

# Molecular Physics

WS 06/07

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## 1. Thermodynamics, Basics (Chapt. 1-5) (+ some statistical physics)

### 1.1. Temperature

Temperature  $T$  is the property that indicates the direction of the flow of energy (heat  $Q$ ) through a thermally conducting, rigid wall.

$$A \xrightarrow{\text{energy}} B \quad \Rightarrow \quad T_A > T_B$$

Thermal equilibrium is established if no change of state occurs when two objects A to B are in thermal contact

### Equipartition Theorem

At temperature  $T$ , the average energy of any quadratic degree of freedom of a molecule is  $\frac{1}{2} k_B T$

If a system contains  $N$  molecules, each with  $f$  degrees of freedom, and there are no other temperature-dependent forms of energy, then its total thermal energy is

$$\boxed{U = N \cdot f \cdot \frac{1}{2} k_B T}$$

### degrees of freedom:

monoatomic molecules  $f = 3$  translation

diatomic molecules  $f = 5$  1x translation  
2x rotation

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# Temperature and Brownian Motion (1-dim.)

Fick's law

$$j(x, t) = -D \frac{\partial c}{\partial x} \quad (1)$$

microscopic origin: random Brownian motion of molecules

continuity equation:  $\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} \quad (2)$

1+2  $\Rightarrow$   $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$  diffusion equation

+ external potential  $U(x) \Rightarrow F = -\frac{\partial U}{\partial x}$   
drift velocity  $v = -\frac{1}{\zeta} \frac{\partial U}{\partial x}$   
 $\zeta = 6\pi\eta r$  (Stokes)

$$\Rightarrow j = -D \frac{\partial c}{\partial x} - \frac{c}{\zeta} \frac{\partial U}{\partial x}$$

in equilibrium:  $c_{eq}(x) \sim e^{-U(x)/k_B T}$   $j_{eq} = 0$

$$\Rightarrow -D \frac{\partial c_{eq}}{\partial x} - \frac{1}{\zeta} c_{eq} \frac{\partial U}{\partial x} = 0$$

$$\Rightarrow \boxed{D = \frac{k_B T}{\zeta}} \quad \text{Einstein relation}$$

## 1.2. Ideal and Real gases

ideal (perfect) gas equation

$$\boxed{pV = nRT} \quad nR = Nk_B \Rightarrow \boxed{pV = Nk_B T}$$

mole concentration

molecules very dilute, no molecular interactions!

mixtures of perfect gases

$$p = \sum_i p_i \quad \text{--- particle pressures}$$

$$p_i = \frac{n_i RT}{V}$$

mole fraction  $x_j = \frac{n_j}{n} \quad n = \sum n_j$

$$p_i = x_j P$$

Real gases:

molecular interactions:

repulsive interactions  $\Rightarrow$  extremely short range,  
 $<$  molecular diameter

attractive interactions  $\Rightarrow$  short range,  
 $\sim \frac{1}{r^6}, r \gg 3$

proof: molecular interactions are short range

typical interaction potentials of 2 molecules

(multiple interactions):

$$U(r) = -C \frac{1}{r^n}$$

$$\rho = \frac{\text{molecules}}{\text{volume}}$$

⇒ total interaction energy of one molecule ( $\sigma$ : diameter) with all the other molecules in a space of size  $L$

$$U_{tot} = \int_{\sigma}^L U(r) \rho 4\pi r^2 dr = -4\pi C \rho \int_{\sigma}^L r^{2-n} dr$$

$$= -\frac{4\pi C \rho}{(n-3)\sigma^{n-3}} \left[ 1 - \left(\frac{L}{\sigma}\right)^{n-3} \right]$$

$$= \begin{cases} -4\pi C \rho / (n-3)\sigma^{n-3} & \text{for } n > 3 \quad L \rightarrow \infty \\ \infty & \text{for } n < 3 \quad L \rightarrow \infty \end{cases}$$

