Summary of Lecture 6

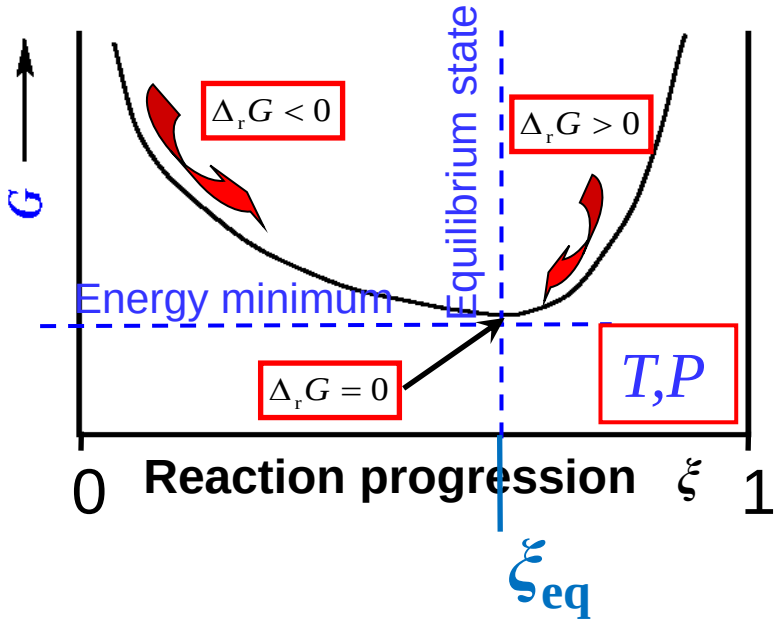
Electrolytic solutions and Electrochemistry

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

$$\Delta_r G = -\nu F E$$

$$E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$$

Nernst equation



reaction

$\Delta_r G < 0$ $E > 0$ →

$\Delta_r G > 0$ $E < 0$ ←

$\Delta_r G = 0$ $E = 0$ ⟷

$$Q = \prod_i a_i^{\nu_i} = \prod_i \gamma_i^{\nu_i} \left(\frac{b_i}{b^{\Theta}} \right)^{\nu_i}$$

Equilibrium:

$$\Delta_r G^{\Theta} = -RT \ln K \quad \Rightarrow \quad E^{\Theta} = +\frac{RT}{\nu F} \ln K$$

$$K = \left[\prod_i \gamma_i^{\nu_i} \left(\frac{b_i}{b^{\Theta}} \right)^{\nu_i} \right]_{eq}$$

Electrolytic solutions and Electrochemistry

Activity as an effective concentration

$$\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i$$

Molarity (mol/L)

$$c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}$$

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\Theta}}$$

$$c^{\Theta} \equiv 1\,\text{mol/L}$$

Molality (mol/kg)

$$b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\Theta}}$$

$$b^{\Theta} \equiv 1\,\text{mol/kg}$$

Mole fraction ( )

$$x_i = \frac{\#\,\text{mol solute } i}{\text{total } \#\,\text{mol in solution}} = \frac{n_i}{n}$$

$$a_i = \gamma_i^{(x)} x_i$$

Standard state **Θ**
(still *T* dependent)

$$P = P^{\Theta}$$

$$a_i^{\Theta} = 1$$

and pure

$$c_i^{\Theta} = 1\,\text{mol/L}$$

$$b_i^{\Theta} = 1\,\text{mol/kg}$$

$$x_i = 1$$

even for ions!

Activity coefficients solutes electrolytic solutions

$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

$$G_m(M_pX_q) = \mu = p\mu_+ + q\mu_-$$

chemical potential of the dissolved salt

average chemical potential per ion

$$\mu_i = \frac{\mu}{p+q} = \frac{\mu^{\text{ideal}}}{p+q} + \frac{RT}{p+q}\ln\left(\gamma_+^p \gamma_-^q\right)$$

Mean activity coefficient

$$\mu_i = \mu_i^{\text{ideal}} + RT\ln\gamma_\pm$$

$$\gamma_\pm \equiv \left(\gamma_+^p \gamma_-^q\right)^{1/s};\ s \equiv p+q$$

Debye-Hückel: $\log\gamma_\pm = -|z_+ z_-|AI^{1/2}$ **limiting law** $(b_i \approx \text{mmol/kg})$

Ionic strength $I = \frac{1}{2}\sum_i z_i^2 \frac{b_i}{b^\Theta}$

(sum over all ions in solution)

$$A = \frac{F^3}{4\pi N_A \ln(10)}\left[\frac{\rho b^\Theta}{2\varepsilon^3 R^3 T^3}\right]^{1/2}$$

A = 0.509 for H_2O @ 298 K

Lecture 7

Thermodynamics of surfaces and interfaces

Atkins (ed. 12, 11): §14C.2-C.4 + 4B.1(c) + Study Guide: P.20
Atkins (ed. 10): §16C.2-C.4 + 4.4(c) + Study Guide: P.20
Atkins (ed. 9): §17.8-17.10 + 4.4(c) + Study Guide: P.20

Statistical Thermodynamics

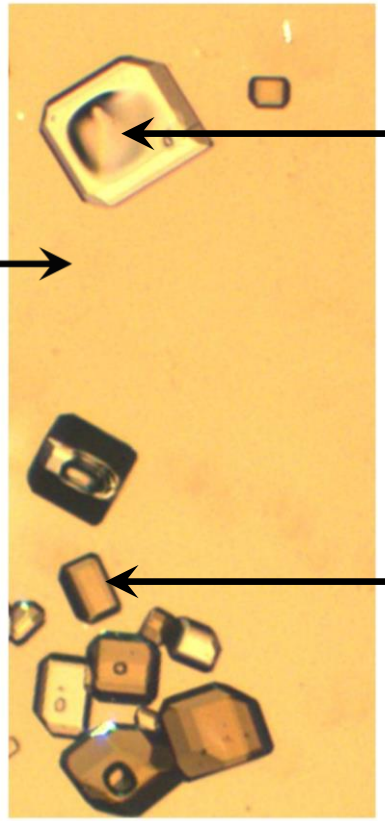
Study Guide: P.21-22

Entropy revisited

Study Guide: P.22-24

Thermodynamics of surfaces and interfaces

Na_2ClO_3 crystals in a saturated solution



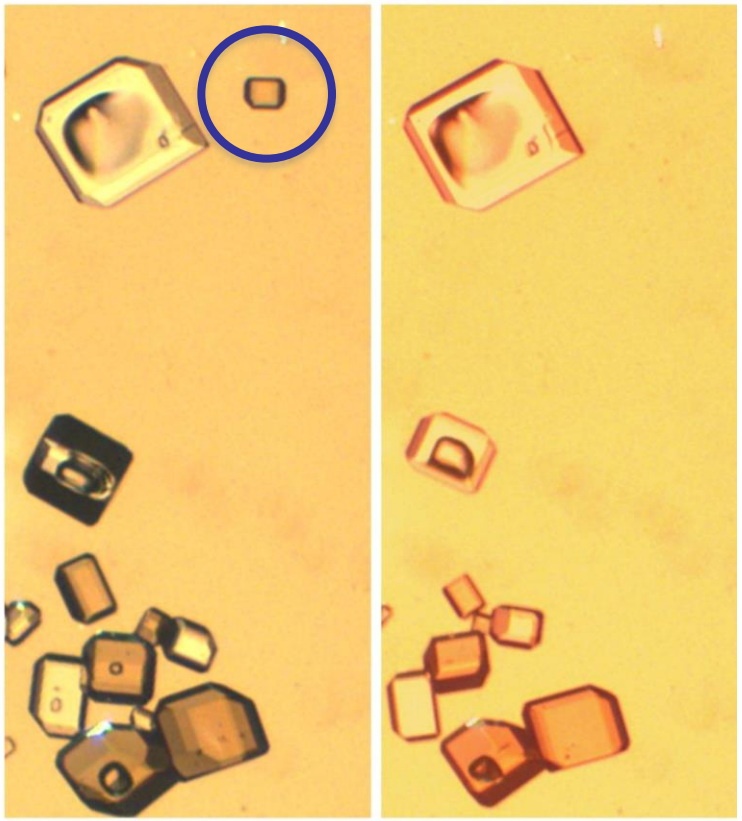
Saturated solution

Optically left rotating crystal

Optically right rotating crystal

Optical active crystals under polarizing microscope

Na_2ClO_3 crystals in a saturated solution



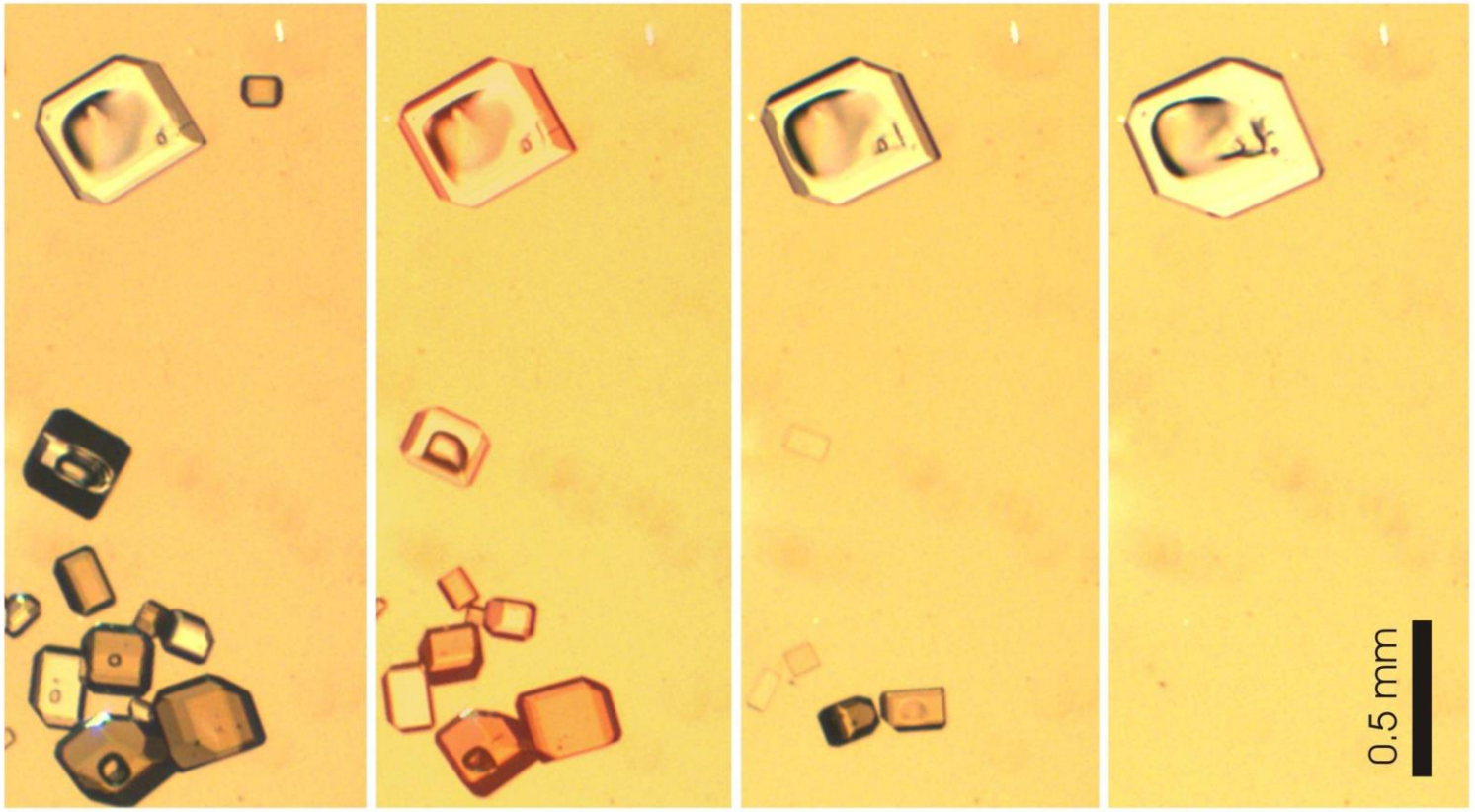
$T = 0$ $T = 1$ day

Wilhelm Ostwald
(1853-1932)

Ostwald ripening
(1896)

Large crystals grow; small crystals dissolve

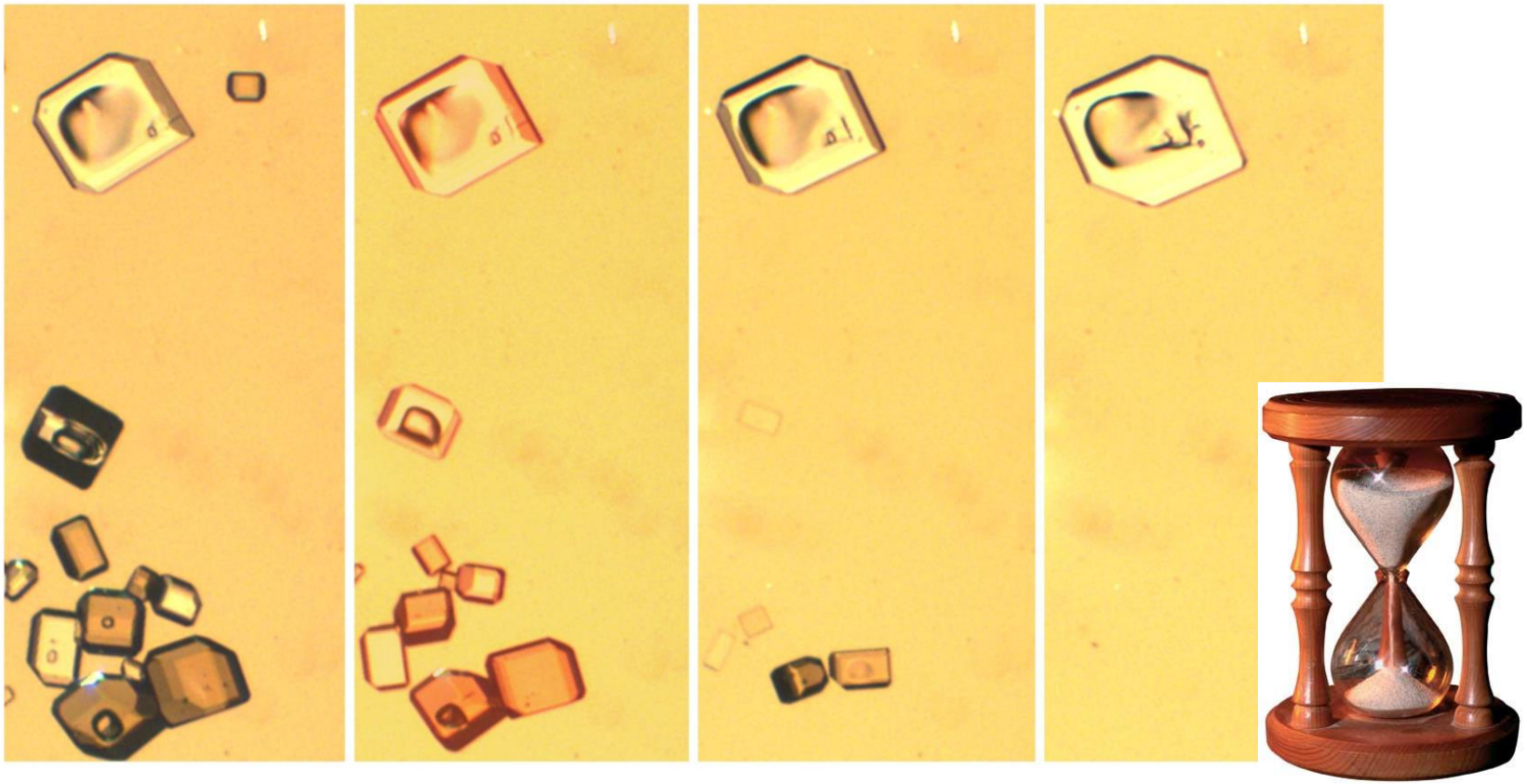
Na_2ClO_3 crystals in a saturated solution



$T = 0$ $T = 1$ day 10 days 30 days

Equilibrium: one single crystal of single handedness!

