The Nature of Thermodynamics

(Lecture 1)

1st semester, 2021

Advanced Thermodynamics (M2794.007900)

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(*) Some phrases in this lecture note are borrowed from the textbook of Ashley H. Carter.

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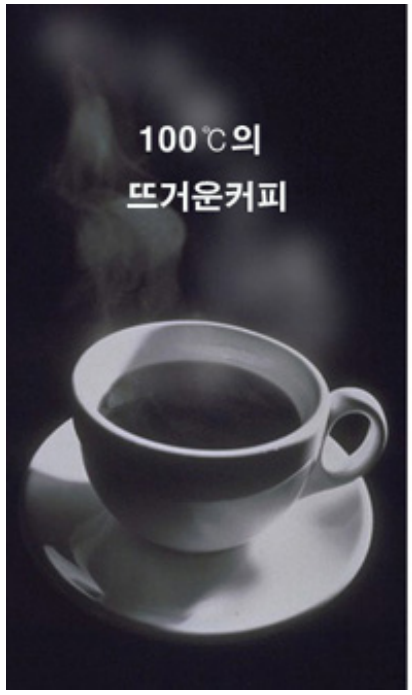
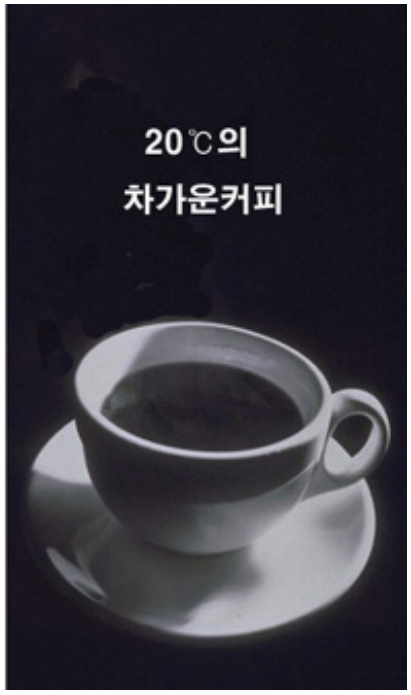
Can you figure out “energy conservation” below?



Energy of coffee
100 J

Heat
XX J



Energy of coffee
20 J

Which occurs “naturally”? (Environment at 20 °C)

