Theo. 4.
Lecture 2.
Felix Yu.
October 22, 2023.

Last time:

Course administration.

Introduction + motivation to thermodynamics + stat. mech.

Today:

Concept of equilibrium.

State function

~~Extensive & intensive variables~~

0th law of thermodynamics

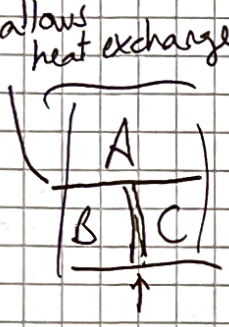
1st law of thermodynamics

Last time, we discussed a system in isolation, where as time goes on, the microscopic degrees of freedom remain dynamic but some meaningful macroscopic averages can be identified to characterize the system. Thermodynamics works solely with such aggregate variables, and this "characterization" is formalized as a "state function" (also called function of state or point function) which is defined for a system after it equilibrates (on some relevant time scale).

In other words, for some system A characterized by the macroscopic variables or coordinates $A_1, A_2, \ldots$, the state function is purely a function of these coordinate $A_1, A_2, \ldots$

By itself, the state function is not useful (and also still very abstract), but its existence is important to mathematically study the equilibrium condition. If system A is in equibrium with system B, then there exists some state function of all the thermodynamic coordinates $A_1, A_2, \ldots; B_1, B_2, \ldots$ that vanishes:

$$f_{AB}(A_1, A_2, \ldots; B_1, B_2, \ldots) = 0$$



The interpretation of this equation is best from the point of view of dynamics: for two systems in equibrium, changing A_1 will induce a change in $A_2, \ldots$ + $B_1, B_2, \ldots$ such that equilibrium is maintained (recall that the total A + B system is isolated).

If system A is also in equilibrium with a system C, then we have

$$f_{AC}(A_1, A_2, \ldots; C_1, C_2, \ldots) = 0$$

Thus, the state variables $A_1, A_2, \ldots; C_1, C_2, \ldots$ are also similarly constrained because of the equilibrium requirement.

Given these constraints, we can isolate/solve for A_1, which will generally require some new functional relationship

$$A_1 = F_{AB}(A_2, \ldots; B_1, B_2, \ldots)$$

$$A_1 = F_{AC}(A_2, \ldots; C_1, C_2, \ldots)$$

Clearly, $F_{AB}(A_2, \ldots; B_1, B_2, \ldots) = F_{AC}(A_2, \ldots; C_1, C_2, \ldots)$

We now postulate (empirically shown to be true):

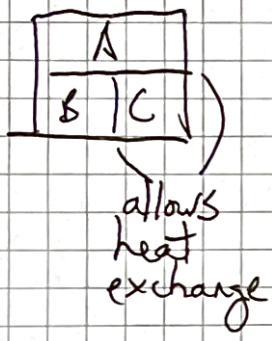
0th law of thermodynamics:

If two systems are separately in equilibrium with a third system, then they are also in equilibrium with each other.

In other words, equilibrium is a transitive property.

Following this postulate, we can conclude there is a constraint of the macroscopic variables of B and C that vanishes:

$$f_{BC}(B_1, B_2, \ldots; C_1, C_2, \ldots) = 0$$



If we replace the barrier between B + C, then nothing changes in the measured coordinates $(B_1, B_2, \ldots) + (C_1, C_2, \ldots)$.

Now, we can consider the full manifold spanned by the $(B_1, B_2, \ldots; C_1, C_2, \ldots)$ coordinate space subject to the equilibrium constraint $f_{BC} = 0$. Since

$$F_{AB}(A_2, \ldots; B_1, B_2, \ldots) = F_{AC}(A_2, \ldots; C_1, C_2, \ldots)$$

is true for the entire manifold, regardless of the A coordinates, (in other words, the A coordinates adjust in response to $\vec{B}$, and communicate this as new arguments in the function F_{AC} so $\vec{C}$ again lies on the original manifold of $f_{BC} = 0$). This lets us simplify $F_{AB} = F_{AC}$ to remove the reference coordinates $A_2, \ldots$ and construct / hypothesize

an equation of state with arguments of system B and C separately:

$$\textcircled{H}(B_1, B_2 \ldots) = \textcircled{H}(C_1, C_2, \ldots)$$

where $\vec{B}$ and $\vec{C}$ are the (possibly distinct) thermodynamic coordinates.

