

Physics 415 - Lecture 6

February 3, 2025

Summary

- Macrostate of a system specified by:
 - Fixed external parameters (x_1, x_2, \dots, x_n) . Ex: $x = V = \text{Volume}$.
 - Additional conditions on the system. Ex: Energy $E = \text{const}$ (closed system).
- Interaction between macroscopic systems A and B (really, ensembles):
 - Interaction leads to change in mean energy \bar{E} of A (say).
 - Interaction types:
 - * Thermal (Heat exchange Q).
 - * Mechanical (Work W).
 - First Law of Thermodynamics (infinitesimal form):

$$dQ = d\bar{E} + dW$$

where $d\bar{E}$ = small change in mean energy, dQ = small heat absorbed by A, dW = small work done *by* A.

Exact and Inexact Differentials (Mathematical Aside)

Explain difference between "d" and "d".

Consider a function $F(x, y)$ of two variables x and y . A small change $x \rightarrow x + dx$, $y \rightarrow y + dy$ leads to $F(x, y) \rightarrow F(x + dx, y + dy)$. The change dF is:

$$dF = F(x + dx, y + dy) - F(x, y)$$

Using Taylor expansion for small dx, dy :

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy$$

Let $A(x, y) = \frac{\partial F}{\partial x}$ and $B(x, y) = \frac{\partial F}{\partial y}$. Then $dF = A(x, y)dx + B(x, y)dy$. This is called an "exact differential". It is the differential of an actual function $F(x, y)$.

- In going from an initial point (x_i, y_i) to a final point (x_f, y_f) , the net change in F is:

$$\Delta F = F(x_f, y_f) - F(x_i, y_i) = \int_i^f dF = \int_i^f (A dx + B dy)$$

- The integral $\int_i^f dF$ is independent of the path taken in the (x, y) -plane between (x_i, y_i) and (x_f, y_f) . F is a "state function".

Now consider infinitesimal quantities of the form $\tilde{A}(x, y)dx + \tilde{B}(x, y)dy$ that are *not* the differential of any function $G(x, y)$. That is, there is no function G such that $\frac{\partial G}{\partial x} = \tilde{A}$ and $\frac{\partial G}{\partial y} = \tilde{B}$ simultaneously (mathematically, this requires $\frac{\partial \tilde{A}}{\partial y} = \frac{\partial \tilde{B}}{\partial x}$). We write such infinitesimal quantities using d :

$$dG = \tilde{A}(x, y)dx + \tilde{B}(x, y)dy \quad (\text{inexact differential})$$

In contrast to an exact differential, the integral

$$\int_i^f dG = \int_i^f (\tilde{A}dx + \tilde{B}dy)$$

is generally dependent on the path taken in the (x, y) -plane between the initial and final points.

Return to Physics

First Law: $dQ = d\bar{E} + dW$.

- $d\bar{E}$ is the difference between mean energies $\bar{E}_f - \bar{E}_i$. It's an exact differential because \bar{E} is a state function. If the system goes from initial macrostate i to final macrostate f , the change $\Delta\bar{E} = \bar{E}_f - \bar{E}_i = \int_i^f d\bar{E}$ is independent of the path (or process) used to go from i to f .
- In contrast, dW and dQ are generally inexact differentials. The total work $W_{if} = \int_i^f dW$ and total heat $Q_{if} = \int_i^f dQ$ do, in general, depend on the process (path) taken from i to f .

Special Cases:

- Thermally isolated system ($Q = 0 \implies dQ = 0$): Then $dW = -d\bar{E}$. The work done $W_{if} = -\Delta\bar{E}$ depends only on the energy difference and is path independent (for adiabatic processes).
- External parameters held fixed ($W = 0 \implies dW = 0$): Then $dQ = d\bar{E}$. The heat absorbed $Q_{if} = \Delta\bar{E}$ is independent of the process (as long as volume, etc., are constant).

Quasi-static Processes

A quasi-static process is one where system A interacts with system B (heat exchange + work) sufficiently slowly such that system A remains in equilibrium throughout the process.

- "How slowly?" depends on the microscopic "relaxation time" τ = time for the system to return to equilibrium if perturbed. The process must occur over times $t \gg \tau$.

For concreteness, consider a system whose Hamiltonian depends on a single external parameter x (e.g., x = Volume V). Let $q = (q_1, \dots, q_S)$ and $p = (p_1, \dots, p_S)$.

$$H = H(q, p; x)$$

If x changes in time, $x(t)$ (e.g., slow change in volume), we have:

$$\frac{dH}{dt} = \sum_i \left(\frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right) + \frac{\partial H}{\partial x} \dot{x}$$

Using Hamilton's equations $\dot{q}_i = \frac{\partial H}{\partial p_i}$ and $\dot{p}_i = -\frac{\partial H}{\partial q_i}$:

$$\begin{aligned}\frac{dH}{dt} &= \sum_i \left(\frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right) + \frac{\partial H}{\partial x} \dot{x} \\ &\implies \frac{dH}{dt} = \frac{\partial H}{\partial x} \dot{x} = \frac{\partial H}{\partial x} \frac{dx}{dt}\end{aligned}$$

Identifying H with the energy E of a specific microstate, $E = H(q, p; x)$, we can write:

$$\frac{dE}{dt} = \frac{\partial H}{\partial x} \frac{dx}{dt} \quad (\text{due to time-variation of } x)$$

In a small time dt , the change in energy for this microstate is:

$$dE = \frac{\partial H}{\partial x} \frac{dx}{dt} dt = \frac{\partial H}{\partial x} dx \quad (*)$$

In a quasi-static process, at each time t the system is in equilibrium. We average $(*)$ over the equilibrium ensemble corresponding to the value of x at time t :

$$d\bar{E} = \frac{\partial \bar{H}}{\partial x} dx$$

This change $d\bar{E}$ is due only to the change in the external parameter x . This corresponds to the work done *on* the system in an infinitesimal step:

$$dW_{on} = \frac{\partial \bar{H}}{\partial x} dx$$

The work done *by* the system is $dW = -dW_{on}$:

$$dW = -\frac{\partial \bar{H}}{\partial x} dx$$

We define the "generalized force" X conjugate to the external parameter x as:

$$X = -\frac{\partial \bar{H}}{\partial x}$$

Then the work done by the system is:

$$dW = X dx$$

(This is analogous to mechanical work $dW = F dx$).