⇒ 
$$U_{tot}(r) = -C \frac{1}{r^n} \quad n > 3$$

⇒ molecular interactions are short range

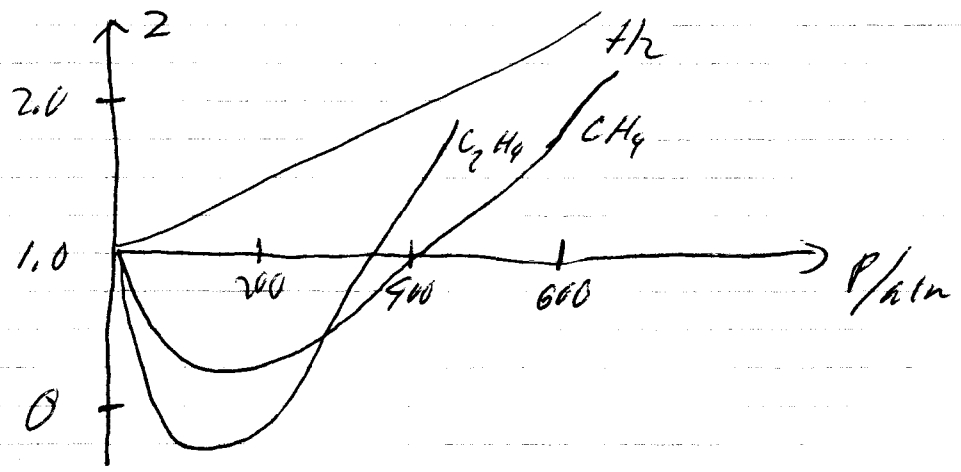
⇒ gas at low pressures ⇒ large molecule separations  
⇒ no interactions

⇒ gas at moderate pressures ⇒ smaller molecule separations  
⇒ attractive interactions  
⇒ higher compressibility

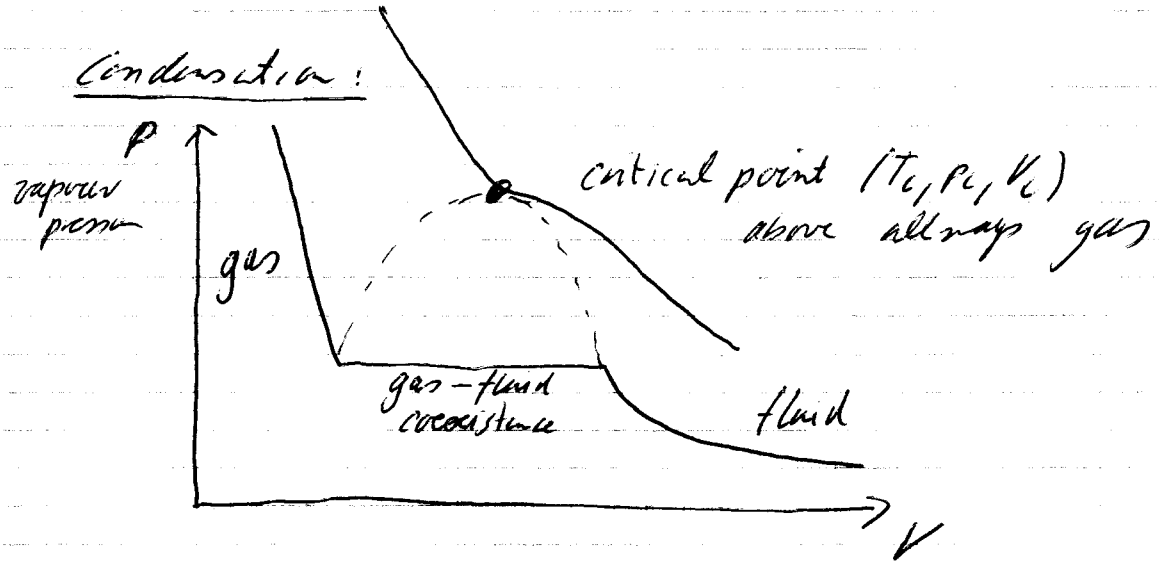
⇒ gas at high pressures ⇒ molecules in close contact  
⇒ repulsive interactions  
⇒ lower compressibility

Compression factor Z

$$Z = \frac{V_{molar}}{V_{molar, ideal}}$$



Condensation:



Van der Waals equation

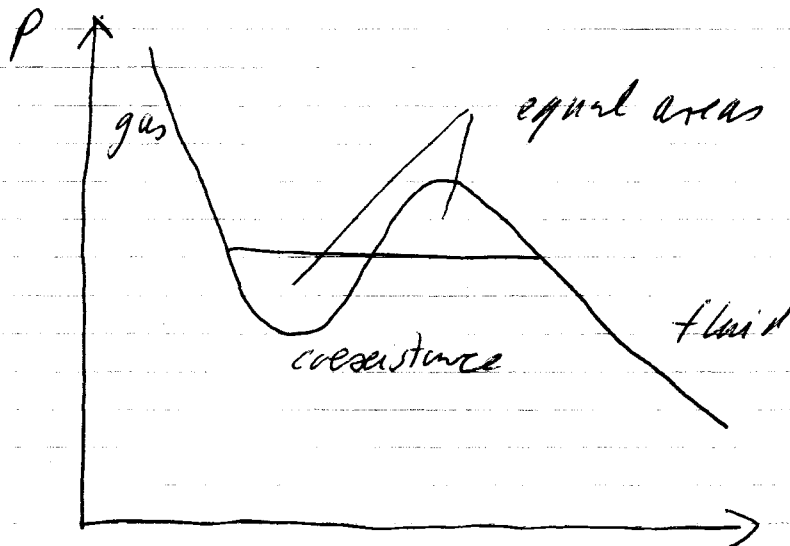
$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

a, b van der Waals coefficients

b:  $nb \approx 4 \times$  total volume taken up by the molecule  
 $\Rightarrow$  repulsion, hard core, exclude

a: attractive interactions lower frequency of collisions and impulses transferred to the walls  
 $\Rightarrow$  higher compressibility

limits, condensation:



# 1.3 Heat and Calorimetry

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## heat, molecular background:

heat: The disorderly molecular motion called thermal motion in the hot surroundings stimulates the molecules in the cooler system to move more and as a result the energy of the system is increased

work: Work is the transfer of energy that makes use of organized motion

## Energy distribution = Boltzmann distribution

number of molecules  $N$  in a sample of  $n$  molecules that will be found in a state with an energy  $E_i$  when it is part of a system in thermal equilibrium at a temperature  $T$

$$N = \frac{n e^{-E_i/k_B T}}{q}$$

$q$  partition fun.

$$q = \begin{cases} \int e^{-E/k_B T} dE & \text{classical} \\ \sum_i e^{-E_i/k_B T} & \text{quantum} \end{cases}$$

# The first law

$$U = q + W$$

↑            ↑  
 internal    heat    work  
 energy

## Reversibility:

A system is in equilibrium with its surrounding if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state

## Heat changes

$$dU = dq + dW_{exp} + dW'$$

$$V = \text{const}, W' = 0$$

$$\Delta U = q_V \Rightarrow \boxed{C_V = \left. \frac{\partial U}{\partial T} \right|_V}$$

heat capacity at constant volume

$$\Rightarrow dU = C_V dT \quad \text{for } V = \text{const}$$

- $C_V$  is a material property
- $C_V \rightarrow \infty \Rightarrow$  heat is absorbed, but no temperature change, latent heat is used for a phase transition e.g. melting of ice



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enthalpy  $H = U + pV$

change in enthalpy is equal to the heat supplied at constant pressure  $dH = dq$  for  $p = \text{const}$