Na_2ClO_3 crystals in a saturated solution



$T = 0$ $T = 1$ day 10 days 30 days

Equilibrium: one single crystal of single handedness!

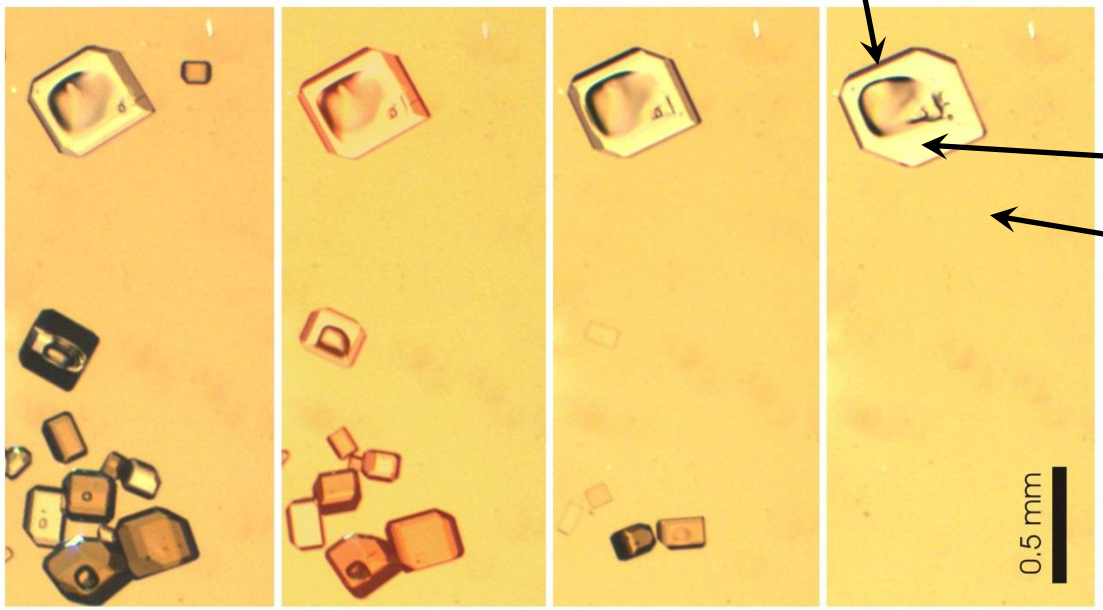
Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$dA = -SdT - PdV + dW_\sigma$$

σ : Interfacial surface

A : Helmholtz free energy



Gibbs-Thomson effect

Interfacial (free) energy between two phases

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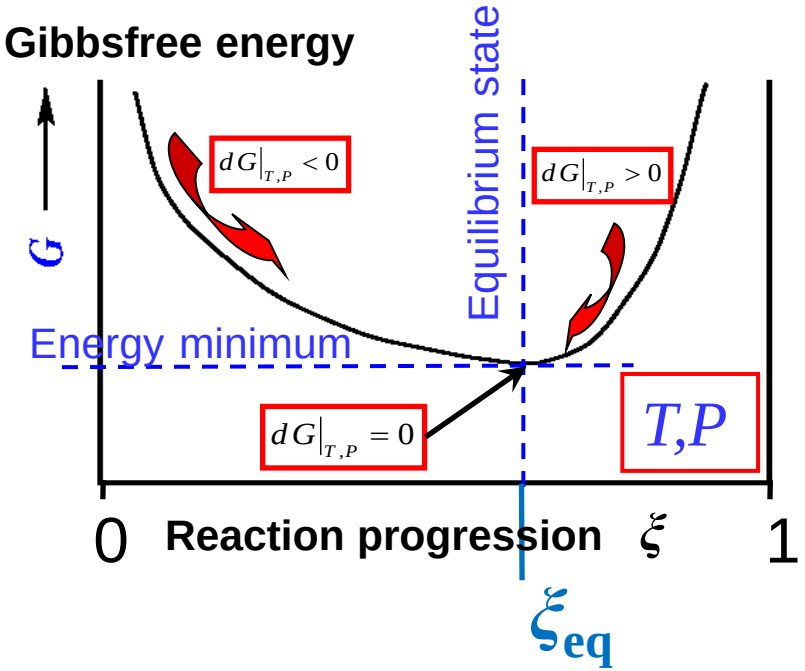

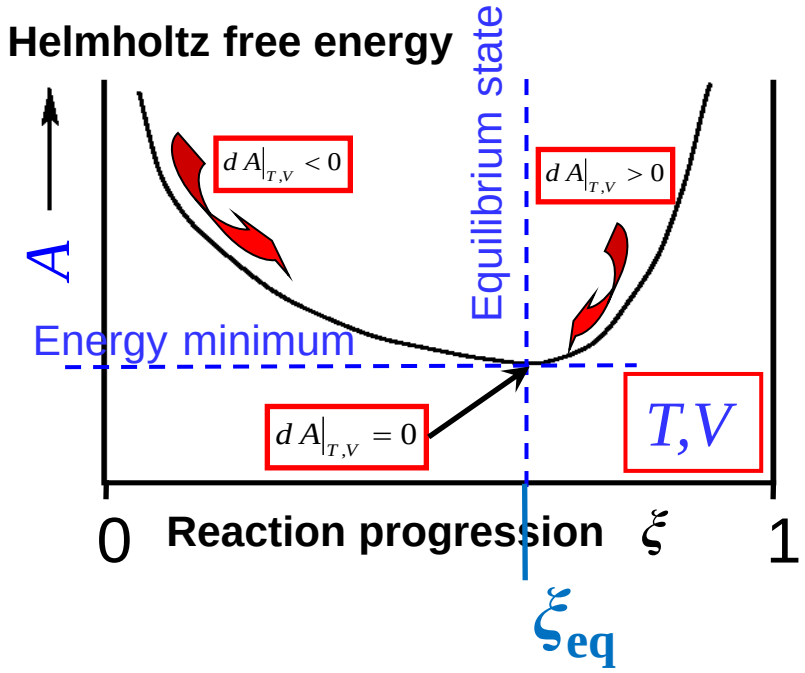

Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$dA = -SdT - PdV + dW_\sigma$$

σ : Interfacial surface

$$dA_{T,V} = dW_\sigma \equiv \gamma d\sigma$$

γ : Interfacial or surface tension

$\gamma > 0$ ➡ Surface tension γ tends to reduce σ

σ (m^2): surface

γ (Jm^{-2}): surface tension

relevant for $P > 1$

Gibbs-Thomson effect

Interfacial (free) energy between two phases

$$dA = -SdT - PdV + dW_\sigma$$

σ : Interfacial surface

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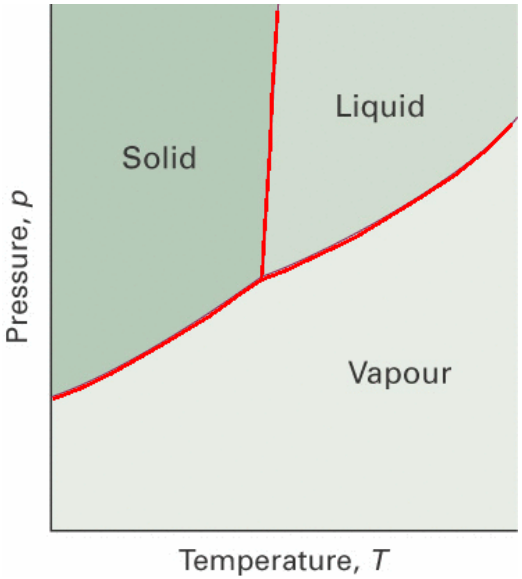
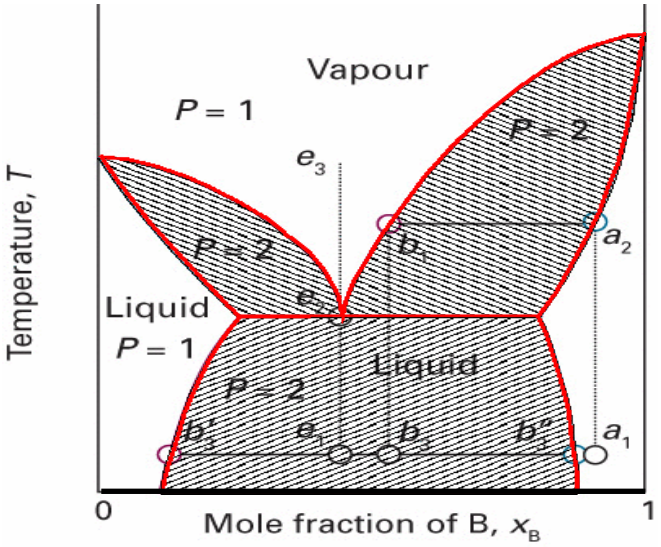
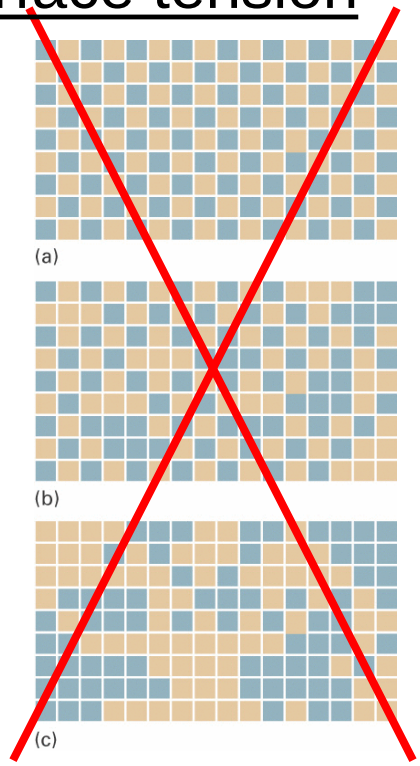


P =2,3



P =2,3



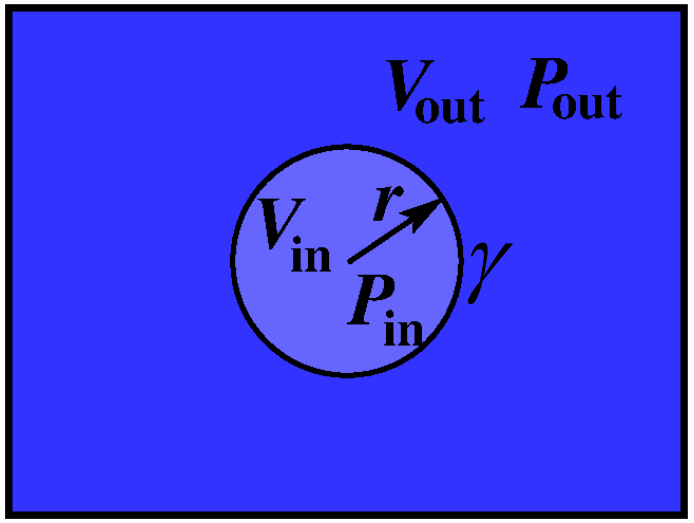
P =1

Gibbs-Thomson effect: Laplace equation

Equilibrium: $$dA = -SdT + dW_V^{\text{rev}} + dW_\sigma^{\text{rev}} = -SdT - PdV + \gamma\, d\sigma = 0$$

Interfacial or surface tension $\gamma > 0$ tends to reduce σ

isotropic γ ➡ smallest surface σ is spherical



$$\gamma \Rightarrow \mathrm{d}\sigma < 0$$

$$P_{in} \Rightarrow \mathrm{d}V_{in} > 0$$

$$P_{out} \Rightarrow \mathrm{d}V_{in} < 0$$

➡ $$dA_T = -P_{in}\, dV_{in} - P_{out}\, dV_{out} + \gamma\, d\sigma = 0$$

Equilibrium: Relation between P_{in}, P_{out} and γ ?

