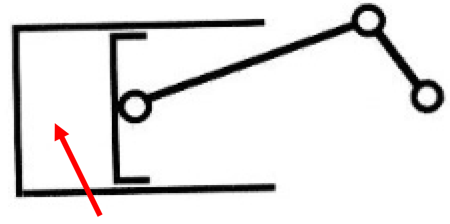
$$pV = nRT$$

where n is the number of moles, and R=8300 J kmole^{-1} K^{-1}.

If 2 systems are each in thermal equilibrium, then, from the 0-th law, they are also in mutual equilibrium if, when brought in thermal contact, there is no net heat transfer from one to the other. They then have the same **temperature** (by our previous definition of temperature as that quantity which equilibrium bodies have in common).

Reversible Processes: These are cyclical processes whereby a system is returned to its original state without any net heat transfer to the environment. (As already noted, this means that there is no change in total entropy S – to be defined below).

THERMODYNAMICS of GASES

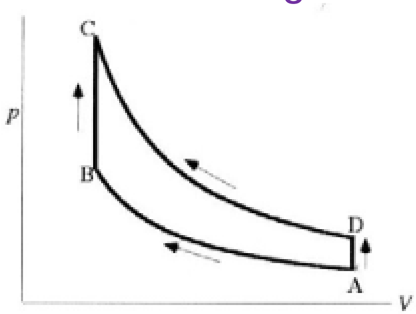


We learn a lot by looking at simple ideal gases. Consider the process where we move a piston in & out, alternatively compressing and expanding the low-density gas inside. The state variables are the pressure p and volume V of the gas.

An infinitesimal change of volume gives, for a slow reversible process, a change δU in internal energy equal to the work δW done on the gas by the piston.

We then have $\delta W = -pdV$ so that $W = -\int_{V1}^{V2} pdV$ (note the sign!)

However if the change is irreversible, heat can flow in or out of the system, or even be generated internally (particularly if the change is rapid). We then must account for this heat in the energy balance – we now have



$$dU = \delta Q - pdV$$

The total heat energy ΔQ involved is reflected in the path taken in the (p, V) plane – it is given by the enclosed area.

We can also define the enthalpy: $H \equiv U + pV$

so that $dH = dU + pdV + Vdp \rightarrow \delta Q + Vdp$

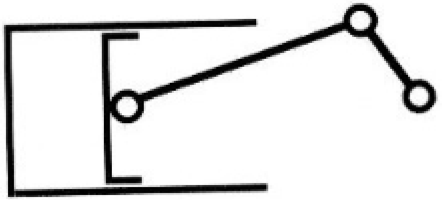
Applies when, eg., we heat the gas in a fixed volume.

IRREVERSIBLE PROCESSES for GASES: ENTROPY

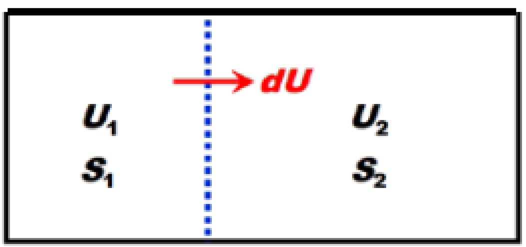
Compare the 2 processes, for the piston at right

(i) Gas slowly pushes piston out

(ii) Gas expands freely (massless frictionless piston)



The first is reversible, the 2nd is irreversible. WHY?



To understand all this better, consider the "Gedankenexperiment" where a partition between 2 systems moves slowly & reversibly. No heat passes between the two – but one gas can do work on the other. Then

(a) Neither S nor U for the total system change; so $dU_1 = - dU_2$, & likewise for S. Hence

$$dS = (dS_1/dU_1)\, dU_1 + (dS_2/dU_2)\, dU_2$$
$$[(dS_1/dU_1) - (dS_2/dU_2)]\; dU = 0$$

so that $dS_1/dU_1 = dS_2/dU_2$ is the same for any 2 systems in eqlbm.

