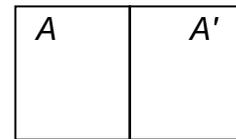


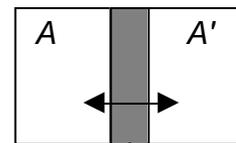
Appendix C extra - Interacting systems

In the first part of this supplement, we discussed a system in isolation, describing its accessible states and the fundamental postulate of statistical mechanics. Now we generalize to systems in interaction. The systems are labeled A and A' , and they interact at their point of contact. The interaction may result in an exchange of several quantities:

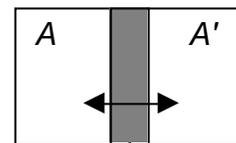
Thermal contact: the energy of a system can change, but not volume or particle number. Temperature is fixed, but the energy of each system changes.



Mechanical contact: volume can change but not energy (insulating piston). Pressure is fixed, but the volume of each system changes.

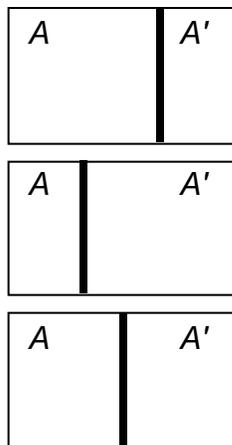


Mechanical plus thermal contact (conducting piston). Temperature and pressure are fixed, volume and energy vary.

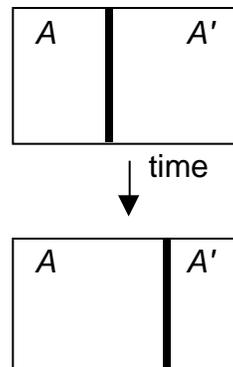


From the ergodic assumption, there is more than one way to measure the energies and volumes of systems in contact:

measure an ensemble of identically prepared systems once



measure one system many times



Constraints and Ω

What happens when two systems are brought in contact, and a constraint that isolated them is removed? For example, consider what happens when a thermal barrier between two gases is removed, but the volume of their container is not altered.



remove the barrier

Once the barrier has been removed, the number of accessible states must be the same, or larger:

$$\Omega_{\text{final}} \geq \Omega_{\text{initial}} \quad (\text{Cx2.1})$$

That is, removing a constraint cannot decrease the number of accessible states. As the probability of the system being in a particular state is proportional to Ω , then the probability of a system returning to its initial state is $\Omega_{\text{initial}} / \Omega_{\text{final}}$.

If the number of accessible states doesn't change during a process, that is

$$\Omega_{\text{final}} = \Omega_{\text{initial}} \quad (\text{reversible}) \quad (\text{Cx2.2})$$

then equilibrium can be maintained during the process and it is reversible. If the number of accessible states increases during a process,

$$\Omega_{\text{final}} > \Omega_{\text{initial}} \quad (\text{irreversible}) \quad (\text{Cx2.3})$$

then the process is irreversible.

For example, if a gas expands to occupy a larger volume by removing a barrier, then it will not go back to its original state if the barrier is reinserted:

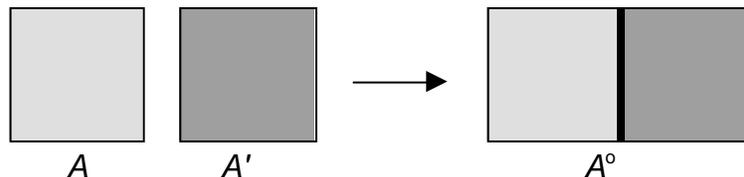


remove the barrier

Systems in thermal contact

Note: the following argument, which follows Reif's Statistical and Thermal Physics, uses discrete energies, but goes over to continuous energies without modification.

Next, consider what happens when we place two systems in thermal contact, but not mechanical contact (i.e., systems can exchange energy, but not volume or material).



Two systems A and A' combine to form A^0 , which is isolated.

Because A^0 is isolated, the total energy of A^0 is constant, even as the subsystems exchange energy. Denoting the energies of A , A' and A^0 as E , E' and E^0 , then

$$E + E' = E^0 = \text{constant} \quad (A^0 \text{ is isolated}) \quad (\text{Cx2.4})$$

The number of accessible states in each system is written as $\Omega(E)$, $\Omega'(E')$ and $\Omega^0(E^0)$. What is the probability $P(E)$ of system A having energy E ? In the isolated system A before contact, it is

$$P_A(E) = \frac{\Omega(E)}{\Omega} = \frac{\Omega(E)}{\Omega_{TOT}} \quad (\text{Cx2.5})$$

$P'_{A'}(E')$ can be similarly expressed. What about the combined system? Call $P_A^0(E)$ the probability of system A having energy E once the systems are in contact. Then

$$P_A^0(E) = \frac{\Omega^0(E)}{\Omega_{TOT}^0} \quad (\text{Cx2.6})$$

with

$$\Omega_{TOT}^0 = \sum_E \Omega^0(E) \quad (\text{Cx2.7})$$

What about $\Omega^0(E)$? For every state in the collection $\Omega(E)$, a total of $1 \times \Omega'(E')$ combined states can be formed (where $E' = E^0 - E$). Hence, for a specific energy division E and E' , there must be a total of

$$\Omega(E)\Omega'(E')$$

states. We sum over all of these combinations to obtain Ω_{TOT}^0 .