Gibbs-Thomson effect: Laplace equation

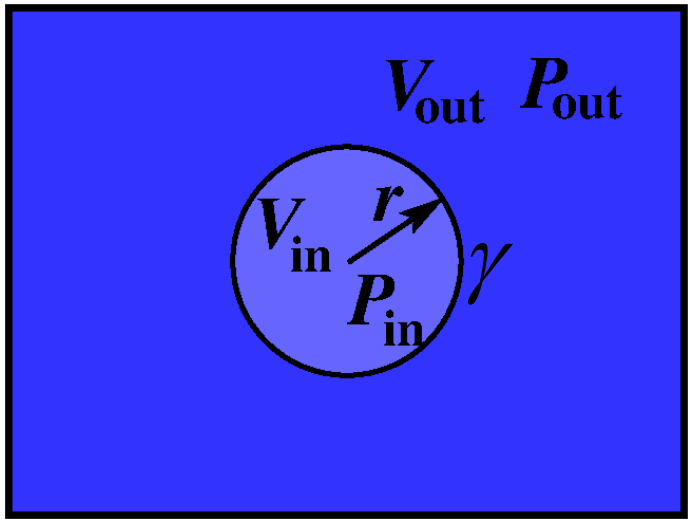
Equilibrium:

$$dA_T = -P_{\text{in}}\,dV_{\text{in}} - P_{\text{out}}\,dV_{\text{out}} + \gamma\,d\sigma = 0$$

σ, V for a sphere: only depend on radius

$$\left(dV_{\text{out}} = -dV_{\text{in}}\right)$$

$$dA_T = -P_{\text{in}}\frac{d\,\frac{4\pi}{3}r^3}{dr}dr + P_{\text{out}}\frac{d\,\frac{4\pi}{3}r^3}{dr}dr + \gamma\frac{d\,4\pi r^2}{dr}dr = 0$$



$$P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r}$$

Laplace equation

Gibbs-Thomson effect: Laplace equation

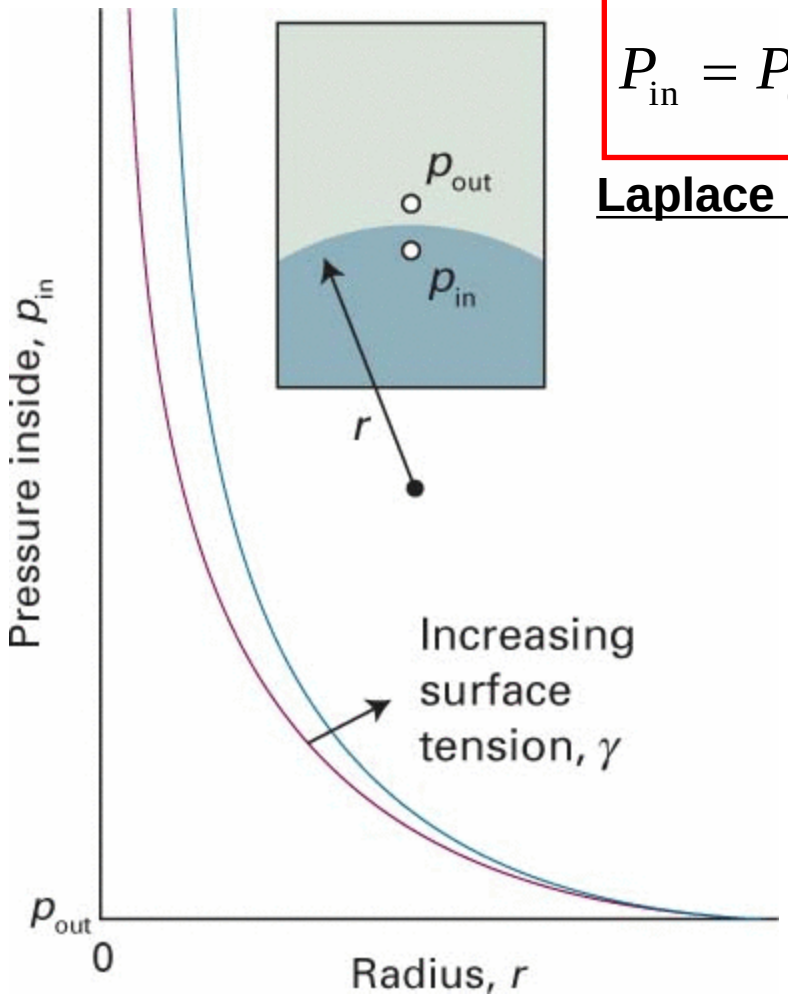
Surface tension γ ($Jm^{-2} = Nm^{-1}$)

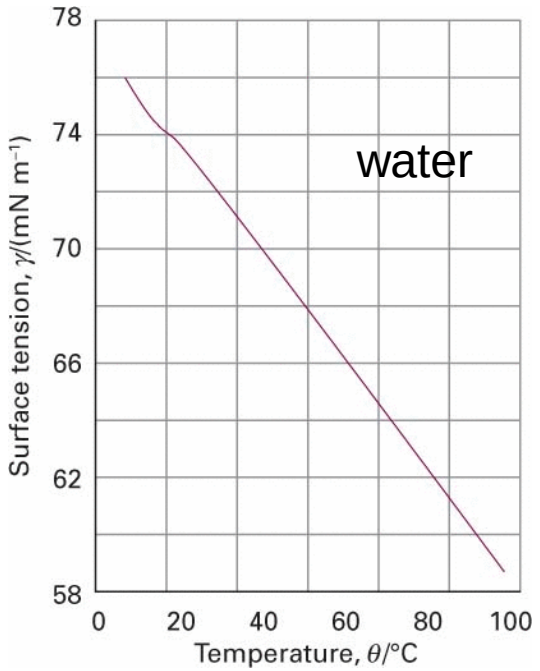
$$P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r}$$

Laplace equation

(293 K, in air)	$\gamma/(\text{mN m}^{-1})$
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

* More values are given in the *Data section*.
Note that $1\ \text{N m}^{-1} = 1\ \text{J m}^{-2}$.



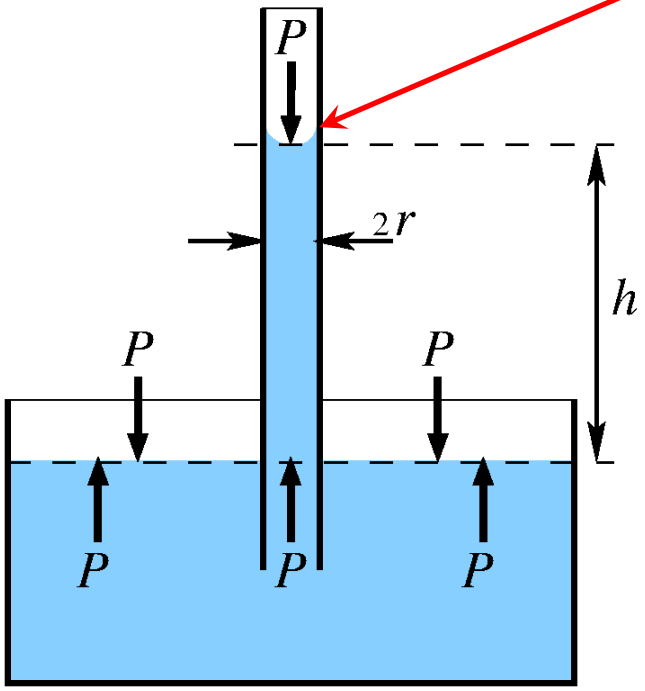


Surface tension and capillary action

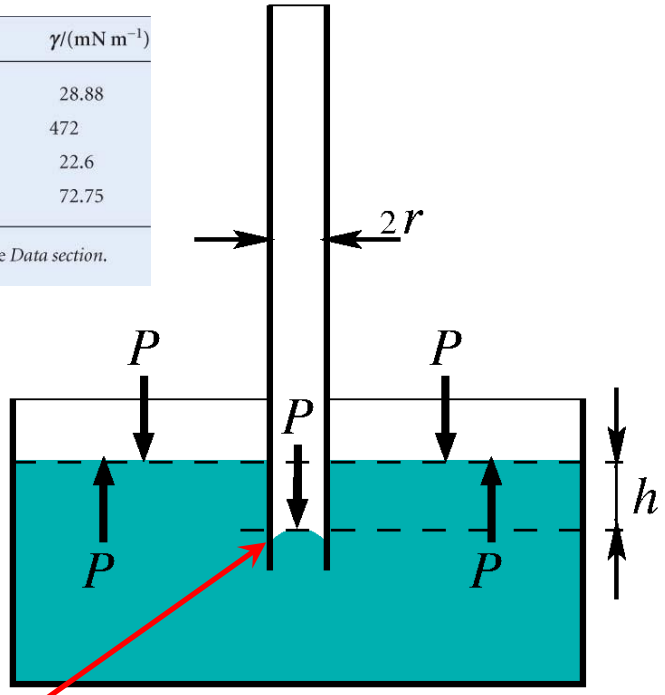
Surface tension and capillary action

Adhesive force between liquid and capillary, e.g. H_2O/glass

capillary rise



capillary depression



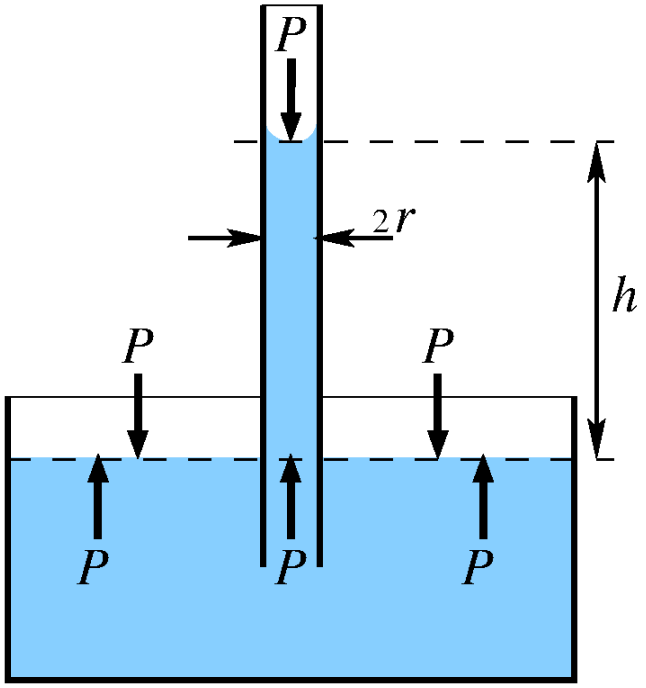
	γ/(mN m^{-1})
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

* More values are given in the *Data section*.
Note that 1 N m^{-1} = 1 J m^{-2}.

Stronger cohesive force within the liquid, e.g. Hg/glass

Surface tension and capillary action

Adhesive force between liquid and capillary



Pressure of a liquid column with cross section A, height h and mass density ρ

$$P(h) = \frac{F(h)}{A} = \frac{m(h)g}{A} = \frac{m(h)gh}{Ah} = \frac{m(h)gh}{V} = \rho gh$$

Surface tension and capillary action

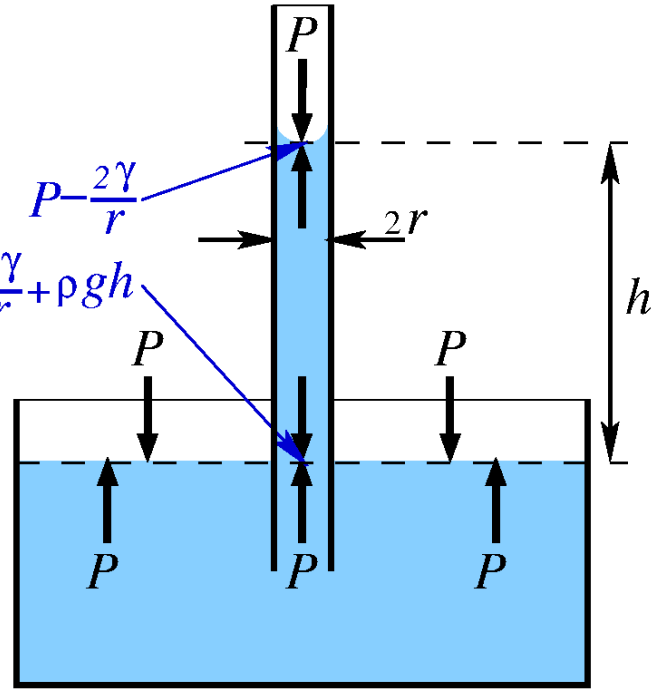
Adhesive force between liquid and capillary

Laplace equation

$$\Delta P = P_{\text{in}} - P_{\text{out}} = \frac{2\gamma}{r}$$

$$P(h) = \rho g h$$

equilibrium $P(h) = \Delta P$



$$P(h) = \frac{F(h)}{A} = \frac{m(h)g}{A} = \frac{m(h)gh}{Ah} = \frac{m(h)gh}{V} = \rho g h$$

Surface tension and capillary action

Adhesive force between liquid and capillary

Laplace equation

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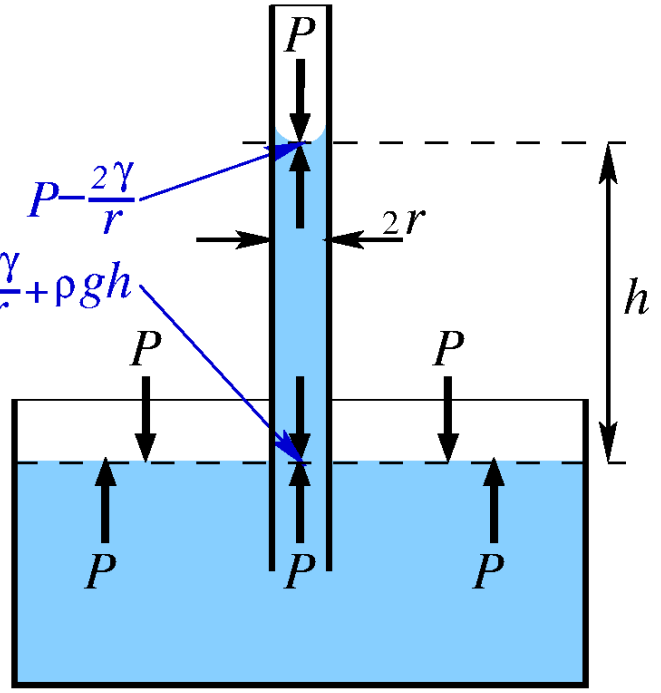
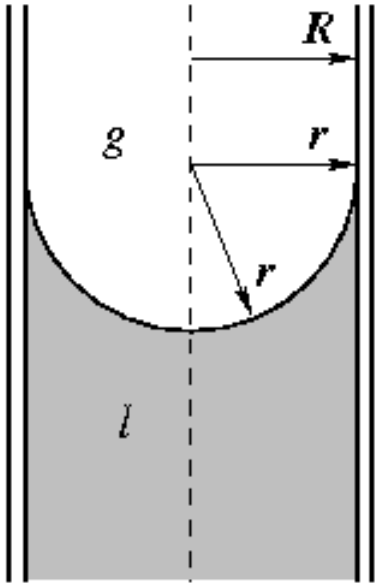


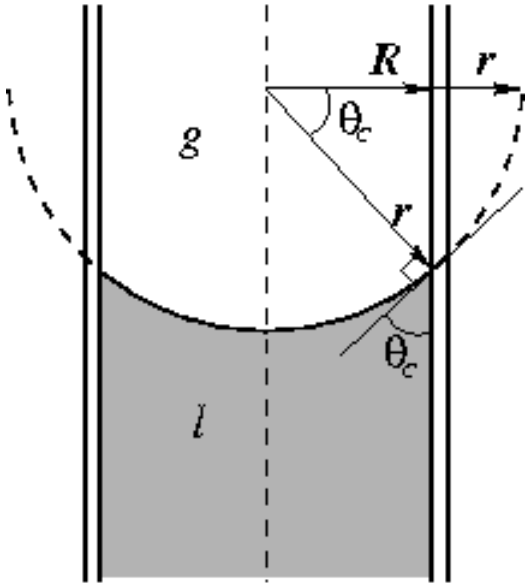
$$h = \frac{2\gamma}{\rho g r}$$ **capillary rise**