Energy of coffee
100 J

1

2

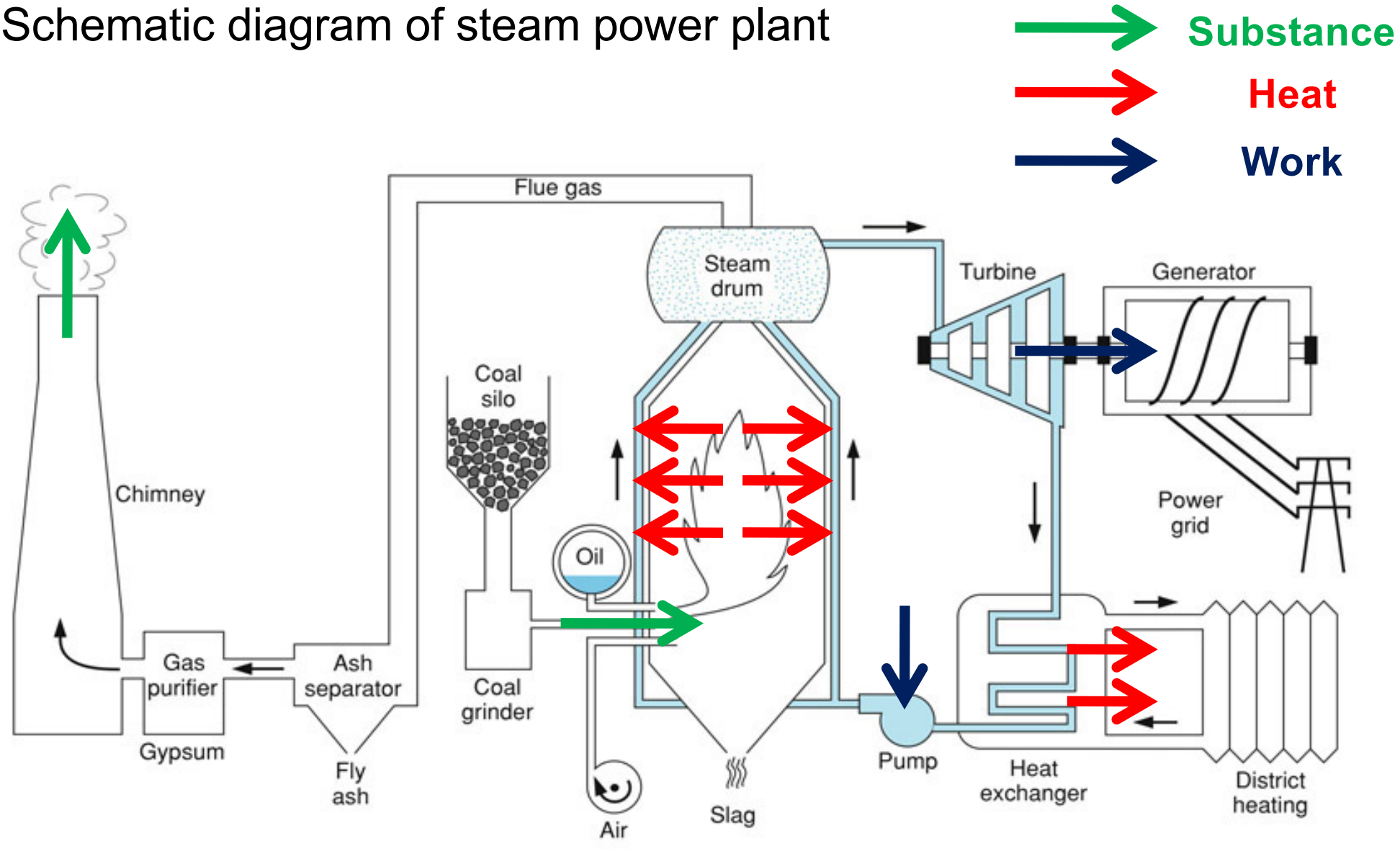
Energy of coffee
20 J

Energy of coffee
120 J

Thermodynamics

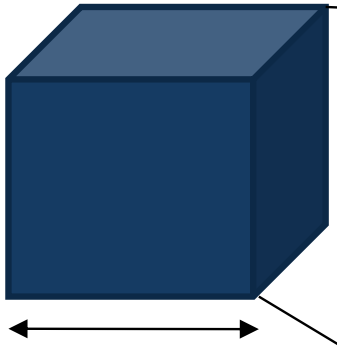
- Thermodynamics: the science of energy and entropy.
- Thermodynamics deals with heat and work and those properties of substances that bear a relation to heat and work.
- Like all sciences, the basis of thermodynamics is experimental observation (empirical). In thermodynamics these findings have been formalized into certain laws, zeroth, first, second and third laws of thermodynamics.
  - 0th law: defines temperature
  - 1st law: defines energy
  - 2nd law: defines entropy
  - 3rd law: gives numerical value to entropy

Schematic diagram of steam power plant



Classical vs. Statistical Thermodynamics

Macroscopic



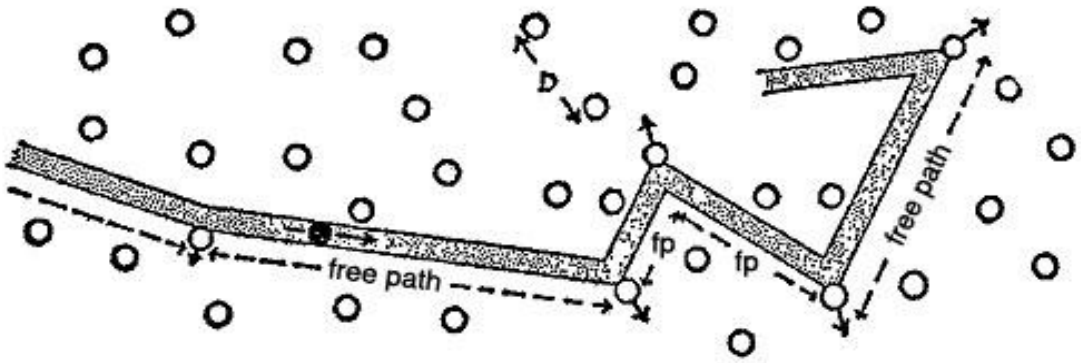
25 mm

Atmospheric P, T

Continuum

Microscopic

10^{20} atoms



Mean free path of a gas molecule

$6*10^{20}$ equations!