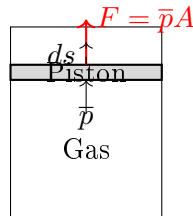
With multiple external parameters (x_1, x_2, \dots, x_n) :

$$dW = \sum_{\alpha=1}^n X_{\alpha} dx_{\alpha}$$

where $X_{\alpha} = -\frac{\partial \bar{H}}{\partial x_{\alpha}}$ is the generalized force conjugate to x_{α} .

Important Example: Work Done by Pressure

Let the external parameter be the volume, $x = V$. Consider a gas in a cylinder with a piston of cross-sectional area A .



The mean force on the piston due to the gas pressure is $F = \bar{p}A$. If the piston moves outward by a small amount ds , the work done *by* the gas is:

$$dW = F \times ds = (\bar{p}A)ds = \bar{p}(Ads)$$

Since $dV = Ads$ is the change in volume, we have:

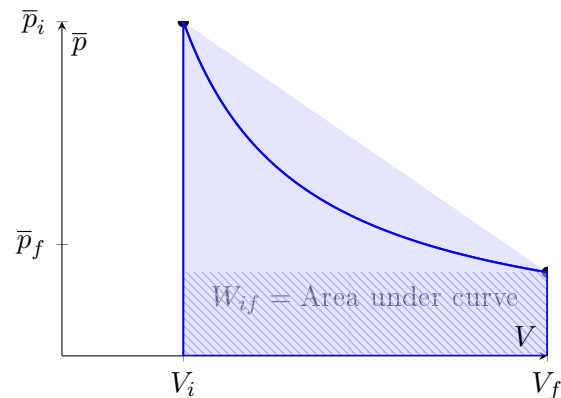
$$dW = \bar{p}dV$$

Here, the generalized force conjugate to volume V is the mean pressure \bar{p} .

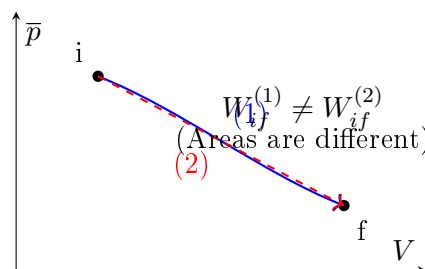
If the change in volume dV is quasi-static, then the system is in equilibrium at each volume V during the process, and we can compute the mean pressure \bar{p} at that volume, $\bar{p} = \bar{p}(V)$. When the system volume changes quasi-statically from $V_i \rightarrow V_f$, the total work done is:

$$W_{if} = \int_{V_i}^{V_f} dW = \int_{V_i}^{V_f} \bar{p}(V)dV$$

Since $\bar{p} = \bar{p}(V)$, we can graph this relationship in a pV -diagram.



Since $dW = \bar{p}dV$ is an inexact differential, the work W_{if} will, in general, depend on the process (the path taken in the pV -diagram).



Approach to Equilibrium

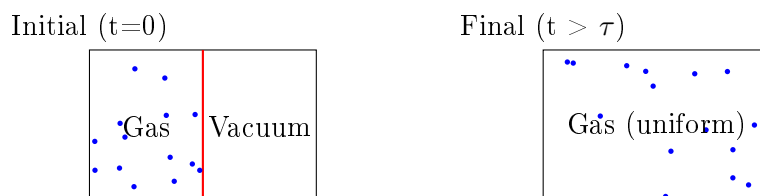
Return briefly to the notion of "equilibrium". Recall: For a given macrostate (determined, e.g., by fixed volume V and conserved total energy E), there are very many accessible μ -states ($\# = \Omega(E)$).

- **Equilibrium:** Probability to find the system in any μ -state, $P(\mu)$, is time-independent (\implies macro parameters are time-independent).
- **Postulate:** An isolated system in equilibrium is equally likely to be in any accessible μ -state.

What if a system is *not* equally likely to be in any accessible μ -state?

- By the postulate above, this situation cannot be equilibrium.
- The system will evolve in time.

Example: Gas initially confined to 1/2 of a box by a partition.



Immediately after the partition is removed, the system is not equally likely to be in any accessible state (since 1/2 of the container is empty). This situation will not last long. The system will evolve with time, and after a relatively short time ($\sim \tau$), the density of particles will be uniform over the entire box. The system reaches a new equilibrium state.

General Principle:

- If at some time t , an isolated system is only in a subset of accessible states, we anticipate a time-evolution toward a distribution in which *all* accessible μ -states are equally likely.
- Similarly, if we perturb an equilibrium system and drive it out of equilibrium, we expect the system will eventually return to equilibrium once the perturbation has been "turned off".
- Associated with the attainment of equilibrium is a time scale τ , the "relaxation time". The value of τ varies significantly between different systems.

(Proof of statements regarding approach to equilibrium is contained in Boltzmann's H-theorem - see Reif App. A.12).