

Thermodynamics

As we mentioned, thermodynamics is founded by statistical mechanics. However, it can also be considered as a self-standing axiomatic theory, based on the following axioms:

- (0) There exist a relation between thermodynamic systems. This relation is called thermodynamic equilibrium, and it is transitive (equivalence relation):
if $A \sim B$ and $B \sim C$, then $A \sim C$.
Here A , B and C label different systems. For example in thermal equilibrium this means a transitive relation between the temperatures of the three systems.
- (1) Energy conservation: the total energy of an isolated system is fixed.
Thus if during some process a system absorbs heat ΔQ , as well as work $\Delta W = -p \Delta V + \dots$ is made on it, then its energy changes by $\Delta E = \Delta Q + \Delta W$.
- (2) In an isolated system the entropy does not decrease.
Thus if during some process a system absorbs heat ΔQ , then its entropy changes by $\Delta S = \Delta Q/T + \Delta S_{\text{internal}} \geq \Delta Q/T$.
- (3) The entropy at absolute zero temperature is zero, or it is independent of other parameters, so can be set to zero. Another form is that the ground state of a quantum system has finite multiplicity (or at least not exponential with N).
A simple consequence is that the heat capacity vanishes at absolute zero temperature:

$$C_X = \left. \frac{\partial Q}{\partial T} \right|_X = T \left. \frac{\partial S}{\partial T} \right|_X \rightarrow 0 \quad \text{if } T \rightarrow 0$$

where the subscript X corresponds to the quantity held fixed, it can be anything suitable, eg. volume or pressure.

Let us suppose now that we bring a thermodynamic system from one state to another. Certain thermodynamic quantities, like work or heat do depend on which path is taken, while others like total energy, entropy, free energy, temperature, pressure etc. are path-independent. We call the latter ones *state variables*.

Now we return to free energies. Consider a system kept at fixed temperature T , which undergoes some change. If it is otherwise isolated from its environment (canonical ensemble), then its energy changes only by the absorbed heat: $\Delta E = \Delta Q$. The change in entropy is

$$\Delta S = \frac{\Delta Q}{T} + \Delta S_{\text{int}} \geq \frac{\Delta Q}{T}$$

since the second law of thermodynamics states that $\Delta S_{\text{int}} \geq 0$. Introducing the Helmholtz free energy as $A(T) = E - TS$, its change is

$$\Delta A = \Delta E - T \Delta S \leq 0,$$

so the free energy never increases during any change or transition. Then it follows that at stable equilibrium it must be minimal. This is a very important point, which makes free energies central in thermodynamics. The corresponding observation in statistical mechanics, where there are always fluctuations, is that the probability of a macroscopic state is proportional to $\exp\left(-\frac{A(T)}{k_B T}\right)$. For a large system the difference between free energies of different states are large: $\Delta A \gg k_B T$, so only the state with the lowest free energy is observed.

The above observations hold for any ensemble, when the appropriate free energy is used. To illustrate this we will have another example. Consider now a system kept at constant temperature T and pressure p , so exchange of heat and volume with its environment is allowed. When undergoing a change, its energy changes by $\Delta E = \Delta Q - p \Delta V$. The change in entropy is

$$\Delta S = \frac{\Delta Q}{T} + \Delta S_{\text{int}} \geq \frac{\Delta Q}{T}$$

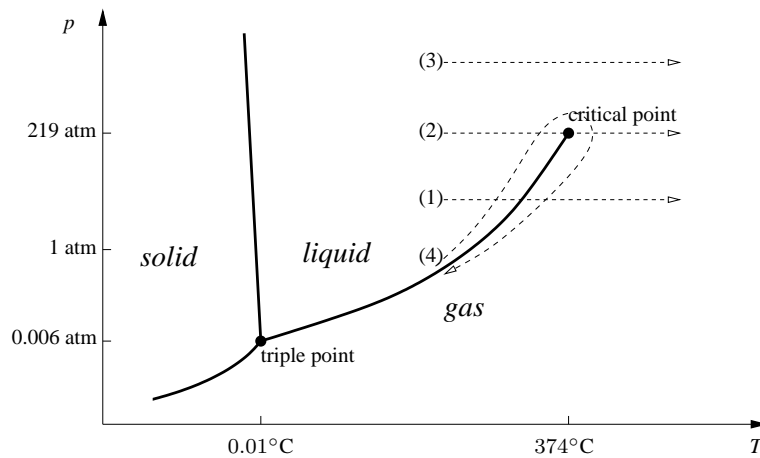


Figure 1: Simplified phase diagram of water. Path (1) corresponds to an abrupt phase transition between the liquid and gas phases, path (2) is a continuous phase transition, while path (3) involves no phase transition as it crosses neither a coexistence line nor a critical point. Since liquid and gas has the same symmetry, it is possible, as in path (4), to move from one side of the coexistence line to the other without a phase transition.

