Lecture 10 - Systems in thermal contact

What's Important:

- heat flow
- heat reservoirs
- thermal contact
- mechanical contact

Text: Reif

Heat flow (not covered in class)

This result is rather intuitive, but is worthwhile establishing nevertheless. Suppose that only an infinitesimally small amount of heat is exchanged between two systems A and A'. Then, the condition of increasing entropy is

$$\Delta S + \Delta S' \geq 0$$

$$\Delta\left(\ln\Omega(E)\right) + \Delta\left(\ln\Omega'(E')\right) \geq 0$$

$$\frac{\Delta\left(\ln\Omega(E)\right)}{\Delta E} \cdot \Delta E + \frac{\Delta\left(\ln\Omega'(E')\right)}{\Delta E'} \cdot \Delta E' \geq 0$$

$$ß \cdot \Delta E + ß' \Delta E' \geq 0$$

For small heat flows,

$$\Delta E \sim Q \qquad \Delta E' \sim -Q$$

such that

$$ßQ - ß'Q \geq 0$$

or

$$(ß - ß')Q \geq 0. \qquad (10.1)$$

What does this tell us about heat flow?

If A is colder than A', then

$ß \geq ß'$ and

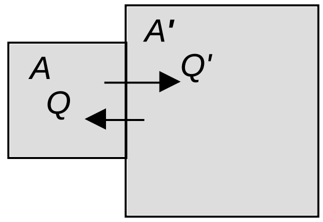
$(ß - ß') \geq 0.$

Eq. (10.1) then says that Q is positive for this situation: heat flows from A' (hot) to A (cold).

Heat reservoirs

We now consider the situation in which our system of interest A is much smaller (fewer accessible states) than system A'. This is the same as saying $\bar{E}' >> \bar{E}$, so any exchange of energy Q has only a negligible effect on $\bar{E}'$. System A' is called a heat reservoir; this strongly asymmetric situation is a very common one in everyday life.

At the reservoir:



Because Q' is small compared to $\bar{E}'$, we can perform a Taylor series expansion for the number of accessible states:

$$\ln\Omega'(E'+Q') = \ln\Omega'(E') + \frac{\partial \ln\Omega'}{\partial E'}\cdot\Delta E' + \frac{1}{2}\frac{\partial^2 \ln\Omega'}{\partial E'^2}(\Delta E')^2 + ...$$

Substituting

$$ß' = \frac{\partial \ln\Omega'}{\partial E'} \qquad \Delta E' \approx Q'$$

this becomes

$$\ln\Omega'(E'+Q') - \ln\Omega'(E') = ß'Q' + \frac{1}{2}\frac{\partial ß'}{\partial E'}(Q')^2 + ...$$

The derivative on the right-hand side is very small, because T varies slowly with E'. Thus, after multiplying by k_B:

$$k_B \ln\Omega'(E'+Q') - k_B \ln\Omega'(E') \approx k_B ß'Q'$$

Replacing $k_B\ln\Omega$ by the entropy, and taking the difference, yields

$$\Delta S' = \frac{Q'}{T'} \qquad \text{(at the reservoir)} \qquad (10.2)$$

In fact, for small changes in any system, this equation is valid

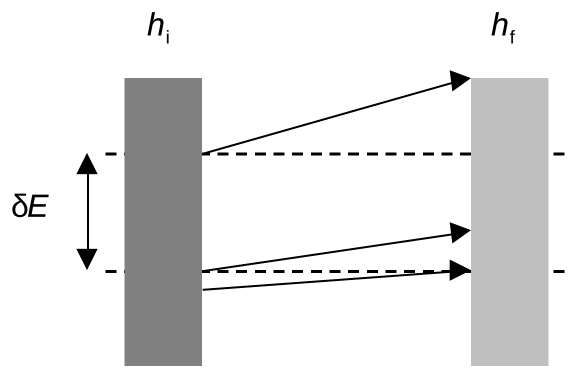
$$dS = \frac{đQ}{T} \qquad \text{(infinitesimal)} \qquad (10.3)$$

Systems in thermal and mechanical contact

The formalism is a little more complicated once mechanical contact is permitted as well as thermal contact. Let's start by considering a single system described by a set of characteristics $h_1 ... h_m$. In particular, we focus on what happens when only a single h is changed.

What happens when h changes from some initial value h_i to a new h_f?

- In the energy range δE, there will be a number of accessible states $\Omega(E)$. Some of these states will move out of δE after h is changed, while others will move in.
- We assume for now that all states move in the same direction (namely *up* in energy).



When h is changed by an amount dh, the energy of each microstate changes by an amount

$$[energyshift] = \frac{\partial E_r}{\partial h} dh \qquad (10.4)$$

For notational ease, break up the set of microstates as follows:

define $Y \equiv \frac{\partial E_r}{\partial h}$

define $\Omega_Y(E,h)$ = [*number of states with characteristic h and energy between E and E+dE Y between Y and Y+dY*]

Initially, then

$$\Omega(E,h_i) = \Sigma_Y \, \Omega_Y(E,h_i). \qquad (10.5)$$

We need to find the flux of states into and out of the energy range δE when h is changed to $h+dh$. Consider the states with a given Y (which will be summed over later in this calculation).

The energy range of states (with Y) that can move for a given dh is

[*energy range*] = $Y\, dh$.

The number of states per unit energy (with Y) is

$\Omega_Y(E,h) / \delta E$.

