Phys. 528 Lecture 1

Laws of thermodynamics

The laws of thermodynamics are phenomenological statements about the behavior of macroscopic systems. It is a central goal of statistical mechanics:

1) To derive the laws of thermo. from fundamental principles based on microscopic dynamics.

The second main goal of stat. mech is:

2) To describe and predict the macroscopic properties of matter. Is a system a gas, liquid, or solid? Is it a metal or

insulator? Is it magnetic? Is it superconducting? What broken symmetry(ies) characterize its low-temperature phase(s)?

The first part of this course will build up the framework of statistical mechanics and focus more on question 1 above. The latter part of this course will turn to goal # 2.

We begin with a review of the four laws of thermodynamics:

0) <u>Zeroth law</u> Transitive property of equilibrium. Two systems are said to be in <u>thermal equilibrium</u> if they can exchange energy but have reached a state where the net rate of energy flow is zero

(fluctuations back and forth may still occur). Two systems are said to be in <u>chemical equilibrium</u> if they can exchange particles but have reached a state where the net flow of particles between them is zero. Two systems are said to be in mechanical equilibrium if they can perform (mechanical) work on each other but have reached a state where the net work done per unit time is zero.

The transitive property of equilibrium states that if system 1 is in equilibrium with system 2, and system 2 is in equilibrium with system 3, then system 1 is in equilibrium with system 3. The zeroth law is a necessary precondition to define thermodynamic variables such as

temperature T (thermal equil.)

chemical potential μ (chemical equil.)

pressure p (mechanical equil.)

1) <u>First law</u> The conservation of energy.

$$\underset{\substack{\uparrow \\ \text{change in} \\ \text{energy of} \\ \text{a system}}}{\Delta E} = \underset{\substack{\uparrow \\ \text{heat} \\ \text{added} \\ \text{to system}}}{Q} + \underset{\substack{\nwarrow \\ \text{work done} \\ \text{on the} \\ \text{system}}}{W}$$

If the heat is added in such a way that the system is never driven (except infinitessimally) out of equilibrium, then

$$Q = T \Delta S$$ (for an isothermal process)

T = temperature of the system

S = entropy of the system

$$\Delta S = \int \frac{dQ}{T}.$$ (for a general reversible process)

Differential form of 1st law:

$$dE = \underset{\substack{\uparrow \\ \text{heat} \\ \text{added} \\ \text{to system}}}{TdS} \; \underset{\substack{\uparrow \\ \text{mechanical} \\ \text{work} \\ \text{done on} \\ \text{system}}}{-\,pdV} \; \underset{\substack{\uparrow \\ \text{chemical/} \\ \text{electrical} \\ \text{work done} \\ \text{on system}}}{+\,\mu dN}$$

2) Second law   Law of increase of entropy. For any closed system,

$$\Delta S \geq 0.$$

There are several statements of the 2nd law, which can be shown to be equivalent:

Clausius statement

No process is possible whose sole effect is to transfer heat from a body at temperature T_1 to a body at a higher temperature $T_2 > T_1$.

Kelvin statement

No process is possible whose sole effect is to convert a given amount of heat Q removed from some system in equilibrium entirely into work.

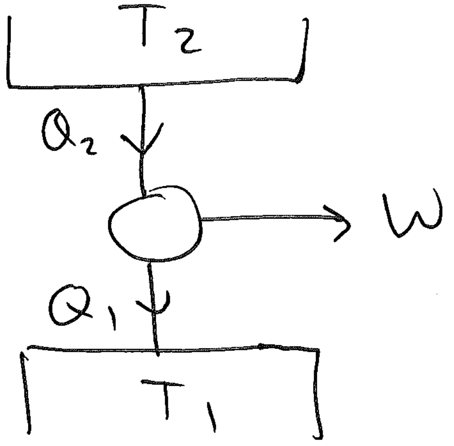
Carnot statement

No heat engine operating between reservoirs at temperatures $T_2 > T_1$ can exceed the Carnot efficiency

$$\eta_c = 1 - \frac{T_1}{T_2}$$

Here T is the absolute temperature (Kelvin).

Proof



1st law: $Q_2 = W + Q_1$

2nd law: $-\frac{Q_2}{T_2} + \frac{Q_1}{T_1} \geq 0$

$$\frac{Q_1}{Q_2} \geq \frac{T_1}{T_2}$$

Efficiency

$$\eta = \frac{W}{Q_2}$$

$$\eta = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2} \leq 1 - \frac{T_1}{T_2}$$

Q.E.D.

Boltzmann

$$S = k_B \ln \Omega$$

Ω = # of microstates consistent with our limited knowledge of the macrostate of a system

3) Third law

$$\lim_{T\to 0} S(T) = \begin{cases} 0, & \text{non-degenerate ground state} \\ k_B \ln g, & g = \text{degeneracy of quantum mechanical ground state.} \end{cases}$$

This implies other quantities also vanish as $T \to 0$:

$$\lim_{T\to 0} C(T) = 0 \quad \text{(specific heat)}$$

$$\lim_{T\to 0} K(T) = 0 \quad \text{(thermal conductance/conductivity)}$$

The third law implies it is practically impossible to cool any system to absolute zero (see pp. 10-11 of Di Castro and Raimondi).