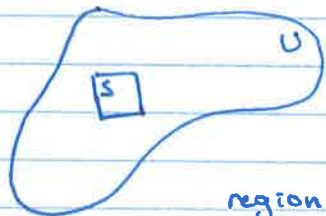


Standard text: Statistical Mechanics
Donald A. McQuarrie

Classical thermodynamics:

This is likely the only discipline in the natural sciences that will never be superseded by a more fundamental theory. This is because it is based directly on experiential observations, and confines itself only to experimental observations.



Let U be the observable universe. Let S be some region of interest containing enough matter that it appears to be continuous. The region S is conventionally called the system, and the rest of the universe is called the surroundings.

First law of thermodynamics: for any thermodynamic system, there is a (state) function E called the internal energy with the property that

$$dE = TdS - pdV$$

E - internal energy
 T - temperature

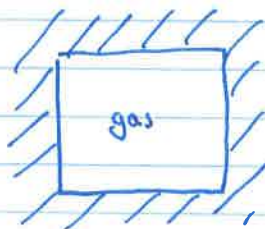
* S - entropy

p - pressure exerted by surroundings

V - volume

where the state of the system is considered to be specified by S and V (independent variables), and $E(S, V)$, $T(S, V)$, and $p(S, V)$ are dependent functions of the state.

$-pdV$ is the change in energy of the system for an infinitesimal change in volume, and TdS is the change in energy of the system when supplied with an infinitesimal amount of heat. That these two should be related to a single conserved quantity (energy) is not at all obvious, and this realization was closely related to the invention of the heat engine and refrigeration.



The internal energy $E(S, V)$ is the natural quantity with units of energy for a system with fixed S and V (rigid and insulating walls) since in these conditions any process for which $\Delta E < 0$ is spontaneous. (system evolves to a min

of energy.



This is not true for a system with fixed T and V (rigid but thermally conducting walls and immersed in a bath of constant temperature).

The natural quantity with units of energy in this case is the Helmholtz free energy $A(T, V)$, since in these conditions any process for which $\Delta A < 0$ is spontaneous.

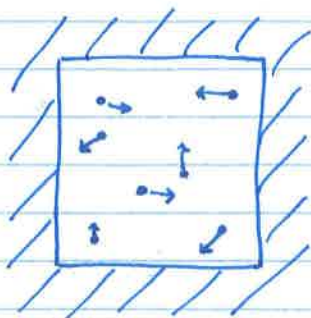
The Helmholtz free energy is entirely equivalent to the internal energy in the sense that there is an invertible map (Legendre transform) from one to the other:

$$\begin{aligned} A(T, V) &= E - TS & dA &= dE - TdS - SdT \\ & & &= TdS - pdV - TdS - SdT \\ & & &= -SdT - pdV \end{aligned}$$

This is enough for our purposes, but note that there is more to classical thermodynamics. In particular, two of the other three laws relate to the mysterious quantity called entropy.

Statistical mechanics:

This is concerned with calculating measurable thermodynamic quantities from the more fundamental properties of the constituent molecules. That is, matter is composed of atoms, and is no longer a continuum.



Suppose that N molecules ~~are~~ are confined to the unit cube ~~with~~ with rigid walls. The state of this system (often called a microstate) is a set of N position vectors \vec{q}_i and N momentum vectors \vec{p}_i , one for each molecule. That is, the microstate corresponds to a point in the phase space $X = \mathbb{R}^{6N}$.

$p = mv$, choice of p instead of v motivated by vol. element on phase space.

Phase space can alternatively be considered a cotangent bundle of configuration space.

There is a function ~~of~~ $U(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$ of the positions of the molecules called the potential energy. This function is in general not

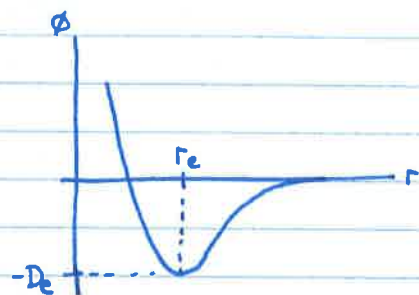
precisely known, but is often successfully approximated by a sum of pairwise interaction potentials $\phi_{ij}(|\bar{q}_i - \bar{q}_j|)$ depending only on the molecular type and separation distance. For a system with a single atomic type this reduces to

$$U = \sum_{i < j} \phi(|\bar{q}_i - \bar{q}_j|)$$

A typical choice for the pairwise interaction potential is the Morse potential:

$$\phi(r) = D_e [e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}]$$

This is constructed to have a zero at infinity and a minimum of depth D_e at radius r_e . The parameter a controls the width of the well.