Thus, the number of states (with Y) that will move from less than E to more than E as h changes by dh is

$$\sigma_y(E) = (\Omega_Y(E,h) / \delta E) \bullet Y\, dh. \qquad (10.6)$$

To find the total number of states, we sum over all Y,

$$\sigma(E) = \Sigma_Y \, \sigma_y(E) = \Sigma_Y \, (\Omega_Y(E,h) / \delta E) \bullet Y\, dh \qquad \text{(move into range)}$$

or

$$\sigma(E) = \Omega(E,h)\frac{1}{\Omega(E,h)}\sum_Y \Omega_Y(E,h)Y\frac{dh}{\delta E}$$

$$= \Omega(E,h)\left[\frac{1}{\Omega(E,h)}\sum_Y \Omega_Y(E,h)Y\right]\frac{dh}{\delta E} \qquad (10.7)$$

$$= \frac{\Omega(E,h)}{\delta E}\overline{Y}\,dh$$

where $\overline{Y}$ is the mean value of Y in the range δE around E.

States move both **into** and **out of** the energy range of interest δE. The number moving out of the range (again assuming positive movement) is

$\sigma(E + \delta E)$ (move out)

Rearranging a little, the net number of states is

$$[net] = \sigma(E) - \sigma(E + \delta E) = -\frac{\delta\sigma}{\delta E}\delta E = -\frac{\partial\sigma}{\partial E}\delta E \qquad (10.8)$$

However, the net number is also

$$\frac{\partial\Omega(E,h)}{\partial h}\cdot dh \qquad (10.9)$$

Thus, subbing (10.7) into (10.8), and equating with (10.9)

$$\frac{\partial\Omega}{\partial h}dh = -\frac{\partial}{\partial E}\left[\frac{\Omega(E,h)}{\delta E}\overline{Y}\,dh\right]\cdot\delta E$$

$$\frac{\partial\Omega}{\partial h} = -\frac{\partial}{\partial E}\left[\Omega(E,h)\overline{Y}\right]$$

$$= -\frac{\partial\Omega}{\partial E}\overline{Y} - \Omega\frac{\partial\overline{Y}}{\partial E}$$

Divide both sides by Ω to give

$$\frac{1}{\Omega}\frac{\partial\Omega}{\partial h} = -\frac{1}{\Omega}\frac{\partial\Omega}{\partial E}\overline{Y} - \frac{\partial\overline{Y}}{\partial E}$$

$$\frac{\partial\ln\Omega}{\partial h} = -\frac{\partial\ln\Omega}{\partial E}\overline{Y} - \frac{\partial\overline{Y}}{\partial E} \qquad (10.10)$$

Now, the first term in Eq. (10.10) on the right hand side is huge compared to the second term. For example,

$\Omega \sim E^{f/2}$ -> $\ln\Omega \sim (f/2)\ln E$

from which

$$\frac{\partial \ln \Omega}{\partial E} \sim \frac{f}{2E}.$$

In other words, the first term grows rapidly with f, while the second term has no f -dependence. Thus,

$$\frac{\partial \ln \Omega}{\partial h} = -\frac{\partial \ln \Omega}{\partial E} \overline{Y}$$

But the inverse temperature ß is defined by

$$\frac{\partial \ln \Omega}{\partial E} = ß$$

and $\overline{Y}$ has the form of a generalized force (derivative of an energy with respect to a generalized coordinate)

$$\overline{Y} = \frac{\partial E_r}{\partial h} = -\phi_h$$

Thus, we have

$$\frac{\partial \ln \Omega}{\partial h} = +ß\phi_h \qquad \text{(generalized force)} \qquad (10.11)$$

Quasi-static processes

As a final step, we apply our results from the microscopic approach of statistical mechanics to the macroscopic language of thermodynamics. Let two systems be placed in mechanical contact, with a time scale slow enough that the energy of the systems changes quasi-statically, maintaining equilibrium during the change. In the process:

$\overline{h}_\alpha$ changes to $\overline{h}_\alpha + d\overline{h}_\alpha$ for coordinate labels α

$\overline{E}$ changes to $\overline{E} + d\overline{E}$ (equilibrium energy)

Then $\ln\Omega$ has the infinitesimal change (just a trivial expansion derivatives)

$$d \ln \Omega = \frac{\partial \ln \Omega}{\partial E} \cdot d\overline{E} + \sum_{\alpha=1}^{m} \frac{\partial \ln \Omega}{\partial h_\alpha} d\overline{h}_\alpha$$

or

$$d \ln\Omega = ß \, d\overline{E} + ß \, \Sigma_\alpha \, \phi_\alpha \, d\overline{h}_\alpha$$

where $\Sigma_\alpha \, \phi_\alpha \, d\overline{h}_\alpha$ is the work from the change in $\overline{h}_\alpha$. Substituting $ß = 1 / k_B T$ and $S = k_B \ln\Omega$, this becomes

$$d\left(\frac{S}{k_B}\right) = \frac{1}{k_B T} d\overline{E} + \frac{1}{k_B T} đW$$

$$T\,dS = d\overline{E} + đW = đQ$$

Thus,

$$dS = \frac{đQ}{T} \qquad \text{(quasi-static; thermal+mechanical contact)}$$

Notes:

- If the process is quasi-static and adiabatic, $dS = 0$. Therefore, if the external parameters of a thermally isolated system are changed quasi-statically, $\Delta S = 0$.
- It can also be shown (see Reif) that the temperatures and pressures of two systems in thermal and mechanical contact are equal.