Physics 207, Lecture 28, Dec. 11

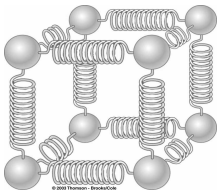
- Agenda: Ch. 21 Finish, Start Ch. 22
  - ❖ Ideal gas at the molecular level, Internal Energy
  - ❖ Molar Specific Heat (Q = m c ΔT = n C ΔT)
  - ❖ Ideal Gas Molar Heat Capacity (and ΔU_{int} = Q + W)
    Constant V: C_v= 3/2 R , Constant P: C_p = 3/2 R + R = 5/2R
  - ❖ Adiabatic processes (no heat transfer)
  - ❖ Heat engines and Second Law of thermodynamics
  - ❖ Reversible/irreversible processes and Entropy

Assignments:

- Problem Set 10 (Ch. 20 & 21) due Tuesday, Dec. 12, 11:59 PM
  Ch. 20: 13,22,38,43,50,**68** Ch.21: 2,16,29,36,70
- Problem Set 11, Ch. 22: 6, 7, 17, 37, 46 (Due, Friday, Dec. 15, 11:59 PM)
- Wednesday, Work on problem set 11

Lecture 28, Exercise *1*

- An atom in a classical solid can be characterized by three independent harmonic oscillators, one for the x, y and z-directions?
- How many degrees of freedom are there?



(A) 1 (B) 2 (C) 3 (D) 4 (E) Some other number

Ideal Gas Molar Heat Capacities

- Definition of molar heat capacities (relates change in the internal energy to the change in temperature)

$$C \equiv \frac{1}{n}\lim_{n\to\infty} Q/\Delta T = \frac{1}{n}\delta Q/\delta T$$

Ideal Gas Internal Energy

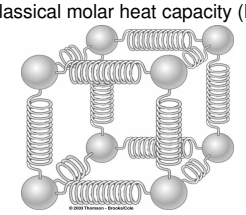
$$K_{\text{tot trans}} = U = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

- There is only microscopic kinetic energy (i.e., no springs) in a monoatomic ideal gas (He, Ne, etc.)
  - ❖ At constant V: Work W is 0 so ΔU = Q → $C_V = \frac{3}{2}R$
  - ❖ At constant P: ΔU = Q + W = Q - P ΔV $C_P = \frac{3}{2}R + R$

$$PV = nRT$$

Lecture 28, Exercise *2*

- An atom in a classical solid can be characterized by three independent harmonic oscillators, one for the x, y and z-directions (U per atom = 3 k_BT) ?
- What is the classical molar heat capacity (P ΔV ≅ 0 !)?



(A) nR (B) 2nR (C) 3nR (D) 4nR (E) Some other number

Adiabatic Processes

- By definition a process in which no heat tranfer (Q) occurs

For an Ideal Gas:

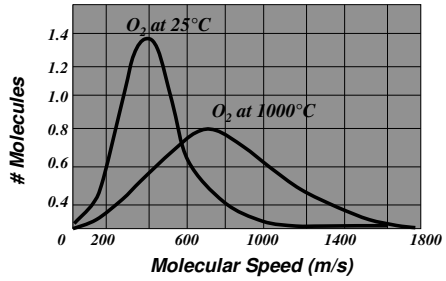
$$PV^{\gamma} = \text{const} \qquad \gamma \equiv \frac{C_P}{C_V}$$

- Adiabatic process:
  - ❖ PV^{γ} is constant
  - ❖ PV=nRT but **not** isothermal
  - ❖ Work (on system) becomes :

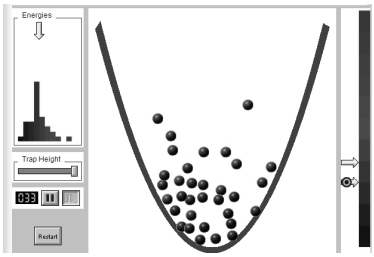
$$W = -\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} \frac{\text{const}}{V^{\gamma}}\frac{dV}{V} = \frac{\text{const}}{\gamma}\left(V_2^{-\gamma} - V_1^{-\gamma}\right)$$

Distribution of Molecular Speeds
Maxwell-Boltzmann Distribution

Very few gas molecules have exactly 3/2 k_BT of energy



Evaporative Cooling in a Bose-Einstein Condensation



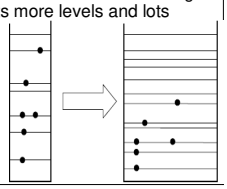
Evaporative cooling can lead to a state change

Granularity, Energy and the Boltzmann Statistics

- There are discrete number accessible energy levels in any finite system. It can be shown that if there are many more levels than particles to fill them the probability is just

$$P(E) = \exp(-E/k_BT)$$

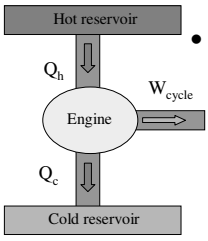
- The energy levels for a Quantum Mechanical (i.e., discrete quantized states) ideal gas is shown before and after a change (highly idealized diagram, imagine lots more levels and lots more particles).

