

Part II: Thermodynamics

II.2 The second law of thermodynamics

Class schedule: Feb 3, 5

Reading assignments: S7-8, R3.1, R3.3-3.6, F11-13; optional: R3.7, F7;

Examples marked with * are important and should be studied carefully and thoroughly.

II.2.1 Interacting systems in equilibrium

Example 1: review: the number of states in a many-particle system: dependence on internal energy and multiplicative property.

Remark: 1. the number of states $\Omega(E)$ increases rapidly with increasing E . 2. $\Omega(E) = \prod_1^N \Omega_i(E_i)$, or the number of states in combined systems is a product of the numbers of states of constituent sub-systems. Understanding this way: by adding another sub-system, new dimensions (new dice) are added to the system, and the “volume” of the system is a product of “lengths” along all dimensions.

*Example 2: energy distribution between two systems in thermal equilibrium through thermal interaction (heat transfer): maximum probability consideration. The system in final equilibrium has the energy distribution that has the largest probability, or largest number of states, with the constraints the system is subject to.

Example 3: sharpness of the probability function

Remark: we’ve deduced the most probable energy distribution starting from the following 3 points: a. the total energy in the combined system is conserved; b. multiplicative property of the number of states; c. in equilibrium, the system is equally likely to be in ANY of ALL the accessible states.

II.2.2 Entropy, Temperature, and the Second Law

Definitions of *entropy* (S) and *absolute temperature* (T): $S \equiv k \ln \Omega$, $\frac{1}{T} = \frac{\partial S}{\partial E}$.

*Example 4: entropy of combined systems: in final equilibrium, the entropy of the combined system is maximized, or the system evolves to the final MACROSCOPIC state which has the largest number of accessible MICROSCOPIC states – largest probability, or largest entropy.

Example 5: dependent and independent variables

The *second law* is formulated as $\Delta S \geq 0$, and is stated in many ways! One of these statements goes: for any two interacting systems, the entropy of the combined systems cannot decrease. Or: interacting systems will reach a final equilibrium with maximized entropy - or largest number of accessible micro-states.

Specificly, systems with thermal interaction will reach *thermal equilibrium* with the same temperature anywhere in the system, i.e., $T_1 = T_2 = \dots = T_i \dots = T$.

*Example 6: Energy distribution in combined systems of thermal equilibrium: specific case and general form. In most systems, $\Omega(E) \sim E^{f/2}$, where f is the degree of freedom (e.g., $f = 3N$ for an ideal monatomic gas), and in thermal equilibrium, $E/f = 1/2kT$.

The unit of *absolute temperature* is degree K (kelvin), and the unit of entropy is Joule / K, same as the unit of $k = 1.38 \times 10^{-23} \text{ Joule/K}$, Boltzmann constant.

Properties of *absolute temperature*:

- In general systems, $T > 0$, as $\Omega(E)$ increases rapidly with increasing E .
- T indicates the direction of heat flow.
- *Zeroth law*: if two systems are each in thermal equilibrium with the third system, then they are in thermal equilibrium with each other. In other words: if $T_1 = T_3$, and $T_2 = T_3$, then $T_1 = T_2$.

Remark: we will be using *absolute temperature* in all following thermal physics problems and discussions. The absolute temperature $T \equiv T_{\text{celsius}} + 273.16K$, or $T_{\text{triplepoint}} \equiv 273.16K$.

II.2.3 Heat Reservoirs

Consider a system A with internal energy E at temperature T , which absorbs a small amount of heat $Q = \Delta E \ll E$. The resultant change in entropy is given by $\Delta S = \frac{Q}{T}$.

In more general form, $dS = \frac{dQ}{T}$, where $dQ \ll E$, or infinitesimal amount of heat. So, while dQ is an inexact differential, $dS = dQ/T$ is an exact differential, which can be determined by the initial and final states as the difference between the two macro-states and is independent of the process or how the system evolves from the initial to the final state.

Equivalently: $dQ = TdS$.

Example 7: calculating the change of the number of states by adding 1 eV heat to a heat reservoir at the temperature 300 K: $\frac{\Omega_f}{\Omega_i} = e^{Q/kT}$

We can achieve $S_f - S_i = \int_i^f dQ/T$ in a process of quasi-static evolution. In other words, if we very slowly (quasi-statically!) heat/cool the system, we can find the entropy change of the system.

Note that until now, we have been only dealing with systems with thermal interactions. However, the expression $TdS = dQ$ is valid for systems with general interactions, as we shall see later. Combined with the first law, it is therefore $TdS = dQ = dE + dW - \mu dN$. For an ideal gas, there is $dS = \frac{dQ}{T} = \frac{dE}{T} + \frac{PdV}{T}$.

Example 8 (Stowe Prob. 8.18, 8.20): calculate the change in entropy and the number of quantum states when a system is heated or when work is done: in these processes, what causes the change in the number of quantum states?

II.2.4 The Third Law

As the energy E of the system decreases, for example, by gradually cooling down the system (reducing T), the entropy S drops rapidly. When E approaches the lowest possible value E_0 ($T \rightarrow 0$), i.e., the ground-state, S approaches zero or a fixed base value S_0 , which ought to be determined at atomic level.

Example 9: the ground-state of H atoms.

Remark: the state variable E or S is being discussed with respect to a reference value, say, a ground-state.

Third law: as T approaches absolute zero, S reaches a base value S_0 , a constant independent of external parameters of the system.

Appendix: dependent and independent variables: in general, given a function $F \equiv F(x_1, x_2, \dots, x_i, \dots, x_M)$ and there are K equations describing the relationship between $x_1, x_2, \dots, x_i, \dots, x_M$ such as $x_j = x_j(x_1, x_2, \dots, x_{M-K})$, for $j = M - K + 1, M - K + 2, \dots, M$, then we say that there are K dependent variables (x_j), and $M - K$ independent variables ($x_i, i = 1, 2, \dots, M - K$). To maximize F , the partial derivative of F with respect to ANY of the INDEPENDENT variable x_i should be zero (i.e., $M - K$ equations to solve), and the partial derivative can be derived as:

$$\frac{\partial F}{\partial x_i} = \left(\frac{\partial F}{\partial x_i} \right)_{x_j} + \sum_{j=M-K+1}^M \frac{\partial F}{\partial x_j} \frac{\partial x_j}{\partial x_i}$$