

Super cooled water in the atmosphere and water freezing

Stable and unstable state of physical systems

Unstable state = **Non-equilibrium state** → It tends to be transferred into **Stable (equilibrium) state**

Stable state = **Equilibrium state** ←

Equilibrium condition for a thermodynamic system

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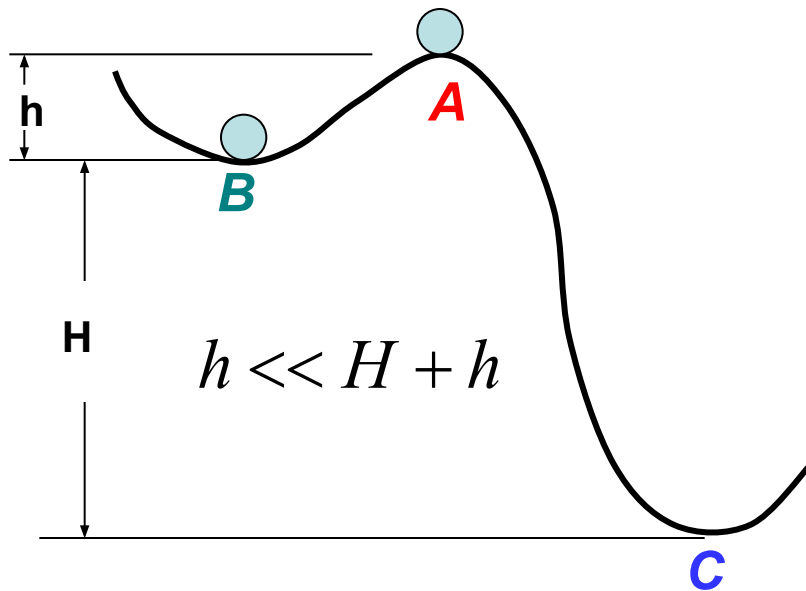
Minimal thermodynamic potential and maximal entropy

A closed thermodynamic system in unstable state after some time will come to

*The time interval needed for a system to be transferred from **unstable** to **stable** state is called **relaxation time***

Metastable state

In some cases the relaxation time is rather long. It happens as the initial state is not really unstable. We say: “the system is in **metastable state**”.



A. Unstable state

B. Metastable state

C. Stable state

Super saturated water vapor and super cooled water in the atmosphere are **metastable thermodynamic systems**.

To start condensation or freezing, some nuclei of the new state are needed

Metastable state

Super saturated water vapor or/and supercooled water droplets

No condensation (crystallization) nuclei

Random molecular condensation (crystallization)

The nuclei can appear due to density fluctuation (random molecules approach each other)

Energy released due to random condensation (crystallization), E_r

Growth the nuclei requires some additional energy E_N . It may come from condensation (crystallization)

There are condensation (crystallization) nuclei

Condensation (crystallization) on some larger nuclei releases additional energy $E_{L.n.}$

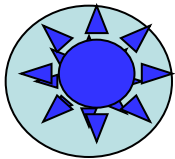
$E_r < E_N$
Process will not go due to energetic disadvantage

Condensation will proceed, and the energy released will be scarified for formation of larger nuclei

$E_r + E_{L.n.} \geq E_N$ Heterophased nuclei

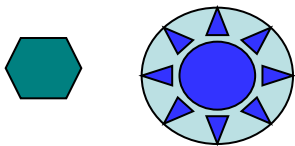
Water droplet freezing process

At the temperature below 0°C, water droplets may freeze becoming ice particles. For the ice phase to appear a nucleus of the ice must be formed inside of the droplet.



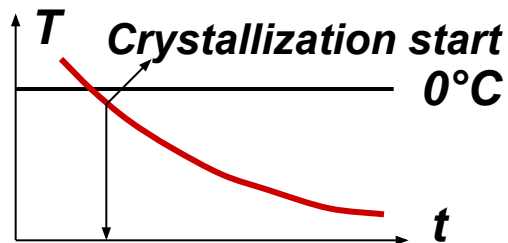
*Such process is called **homogenous phase transfer***

*The new phase can appear on foreign body (heterogeneous nucleus). Such kind of bodies are called **crystallization nuclei**. Accordingly this process is called **heterogeneous phase transfer***



*In the atmosphere both **homogenous** and **heterogeneous phase transfer** may take place*

Heterogeneous ice formation assumes existence of special crystallization nuclei. At present, meteorologists believe that condensation nuclei become (at least partly) crystallization ones as the air temperature grows down below 0°C



Crystallization nuclei are present.

Heterogeneous phase transfer



Crystallization nuclei are not present.

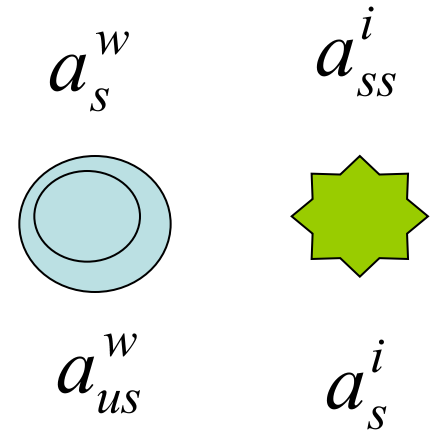
Homogenous phase transfer

It is believed that amount of crystallization nuclei in the atmosphere is rather small. Therefore, the major role in crystallization process is played the **homogenous phase transfer. This conclusion is supported by the observed facts of super cooled water droplet clouds ($T=-12\dots-20^{\circ}\text{C}$) existence for a long time.**

