Introduction to Nonequilibrium Statistical Physics, C. Jarzynski, Spring 2020

Brief review of relevant thermodynamics

These notes are not intended as a comprehensive or particularly careful summary of thermodynamics. Rather, they represent a brief, informal review of some of the concepts and results of classical thermodynamics that will be relevant for this course.

The first and second laws as enunciated by Rudolf Clausius (1865):

1) The energy of the universe is constant.

2) The entropy of the universe tends toward a maximum.

Thermodynamics provides a conceptual framework that converts these rather grandiose statements into meaningful predictions about the world around us. This framework organizes our thoughts about the manner in which macroscopic systems exchange energy and matter, and it is constructed around a number of concepts, including:

- **Equilibrium states.** Phenomenologically, we observe that when a macroscopic system is left undisturbed, it relaxes spontaneously to a state in which nothing appears to be happening. We refer to such a state as an *equilibrium state.*

- **State functions.** A state function is some observable whose value is determined uniquely by the equilibrium state. Internal energy, U, and entropy, S, are state functions.

- **Thermodynamic processes.** For our purposes, a thermodynamic process is a sequence of events during which a system of interest evolves from one equilibrium state, A, to another equilibrium state, B. The system need not be in equilibrium at intermediate times. During a thermodynamic process, the system of interest might interact with other systems – we refer to the latter as the *surroundings.*

- **Reversible processes.** During a reversible process – a special case of a thermodynamic process – the system of interest and its surroundings remain in equilibrium with one another at all times. The concept of reversibility is an idealization, typically associated with infinitely slow changes. If a reversible process takes a system and its surroundings from an initial state to a final state, then there exists another reversible process that can bring both the system *and its surroundings* back to the initial state.

First Law of Thermodynamics

The first law is expressed by the equation

$$\Delta U = W + Q \tag{1}$$

$\Delta U = U_B - U_A$ denotes the net change in the internal energy of a system during a process from state A to state B. W is the *work* performed on the system during this process, and Q is the *heat* absorbed by the system. Work is a transfer of energy due to macroscopic displacements against forces, such as a piston pushing into a gas or the flow of electric current across a voltage difference. Heat is the spontaneous transfer of energy that occurs between bodies at different temperatures, as energy flows from the hotter to the colder body. The infinitesimal form of the first law is $dU = đW + đQ$. Here $đW$ and $đQ$ are inexact differential, reflecting the fact that work and heat are not state functions.

It is useful to introduce here the concept of a *thermal reservoir*, or *heat bath*, which is a system that exchanges energy in the form of heat, but not work, with the system of interest. A thermal reservoir is viewed as being infinitely large, hence its temperature remains constant even as it gains or loses energy. In the following discussion of the second law, we imagine a system of interest that undergoes a thermodynamic process in the presence of a number of thermal reservoirs. These reservoirs constitute the system's surroundings.

Second Law of Thermodynamics

There are various equivalent statements of the second law. One of these is the *Clausius inequality*, which applies to a process from state A to state B:

$$\int_A^B \frac{đQ}{T} \leq \Delta S \tag{2}$$

$\Delta S = S_B - S_A$ is the net change in the entropy of the system, $đQ$ is the energy absorbed as heat by the system during an infinitesimal portion of the process, and T is the absolute temperature of the reservoir from which that energy is absorbed. When the process is reversible, the inequality becomes an equality ($=$). When the process is irreversible, the inequality is strict ($<$).

The Clausius *equality* – that is, Eq. 2 for reversible processes – is a deep statement about the natural world. It tells us that the integral appearing on the left takes the same value for any reversible process from state A to state B. This statement defines the entropy difference $S_B - S_A$, and therefore defines entropy as a state function, up to an additive constant.

Let us consider implications of the Clausius inequality in a variety of situations.

- When there are no thermal reservoirs, Eq. 2 gives $\Delta S \geq 0$: in the absence of heat exchange, a system's entropy never decreases.