Exercise 26

Surface tension and capillary action

$\theta_c = 0$





$$\cos\theta_c = \frac{R}{r}$$

$\theta_c = 0$ $\quad r = R$

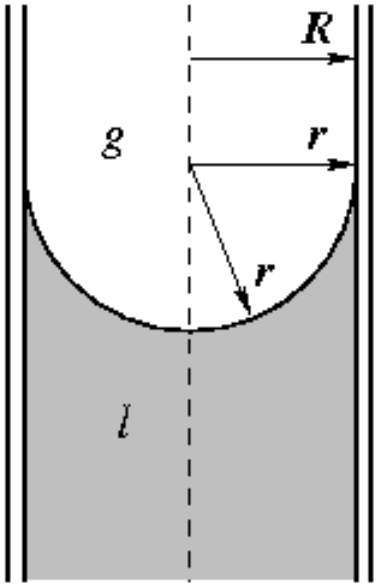
$\theta_c \neq 0$ $\quad r > R$

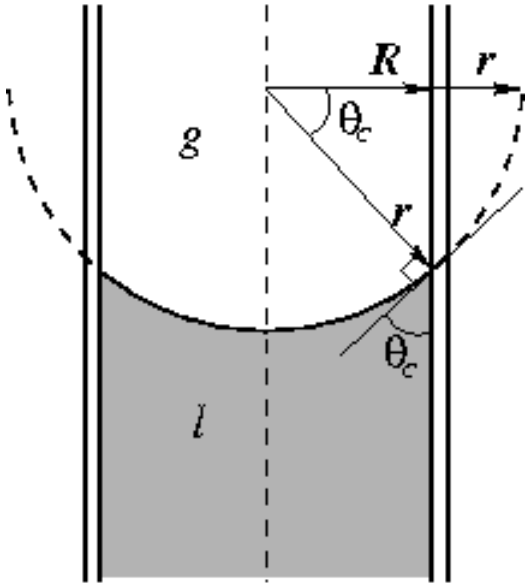
$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}$$

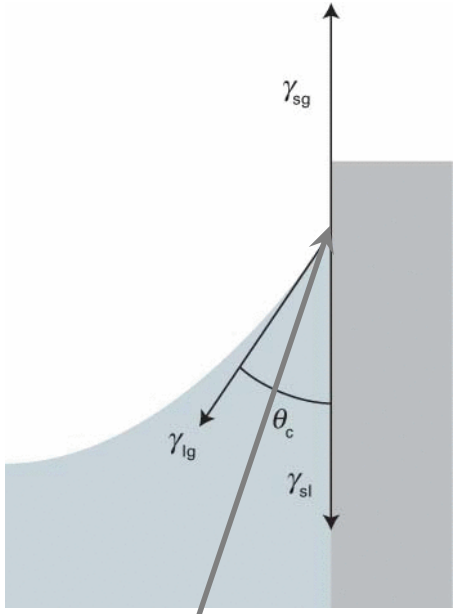
$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}\cos\theta_c$$

Surface tension and capillary action

equilibrium situations







$$\theta_c = 0$$

$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}$$

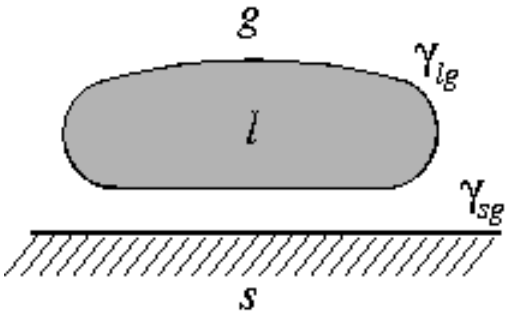
$$\theta_c \neq 0$$

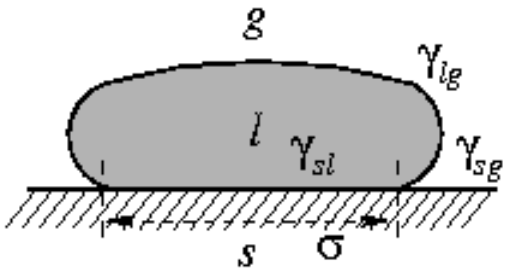
$$h = \frac{2\gamma}{\rho g r} = \frac{2\gamma}{\rho g R}\cos\theta_c$$

Each interfacial tension tries to reduce its corresponding surface

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c$$

Surface tension and wetting



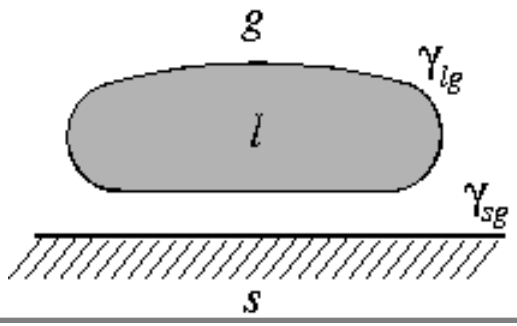


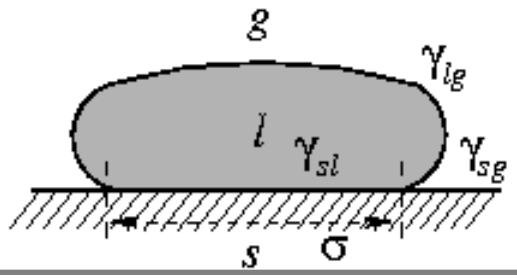
$$w_{adh} = -\frac{W}{\sigma}$$

specific work (J/m^2)of adhesion

(γ is always trying to reduce the corresponding surface)

Surface tension and wetting

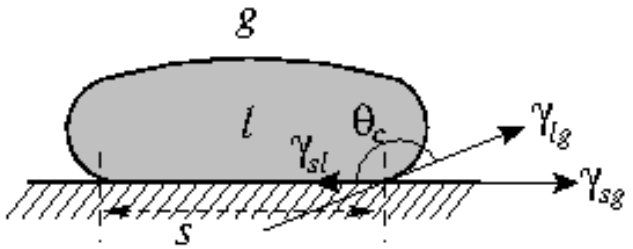




$$w_{adh} = -\frac{W}{\sigma} = -\frac{\gamma_{sl}\sigma - \gamma_{sg}\sigma - \gamma_{lg}\sigma}{\sigma} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$$

specific work (J/m²) of adhesion

(γ is always trying to reduce the corresponding surface)

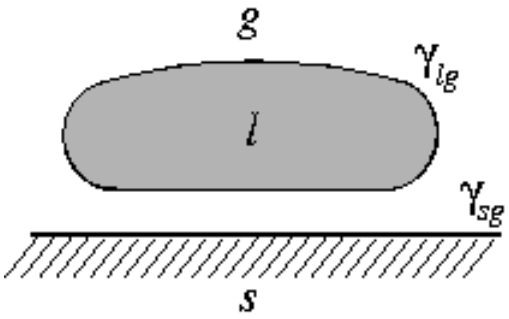


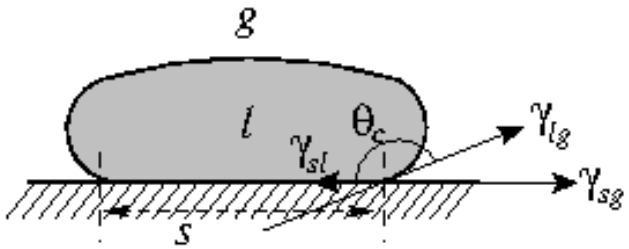
$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c$$

(equilibrium)

horizontal Force (N/m) balance

Surface tension and wetting



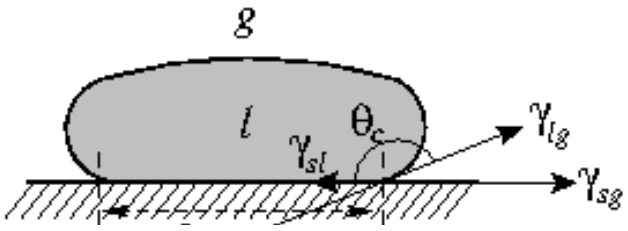


Work (J/m²) $w_{adh} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$

Force (N/m) $\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c$

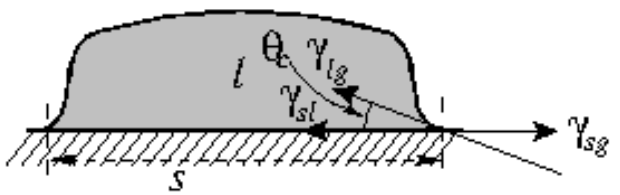
$$\cos\theta_c = \frac{w_{adh}}{\gamma_{lg}} - 1$$

$$0 < \frac{w_{adh}}{\gamma_{lg}} < 1 \Leftrightarrow 180^\circ < \theta_c < 90^\circ$$



partial dewetting

$$1 < \frac{w_{adh}}{\gamma_{lg}} < 2 \Leftrightarrow 90^\circ < \theta_c < 0^\circ$$

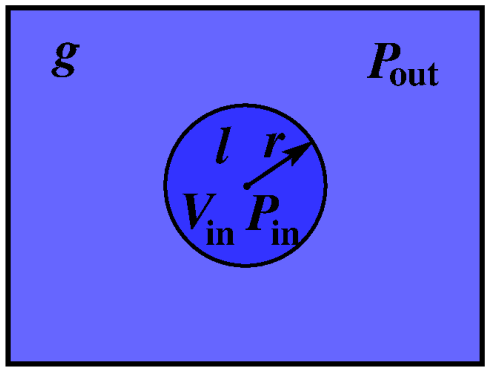


partial wetting

Kelvin equation

Kelvin equation and nucleation

nucleation barrier for condensation ($g \rightarrow l$) @ $T < T_{vap}$



$$\Delta P = P_{in} - P_{out} = \frac{2\gamma}{r}$$ **Laplace equation**

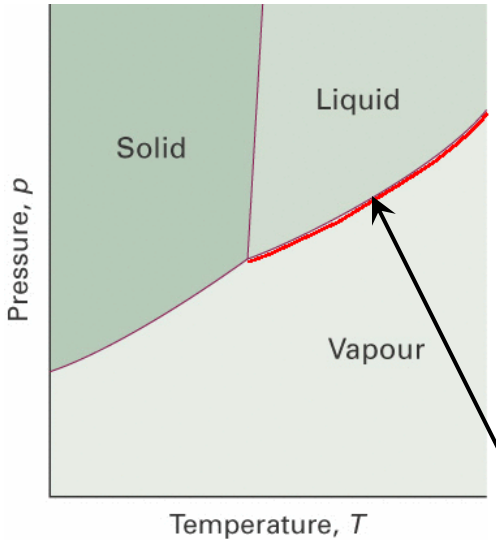
Surface tension will change P_g

revert to Gibbs free energy

$$d\mu_{l,g} = -S_{m,l,g}\,dT + V_{m,l,g}\,dP$$

equilibrium $d\mu_g = d\mu_l$

(pure compound)

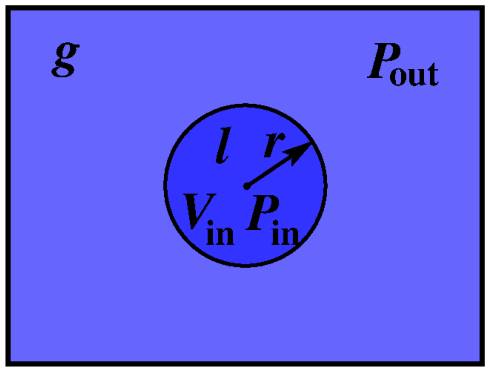


$$\int_{P^*}^{P_g} V_{m,g}\,dP = \int_{P^*}^{P^*+\Delta P} V_{m,l}\,dP$$ @ **constant T**

$$P^* = P^*(T)$$

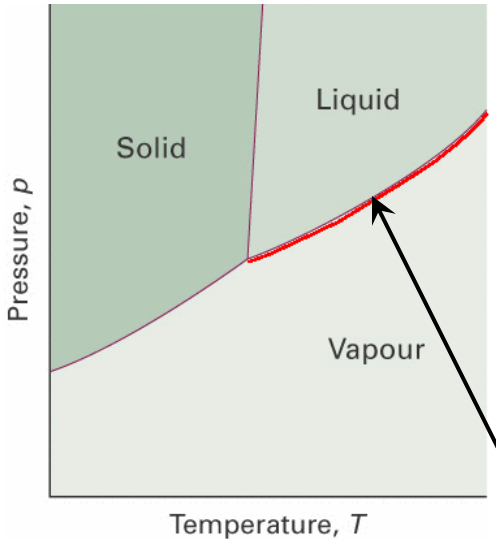
Kelvin equation and nucleation

nucleation barrier for condensation ($g \rightarrow l$) @ $T < T_{vap}$



$$\Delta P = P_{in} - P_{out} = \frac{2\gamma}{r}$$

$$\int_{P^*}^{P_g} V_{m,g}\, dP = \int_{P^*}^{P^*+\Delta P} V_{m,l}\, dP$$



$$\int_{P^*}^{P_g} \frac{RT}{P}\, dP \approx V_{m,l} \int_{P^*}^{P^*+\Delta P} dP$$

$$RT \ln \frac{P_g}{P^*} \approx V_{m,l}\Delta P = V_{m,l} \frac{2\gamma}{r}$$

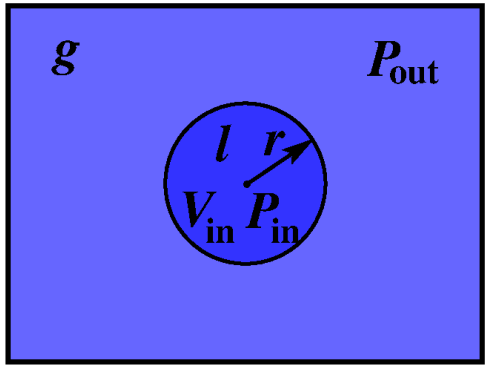
$$P_g = P^* \exp\left[\frac{2\gamma V_{m,l}}{rRT}\right]$$

