

## Basic Assumptions

### 1. Existence of Quantum States

Any system at any instance is in one of a **countable** set of *states*, each with an associated *energy*.

### 2. Principle of Equal *A Priori* Probabilities (P.E.A.P.P.)

An *isolated system* in *equilibrium* visits all of its accessible states with equal probability.

### 3. Principle of Maximum Probability

In *equilibrium*, *macroscopic variables* are such that the total number of accessible states is maximized.

One should think of quantum states to be stationary states of the Schrödinger or Dirac equation. An isolated system is a system that only interacts with its own degrees of freedoms. Equilibrium is reached when a system's macroscopic variables no longer change with time, where a macroscopic variable is a quantum expectation value within some coarse-grained window.

## Microcanonical Ensemble

Given an appropriate coarse-graining scale for the energy  $\delta E$ , the total number of accessible states ( $\Gamma \in \mathbb{Z}^*$ ) of  $N$  particles in a box of volume  $V$  with a total energy of  $E \pm \delta E$  only depends on these three parameters  $\Gamma(N, V, E)$ . This set of states is known as the *microcanonical ensemble*. This is the ensemble accessed by an isolated system.

## Temperature, Pressure and Chemical Potential

When two originally isolated systems with states  $\Gamma_1(N_1, V_1, E_1)$  and  $\Gamma_2(N_2, V_2, E_2)$  are considered together, the total number of accessible states is  $\Gamma = \Gamma_1 \Gamma_2$  by counting. If they are allowed to exchange one of  $X = N, V, E$ , then by the principle of maximum probability, this variable  $X$  must change in a way such that  $d\Gamma \geq 0$ . Consider the transfer of  $dE_1 > 0$  (a few quanta of) energy from system 2 to 1

$$\begin{aligned} d\Gamma &= d(\Gamma_1 \Gamma_2) = d\Gamma_1 \Gamma_2 + \Gamma_1 d\Gamma_2 \\ &= \frac{\partial \Gamma_1}{\partial E_1} dE_1 \Gamma_2 + \Gamma_1 \frac{\partial \Gamma_2}{\partial E_2} dE_2 \\ &= \frac{\partial \Gamma_1}{\partial E_1} dE_1 \Gamma_2 - \Gamma_1 \frac{\partial \Gamma_2}{\partial E_2} dE_1 \geq 0 \\ &\Rightarrow \boxed{\frac{\partial}{\partial E_1} \ln \Gamma_1 \geq \frac{\partial}{\partial E_2} \ln \Gamma_2}. \end{aligned} \tag{1}$$

Equation (1) also applies to number of particles and volume.

$\frac{\partial}{\partial N_1} \ln \Gamma_1 \geq \frac{\partial}{\partial N_2} \ln \Gamma_2$  for a particle to flow from system 2 to 1.

$\frac{\partial}{\partial V_1} \ln \Gamma_1 \geq \frac{\partial}{\partial V_2} \ln \Gamma_2$  for some volume  $dV_1 > 0$  to flow from system 2 to 1.

Equation (1) is verified by our daily experience of temperature and pressure. Unfortunately, we will have to jump through some hoops of definitions to see that. These definitions were made before the advent of quantum mechanics and thus statistical mechanics. OK, let's define stuff. Firstly, define **entropy** as

$$S \equiv k_B \ln \Gamma. \tag{2}$$

Now, recall  $\Gamma(N, V, E)$ , so  $S(N, V, E)$ , thus  $E(N, V, S)$ , now define

$$\begin{cases} T \equiv \frac{\partial E}{\partial S} \Big|_{N,V} \\ P \equiv - \frac{\partial E}{\partial V} \Big|_{N,S} \\ \mu \equiv \frac{\partial E}{\partial N} \Big|_{V,S} \end{cases}, \quad (3)$$

where  $T, P, \mu$  are temperature, pressure and chemical potential, respectively. This gives rise to the definition of the **thermal dynamic identity** of the microcanonical ensemble, which should be committed to memory

$$\boxed{dE = TdS - PdV + \mu dN}. \quad (4)$$

From the thermal dynamic identity we can derive the derivatives of entropy

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \Rightarrow \begin{cases} \frac{\partial S}{\partial E} \Big|_{V,N} = \frac{1}{T} \\ \frac{\partial S}{\partial V} \Big|_{N,E} = \frac{P}{T} \\ \frac{\partial S}{\partial N} \Big|_{V,E} = - \frac{\mu}{T} \end{cases}. \quad (5)$$

Notice that what's held constant in a partial derivative is determined by the ensemble control variables. In this case the microcanonical ensemble control variables are  $N, V, E$ , so  $\frac{\partial}{\partial E}$  must hold  $N, V$  constant and so on. With this understanding, I will drop the  $|_{N,V}$  etc. for simplicity. Finally, (1) can be written in terms of entropy derivatives

$$\frac{\partial}{\partial X_1} \ln \Gamma_1 \geq \frac{\partial}{\partial X_2} \ln \Gamma_2 \Rightarrow \frac{\partial S_1}{\partial X_1} \geq \frac{\partial S_2}{\partial X_2} \Rightarrow \boxed{\begin{cases} T_2 \geq T_1 \\ P_1 \geq P_2 \\ \mu_2 \geq \mu_1 \end{cases}}, \quad (6)$$

where I have assumed positive temperature for comparison with day-to-day life. In conclusion, (1) implies energy flows from hot to cold system, volume flows from low pressure to high pressure system, particles flow from high chemical potential system to low chemical potential system. To interpret volume flow, consider heating up one side of a cylinder of air divided by a mobile separator. As the gas heats up its pressure increases and pushes the cylinder towards the low-pressure side. Here volume flows from the low pressure system to the high pressure system.

Equation (1) is the simplest result of the basic assumptions that can be compared to intuition. Notice all three assumptions are invoked during its derivation. The very definition of  $\Gamma$  invokes the existence of quantum states. P.E.A.P.P. allows us to calculate probability by counting states. Finally the direction of the inequality is determined by the principle of maximum probability. There are also the additional subtle definitions of isolated system, equilibrium, microcanonical ensemble and coarse-graining scale.