Classical Thermodynamics
-Averaged effect of many molecules

Statistical Thermodynamics
- Statistical and probabilistic approach

Classical vs. Statistical Thermodynamics

- Classical thermodynamics deals with experimental laws without considering the nature of matter.
  - Phenomenological theory to describe the macroscopic properties of matter, most of which are measurable
  - No discussion on the fine structure of material substances
  - In practice, this is quite useful!
- Statistical thermodynamics deals with molecular constitution of matter and provides a deeper foundation on which the laws of thermodynamics exist.
  - Kinetic theory was firstly introduced to understand the macroscopic properties of a gas, in terms of averaged properties of molecules, and expanded into the statistical thermodynamics.
  - Statistical thermodynamics encompasses the ideas of quantum mechanics with statistical approach.

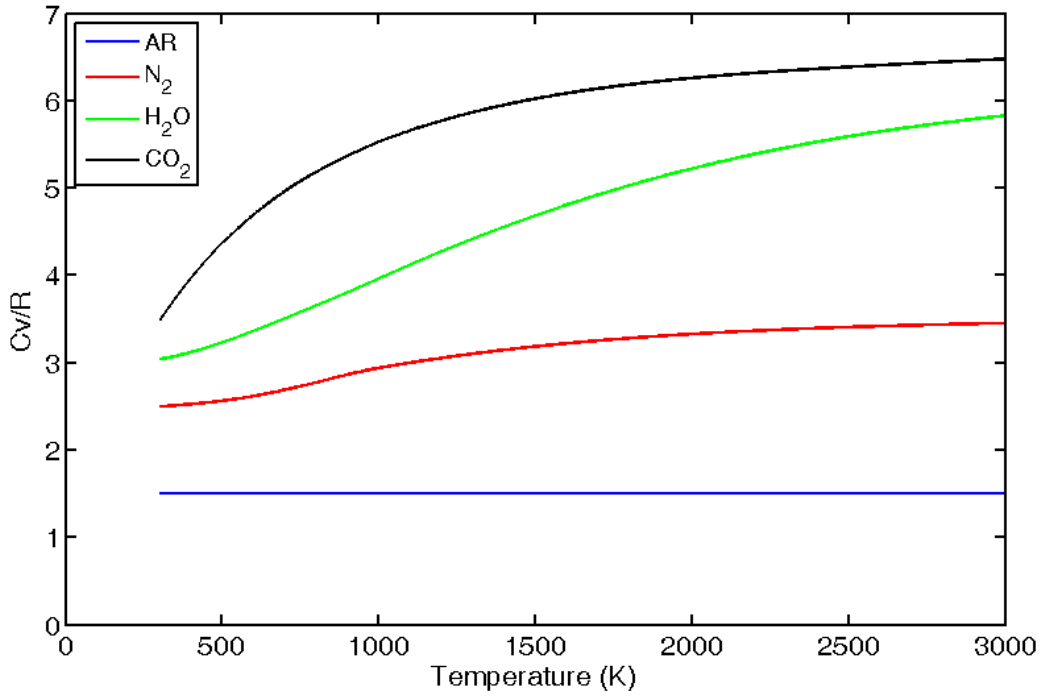
Specific Heats of Pure Substance

Ar (monatomic): $\tilde{c}_v = \tilde{c}_{v_{tr}} = (3/2)k_B$

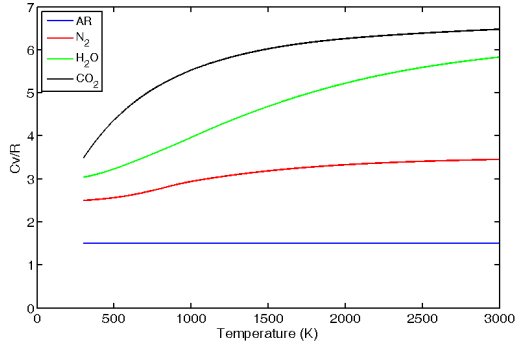
N_2 (diatomic): $\tilde{c}_v = \tilde{c}_{v_{tr}} + \tilde{c}_{v_{rot}} + \tilde{c}_{v_{vib}} = (5/2 \sim 7/2)k_B$

