Honors Classical Physics I

PHY141
Lecture 40
Thermodynamics & Statistics

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Other Machines

Refrigerator, air conditioner, heat pump:

- A refrigerator moves heat $Q_C$ from inside a cold box at temperature $T_C$ to the hotter outside at $T_H$

- A Carnot refrigerator is a Carnot engine running in the anticlockwise cycle:
  - it takes heat from a Cold reservoir at $T_C$ and “pumps” it into a high-temperature $T_H$ Hot reservoir,
  - while consuming $W$ ...

- **Coefficient of Performance** $COP$ is defined as:
  - the extracted heat $Q_C$ over the net work input $W$

  $$COP \equiv \frac{|Q_C|}{W} = \frac{|Q_C|}{(Q_H + Q_C)}$$

  $$\leq COP_{\text{Carnot}} = \frac{T_C}{(T_H - T_C)} = \left(\frac{T_H}{T_C} - 1\right)^{-1}$$

- Note: for a heat pump it is rather $Q_H/W$; $Q_H$ is the heat *delivered into* the house!
(Ir)reversible Processes

Reversible processes are processes that occur under quasi-equilibrium conditions: i.e. temperature and pressure differences are kept small, so that the path can be exactly reversed:

- We've met such a situation already: a gas expanding from 1 L to 2 L, ending at the same temperature as it started at. The two extremes:
  1. slow ISOTHERMAL expansion, $\Delta E_{\text{int}}=0$, moving a piston outwards while ADDING HEAT to the gas to counteract the cooling... Work $W=Q$ is done by the gas (piston moves out)

Q₁ ≠ Q₂!

This is a reversible process: extracting heat, while pressing the piston slowly in again will “recover” the original heat by doing the same work again...

2. “explosive” expansion (“FREE EXPANSION”) into a vacuum space of equal volume (thereby doubling the original volume). NO HEAT is added, but still the temperature stays constant (as observed by experiment). In this case: $W=0$, $Q=0$, and $\Delta E_{\text{int}} = 0$.

However, this process is IRREVERSIBLE, because to get back to the original state, we will have to do work as in 1, and thus take a DIFFERENT PATH back! the expanded gas will NEVER spontaneously regroup in one-half of the volume...

This can be traced back to the fact that the typical system contains an extremely large number of molecules (1 L at STP contains $2.7 \times 10^{22}$)
(Ir)reversible Processes – cont’d

• Note that the reversible isothermal expansion process and the free expansion process have exactly the same start and end points in the \( p-V \) diagram.

• The reversible process follows the isotherm:

\[
pV = \text{const.} \implies Q = W = nRT \ln(V_2/V_1)
\]

• However, the irreversible process does **not** follow a well-defined path in the \( p-V \) diagram: \( Q = W = 0 \), i.e. zero area under the curve \( p(V) \)!
Reversible Process Cycle

- only a QUASI-EQUILIBRIUM process is reversible (small $T$ or $p$ gradients!), e.g.:
  - slow ISOTHERMAL: no (large) $\Delta T$;
  - slow ADIABATIC ($Q = 0$)
  - Carnot engine works between constant temperature reservoirs:
- the CARNOT cycle has the best efficiency theoretically possible: $\varepsilon_{\text{Carnot}} = 1 - T_C/T_H$, i.e. always $< 100\%$!!
- any reversible cycle can be approximated by a sum of tiny Carnot cycles and will have the same (Carnot) efficiency if working between the same constant-temperature baths!
  - Engines working between non-constant temperature reservoirs are less efficient!
  - Any irreversible cycle is less efficient than the Carnot cycle: $\varepsilon \equiv 1 + Q_C/Q_H < \varepsilon_{\text{Carnot}} = 1 - T_C/T_H$
  - Real engines always have some irreversibility and thus are less efficient than the Carnot theoretical maximum...
Recap: Adiabatic Process

Some thermodynamic processes occur without exchange of heat with the environment, either because they are very rapid, or because the system is isolated or well insulated... a thermodynamic process where \( Q = 0 \) is called **ADIABATIC**

- for an adiabatic process \( Q = 0 \) by definition:
  
  1st Law: \( dQ = dE_{\text{int}} + dW = 0 \) (thus: \( W = -\Delta E_{\text{int}} = -nC_v\Delta T \))

  \[
  \Rightarrow dE_{\text{int}} = nC_v dT = -dW = -pdV = -nRT \frac{dV}{V}
  \]

- this leads to a differential equation:

  \[
  \frac{dT}{T} = -\frac{R}{C_v} \frac{dV}{V} \quad \Rightarrow \quad \ln T_2 - \ln T_1 = -\frac{R}{C_v} (\ln V_2 - \ln V_1);
  \]

  with \( \frac{R}{C_v} = \frac{C_p - C_v}{C_v} \equiv \gamma - 1 \) (\( \gamma \equiv \frac{C_p}{C_v} \)):

  \[
  \ln T_2 + (\gamma - 1) \ln V_2 = \ln T_1 + (\gamma - 1) \ln V_1 \quad \Rightarrow \quad T_2 V_2^{\gamma - 1} = T_1 V_1^{\gamma - 1} = \text{const.}
  \]

  \( TV^{\gamma - 1} = \text{const.} \), or: \( pV^\gamma = \text{const.} \), or \( p^{1-\gamma} T^\gamma = \text{const.} \)

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Randomness and Entropy $S$

A typical system contains a very large number of molecules which make random motions (collisions with walls, each other).