We will then define the temperature T so that

$dU = T\,dS$ ie., $T \equiv \left(\frac{\partial U}{\partial S}\right)_V$

(b) We now consider the change in energy when both *S* and *V* change. We have

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - pdV$$

from the last slide, and from $p = -\left(\frac{\partial U}{\partial V}\right)_S$

Thus we have $\boxed{dS = \frac{\delta Q}{T}}$ ENTROPY in terms of HEAT

THERMODYNAMIC POTENTIALS for GASES

Let's define the quantities (related via Legendre transformations):

Internal energy:	U		
Enthalpy:	H	$=$	$U + pV$
Helmholtz Free Energy:	F	$=$	$U - TS$
Gibbs Free Energy:	G	$=$	$U - TS + pV$

With infinitesimals given by

Internal energy:	$\mathrm{d}U$	$=$	$T\mathrm{d}S - p\mathrm{d}V$
Enthalpy:	$\mathrm{d}H$	$=$	$T\mathrm{d}S + V\mathrm{d}p$
Helmholtz Free Energy:	$\mathrm{d}F$	$=$	$-S\mathrm{d}T - p\mathrm{d}V$
Gibbs Free Energy:	$\mathrm{d}G$	$=$	$-S\mathrm{d}T + V\mathrm{d}p$

With these we can define changes involving any pair of variables, viz., any of

$$(\mathrm{d}S, \mathrm{d}V),\ \text{or}\ (\mathrm{d}S, \mathrm{d}P),\ \text{or}\ (\mathrm{d}T, \mathrm{d}V),\ \text{or}\ (\mathrm{d}T, \mathrm{d}P).$$

We can then define changes in which some preferred variable is held constant. For example, starting from *F* we have

$$p = -\left(\frac{\partial F}{dV}\right)_T \quad \& \quad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

An important such set of derivatives are the "specific heats"

$$dU = \delta Q - pdV$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q}{\partial T}\right)_V$$

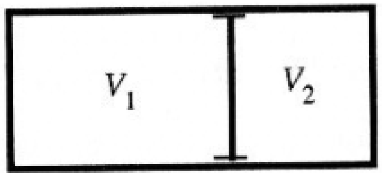
$$dH = \delta Q + Vdp$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_p$$

FREE ENERGY for GASES

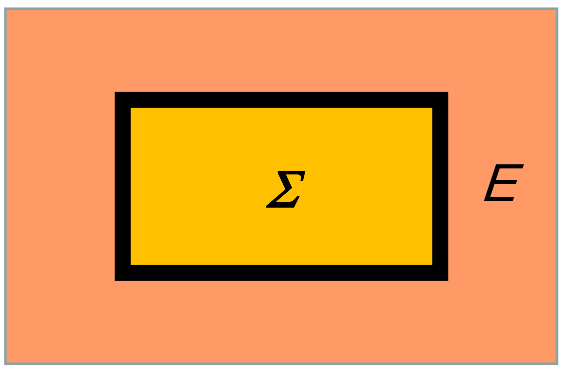
To see how these thermodynamic potentials work, let's look at the Helmholtz Free energy (usually just called the Free energy.

Suppose we first ignore temperature, and ask how the energy balances for 2 gases separated by a movable Partition. Moving the partition gives an energy change



$dU = -p_1 dV_1 - p_2 dV_2$ However, $dV_1 = dV = -dV_2$

Thus at equilibrium we have: $dU = 0$ (so that U is minimized)



Now suppose we have a system Σ in contact with a massive thermal bath E at temperature T (so Σ must also be at temperature T). Consider the free energy F, defined as $F = U - TS$

Notice that

$$dF = dU - TdS - SdT = TdS - pdV - TdS - SdT$$

so that we get $dF = -SdT - pdV$

We can also divide Σ into 2 partitions, & make the same argument as above, at constant T; we then get

$$dF = dF_1 + dF_2 = -p_1 dV_1 - p_2 dV_2 \quad \rightarrow \quad dF = 0$$

(F is minimized)

It is also useful to note that

$$U = F + TS \quad = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial (F/T)}{\partial T}\right)_V = \left(\frac{\partial (\beta F)}{\partial \beta}\right)_V$$

Side Note: MAXWELL RELATIONS, etc.

When people actually use thermodynamics to treat macroscopic systems in equilibrium they often use various identities relating the differentials of state functions like F, G, U, etc.