H_2O (non-linear polyatomic): $\tilde{c}_v = (3/2)k_B + (3/2)k_B + (3\times 3 - 6)k_B = (3 \sim 6)k_B$

CO_2 (linear polyatomic): $\tilde{c}_v = (3/2)k_B + k_B + (3\times 3 - 5)k_B = (5/2 \sim 13/2)k_B$



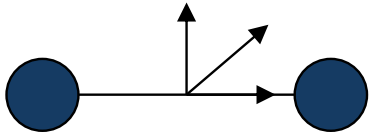
Specific Heats of Pure Substance



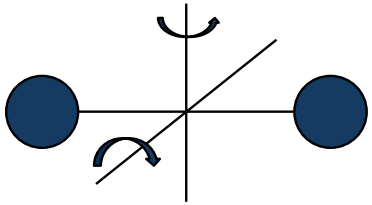
- Classical thermodynamics

$$c = \frac{1}{m}\left(\frac{\delta Q}{dT}\right) = \frac{\delta q}{dT} \quad (\mathrm{J/kg \cdot K})$$

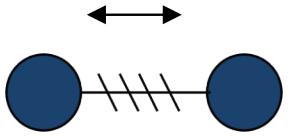
- Equipartition theory: The mean value of energy of a molecule corresponding to each degree of freedom of motion is $(R_u T)/2$ (per mole).



Translation = 3 * $R_u/2$



Rotation = 2 * $R_u/2$

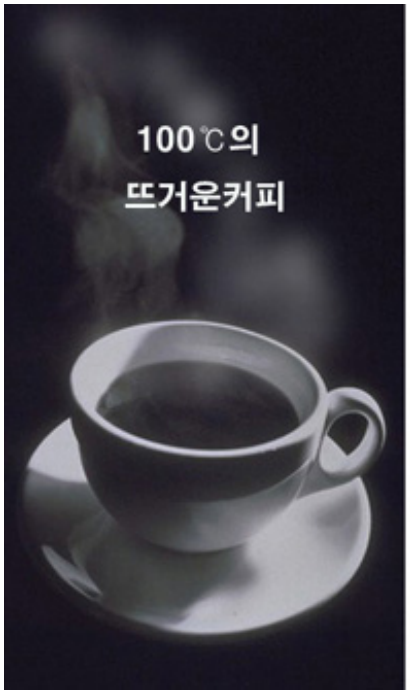


Vibration = 2 * $R_u/2$

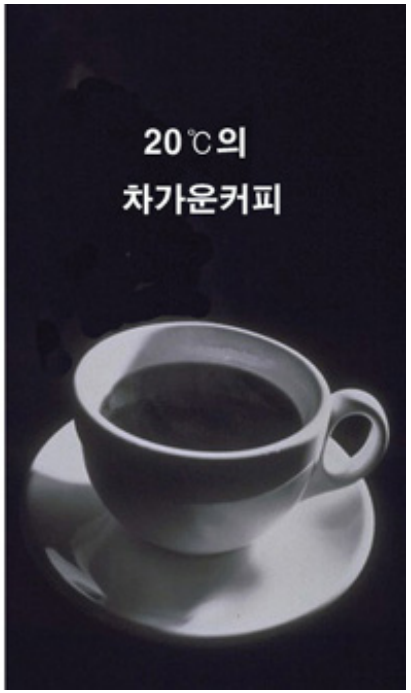
- Statistical thermodynamics: Statistical energy (or specific heat) of numerous molecules based on their quantum mechanical states and distributions.

ex) Vibration $\hat{c}_{v,vib} \equiv \left(\frac{\partial \hat{e}_{vib}}{\partial T}\right)_V = \hat{R}\left(\frac{\Theta_{\mathrm{vib}}}{\mathrm{T}}\right)^2 \frac{\exp(\Theta_{vib}/T)}{\left[\exp(\Theta_{vib}/T)-1\right]^2}$

What do we need to know?



substance, system, state, property, process, work, heat, matter transfer, energy, entropy..