In this way, it becomes possible to say that an equilibrium condition is meaningful even when the coordinate spaces of $\vec{B}$ & $\vec{C}$ are completely orthogonal.

Examples: gas (V, P) + wire $(L, \text{tension } F)$

Kardar 1.7, 1.8, 1.9

$$\left(P + \frac{a}{V^2}\right)(V-b)(L-L_0) - c\left(F - K(L-L_0)\right) = 0$$

paramagnet + gas: (M, B) (V, P)

lower case letters are parameters

$$\left(P + \frac{a}{V^2}\right)(V-b)M - \lambda B = 0$$

$$\Rightarrow \textcircled{H} \alpha\left(P - \frac{a}{V^2}\right)(V-b) = c\left(\frac{F}{L-L_0} - K\right) = \lambda\frac{B}{M}$$

van der Waals gas $\left(P + \frac{a}{V^2}\right)(V-b) = N k_B T$

Curie paramagnet $M = \frac{N \mu_B^2 B}{3 k_B T}$

Hooke's law for rubber $F = \frac{K + DT}{L - L_0}(L - L_0)$

Three equations of state that we will revisit later.

A more intuitive picture of the manifold constraint.

Consider an irregular shape of iron sitting on a set of springs with gravity pulling down.

Given the iron is at rest, the net force (and torque) is zero. We can label this constraint by knowing the location of each spring and its tension. Suppose now that we tighten / loosen remove one spring (or a set of springs) or add more springs with various points of contact. The previously individual forces of the springs will adjust to compensate the new distribution and we will again have a static system. We could also remove all springs below and instead attach ropes to the ceiling and keep the object stable. The equivalence of each configuration of springs illustrates the tradeoff between $\vec{B}$ & $\vec{C}$ for a fixed empirical temperature / equilibrium condition. Now, changing the weight of the object or its shape will identify a new

set of coordinates $\vec{B}$ & $\vec{C}$ that are themselves interchangable. In fact, within reason, the test object can always be balanced, so we can meaningfully remove it and study the coordinate ~~space~~ space for equilibrium without reference to a fixed temperature/object.

Note: The movement in coordinate space along the constraint of constant temperature is an isotherm. Similarly, constant pressure as a constraint gives an isobar & constant volume is an isovolumetric process. or isochoric process.

Another note: Empirical temperture is a fancy phrase to abstract the notion of temperature to situations where an intuitive visualization / picture of temperature is not meaningful. (We will later define temperature via $dE = TdS$, which is even more abstract.) It is easiest to think of empirical temperature as a calculable ~~thing~~ quantity ~~that~~ of thermodynamic coordinates that matches ~~it~~ across systems in equilibrium.

Note 3: Temperature & the Kelvin scale is then defined via ideal gas law & triple point of water:

$$T(K) \equiv 273.16 \cdot \left(\frac{\lim_{P \to 0} (PV)_{\text{system}}}{\lim_{P \to 0} (PV)_{\text{ice-water-gas}}} \right)$$

Now, we should emphasize that state functions have no history. (Because they have no future?)

Time evolution of an isolated system at equilibrium does not change anything, and so if two systems arrive to the same state function, you cannot extract which system started in what configuration.

This leads to a statement of the 1st law of thermodynamics:

The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial & final states. It does not depend on the means of the work performed nor any intermediate stage.

We will study the consequences of this law next time.

Next time:

1st law

Path (in)dependence

(Inexact differentials

Generalized displacements & conjugate generalized forces

Extensive & intensive variables