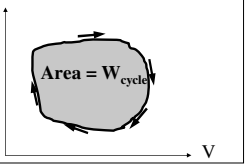


- Here we increase the box size slowly and perform a "quasistatic, adiabatic expansion"

Chapter 22: Heat Engines and the 2nd Law of Thermodynamics

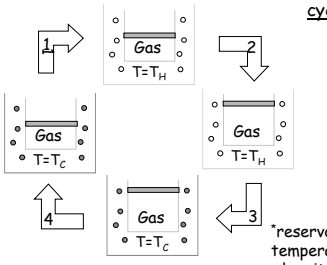
- A schematic representation of a heat engine. The engine receives energy Q_h from the hot reservoir, expels energy Q_c to the cold reservoir, and does work W.
- If working substance is a gas then we can use the PV diagram to track the process.



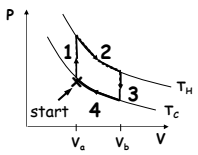


Heat Engines

- Example: The Stirling cycle



We can represent this cycle on a P-V diagram:



*reservoir: large body whose temperature does not change when it absorbs or gives up heat

Heat Engines and the 2nd Law of Thermodynamics

- A heat engine goes through a cycle (start and stop at the same point, same state variables)
  - 1st Law gives

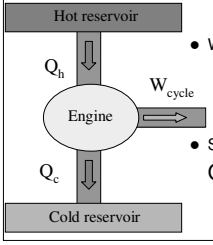
$$\Delta U = Q + W = 0$$

- What goes in must come out
  - 1st Law gives

$$Q_h = Q_c + W_{cycle} \quad (Q\text{'s} > 0)$$

- So (cycle mean net work on world)

$$Q_{net} = |Q_h| - |Q_c| = -W_{system} = W_{cycle}$$



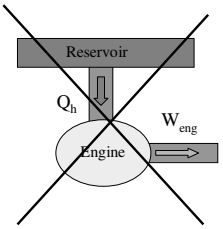
Efficiency of a Heat Engine

- How can we define a "figure of merit" for a heat engine?
- Define the efficiency ε as:

$$\varepsilon = \frac{W_{\text{cycle}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

Observation: It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work

Heat Engines and the 2nd Law of Thermodynamics



It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work.

This leads to the 2nd Law

Equivalently, heat flows from a high temperature reservoir to a low temperature reservoir

Lecture 28: *Exercise 3* Efficiency

- Consider two heat engines:
  - Engine I:
    - Requires Q_{in} = 100 J of heat added to system to get W=10 J of work (done on world in cycle)
  - Engine II:
    - To get W=10 J of work, Q_{out} = 100 J of heat is exhausted to the environment
- Compare ε_I, the efficiency of engine I, to ε_{II}, the efficiency of engine II.

$$\varepsilon = \frac{W_{cycle}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

(A) $\varepsilon_I < \varepsilon_{II}$

(B) $\varepsilon_I > \varepsilon_{II}$ (C) Not enough data to determine

Reversible/irreversible processes and the best engine, ever

- Reversible process:
  - Every state along some path is an equilibrium state
  - The system can be returned to its initial conditions along the same path
- Irreversible process;
  - Process which is not reversible !
- All real physical processes are irreversible
  - e.g. energy is lost through friction and the initial conditions cannot be reached along the same path
  - However, some processes are almost reversible
    - If they occur slowly enough (so that system is almost in equilibrium)

The Carnot cycle

Carnot Cycle

Named for Sadi Carnot (1796- 1832)

(1) Isothermal expansion
(2) Adiabatic expansion
(3) Isothermal compression
(4) Adiabatic compression

The Carnot Engine (the best you can do)

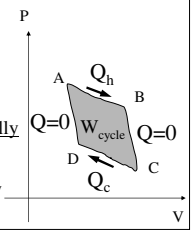
- No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

A. A→B, the gas expands isothermally while in contact with a reservoir at T_h

B. B→C, the gas expands adiabatically ($Q=0$, $\Delta U=W_{B\to C}$,$T_h \to T_c$), PV^γ=constant

C. C→D, the gas is compressed isothermally while in contact with a reservoir at T_c

D. D→A, the gas compresses adiabatically ($Q=0$, $\Delta U=W_{D\to A}$,$T_c \to T_h$)



Carnot Cycle Efficiency

$$\varepsilon_{Carnot} = 1 - Q_c/Q_h$$

$$Q_{A\to B} = Q_h = W_{AB} = nRT_h \ln(V_B/V_A)$$

$$Q_{C\to D} = Q_c = W_{CD} = nRT_c \ln(V_D/V_C)$$

(work done by gas)