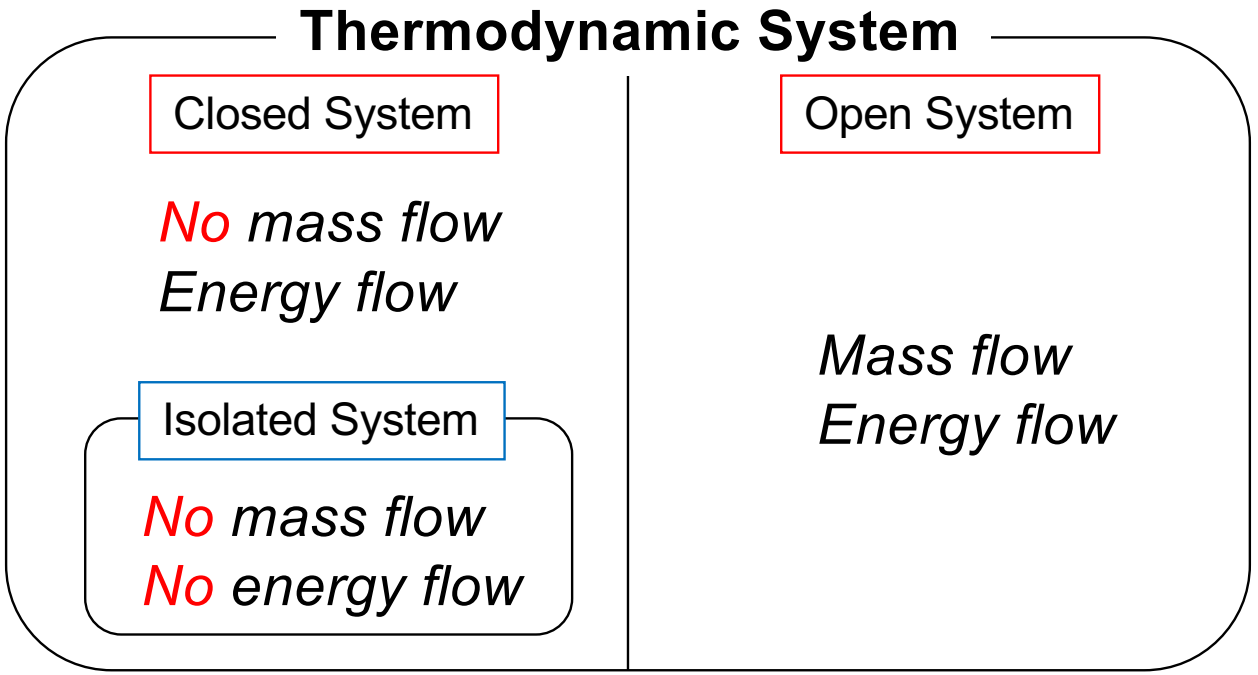


Thermodynamic Systems

- Thermodynamic system: a device or combination of devices containing a quantity of matter that is being studied

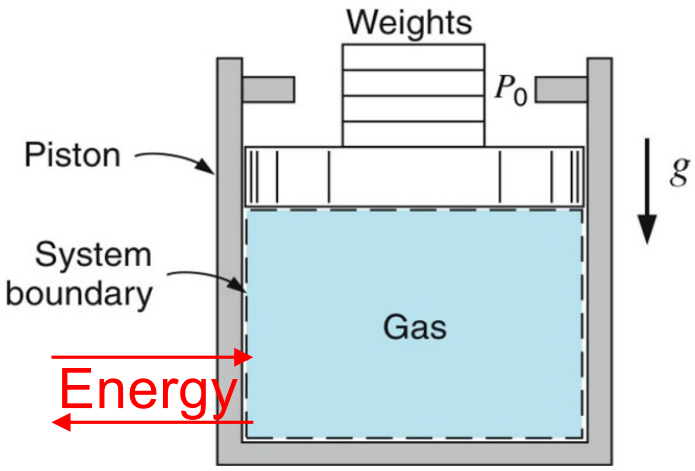
  → Classified as to whether they are open, closed, or isolated