Intuitively, the molecules act as soft spheres with a preferred separation and a penalty for overlapping. Occasionally a purely repulsive potential

$$\phi(r) = D_e e^{-2a(r-r_e)}$$

can be useful instead, since this has the property of converging to the hard sphere potential in the limit $a \rightarrow \infty$.

There is a second function $K(\bar{p}_1, \bar{p}_2, \dots, \bar{p}_N)$ of the momenta of the molecules called the kinetic energy and defined as

$$K = \sum_i \frac{1}{2m_i} |\bar{p}_i|^2$$

where m_i is the mass of the i^{th} molecule. As suggested by the notation, this is the energy of motion.

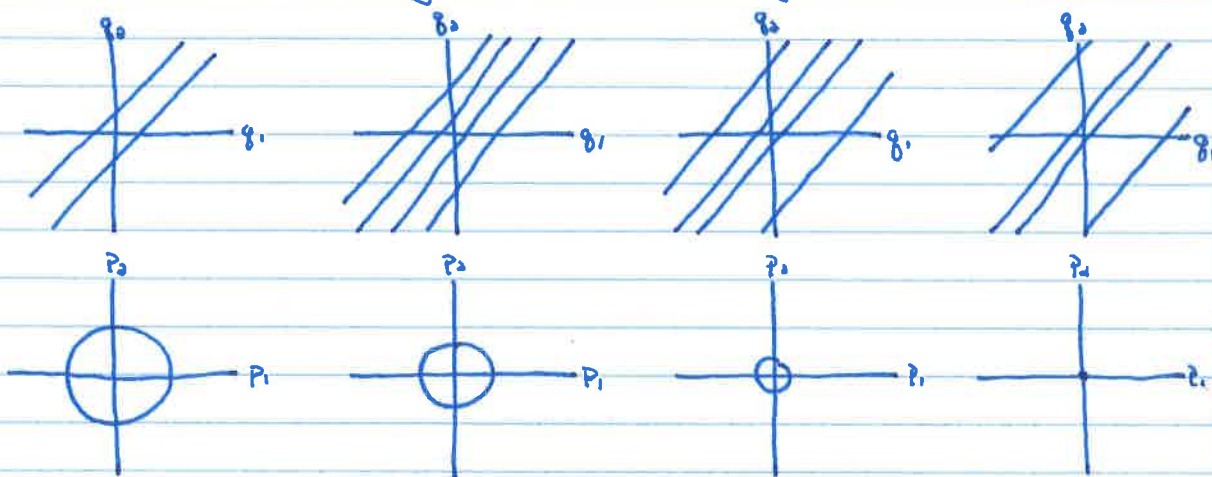
The Hamiltonian is defined as the sum of the potential and kinetic energies, and specifies the evolution equations for the system:

$$H = U + K \quad \frac{\partial H}{\partial \bar{q}_i} = -\frac{\partial \phi}{\partial r} \quad \frac{\partial H}{\partial \bar{p}_i} = \frac{\partial \bar{q}_i}{\partial t}$$

For this particular system, this is supplemented by the condition that the component of the momentum perpendicular to a wall is

reversed when the particle impacts a wall. This specifies a trajectory through the phase space X .

Notice that the isolation of the system and the conservation of energy imply that the Hamiltonian is equal to some constant E . This confines the trajectory to one of a continuous family of codimension-one subspaces. Roughly, these consist of the sublevel set of ~~U~~ $U \leq E$ in the position subspace crossed with a sphere of radius $\sqrt{2m(E-U)}$ in the momentum subspace. For two identical particles in \mathbb{R}^2 , this looks something like the following:



Fundamental assumption of statistical mechanics:

For a system in thermodynamic equilibrium and for an appropriately constructed potential energy U , the following four methods of calculating a given thermodynamic quantity are the same:

1. The time average of the quantity along the given trajectory through the configuration space in the long time limit:

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(x(t)) dt \quad x \in X$$



The motivation for this is that our observation time is generally much longer than the lifetime of a microstate. Notice that this is assumed to be independent of the zero of time.