- When there is a single reservoir, at temperature T, and the system begins and ends in equilibrium with that reservoir, Eq. 2 becomes

$$\frac{Q}{T} \leq \Delta S \tag{3}$$

where $Q = \int_A^B đQ$ is the net heat absorbed by the system. Combining this result with the first law, Eq. 1, simple manipulations give us $W \geq \Delta U - T\Delta S$, or more compactly

$$W \geq \Delta F \equiv F_B - F_A \tag{4}$$

where $F = U - TS$ is the system's Helmholtz free energy. Eq. 4 is often called the *maximum work theorem*, in reference to the greatest amount of work that can be delivered by bringing the system from a state of higher free energy to a state of lower free energy. [1]

- When there is a single reservoir and the process is *cyclic* – that is, the system begins and ends in the same state – then Eq. 4 implies

$$W \geq 0 \geq Q \tag{5}$$

since $\Delta F = \Delta U = 0$. Energy is supplied *to* the system as work, and an equal amount of energy flows *from* the system into the reservoir as heat. This result is known as the *Kelvin-Planck statement* of the second law: "No process is possible whose sole result is the absorption of heat from a reservoir and its complete conversion to work" – in other words, we can't have $W < 0 < Q$ for a cyclic process involving a single thermal reservoir.

- When two reservoirs are present – one hot, one cold – and we consider cyclic processes for which $W = 0$, Eq. 2 becomes

$$\frac{Q_c}{T_c} + \frac{Q_h}{T_h} \leq 0 \tag{6}$$

where Q_c is the heat absorbed from the cold reservoir, at temperature T_c, and Q_h, T_h are defined similarly for the hot reservoir. Combining Eq. 6 with the first law ($Q_c + Q_h = 0$) we

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[1] $W_{\text{delivered}} = -W \leq F_A - F_B$

get

$$Q_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right) \leq 0 \tag{7}$$

hence

$$Q_h \geq 0 \geq Q_c \tag{8}$$

Energy is transferred from the hot reservoir, via the system, into the cold reservoir, and not the other way around. This is expressed by the *Clausius statement* of the second law: “No process is possible whose sole result is the transfer of heat from a cooler to a warmer body”. In order to transfer heat from a cooler to a warmer body, we must supply energy in the form of work – this is why refrigerators and air conditioners require a power supply.

• Finally, when two reservoirs are present and we consider cyclic processes in which work is extracted from the system ($W < 0$), Eq. 6 combines with the first law to give

$$W, Q_c \leq 0 \leq Q_h \quad , \quad \eta \equiv \frac{|W|}{|Q_h|} \leq 1 - \frac{T_c}{T_h} \equiv \eta_C \tag{9}$$

These equations describe the operation of a heat engine: energy is absorbed from the hot reservoir, some of that energy is delivered as work, and the rest goes into the cold reservoir. The engine’s efficiency η, defined as the ratio of the work delivered to the heat withdrawn from the hot reservoir, can be no greater than η_C, the *Carnot efficiency.* A heat engine that operates with efficiency $\eta = \eta_C$ is called a Carnot engine. The result $\eta \leq \eta_C$ is the *Carnot statement* of the second law: “No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs”.

While Eqs. 4, 5, 8 and 9 have been presented above as consequences of the Clausius inequality under various situations, in fact these statements, including Eq. 2, are logically equivalent: any one of them can be derived from any other. Thus if the Kelvin-Planck statement, Eq. 5, holds for all systems (as it indeed does!) then it follows that the Clausius inequality, Eq. 2, must also hold for all systems, and so forth. To illustrate it another way, if a magic rubber band could be used to convert heat from a single reservoir into work (violating Eq. 5), then the same rubber band could be used to transfer heat from a cooler to a warmer body without requiring work (violating Eq. 8), or to construct a heat engine with efficiency $\eta > \eta_C$ (violating Eq. 9) – and all of these outcomes violate the Clausius inequality (Eq. 2).