- Surroundings: everything external to thermodynamic system

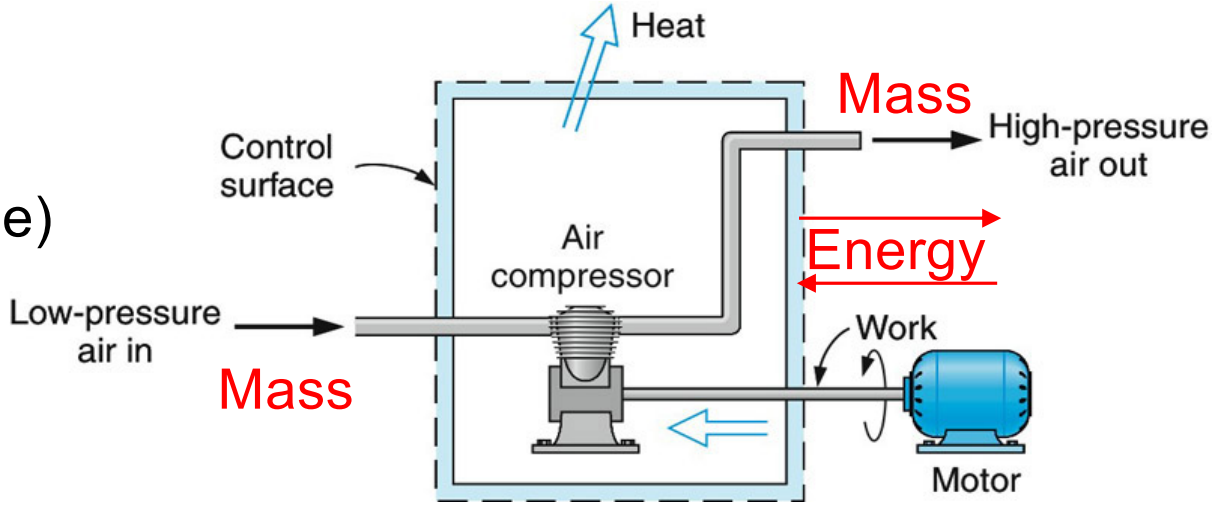


Thermodynamic Systems

Closed system(↔Control Mass)
- Mass transfer NO (fixed mass)
- Energy transfer allowed



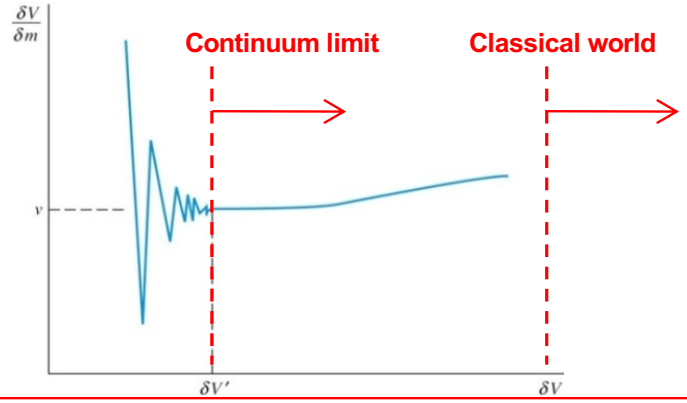
Open system (↔Control Volume)
- Mass transfer YES
- Energy transfer allowed



Thermodynamic Properties

- Definition: observables for the macroscopic behavior of a system
  - Extensive property: mass, volume, energy, etc. (proportional to mass)
  - Intensive property: pressure, temperature, etc. (independent of mass)

  (*) Specific property (extensive property / mass → Intensive property): density, etc.
- Classical thermodynamics is a continuum theory, and the properties vary smoothly from point to point in the system.
- For example, let's consider specific volume = volume / mass.