MAXWELL RELATIONS: Consider the 2 possible partial derivatives of F, obtained by holding one of the 2 free differentials constant, and allowing the other to vary. These are just

$$p = -\left(\frac{\partial F}{dV}\right)_T \quad \text{(pressure)} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{(entropy)}$$

Now let's differentiate each with respect to the other free variable, ie., consider

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T};$$

Now, if the free energy F is an analytic function of its variables, these 2 quantities must be the same. Thus we establish that

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

Thus by measuring the latter (which is easy) we can find the former

There are more complicated relations (eg., the "triple product rule", discussed on the notes. I will set some simple homework questions to help you get used to the Maxwell relations

THERMODYNAMICS – MORE GENERAL ANALYSIS

We now consider the more general case – ie., not tied to gases – where one has a set $\{ x_j \}$ of all the relevant intensive variables, and a set $\{ Y_j \}$ of their conjugate extensive variables, such that

$$dQ = dU - \Sigma_j x_j Y_j$$

Some examples:

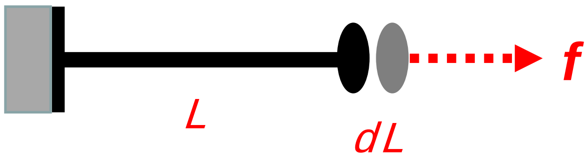
Work done by force	**infinitesimal dW**	**term in TD potential**
Volume change (pressure)	$dW = -p\,dV$	$-pV$
Length change (tension)	$dW = f\,dL$	fL
Areal change (surface tension)	$dW = \gamma\,dA$	γA
Strain (stress)	$dW = \sigma_{ij}\,d\varepsilon^{ij}$	$\sigma_{ij}\,\varepsilon^{ij}$
Electric polarization (E field)	$dW = \mathbf{E}.\,d\mathbf{p}$	$\mathbf{E}.\mathbf{p}$
Magnetization (B field)	$dW = \mathbf{B}.\,d\mathbf{M}$	$\mathbf{B}.\mathbf{M}$
Particle number (chemical potential)	$dW = \mu\,dN$	μN
Rotation (angular momentum)	$dW = \mathbf{\Omega}\,.\,d\mathbf{L}$	$\mathbf{\Omega}\,.\mathbf{L}$

We can then write down all the differential relations as for gases. Suppose, eg. the relevant variables are (T,S) and (M, B). We then have

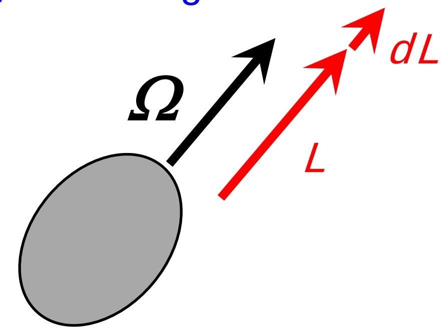
Internal energy:	dU	$= TdS - \mathbf{B}.\,d\mathbf{M}$
Enthalpy:	dH	$= TdS + \mathbf{M}.\,d\mathbf{B}$
Helmholtz Free Energy:	dF	$= -SdT - \mathbf{B}.\,d\mathbf{M}$
Gibbs Free Energy:	dG	$= -SdT + \mathbf{M}.\,d\mathbf{B}$

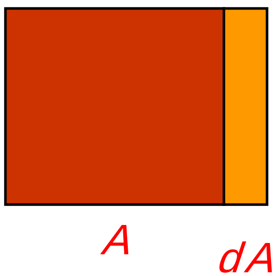
MORE on these EXAMPLES

MECHANICAL CHANGES: We've already seen the example of the mechanical work $dW = -pdV$ done by an externally applied pressure on a 3-d gas. We can do the same thing for a 2-d surface, or for a 1-d wire, spring, or string.



$$dW = fdL$$



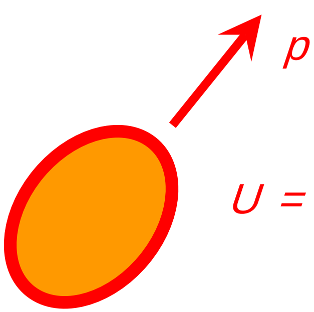


$$dW = \gamma\, dA$$

The same applies to changes in rotational motion & rotational energy

NB: More generally one has tensorial relations for these mechanical quantities

EM CHANGES: electrical and magnetic changes involve energy associated with the EM field