Numerical example

Let systems 1 and 2 have allowed energies $E = 1,2$ and $E' = 1,2$, with accessible states according to

| | | |
|-------------|---|---|
| E | 1 | 2 |
| # of states | 2 | 4 |

| | | |
|-------------|---|---|
| E' | 1 | 2 |
| # of states | 8 | 2 |

From this, we find:

of combined states is

| | | |
|---------|----|---|
| E' | 1 | 2 |
| $E = 1$ | 16 | 4 |
| 2 | 32 | 8 |

with total energy E° given by

| | | |
|---------|---|---|
| E' | 1 | 2 |
| $E = 1$ | 2 | 3 |
| 2 | 3 | 4 |

Information from these two tables generate the number of combined states as a function of E° :

| | | | |
|-------------|----|------|---|
| E° | 2 | 3 | 4 |
| # of states | 16 | 32+4 | 8 |

for a total of $\Omega_{\text{TOT}}^\circ = 60$ states ($16 + 32 + 4 + 8$).

Dividing the entries in the table by $\Omega_{\text{TOT}}^\circ$ yields the fractional distribution of combined states:

| | | | |
|--------------------|------|-----|------|
| E° | 2 | 3 | 4 |
| fraction of states | 0.27 | 0.6 | 0.13 |

Now, let's see the effects of constraints. If we ask, "what are the number of states of the combined system Ω° as a function of the energy E of the subsystem", we would find (add rows in the "combined states" table):

| | | | |
|-------------------|----|----|-------------------------------|
| E | 1 | 2 | (NO constraint on E°) |
| $\Omega^\circ(E)$ | 20 | 40 | |

As expected, the *fractional* distribution of combined states is the same, as a function of E , as the uncombined subsystem. The same would be true if we calculated Ω° as a function of E' (by adding columns).

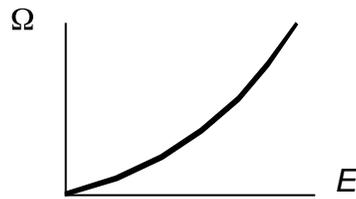
BUT, if we place a constraint on E° , the fractional distributions of the subsystems changes. Say we demand $E^\circ = 3$. Then the number of states Ω° as a function of E of the subsystem changes to (cross diagonal in the table)

| | | | |
|-------------------|---|----|------------------------------|
| E | 1 | 2 | (constraint $E^\circ = 3$). |
| $\Omega^\circ(E)$ | 4 | 32 | |

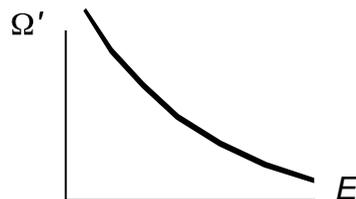
Hence, once the systems are put in thermal contact, and constraints are placed on the energy of the combined system, then the probability distribution in a subsystem may be changed.

The mean value of E to which subsystem A changes once the systems are placed in thermal contact (and the total energy is constrained!) can be calculated from the distribution of total states P^o , as a function of E . Let's move away from our numerical example, and consider the problem in general.

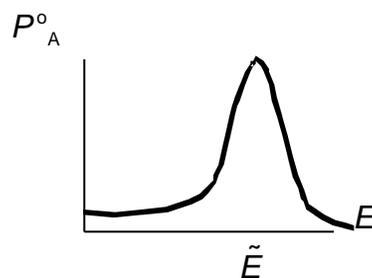
The number of states Ω of A as a function of E generally increases rapidly with E :



The number of states Ω' of A' generally increases rapidly with E' , and hence generally **d**ecreases rapidly with $E = E^o - E'$ for fixed E^o



Hence, the probability P_A^o for system A , once its in contact with A' and the total energy is constrained, looks like



The most likely energy of A is now at \tilde{E} , which can be found by the usual calculus procedure of setting a derivative equal to zero. In this case, we take the derivative of the natural logarithm of P_A^o :

P_A^o is a maximum when

$$\frac{\partial \ln P_A^o(E)}{\partial E} = 0$$

whence

$$\begin{aligned} \frac{\partial}{\partial E} (\ln \Omega(E) + \ln \Omega'(E') - \ln \Omega_{TOT}^0(E)) &= 0 \\ \frac{\partial}{\partial E} \ln \Omega(E) - \frac{\partial}{\partial E'} \ln \Omega'(E') - 0 &= 0 && \text{(Cx2.8) } (\Omega_{TOT}^0 \text{ does not depend on } E) \\ \frac{\partial}{\partial E} \ln \Omega(E) &= \frac{\partial}{\partial E'} \ln \Omega'(E') \end{aligned}$$

Note that a minus sign arises in changing from $\partial/\partial E$ to $\partial/\partial E'$.

This equation by itself does not specify \tilde{E} : rather, it gives a family of E - E' values for which the slopes of the two distributions agree. To determine which member of the family is the solution, one must impose the condition

$$E' = E^0 - E.$$

At equilibrium, $\ln \Omega / E$ is the same for both systems in thermal contact, according to Eq. (Cx2.8). Thus, $\ln \Omega / E$ is a very useful quantity, which we define as β :

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{1}{k_B T} \quad \text{(Cx2.9)}$$

Units:

β^{-1} has units of energy

k_B is a constant, with units of energy

T is a dimensionless parameter, identified with temperature.

As will be shown, $\ln \Omega$ is also a useful quantity. Using the same constant k_B , we define another quantity called the entropy

$$S = k_B \ln \Omega. \quad \text{(Cx2.10)}$$

Hence, the temperature can alternately be extracted from

$$T = \frac{\partial S}{\partial E} \quad \text{(Cx2.11)}$$

At equilibrium, maximizing P implies that

$S + S'$ is a maximum

$T = T'$ (systems in thermal contact have the same temperature).