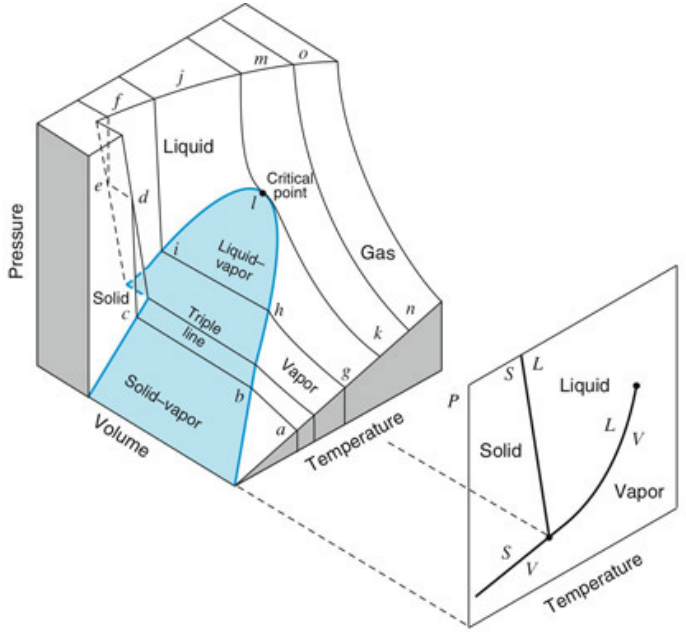


There is certain minimum volume (or dimension) for the validity of the continuum assumption!

To give you some sense,
1 kmol of molecules
→ 22.4 m^3 and 6.02×10^{26} molecules
→2.69×10^{25} molecules/m^3
→2.69×10^{16} molecules/mm^3
→2.69×10^{7} molecules/um^3
→??? molecules/nm^3

Thermodynamic States

- State: condition at which a thermodynamic system is uniquely specified
- Equilibrium state: the properties of the system are uniform throughout and don't change with time
- State variables: properties that describe (local) equilibrium states
- Equation of state (EOS): functional relationship among the state variables for a equilibrium system, typically given in *P*-*V*-*T* relation



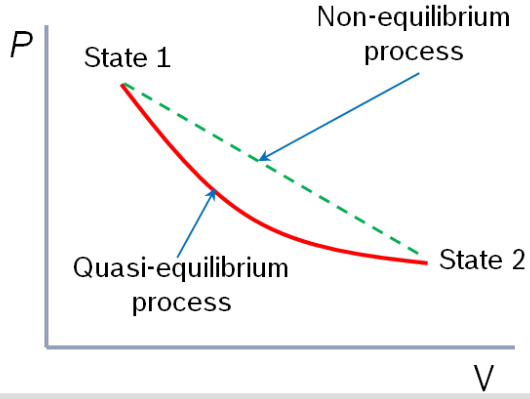
e.g. ideal gas EOS,
van der Waals EOS, etc.

or

$$\mathrm{F}(P,V,T)=0 \; or \; P=f(V,T)$$

Thermodynamic Process

- Process: path of state change
- States during a process?
  - Quasi-equilibrium (or Quasi-static) process: at any instant, the system is very close to an equilibrium state
  - Non-equilibrium process
- Reversible vs. Irreversible?
  - Reversible process: a quasi-equilibrium process without any dissipative forces, whose direction can be reversed by an infinitesimal change
  - Irreversible process: a process involving a finite change with dissipation
- Iso-(property) process: constant (property)
  - Isothermal: T=const.
  - Isobaric: P=const.
  - Isochoric: V=const.