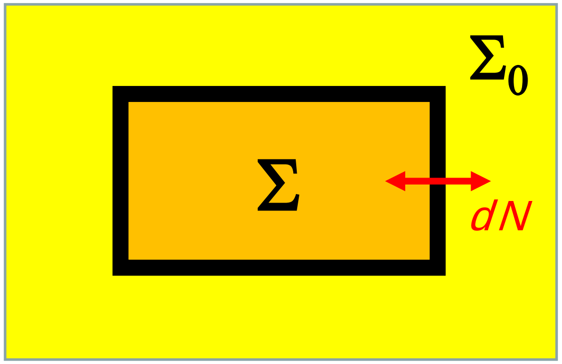
and the same for magnetic systems; we will discuss this more later

$U = E.p$

NB: Again, more generally one has tensorial relations for these electromagnetic quantities

PARTICLE EXCHANGE & CHEMICAL POTENTIAL

One of the most important Thermodynamic potentials allows us to deal with a change in particle number N in the system – this is crucial in everything from chemistry to nuclear physics.



We suppose a thermal bath Σ_0 at temperature T to be in thermal equilibrium with a system Σ. Heat & energy can flow between the two, & also particles. If we want we can even allow the volume of the system Σ to change. Then we have:

$$dU = TdS - pdV + \mu dN$$

so that the chemical potential μ is the energy required to add a particle to Σ

We can then define the following thermodynamic potential differentials

Internal energy:	dU	$=$	$TdS - pdV + \mu dN$
Enthalpy:	dH	$=$	$TdS + Vdp + \mu dN$
Helmholtz Free Energy:	dF	$=$	$-SdT - pdV + \mu dN$
Gibbs Free Energy:	dG	$=$	$-SdT + Vdp + \mu dN$

Two derivatives are then very useful, in the experimental determination of the chemical potential:

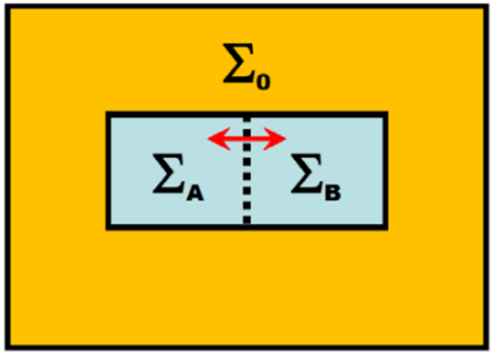
(i) Free Energy *F(T,V,N)*

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

(ii) Gibbs Free energy *G(T,p,N)*

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

PARTICLE EXCHANGE BETWEEN 2 SYSTEMS



Now we consider a situation where particle exchange occurs between 2 systems (but not with the bath). Thus both energy & particles can be exchanged between Σ_A & Σ_B, & energy between all 3 systems. Everything is at temperature T. We thus have

$U_{tot} = U_0 + U_a + U_b$ (constant) $N = N_a + N_b$ (constant)

Now, to find the equilibrium conditions, we note that $dN = -dN_a = dN_b$ and $dU = -dU_a = dU_b$. However, $dU = 0$ since the partition is not moveable.

We then have

$$dS_{tot} = \left[\left(\frac{\partial S_b}{\partial N_b}\right)_U - \left(\frac{\partial S_a}{\partial N_a}\right)_U\right] dN + \left[\left(\frac{\partial S_b}{\partial U_b}\right)_N - \left(\frac{\partial S_a}{\partial U_a}\right)_N\right] dU \quad = \left[\left(\frac{\partial S_b}{\partial N_b}\right)_U - \left(\frac{\partial S_a}{\partial N_a}\right)_U\right] dN$$

from which it follows that when eqlbm is reached (so $dN = 0$) we have

$$\left(\frac{\partial S_b}{\partial N_b}\right)_U = \left(\frac{\partial S_a}{\partial N_a}\right)_U$$

However, we note that $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V\ldots}$ → $\mu_A = \mu_B = \mu$

Eqlbm is reached by particle transfer. Suppose that $\mu_A > \mu_B$. Then a transfer dN from A to B gives

$$dF = \left(\frac{\partial F_a}{\partial N_a}\right)_{T,V} dN_a + \left(\frac{\partial F_b}{\partial N_b}\right)_{T,V} dN_b$$

However $dN_b = -dN_a = dN$

so that $dF = (\mu_b - \mu_a) dN$

and F is minimized at eqlbm, when $dF = 0$