Kelvin equation

$$P^* = P^*(T)$$

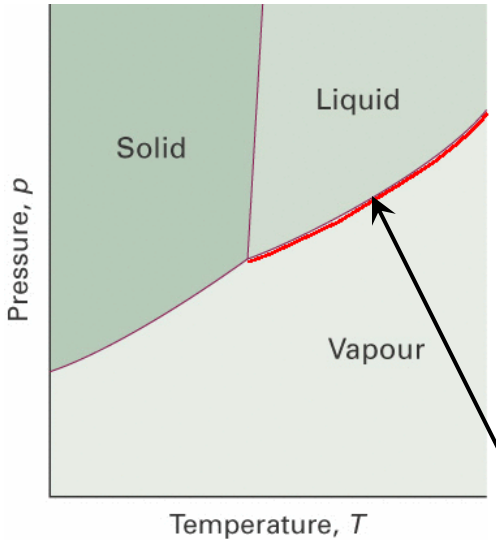
Kelvin equation and nucleation

nucleation barrier for condensation ($g \rightarrow l$) @ $T < T_{vap}$



$$P_g = P^* \exp\left[\frac{2\gamma V_{m,l}}{rRT}\right]$$

Kelvin equation



$P^* = P^*(T)$

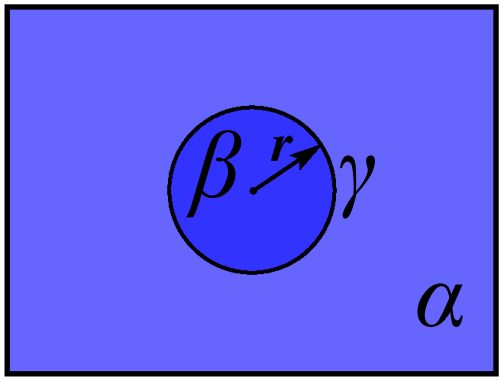
Consider an undercooled gas:

$$P_g(r) > P^*$$

→small droplets evaporate
→condensation nucleation barrier

Nucleation of solid phase $\beta(s)$ from liquid $\alpha(l)$

- revert to Gibbs free energy
- classical nucleation theory
  - spherical nucleus, radius r
  - driving force: $\Delta\mu = \mu_\beta - \mu_\alpha$
  - surface free energy: γ
  - molar volume of phase β: V_m



Nucleation of solid phase $\beta(s)$ from liquid $\alpha(l)$

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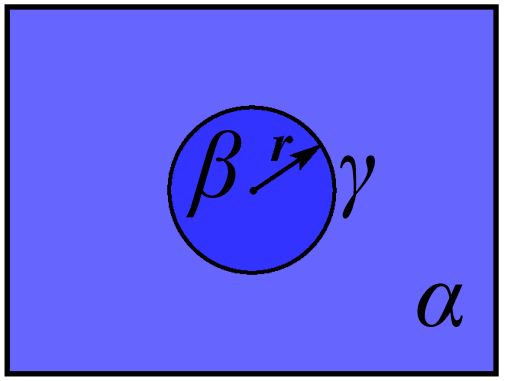


$$\Delta G_V = n_\beta \Delta\mu = \frac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu$$

$$\Delta G_\sigma = +4\pi r^2 \gamma$$

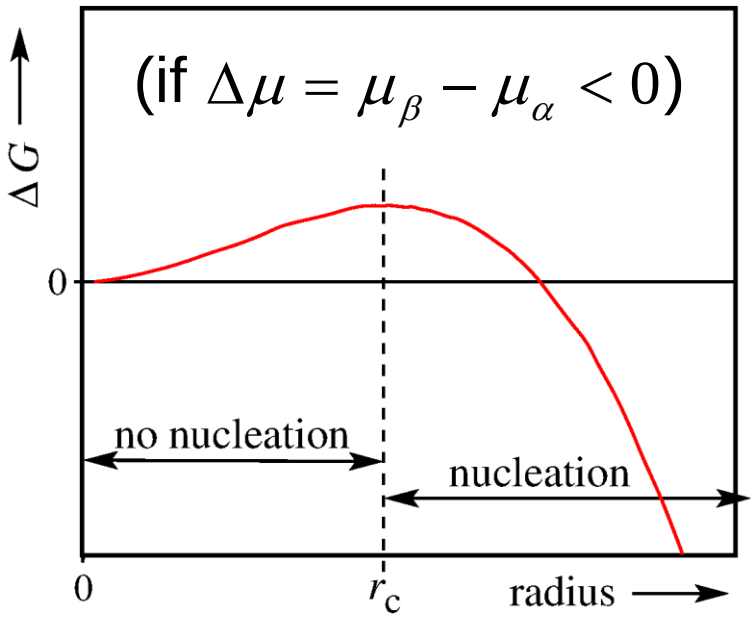
$$\Delta G = \frac{\frac{4}{3}\pi r^3}{V_\mathrm{m}}\Delta\mu + 4\pi r^2\gamma$$

gain **cost**

(if $\Delta\mu = \mu_\beta - \mu_\alpha < 0$)

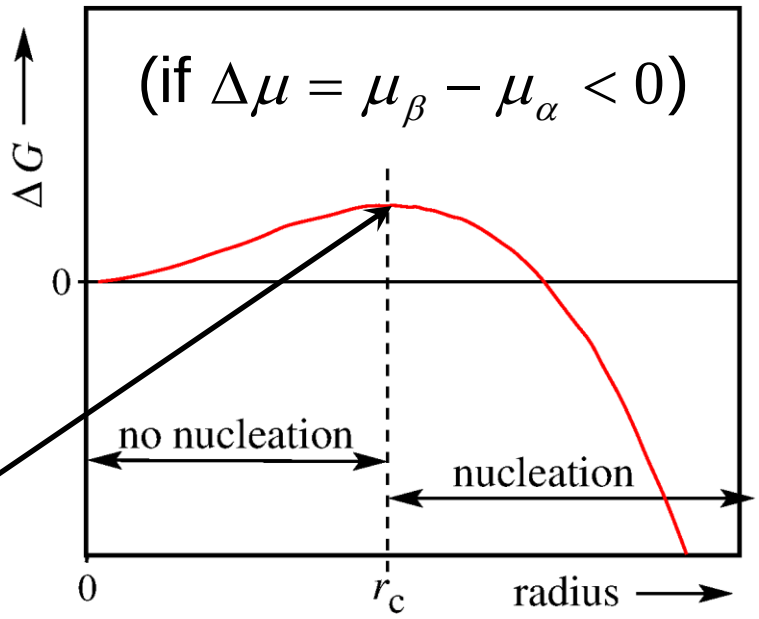
Nucleation of solid phase $\beta(s)$ from liquid $\alpha(l)$

$$\Delta G = \frac{\frac{4}{3}\pi r^3}{V_m}\Delta\mu + 4\pi r^2\gamma$$



Nucleation of solid phase $\beta(s)$ from liquid $\alpha(l)$

$$\Delta G = \frac{\frac{4}{3}\pi r^3}{V_m}\Delta\mu + 4\pi r^2\gamma$$



critical radius r_c:

$$\left.\frac{d\Delta G}{dr}\right|_{r_c} = 0$$

$$G_c = \frac{16\pi^2 V_m^2 \gamma^3}{3\Delta\mu^2};\ r_c = \frac{2\gamma V_m}{\Delta\mu}$$

Exercise 27

nucleation barrier depends on supersaturation ($\Delta\mu = \Delta\mu(T)$)

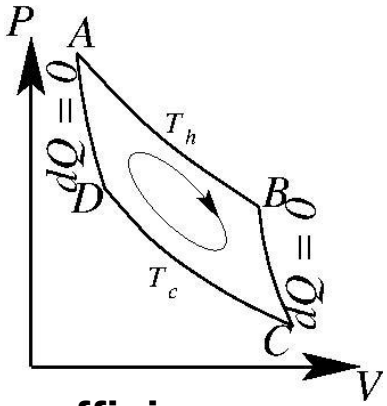
-low $\Delta\mu$: no nucleation

-high $\Delta\mu$: easy nucleation

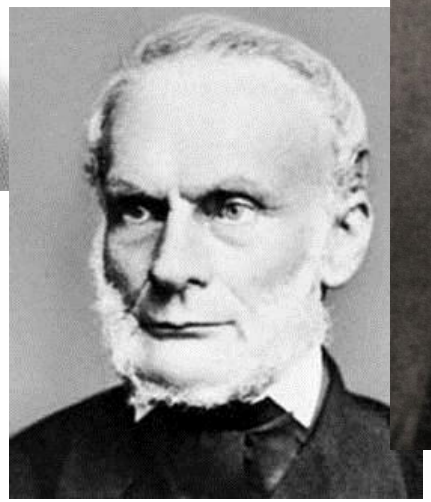
Statistical Thermodynamics: Boltzmann distribution

Statistical Thermodynamics: History

Carnot 1824



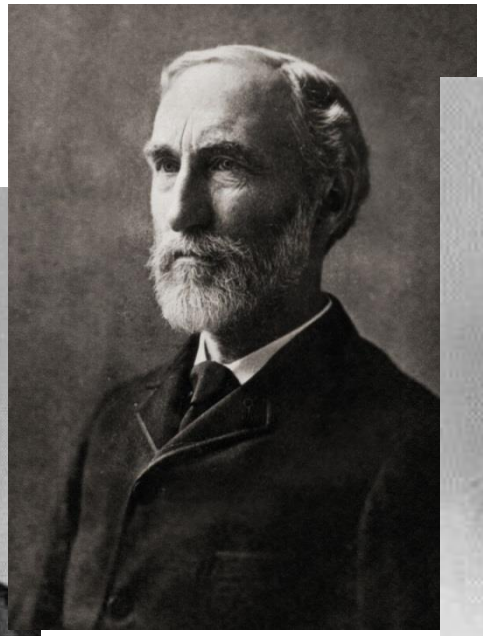
efficiency



Clausius 1856

$$dS = \frac{dQ^{\text{rev}}}{T}$$

entropy



Gibbs 1870

$$G = H - TS$$

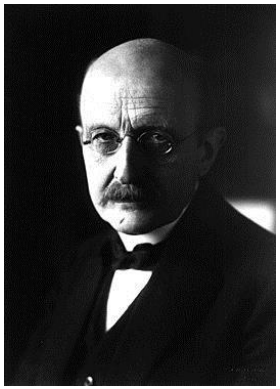
free energy

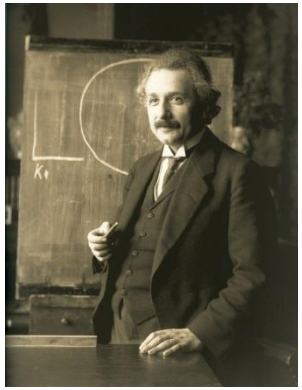
Boltzmann 1896

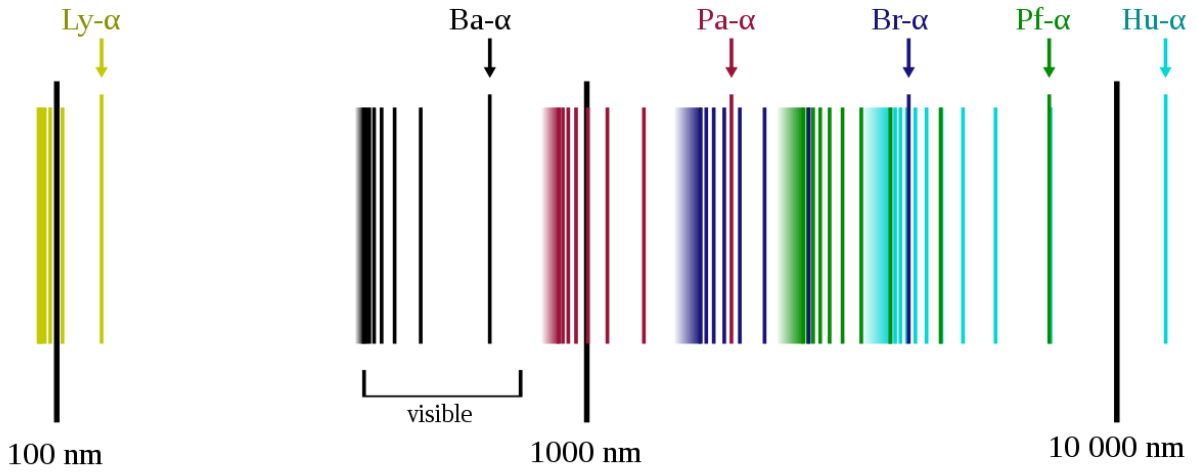
$$S = k \ln W$$

statistical thermodynamics

Statistical Thermodynamics: History







The discrete part of the emission spectrum of hydrogen

Quantum Mechanics:
discrete energy spectrum

$$E(v) \rightarrow \varepsilon_i$$

ε_i is the energy of a molecule in quantum state or quantum level i

discrete energy levels $0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \cdots$

Source: https://en.wikipedia.org/wiki/Discrete_spectrum

Statistical Thermodynamics: Boltzmann distribution

Boltzmann distribution:

Average number of molecules in quantum state ε_i

$$n_i = N \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{\sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]}$$

Total number of molecules

$$k = 1.38 \cdot 10^{-23}\ \mathrm{J/K}$$

$$\sum_i \frac{n_i}{N} = \frac{\sum_i \exp\left[-\frac{\varepsilon_i}{kT}\right]}{\sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]} = 1$$

Boltzmann distribution is normalized

Statistical Thermodynamics: Boltzmann distribution

Boltzmann distribution:

$$n_i = N \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{\sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]}$$

$$q \equiv \sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]$$

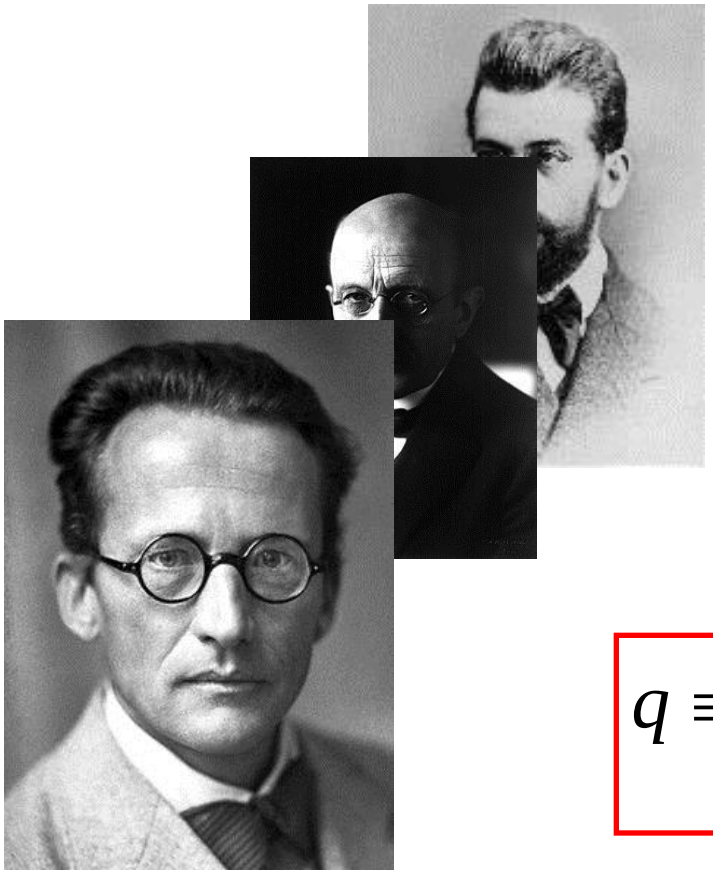
Partition function

Partition function:

- normalizes the distribution

- is a measure for the number of thermally accessible states

Statistical Thermodynamics: Boltzmann distribution



Boltzmann distribution:

$$\frac{n_i}{N} = \frac{\exp\left[-\beta\varepsilon_i\right]}{q}$$

$$\beta \equiv \frac{1}{kT}$$

$$q \equiv \sum_j \exp\left[-\beta\varepsilon_j\right]$$

Partition function

$$\frac{n_i}{N} = P_i$$

Chance P_i of a molecule to be in a quantum state i with energy ε_i

Statistical Thermodynamics: Boltzmann distribution

Alternative interpretation

$$\frac{n_i}{N} = P_i$$

Chance P_i of a molecule to be in a quantum state i with energy ε_i

Boltzmann distribution

$$P_i = \frac{n_i}{N} = \frac{\exp\left[-\beta\varepsilon_i\right]}{q}$$

Partition function

$$q = \sum_j \exp\left[-\beta\varepsilon_j\right] \qquad \left(\beta \equiv \frac{1}{kT}\right)$$

Example: Internal energy averaged over all quantum states

$$< U >= N\sum_i \varepsilon_i P_i = \frac{N}{q}\sum_i \varepsilon_i \exp\left[-\beta\varepsilon_i\right] = \frac{-N}{q}\left[\frac{\partial q}{\partial \beta}\right]$$

Study Guide page 21

Statistical Thermodynamics: Boltzmann distribution

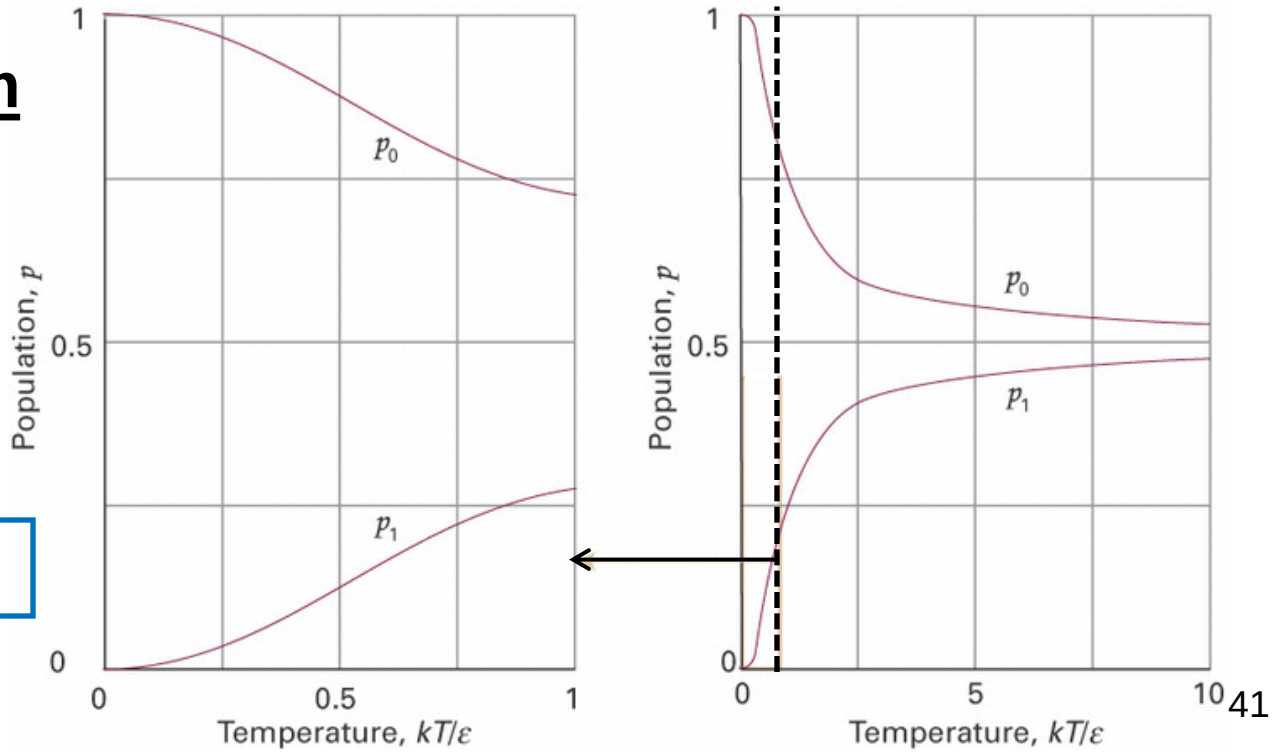
$$P_i = \frac{n_i}{N} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{q} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{\exp\left[-\frac{\varepsilon_0}{kT}\right] + \exp\left[-\frac{\varepsilon_1}{kT}\right]}$$

Two level system

$\varepsilon_0 = 0$ $\varepsilon_1 = \varepsilon$

choice

Exercise 28-29



Statistical Thermodynamics: Boltzmann entropy

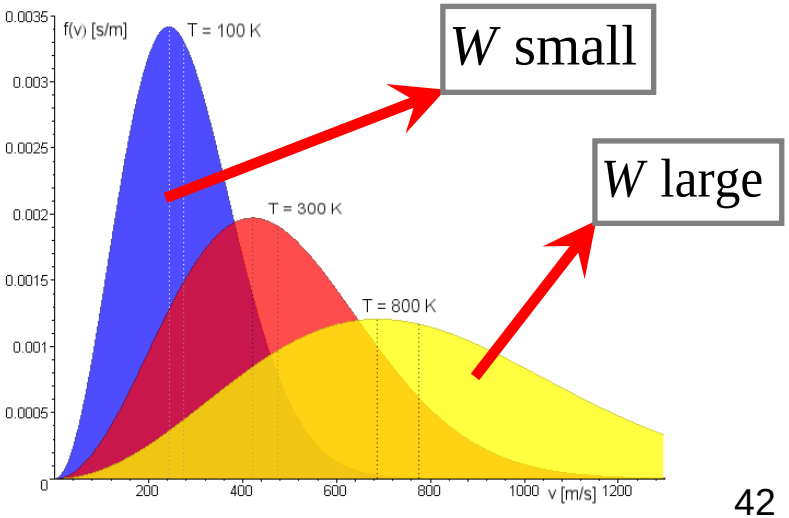
Ludwig Boltzmann
1844-1906

1877: Boltzmann entropy

S : measure for "statistical mixedupness"

$$S \equiv k \ln W$$

W is the number of micro states of a system in equilibrium as a macro state



S increases with T

$$S \xrightarrow{(T \to 0)} 0 \quad \Rightarrow \quad S(T=0) = 0$$

Particle velocity v increases with T

Statistical Thermodynamics: Boltzmann entropy

$$S \equiv k \ln W$$

$$S_1 = k \ln W_1 \quad + \quad S_2 = k \ln W_2 \quad \longrightarrow \quad W = W_1 W_2$$

(ideal mixtures)

$$S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln W_1 W_2 = k \ln W = S$$

(only for ideal mixtures)

Statistical *vs*. Classical Thermodynamics

Is entropy S a measure for disorder or chaos?

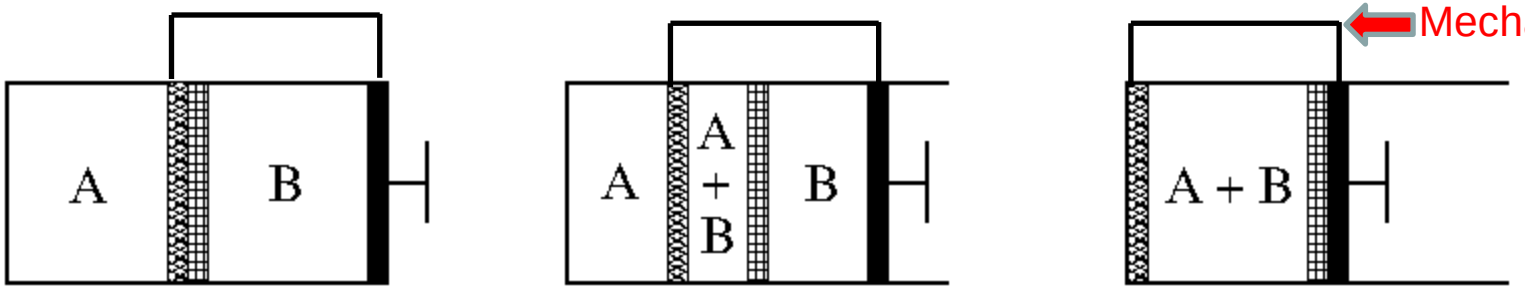
To test this we perform three "Gedanken" experiments

- **Classical thermodynamics**
- **Perfect gases A and B**
- **Clever design of experiment**

(Study Guide: p.22-24)

Classical: Entropy change for changing volume

1



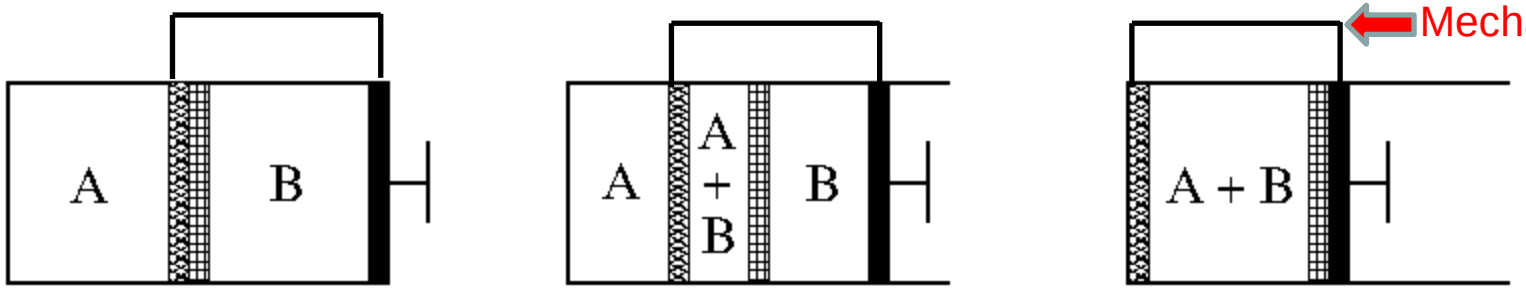
Mechanical coupling

Semi-permeable for A

Semi-permeable for B (fixed position)

Classical: Entropy change for changing volume

1



Semi-permeable for A

Semi-permeable for B (fixed position)

$$V_A' = V_A \qquad V_B' = V_B$$

$$dV_A = dV_B = 0$$

Reversible, isothermal, isochoric "compression"

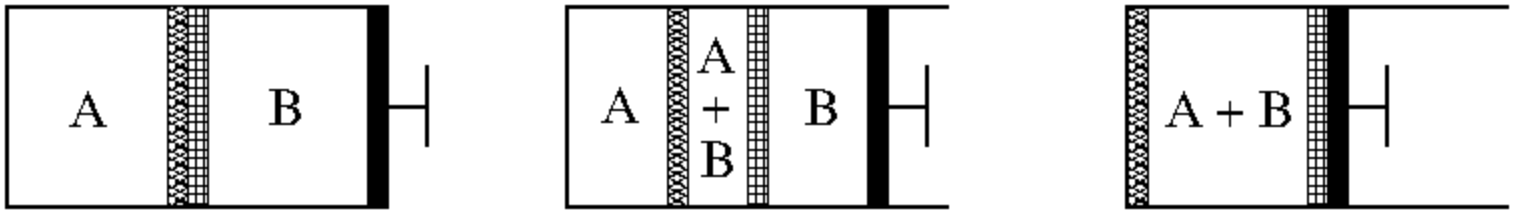
(for both gases) $dW = -PdV = 0$

$dT = 0 \rightarrow dU = 0$

$$dU = dQ + dW \rightarrow dQ_A^{rev} = dQ_B^{rev} = 0 \rightarrow \Delta S = 0$$

Classical: Entropy change for changing volume

1



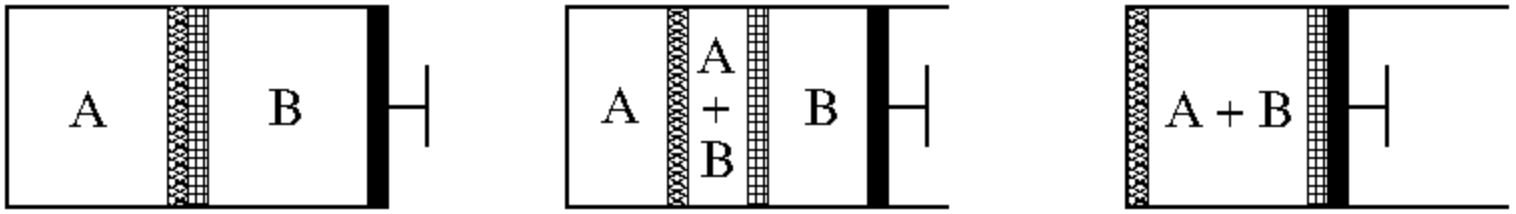
$$V_i' = V_i$$

Reversible, isothermal, isochoric "compression"

$$\Delta S_i = 0$$

Classical: Entropy change for changing volume

1

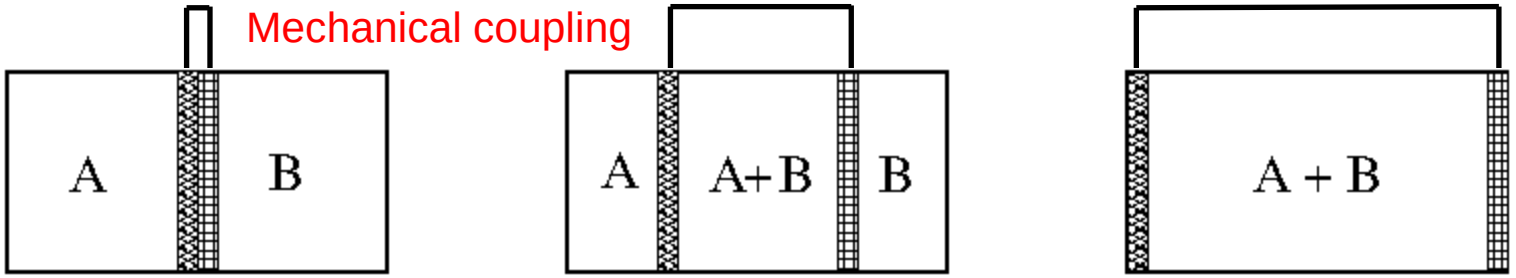


$$V_i' = V_i$$

Reversible, isothermal, isochoric "compression"