- E.g. when a billiard ball is dropped onto the table, the kinetic energy of motion of the ball will be (partially) conveyed to the molecules in the table, which transmit this energy on by successive, and randomizing collisions:
  - The originally "organized" macroscopic motion of the billiard ball is (partially) converted into additional random motion (internal energy) of molecules in the table... Randomness is increased!
  - The original energy is now in random motion energy and is (partially) unavailable for conversion back into useful energy...

- E.g. in a small reversible and isothermal (const. $T \Rightarrow \Delta E_{\text{int}}=0$) expansion $dV$ of a gas, the "randomness" of the molecules increases, simply because their relative position uncertainty increases as $dV/V$:
  - Isothermal process $\Rightarrow$ heat $dQ= pdV = nRT dV /V \Rightarrow dQ / T = nR dV /V$
  - We take $dS \equiv dQ /T$ as a measure of the increase in randomness!

$S$ is called the system's ENTROPY

- In a REVERSIBLE process: $\Delta S = S_2 - S_1 = \int_1^2 dQ / T$
- In a REVERSIBLE ISOTHERMAL process $\Delta S = Q / T$
- Entropy $S$ is a STATE VARIABLE (as $p, T, V, n, E_{\text{int}}$)
the change in Entropy of a system in a given process ...

A. depends on the detailed path in the $p-V$ diagram
B. can only be calculated if the process is reversible
C. depends only on the end points of the process
Entropy Change

Entropy change $dS$ in an arbitrary reversible process for an ideal gas:

$$dQ = dE_{\text{int}} + dW = nC_V dT + pdV$$

$$dS \equiv \frac{dQ}{T}_{\text{rev}} = nC_V \frac{dT}{T} + \frac{pdV}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

- note, that the right-hand side can always be simply integrated (unlike $dQ$!), because $C_V$ is (at worst) a function of $T$ only.

- the entropy change $\Delta S = \int^2_1 dS$ is perfectly determined, and only depends on the endpoints $(p_1, V_1, T_1), (p_2, V_2, T_2)$: i.e. $S$ is a STATE VARIABLE!

- in any CYCLICAL reversible process, the $\Delta S$ of the system over a complete cycle is ZERO

- taking (for simplicity) $C_p = C_V + R$ constant:

$$\Delta S = \int^2_1 dS = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \text{(expressed in } T, V)$$

$$= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{T_2 p_1}{T_1 p_2} = nC_V \ln \frac{T_2}{T_1} + nR \left( \ln \frac{T_2}{T_1} - \ln \frac{p_2}{p_1} \right)$$

$$= nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1} \quad \text{(in } T, p) = nC_V \ln \frac{p_2}{p_1} + nC_p \ln \frac{V_2}{V_1} \quad \text{(in } V, p)$$
Entropy Examples

• 0.50 kg of 0 °C ice heated to water of 100 °C at 1 atm:
  • \[ \Delta S_f = mL_{f,\text{water}}/T = mL_{\text{water}}/273 = 612 \text{ J/K} \]
  • \[ \Delta S_h = \int mc_{\text{water}}dT/T = mc_{\text{water}} \ln(373/273) = 653 \text{ J/K} \]

• a **reversible isothermal** process: \((dQ = pdV)\)
  • \[ \Delta S = \int^2 pdV/T = \int^2 nRdV/V = nR \ln(V_2/V_1) = nR \ln(p_1/p_2) \]

• a **reversible isobaric** process: \((dQ = nC_p dT)\)
  • \[ \Delta S = nC_p \ln(T_2/T_1) \]

• a **reversible adiabatic** process: \((dQ = 0)\)
  • \[ \Delta S = \int_1^2 dQ/T|_{\text{rev}} = 0 \]
  ➢ in the latter three processes the entropy change of the environment (typically) balances \(\Delta S\) of the **reversible** process, so that the **net entropy change** of the “universe” is **zero**

• an **IRREVERSIBLE adiabatic** process (called “free expansion”):
  - we need a **reversible path** between 1 \(\rightarrow\) 2 in order to calculate \(\Delta S\): a **reversible isothermal** process is the obvious choice (Note: \(Q\) is NOT a state variable!)
    • \[ \Delta S = \int nRdV/V = nR \ln(V_2/V_1), \text{ i.e. an increase in the entropy of the gas ...} \]
    • because no heat is exchanged with the environment \((Q_{\text{env}} = 0)\) the entropy of the environment is unchanged ➢ the **net entropy of the universe increased** in this **irreversible** process!