Temperature

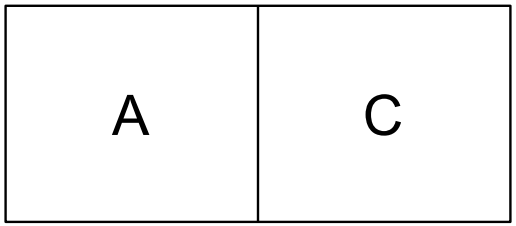
- Temperature: Sense of hotness or coldness, however, difficult to be rigorously defined
- Two objects in thermal contact for a long time → no change anymore → thermal equilibrium
- The Zeroth Law of Thermodynamics
  - Basis of temperature measurement
  - *If two systems are separately in thermal equilibrium with a third system, they are in equilibrium with each other*.

$$\text{if} \quad T_A = T_{thermometer}$$
$$T_B = T_{thermometer}$$
$$\text{then,} \quad T_A = T_B$$

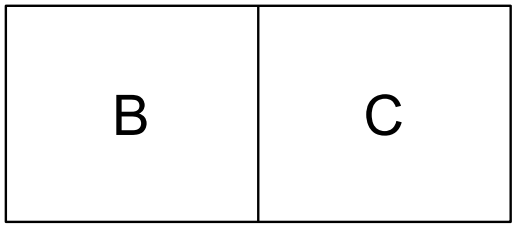
  - The zeroth law precedes 1st and 2nd law of thermodynamics.

Zeroth Law of Thermodynamics and Temperature

- The Zeroth Law of Thermodynamics
  - *If two systems are separately in thermal equilibrium with a third system, they are in equilibrium with each other*.



Systems A and C
in thermal equilibrium
through diathermal wall



Systems B and C
in thermal equilibrium
through diathermal wall

- By the equation of state for system C, its equilibrium state can be determined by measuring (P_c, V_c), or two independent properties.

Zeroth Law of Thermodynamics and Temperature (cont'd)

- From observation (yes, it's thermodynamics!), when thermal equilibrium between systems A and C (no more change in state by heat transfer) is achieved, the only single property can determine the equilibrium state of system A. For example, once P_A is given, V_A is uniquely determined. That is,

$$F_1(P_A, V_A, P_C, V_C)=0$$

- Re-arrange for P_c, $P_C=f_1(P_A, V_A, V_C)$
- Similarly for thermal equilibrium between systems B and C,

$$P_C=f_2(P_B, V_B, V_C)$$

- By equating these two equations for P_c, $f_1(P_A, V_A, V_C)=f_2(P_B, V_B, V_C)$
- Re-arrange for P_A, $P_A=g(V_A, P_B, V_B, V_C)$

Zeroth Law of Thermodynamics and Temperature (cont'd)

- According to the zeroth law of thermodynamics, systems A and B are in thermal equilibrium, and similarly,

$$F_2(P_A, V_A, P_B, V_B)=0$$

- Re-arrange for P_A, $P_A=f_3(V_A, P_B, V_B)$
- By comparing two arbitrary functions for P_A, i.e. g and f_3,

$$P_A=g(V_A, P_B, V_B, V_C) \quad and \quad P_A=f_3(V_A, P_B, V_B)$$

- g should NOT be a function of V_c. Since function g originates from

$$f_1(P_A, V_A, V_C)=f_2(P_B, V_B, V_C)$$

- Then, functions f_1 and f_2 should have a form to cancel functions of V_c out by the above equation, i.e.,

$$f_1 = \emptyset_A(P_A, V_A)\zeta(V_C) + \eta(V_C)$$
$$f_2 = \emptyset_B(P_B, V_B)\zeta(V_C) + \eta(V_C)$$

Zeroth Law of Thermodynamics and Temperature (cont'd)

- Finally, by the equations,

$$f_1(P_A, V_A, V_C) = f_2(P_B, V_B, V_C) \qquad \begin{aligned} f_1 &= \emptyset_A(P_A, V_A)\zeta(V_C) + \eta(V_C) \\ f_2 &= \emptyset_B(P_B, V_B)\zeta(V_C) + \eta(V_C) \end{aligned}$$

- Then, for certain unknown function Φ, $\emptyset_A(P_A, V_A) = \emptyset_B(P_B, V_B)$
- By extending to any system in thermal equilibrium,

$$\emptyset_A(P_A, V_A) = \emptyset_B(P_B, V_B) = \emptyset_C(P_C, V_C) = \emptyset_D(P_D, V_D) = \cdots$$

- One can define *T* (empirical temperature) for that unknown function, Φ, which becomes the same among the systems in thermal equilibrium. Or "temperature" is the property that can be derived from the thermal equilibrium.