

0.1 Assumptions

- No uncertainty in energy states.
- Each system is a pure system.
- An isolated system is equally likely to be in any available state.
- The average of a property over all available microstates is the macroscopic value.

1 MicroCanonical

For a system with constant number, volume, and energy, the number of microstates is

$$\Omega = \Omega(N, V, E).$$

Now take an ensemble or collection of systems like this. Then,

$$E_{tot} = AE$$

$$N_{tot} = AN$$

$$V_{tot} = AV.$$

Since we have no reason to favor one system over the other, we assume each state with the same N, V, E is equally probable. This is known as the principle of equal *a priori* probabilities.

2 Canonical

2.1 Deriving the Partition Function

Now let's take an ensemble of systems with the same temperature, volume, and number. The ensemble is put into a heat bath until it is fully equilibrated, and then moved into perfect thermal insulation. The entire ensemble then becomes a system in the microcanonical ensemble.

We know that the system must obey,

$$A = \sum_j a_j$$

$$E_{tot} = \sum_j a_j E_j \text{ where } a_j \text{ is the occupancy number of state } j.$$

We also know that for each energy E_j , $\Omega(E_j)$ unique quantum states exist. We do not know the occupancy number of states, however.

We do know (assumption) that for the microcanonical ensemble each state is equally likely. This means that each state for the entire canonical ensemble

is equally likely since the entire canonical ensemble is a system in the micro-canonical ensemble; that is all combinations of occupancy numbers is equally likely.

The number of distributions of occupancy numbers is given by

$$W(\vec{a}) = \frac{A!}{\prod_j a_j!}.$$

This a multinomial coefficient meaning that at large A it is very sharply peaked; in fact, arbitrarily so at large enough A . The probability of being in state j is then,

$$P_j = \frac{\bar{a}_j}{A} = \frac{\sum_a W(\vec{a}) a_j(\vec{a})}{A \sum_a W(\vec{a})}.$$

At infinite number of systems in an ensemble, all contributions besides the most common become completely negligible, thus

$$P_j = \frac{\bar{a}_j}{A} = \frac{a_j^*}{A}.$$

We now have a maximization problem with the following constraints.

$$A = \sum_j a_j$$

$$E_{tot} = \sum_j a_j E_j.$$

Since \ln is a monotonic function and, thus, will preserve maxima and minima of inputted functions, $\ln(W(\vec{a}))$ can be maximized instead of $W(\vec{a})$. For further calculations it behooves us to recognize that

$$\ln(W) = \ln(A!) - \sum_j \ln(a_j!).$$

Note the first term is constant and the second is approximately

$$- \sum_j a_j \ln(a_j) + \sum_j a_j.$$

Then,

$$\frac{\partial(\ln W(\vec{a}) - \alpha \sum_j a_j - \beta \sum_j a_j E_j)}{\partial a_k} = 0.$$

For each k then,

$$\ln(a_k^*) + \alpha + 1 + \beta E_k =$$

or

$$a_k^* = e^{-\alpha'} e^{-\beta E_k}.$$

Summing over all (a_j^*) gives,

$$A = e^{-\alpha'} \sum_j e^{-\beta E_j}.$$

Finally,

$$P_j = \frac{e^{-\alpha'} e^{-\beta E_k}}{e^{-\alpha'} \sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}}.$$

We call the denominator Q and label it the partition function. We know show the ensemble energy and some of its derivatives.

2.2 Finding β

$$\begin{aligned}\bar{E} &= \frac{\sum_j E_j e^{-\beta E_j}}{Q} \\ p_j &= - \left(\frac{\partial E}{\partial V} \right)_N \\ \bar{p} &= - \frac{\sum_j \left(\frac{\partial E}{\partial V} \right)_N e^{-\beta E_j}}{Q}.\end{aligned}$$

We can then find,

$$\left(\frac{\partial \bar{E}}{\partial V} \right)_{N,\beta} = -\bar{p} + \beta \bar{E} \bar{p} - \beta \bar{E} \bar{p}$$

and

$$\left(\frac{\partial \bar{p}}{\partial \beta} \right)_{N,V} = \bar{E} \bar{p} - \bar{E} p.$$

Comparing the thermodynamic and ensemble averages we see,

$$\left(\frac{\partial \bar{E}}{\partial V} \right)_{N,\beta} + \beta \left(\frac{\partial \bar{p}}{\partial \beta} \right)_{N,V} = -\bar{p},$$

$$\left(\frac{\partial E}{\partial V} \right)_{N,T} - T \left(\frac{\partial p}{\partial T} \right)_{N,V} = -p.$$

One can see from this that $\beta = \frac{k}{T}$. k will be the same for any system as can be seen from a thought experiment where the ensemble consists of two system composites with the same N, V, T . They individual systems will be in equilibrium and from prior calculations the partition function and probability functions are completely separable. This requires they have the same constant k .

2.3 Entropy

Let

$$f = \ln Q.$$

Then,

$$df = \left(\frac{\partial f}{\partial \beta} \right)_{E_j} d\beta + \sum_k \left(\frac{\partial f}{\partial E_k} \right)_{\beta, E_j \neq k} dE_k.$$

This derivative is equivalent of slightly changing the volumes of all systems which changes the energy levels (which is nothing but PV work) and slightly change the temperature before isolated the ensemble again.

This becomes with some manipulation,

$$df = -\bar{E}d\beta - \beta \sum_k P_k dE_k$$

$$d(f + \beta \bar{E}) = \beta \left(d\bar{E} - \sum_k P_k dE_k \right).$$

The first term is the average energy increase in a system, while the second is the average work done on a system meaning the argument in parenthesis is nothing but the reversible heat. This requires that β is an integrating factor of f .

$$d(f + \beta \bar{E}) = \beta q_{rev}$$

$$d \left(f + \frac{\bar{E}}{kT} \right) = \frac{q_{rev}}{kT}.$$

Thermodynamically the left side must be dS/k , so finally,

$$dS = \frac{d\bar{E}}{T} + k d(\ln Q).$$

2.4 Spontaneous Processes

One can think of spontaneous processes as processes that occur because an increase in available states.

We take the known relation,

$$A(N, V, T) = -kT \ln Q(N, V, T).$$

In addition, one can also recognize that a summation over energy levels rather than states can be done.

$$Q = \sum_l \Omega(N, V, E_l) e^{-\beta E_l}.$$

For a spontaneous process we require that,

$$\Omega_2 \geq \Omega_1.$$

Then,

$$Q_2 - Q_1 = \sum_l (\Omega_2 - \Omega_1) e^{-\beta E_l} \geq 0.$$

Finally,

$$\Delta A = A_2 - A_1 = -kT \ln \frac{Q_2}{Q_1} < 0.$$