$\Rightarrow$  heat capacity at constant pressure

$$H = U + pV = U + nRT \quad \text{ideal gas}$$

$$\Rightarrow \Delta H = \Delta U = \Delta nRT$$

$\Rightarrow$  heat capacity at constant pressure

$$C_p = \left. \frac{\partial H}{\partial T} \right|_p$$

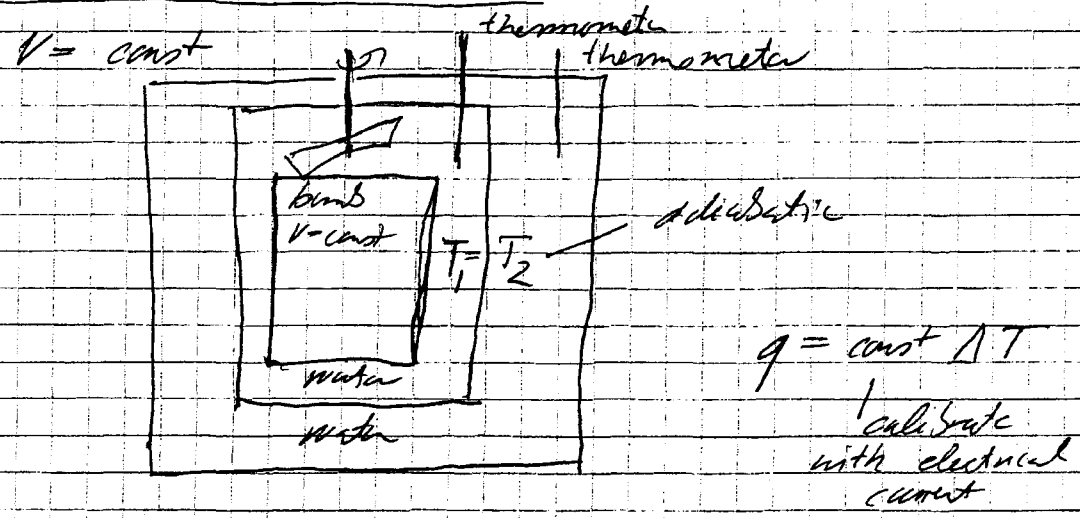
• for a perfect gas:  $C_p - C_v = nR$

•  $C_p$  is only independent of temperature for ideal monatomic gases

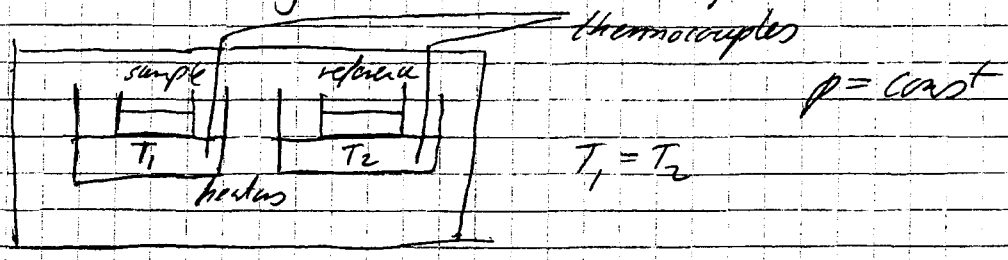
$$C_{p,m} \approx a + bT + \frac{c}{T^2}$$

Calorimetry (measuring heat changes)

(i) adiabatic bomb calorimeter



(ii) differential scanning calorimeter (DSC)



linear scan  $T = T_0 + \alpha t$

e.g. a endothermic process in the sample requires more heating in the sample to maintain  $T_1 = T_2$

$$q_p + q_{prex} = (C_p + C_{prex}) \Delta T \Rightarrow$$

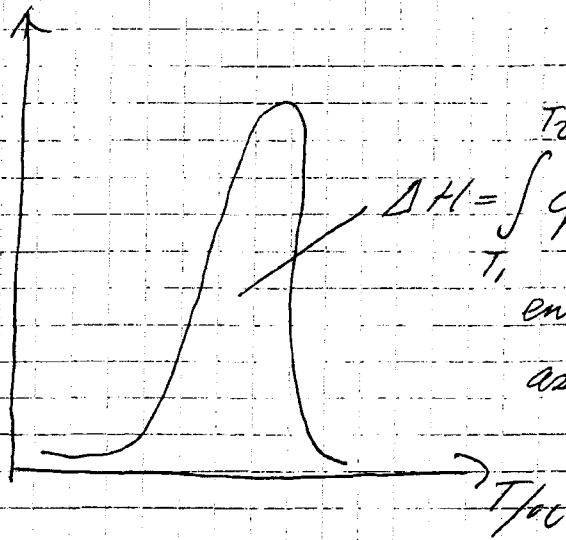
↑  
physical or chemical change in sample

↑  
apparent change in heat capacity

$$\Rightarrow C_{prex} = \frac{q_{prex}}{\Delta T} = \frac{1}{\alpha} \frac{q_{prex}}{t}$$

= electrical power necessary to equalize the temperature

$C_{p,ex}/mg$



- assess the stability of proteins, nucleic acids and membranes
- large molecules attain complex three-dimensional structures due to intra- and inter-molecular interactions such as hydrogen bonding and hydrophobic interactions. disruption of these interactions is an endothermic process that can be studied with a DSC
- phase changes in lipid membranes, insertion of proteins, demixing of lipid mixtures  $\rightarrow$  lipid rafts
- unfolding of protein, e.g. tau protein and Alzheimer
- melting of DNA