But $P_AV_A=P_BV_B=nRT_h$ and $P_CV_C=P_DV_D=nRT_c$

so $P_B/P_A=V_A/V_B$ and $P_C/P_D=V_D/V_C$

as well as $P_BV_B^\gamma=P_CV_C^\gamma$ and $P_DV_D^\gamma=P_AV_A^\gamma$

with $P_BV_B^\gamma/P_AV_A^\gamma=P_CV_C^\gamma/P_DV_D^\gamma$ thus

$$\to \quad (V_B/V_A)=(V_D/V_C)$$

$$Q_c/Q_h = T_c/T_h$$

Finally

$$\varepsilon_{Carnot} = 1 - T_c/T_h$$

The Carnot Engine

- Carnot showed that the thermal efficiency of a Carnot engine is:

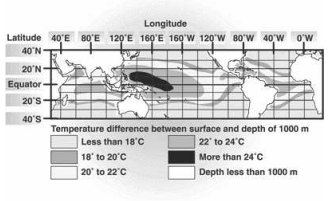
$$\varepsilon_{\text{Carnot cycle}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

- All real engines are less efficient than the Carnot engine because they operate irreversibly due to the path and friction as they complete a cycle in a brief time period.

Power from ocean thermal gradients… oceans contain large amounts of energy

Carnot Cycle Efficiency

$\varepsilon_{\text{Carnot}} = 1 - Q_c/Q_h = 1 - T_c/T_h$



See: http://www.nrel.gov/otec/what.html

Ocean Conversion Efficiency

$\varepsilon_{\text{Carnot}} = 1 - Q_c/Q_h = 1 - T_c/T_h$

$\varepsilon_{\text{Carnot}} = 1 - T_c/T_h = 1 - 275\text{ K}/300\text{ K}$

$= 0.083$ (even before internal losses and assuming a REAL cycle)

Still: "This potential is estimated to be about 10^{13} watts of base load power generation, according to some experts. The cold, deep seawater used in the OTEC process is also rich in nutrients, and it can be used to culture both marine organisms and plant life near the shore or on land."

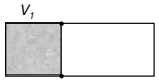
"Energy conversion efficiencies as high as 97% were achieved."

See: http://www.nrel.gov/otec/what.html

So $\varepsilon = 1 - Q_c/Q_h$ always correct but

$\varepsilon_{\text{Carnot}} = 1 - T_c/T_h$ only reflects a Carnot cycle

Lecture 28: *Exercises 4 and 5*
Free Expansion and the 2nd Law



You have an ideal gas in a box of volume V_1. Suddenly you remove the partition and the gas now occupies a large volume V_2.

(1) How much work was done by the system?

(2) What is the final temperature (T_2)?

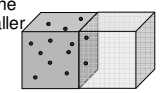
(3) Can the partition be reinstalled with all of the gas molecules back in V_1

1: (A) $W > 0$ (B) $W = 0$ (C) $W < 0$

2: (A) $T_2 > T_1$ (B) $T_2 = T_1$ (C) $T_2 > T_1$

Entropy and the 2nd Law

- Will the atoms go back?
  - Although possible, it is quite improbable
  - The are many more ways to distribute the atoms in the larger volume that the smaller one.
- Disorderly arrangements are much more probable than orderly ones



all atoms no atoms

- Isolated systems tend toward greater disorder
  - Entropy (S) is a measure of that disorder
  - Entropy (ΔS) increases in all natural processes. (The 2nd Law)
  - Entropy and temperature, as defined, guarantees the proper direction of heat flow.

Entropy and the 2nd Law

- In a reversible process the total entropy remains constant, $\Delta S = 0$!
- In a process involving heat transfer the change in entropy ΔS between the starting and final state is given by the heat transferred Q divided by the absolute temperature T of the system.

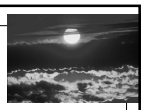
$$\Delta S \equiv \frac{Q}{T}$$

- The 2nd Law of Thermodynamics

"There is a quantity known as entropy that in a closed system always remains the same (reversible) or increases (irreversible)."

- Entropy, when constructed from a microscopic model, is a measure of disorder in a system.

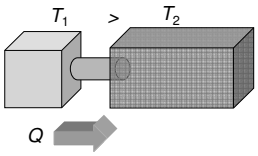
Entropy, Temperature and Heat



- Example: Q joules transfer between two thermal reservoirs as shown below
- Compare the total change in entropy.

$$\Delta S = (-Q/T_1) + (+Q / T_2) > 0$$

because $T_1 > T_2$



Entropy and Thermodynamic processes

Examples of Entropy Changes:

Assume a reversible change in volume and temperature of an ideal gas by expansion against a piston held at constant pressure ($dU = dQ – P\,dV$ with $PV = nRT$ and $dU/dT = C_v$):

$$\Delta S = \int_i^f dQ/T = \int_i^f (dU + PdV) / T$$

$$\Delta S = \int_i^f \{C_v dT / T + nR(dV/V)\}$$

$$\Delta S = nC_v \ln (T_f / T_i) + nR \ln (V_f / V_i)$$

Ice melting:

$$\Delta S = \int_i^f dQ/T = Q/T_{melting} = m L_f / T_{melting}$$

The Laws of Thermodynamics

- First Law
  You can't get something for nothing.
- Second Law
  You can't break even.
- **Do not forget: Entropy, S, is a state variable**

Recap, Lecture 28

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