Because a thermal reservoir, by definition, exchanges energy only as heat and not as work, the net change in the entropy of a reservoir is given by

$$\Delta S_{\text{res}} = \frac{Q_{\text{res}}}{T_{\text{res}}} \tag{10}$$

where Q_{res} is the energy absorbed as heat by the reservoir during a process, and T_{res} is its temperature. This remains true even if the process is irreversible. (Exercise: show that Eq. 10 follows from the definition of a thermal reservoir, combined with Eq. 2.) Using this result, we rewrite the left side of Eq. 2:

$$\int_A^B \frac{đQ}{T} = \sum_r \frac{Q_r}{T_r} = -\sum_r \Delta S_r \tag{11}$$

where Q_r is the heat absorbed by the system from the r'th reservoir, whose temperature is T_r, and ΔS_r is the net change in the reservoir's entropy, during the process. The minus sign arises because $Q_r = -Q_{\text{res},r}$: the heat absorbed by the system is equal to the heat released by the reservoir, or vice versa. Using this result, Eq. 2 can be rewritten as

$$\Delta S + \sum_r \Delta S_r \geq 0 \tag{12}$$

in other words the combined entropy of the system and its surroundings never decreases. This is a local version of Clausius's statement about the entropy of the universe (p. 1).

Thermodynamics of Equilibrium States

Eq. 2 implies the relation

$$đQ \overset{\text{rev}}{=} T\,dS \tag{13}$$

where $đQ$ denotes the small quantity of heat absorbed by the system from a reservoir at temperature T, and dS is the small change in the system's entropy, during a short portion of a reversible process (as indicated by $\overset{\text{rev}}{=}$).[2] For the pedagogical example of a rubber band that is stretched or contracted reversibly in the presence of a reservoir, Eq. 13 can be combined with the first law to give

$$dU \overset{\text{rev}}{=} T\,dS + \mathcal{F}\,dL \tag{14}$$

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[2] It is tempting to drop the assumption of reversibility and write $đQ/T \leq dS$, but if the process is irreversible then the system's entropy might not be well defined at intermediate times.

where $\mathcal{F}$ is the tension in the rubber and dL denotes an infinitesimal change in its length, i.e. $đW = \mathcal{F}\, dL$. Eq. 14 implies that the rubber band's internal energy, in equilibrium, can be expressed as a function of its entropy and length,

$$U = U(S, L) \tag{15}$$

with the partial derivatives

$$\left.\frac{\partial U}{\partial S}\right)_L = T \quad , \quad \left.\frac{\partial U}{\partial L}\right)_S = \mathcal{F} \tag{16}$$

The function $U(S, L)$ is a convex function of its arguments, hence $\partial^2 U/\partial S^2 \geq 0$ and $\partial^2 U/\partial L^2 \geq 0$, equivalently

$$\left.\frac{\partial T}{\partial S}\right)_L \geq 0 \qquad , \qquad \left.\frac{\partial \mathcal{F}}{\partial L}\right)_S \geq 0 \tag{17}$$

These inequalities reflect the thermodynamic stability of equilibrium states. I will not discuss this point in detail here, but it should be clear that these inequalities are intuitively plausible: when we add heat to a rubber band we expect its temperature will not decrease, and when we stretch a rubber band we expect its tension will not decrease.

In the discussion surrounding Eqs. 1 - 12 I have sketched a formulation of the first and second laws of thermodynamics that focuses on thermodynamic processes, and specifically on the exchanges of energy, via heat and work, that occur during such processes. This formulation was developed in the nineteenth century in Europe, and is associated with names such as Carnot, Clausius, Joule, Helmholtz, and William Thomson (Baron Kelvin), among others. This will be the formulation that is most directly relevant to the remainder of this course.

An alternative formulation of the laws of thermodynamics focuses on equilibrium states rather than on processes. In Eqs. 13 - 17 I have just scratched the surface of this approach, which was pioneered by Gibbs in the United States. A clear exposition of this formulation can be found in the classic book, *Thermodynamics and An Introduction to Thermostatistics* by Herbert Callen (2nd ed., 1985, John Wiley and Sons, New York).