$$\Delta S_i = 0$$

2

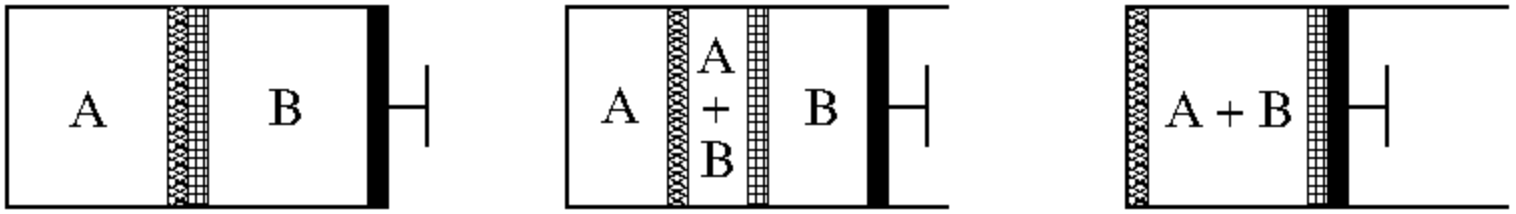


Semi-permeable membranes

Reversible, isothermal, isobaric expansion

Classical: Entropy change for changing volume

1



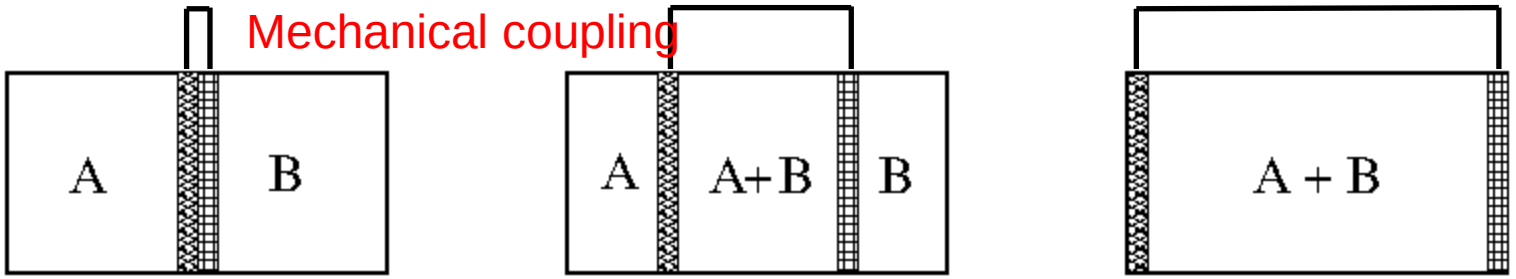
$$V_i' = V_i$$

Reversible, isothermal, isochoric "compression"

$$\Delta S_i = 0$$

2

Mechanical coupling



Semi-permeable membranes

Reversible, isothermal, isobaric expansion

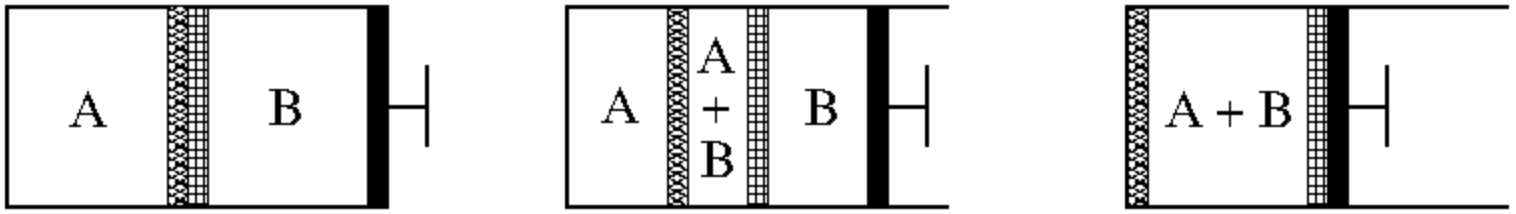
$$dT = 0 \Rightarrow dU = 0$$ **(for both gases)**

$$\Rightarrow dU = 0 \Rightarrow Q = -\int dW = -\int P dV = nRT \ln \frac{V^{\text{final}}}{V^{\text{initial}}} = nRT \ln 2$$

in total $\Rightarrow$ $$\Delta S = (n_A + n_B) R \ln 2$$

Classical: Entropy change for changing volume

1

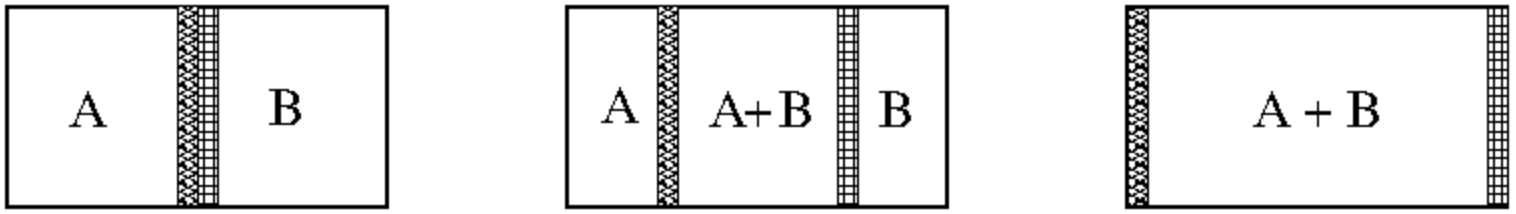


$$V_i' = V_i$$

Reversible, isothermal, isochoric "compression"

$$\Delta S_i = 0$$

2



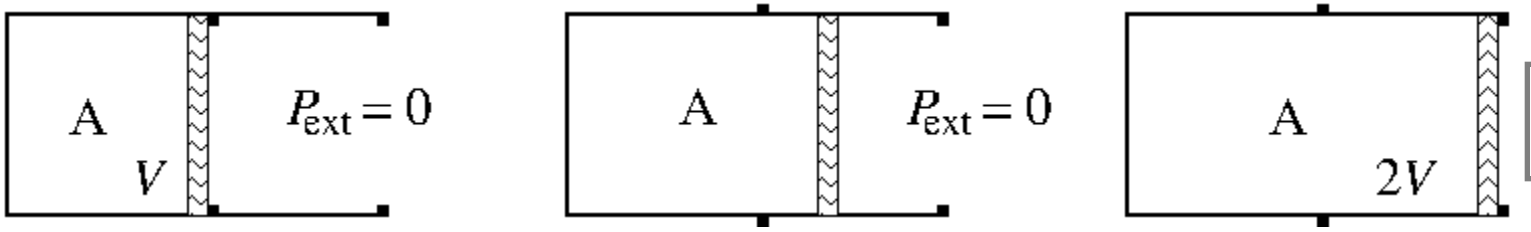
$$V_i' = 2V_i$$

Reversible, isothermal, isobaric expansion

$$\Delta S = \left(n_{\mathrm{A}} + n_{\mathrm{B}}\right) R \ln 2$$

Classical: Entropy change for changing volume

3



$$V_A' = 2V_A$$

Irreversible, isothermal expansion, with $P_{ext} = 0$

$$P_{ext} = 0 \Rightarrow dW = -P_{ext}\,dV = 0$$

$$dT = 0 \Rightarrow dU = 0 \Rightarrow dQ = -dW$$

(perfect gas)

$$\Rightarrow dQ^{irr} = 0$$

(irreversible)

$$dQ^{irr} = 0 \Rightarrow dS \equiv \frac{dQ^{rev}}{T} = ?$$

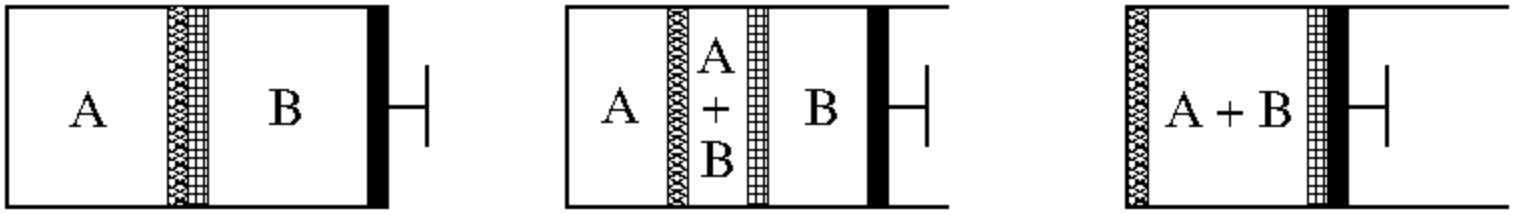
Exercise 30

Reversible alternative

$$\Rightarrow \Delta S = nR \ln \frac{V_2}{V_1} = nR \ln 2$$

Classical: Entropy change for changing volume

1

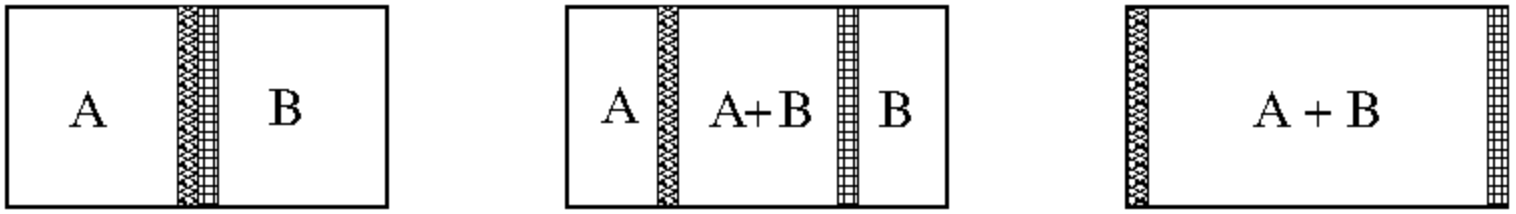


$$V_i' = V_i$$

Reversible, isothermal, isochoric "compression"

$$\Delta S_i = 0$$

2

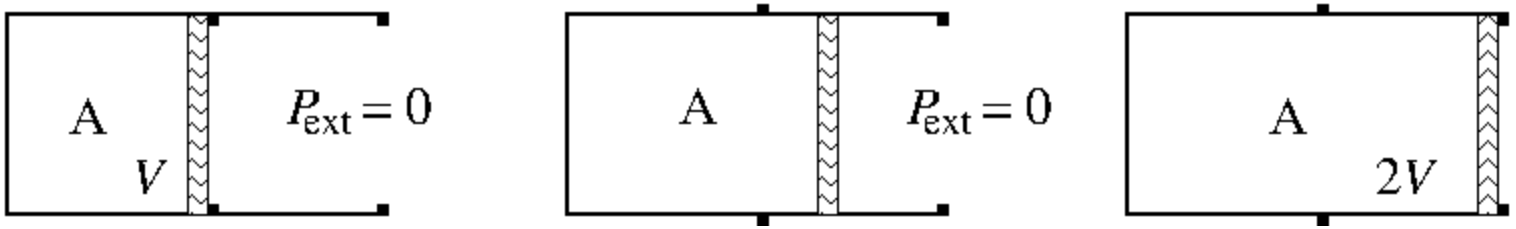


$$V_i' = 2V_i$$

Reversible, isothermal, isobaric expansion

$$\Delta S = \left(n_{\mathrm{A}} + n_{\mathrm{B}}\right) R \ln 2$$

3



$$V_{\mathrm{A}}' = 2V_{\mathrm{A}}$$

Irreversible, isothermal expansion, with $P_{\mathrm{ext}} = 0$

$$\Delta S = nR \ln 2$$

Classical: Entropy change for changing volume

Exp.		ΔS	ΔS_{sur}	ΔS_{tot}	rev./irr.
1		0	0	0	**reversible**
2		$(n_A+n_B)R \ln 2$	$-(n_A+n_B)R \ln 2$	0	**reversible**
3		$nR \ln 2$	0	$nR \ln 2$	**irreversible**

Experiment 1: mixing → disorder increases, but $\Delta V = 0, \Delta S = 0$

Experiment 2: mixing → disorder increases, but $\Delta V \neq 0, \Delta S \neq 0$

Experiment 3: no mixing → disorder constant $\Delta V \neq 0, \Delta S \neq 0$

Besides Q^{rev} and T also V determines the entropy S

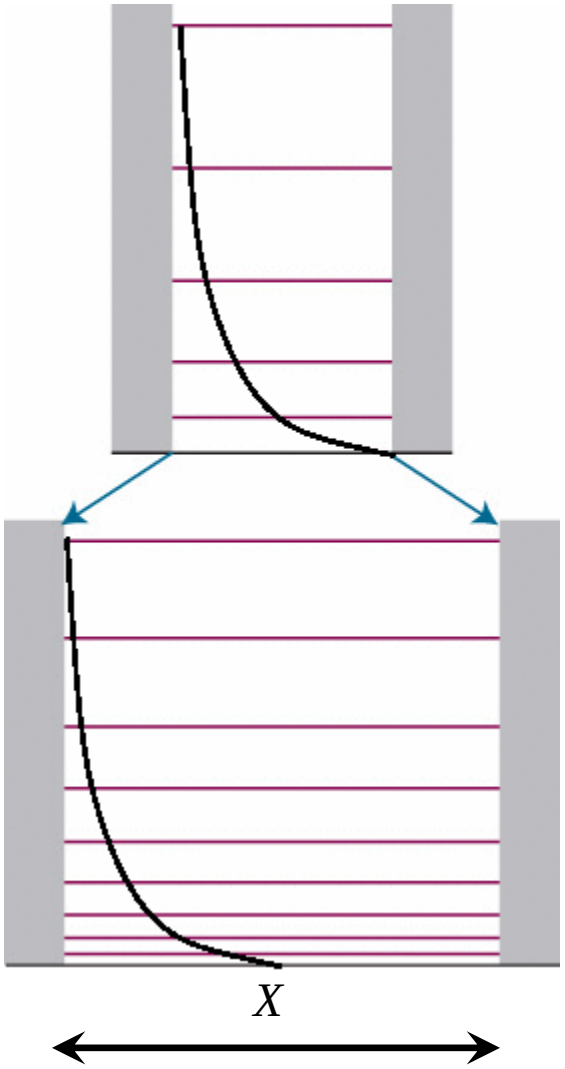
Q.M.: Entropy change for changing volume