If we now introduce the Gibbs free energy: $G(T, p) = E - TS + pV$, its change is

$$\Delta G = \Delta E - T\Delta S + p\Delta V \leq 0$$

non-positive again. The Gibbs free energy is the relevant quantity for constant T, p environments, like in biochemical reactions.

Phase transitions

As we mentioned in the beginning of this lecture, complex systems display a nontrivial collective behaviour of the constituents. Phase transitions are the most spectacular of these emergent phenomena. They correspond to sudden change in behaviour by a small change in the controlling parameters.

Probably the first example to come to mind is the melting of ice, and boiling of water – those in the domain of Physics are the best understood, since the microscopic interactions are completely known. There are many other, potentially more contested examples as well, like the fall of communism in East Europe around 1989.

Coming back to Physics, the transition occurs between different phases. The possible phases include the grade school examples of solids, liquids and gases, but there are many more, like magnets, a whole zoo of liquid crystals, superconductors, superfluids, different crystal structures of the same material etc.

When considering phases, *symmetry* is an important concept. It can be thought of as a collection of operations that map a system back to itself. If two states have different symmetry, these are necessarily different phases. However, it is possible to have two different phases with the same symmetry, like both liquids and gases are homogenous (translation invariant in a statistical sense) and isotropic (all directions are equivalent). When state A and state B corresponds to phases of different symmetry, any path connecting A and B has at some point a jump in symmetry, thus it necessarily involves a phase transition. However, when the phases are of the same symmetry, it is possible, as in Fig. 1, to move from A to B without a phase transition.

Order parameter field

The first step to describe a phase transition is to define an *order parameter field*. This is an extraction of the relevant quantities from a large number of degrees of freedom. This is not straightforward to do, and represents a very important step in understanding the phase transition. A few examples:

liquids and gases: the order parameter field is the density ρ : it is a *scalar* assigned to each point in space.

magnets: the order parameter field is the locally averaged magnetisation: it is a *vector* \mathbf{v} at each space point.

With the extra restriction of fixed temperature, $|\mathbf{v}|$ becomes fixed: corresponding to a point on the surface of a *sphere*.

nematic liquid crystals: these consist of thin rod molecules, which have an orientational order. The order parameter field is the locally averaged orientation \mathbf{d} . Since the two ends of the molecules are equivalent, a 180° rotation does not change the orientation. Mathematically this property can be expressed as $\mathbf{d} = -\mathbf{d}$: these objects are called *directors*.

With the extra restriction of fixed temperature, $|\mathbf{d}|$ becomes fixed, corresponding to a point on a *hemisphere*.

crystals: the order parameter field is the local translation needed to return an atom to a perfect lattice site.

Since all perfect lattice sites are equivalent, this means that our object does not change if we add integer times a lattice vector. Eg. in two dimensions this means $\mathbf{u} = \mathbf{u} + ma_x\hat{x} + na_y\hat{y}$, where a_x and a_y are the lattice constants and \hat{x} and \hat{y} are the lattice directions. These objects are often called *wrapped vectors*. They can be represented by a rectangle, where the pairs of opposite sides are identified, which is topologically equivalent to the surface of a torus.

superconductors: the order parameter field is a complex number Ψ , corresponding to the quantum mechanical phase of the condensed state.

At fixed temperature $|\Psi|$ is fixed, ie. a point on a *circle*.

Topological defects

A phase is often not perfect: the order parameter field is not uniform everywhere. Often these are small fluctuations that can return easily to the perfect state, but sometimes this is not the case. We call *defect* a “tear” (some sort of singularity or discontinuity) in the order parameter field, and *topological defect* is a “tear which cannot be patched”. This means that no continuous local deformation of the order parameter field can remove the defect.

The simplest example is a vortex line superconductor at fixed T . If we consider a closed path encircling the line, the order parameter goes around the circle in the order parameter space. The lack of defect would correspond to the order parameter being constant as we follow the closed path. Since it is not possible to deform continuously the order parameter field from the initial state where following the closed path we go around the circle in the order parameter space to a final state where we don't move in the order parameter space, this is a topological defect. A rigorous treatment of this phenomena belongs to the *topology* branch of Mathematics. It follows that the vortex line cannot end (in reality it can only end at the boundary of the sample).

Another example is a crystal, where in half of the domain there is an extra layer of atoms. The edge of this layer is a line defect: encircling it corresponds to moving on a closed loop on the torus of the order parameter space, which cannot be contracted continuously to a single point.

Our last example is nematic liquid crystals at fixed T . The order parameter space is a hemisphere, where one can select a closed loop which cannot be contracted continuously to a single point. This means that nematic liquid crystals can have line defects. This is in contrast with three-dimensional magnets, which do not have line defects: there the order parameter space is a full sphere: there any circle can be contracted to a point, just imagine to move them to the north pole.