Quantum mechanics

Boltzmann distribution

$$\frac{n_i}{N}$$

"Particle in a box problem"



$$\varepsilon_i = \left(i^2 - 1\right)\frac{h^2}{8mX^2}$$

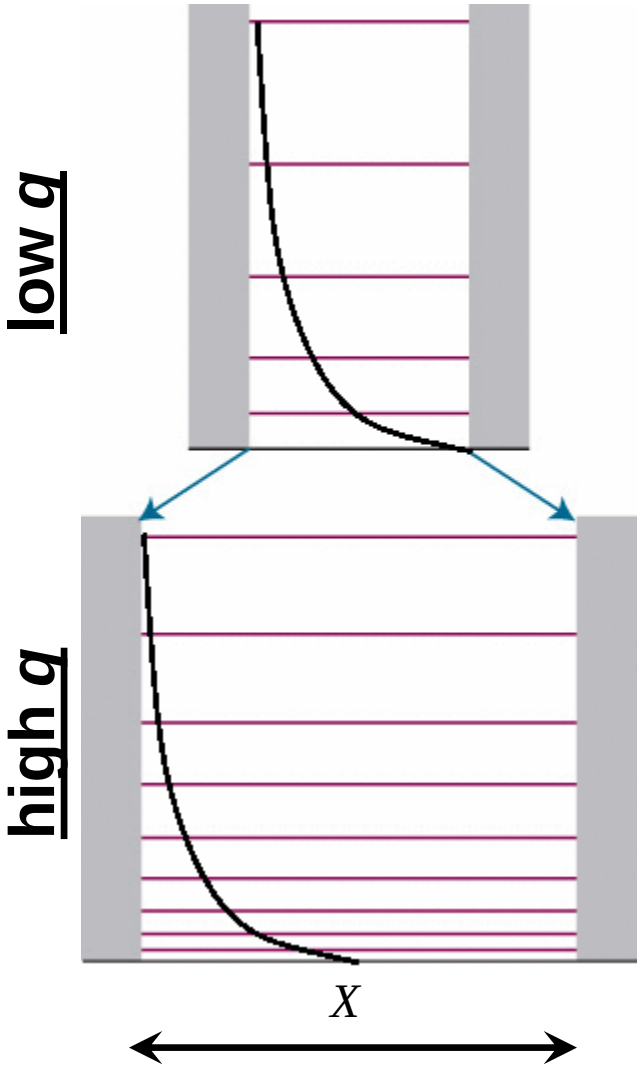
3 D box: $V = XYZ$

$$q = \frac{V}{\Lambda^3} \qquad \Lambda = \frac{h}{\sqrt{2\pi\, mkT}}$$

$$\frac{n_i}{N} = \frac{\exp\left[-\beta\varepsilon_i\right]}{q} = \Lambda^3 \frac{\exp\left[-\beta\varepsilon_i\right]}{V}$$

Q.M.: Entropy change for changing volume

Boltzmann entropy $S = k \ln W$



$$\frac{n_i}{N} = \frac{\exp\left[-\beta\varepsilon_i\right]}{q}$$

$$q = \frac{V}{\Lambda^3}$$

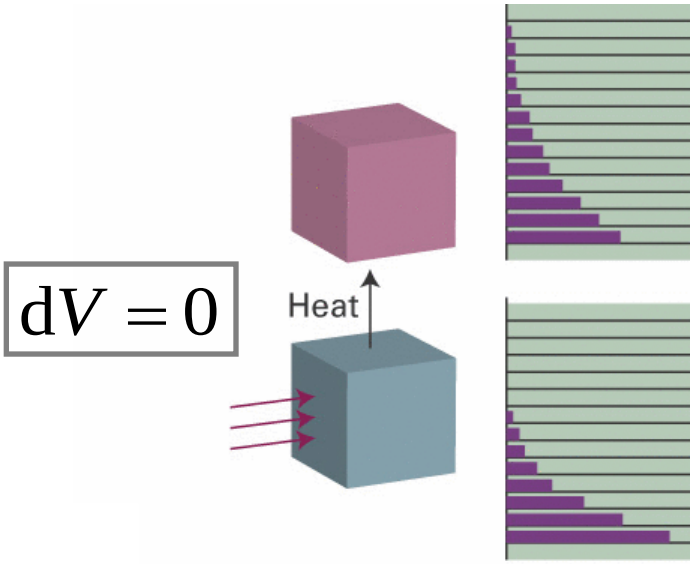
q **is a measure for the number of thermally accessible states**

$$V \uparrow \Rightarrow q \uparrow \Rightarrow W \uparrow \Rightarrow S = k \ln W \uparrow$$

$$S = S(V)$$

Exercise 30

Two ways to change Boltzmann entropy

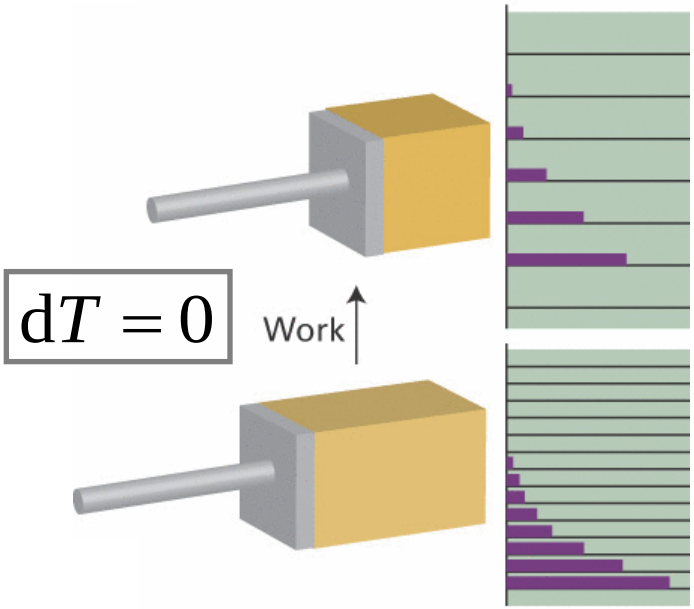


$dV = 0$

$S = k \ln W$ W: **# micro-states**

$$T \uparrow \Rightarrow q \uparrow \Rightarrow W \uparrow \Rightarrow S = k \ln W \uparrow$$

Perfect atomic gas: $\Delta S = \frac{3}{2} nR \ln \frac{T_f}{T_i}$



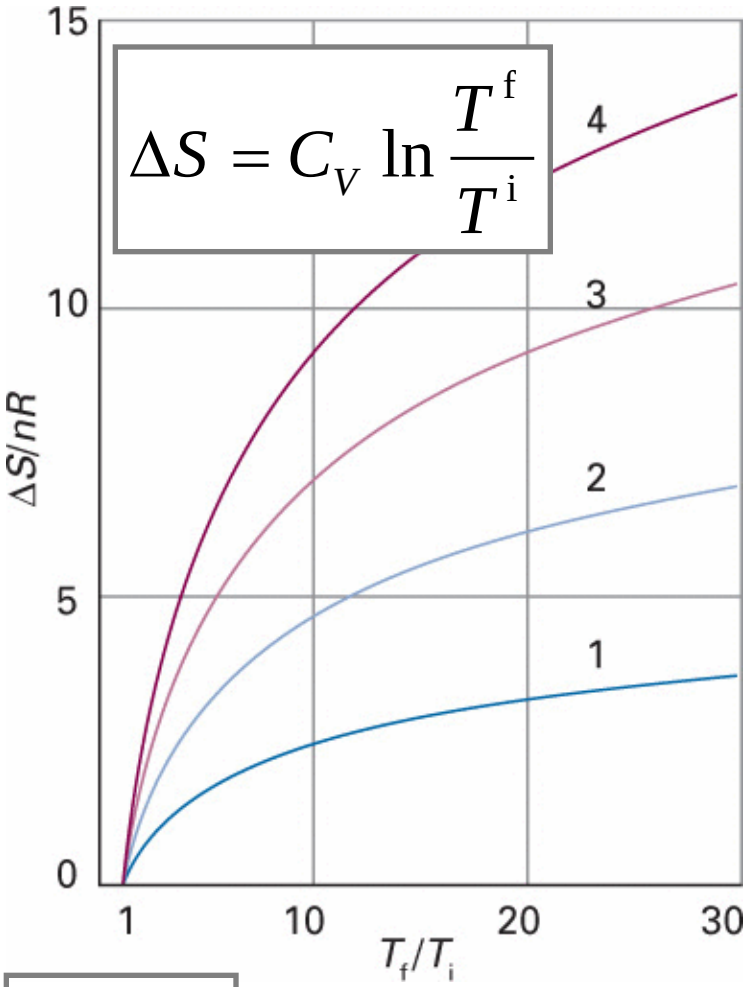
$dT = 0$

$$V \downarrow \Rightarrow q \downarrow \Rightarrow W \downarrow \Rightarrow S = k \ln W \downarrow$$

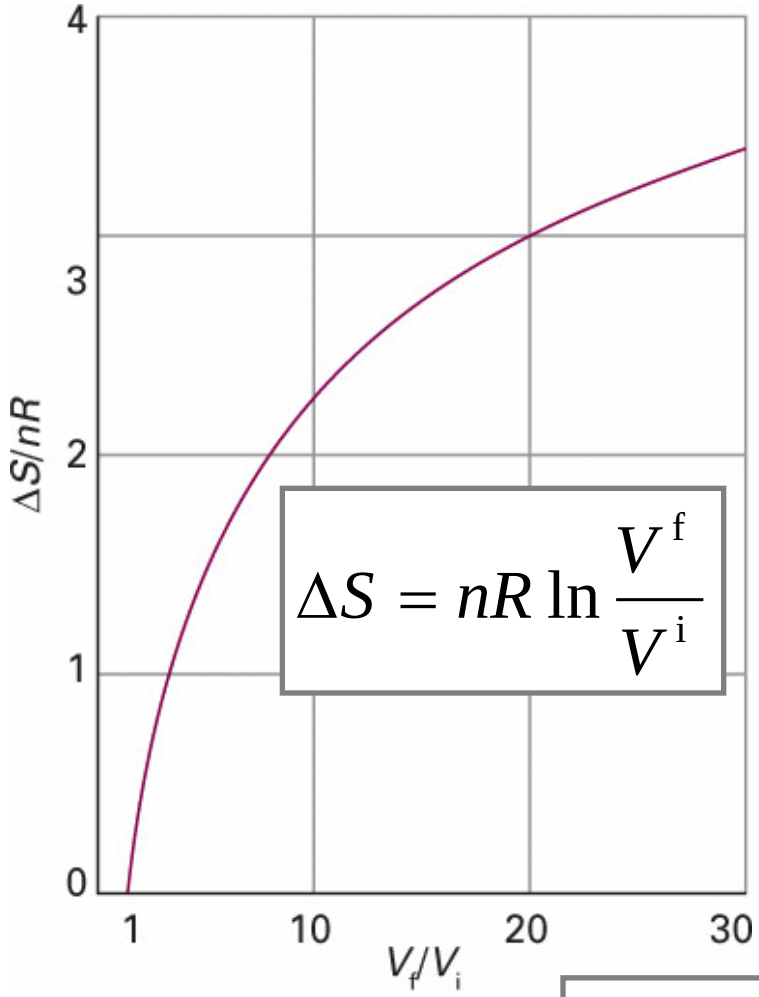
Perfect atomic gas: $\Delta S = nR \ln \frac{V_f}{V_i}$

Two ways to change Boltzmann entropy

$$S = k \ln W$$



$\mathrm{d}V = 0$ **(for 4 constant C_V values)**



$\mathrm{d}T = 0$

Formulae first year course Thermodynamics

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\mathrm{dU} = \mathrm{dQ} + \mathrm{dW}, \quad \text{so} \quad \Delta\mathrm{U} = \int \mathrm{dQ} + \int \mathrm{dW} = \mathrm{Q} + \mathrm{W}$$

$$\mathrm{dQ|_V} = \mathrm{C_V dT}, \quad \text{where} \quad \mathrm{C_V} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

$$\mathrm{dQ|_P} = \mathrm{C_P dT}, \quad \text{where} \quad \mathrm{C_P} = \left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

$$\mathrm{dS} = \frac{\mathrm{dQ^{rev}}}{\mathrm{T}} \geq \frac{\mathrm{dQ}}{\mathrm{T}}$$

$$\mathrm{dS_{tot}} = \mathrm{dS} + \mathrm{dS_{surr}} \geq 0$$

$$S = k \ln W$$

$$\mathrm{dU} = -\mathrm{PdV} + \mathrm{TdS} + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \mathrm{dn_i}$$

$$H = U + PV$$

$$\mathrm{dH} = \mathrm{VdP} + \mathrm{TdS} + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \mathrm{dn_i}$$

$$A = U - TS$$

$$\mathrm{dA} = -\mathrm{PdV} - \mathrm{SdT} + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \mathrm{dn_i}$$

$$G = H - TS$$

$$\mathrm{dG} = \mathrm{VdP} - \mathrm{SdT} + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \mathrm{dn_i}$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT \ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$\Delta_r G^{\ominus} = -RT \ln K \quad \text{with} \quad K = \left(\prod_i a_i^{\nu_i}\right)_{eq}$$

$$\Delta_r G = -\nu F E, \quad \text{so} \quad E = E^{\ominus} - \frac{RT}{\nu F} \ln Q$$

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$$\mathrm{dW} = -\mathrm{P_{ext}} \mathrm{dV} + \mathrm{dW'} \quad \text{and} \quad \mathrm{dW'_{max}} = (\mathrm{dG})_{\mathrm{P,T}} \quad \text{and} \quad \mathrm{dW'} = \mathrm{Edq}$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_{\mathrm{j}} = 0$$

$$\Delta^{\mathrm{ideal}}_{\mathrm{mix}} S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T}\right)_{P,W',n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\sum_j n_j \mathrm{d}\mu_{\mathrm{j}} = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \Delta_{\mathrm{trs}} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -\Delta_{\mathrm{trs}} S$$

$$P = P^* \exp\left(\frac{V_m \Delta P}{RT}\right)$$

$$\frac{\mathrm{dP}}{\mathrm{dT}} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V} = \frac{\Delta_{\mathrm{trs}} H}{T \Delta_{\mathrm{trs}} V}$$

$$\frac{\mathrm{d} \ln \mathrm{P}}{\mathrm{dT}} \approx \frac{\Delta_{\mathrm{trs}} H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}} H}\right) x_B \qquad \ln x_B = \frac{\Delta_{\mathrm{fus}} H}{R}\left[\frac{1}{T_{\mathrm{fus}}} - \frac{1}{T}\right]$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i = \mu_i^{\ominus} + RT \ln x_i + RT \ln \gamma_i$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i = \mu_i^{\ominus} + RT \ln \frac{b_i}{b^{\ominus}} + RT \ln \gamma_i$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\gamma_\pm = \left(\gamma_+^p \gamma_-^q\right)^{\frac{1}{p+q}}$$

$$\log \gamma_\pm = -|z_+ z_-| A \sqrt{I}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}$$

$$P_{in} = P_{out} + \frac{2\gamma}{r} \qquad P = \rho g h$$

$$w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \qquad \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \Theta_c$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad < X >= N < x >= N \sum_i x_i \frac{n_i}{N}$$

Notes for the exam and studying

- **Q&A:**

  ---- Q&A: 22/10, 10:30 in HG00.062

- **After having completed your preparation:**

  Go through all equations of both formulae sheets

  ---- Be sure to understand the meaning of each symbol

  ---- Be sure to understand when the formula can be used

- **At any time:**

  ---- Email me for any question: h.meekes@science.ru.nl

Fill out the course survey

The PC (OLC) uses the results to evaluate the course and lecturer

The lecturer(s) always would like to know how to improve the course

We want your input!!