Distillation

Suppose there is a super cooled clouds consisting of water drops and ice crystals

Absolute humidity (AH)	Over water	Over ice	In cloud
Saturated AH	a_s^w	a_s^i	a_s^c
Under saturated	a_{us}^w	a_{us}^i	a_{us}^c
Super saturated	a_{ss}^w	a_{ss}^i	a_{ss}^c



Initial time $a^c = a^w = a_s^w$ $a_s^w > a_s^i$ $a_s^w = a_{ss}^i$
 Next time $a^c = a^w < a_s^w$ $a_{us}^w = a_s^i$ **Drops evaporate**

W.V. sublimates on ice crystal

**And so on until all drops become evaporated.
 However this process is quite long, practically, it is infinite.**

Theory of distillation

<i>Water droplets</i>	<i>Designation</i>	<i>Ice crystals</i>
n_1	<i>Volume concentration of droplets (ice crystals)</i>	n_2
r_1	<i>Radius of droplets (crystals)</i>	R_2
ρ_1	<i>Density of water (ice)</i>	ρ_2

The following equation set is to be solved to obtain unknown quantities r_1 and r_2 and a at a given moment of time.

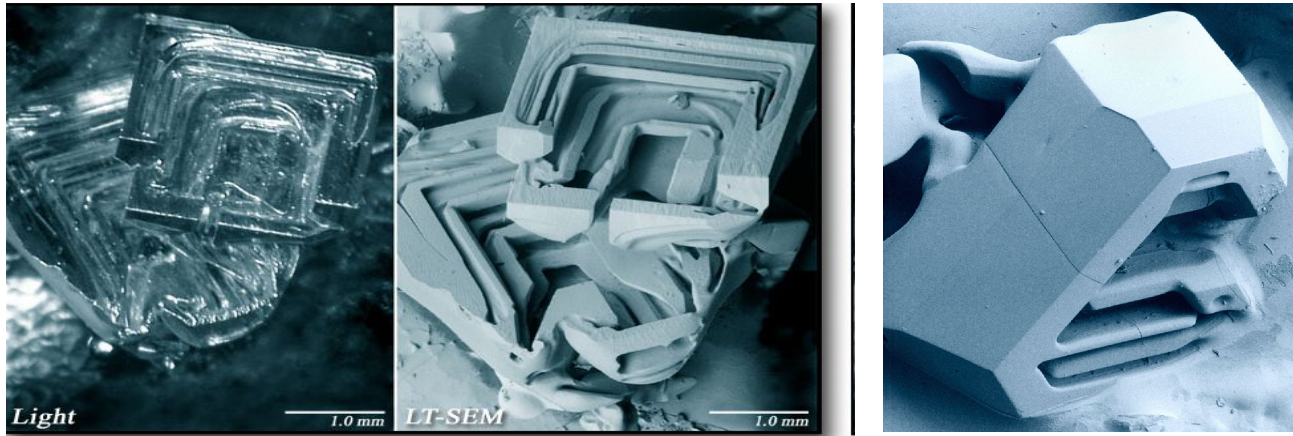
$$\rho_1 r_1 \frac{dr}{dt} = D(a - a_1)$$

$$a + \frac{4}{3} \pi r_1^3 n_1 \rho_1 + \frac{4}{3} \pi r_2^3 n_2 \rho_2 = const$$

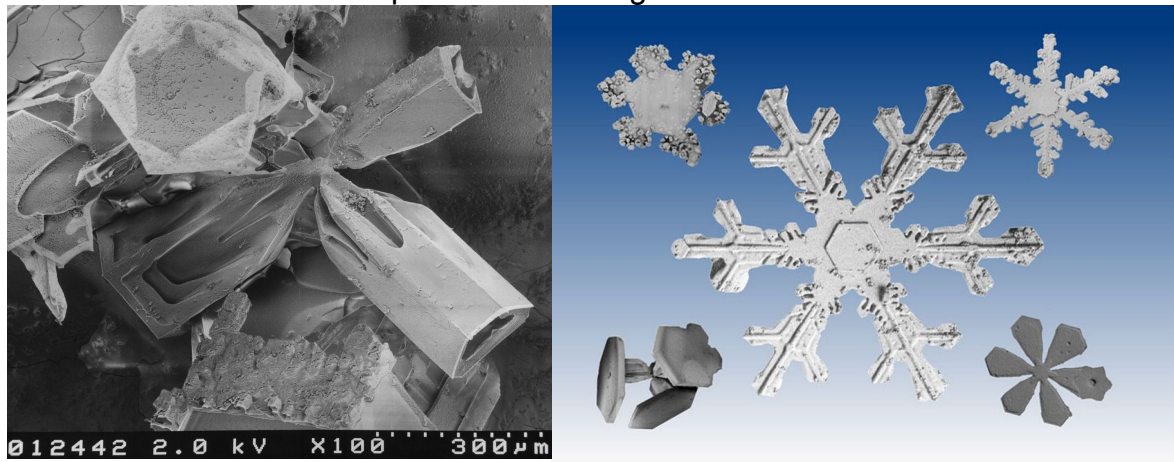
$$\rho_2 r_2 \frac{dr}{dt} = D(a - a_2)$$

D denotes diffusion of the water molecules

Low Temperature Scanning Electron Microscope (LT-SEM)

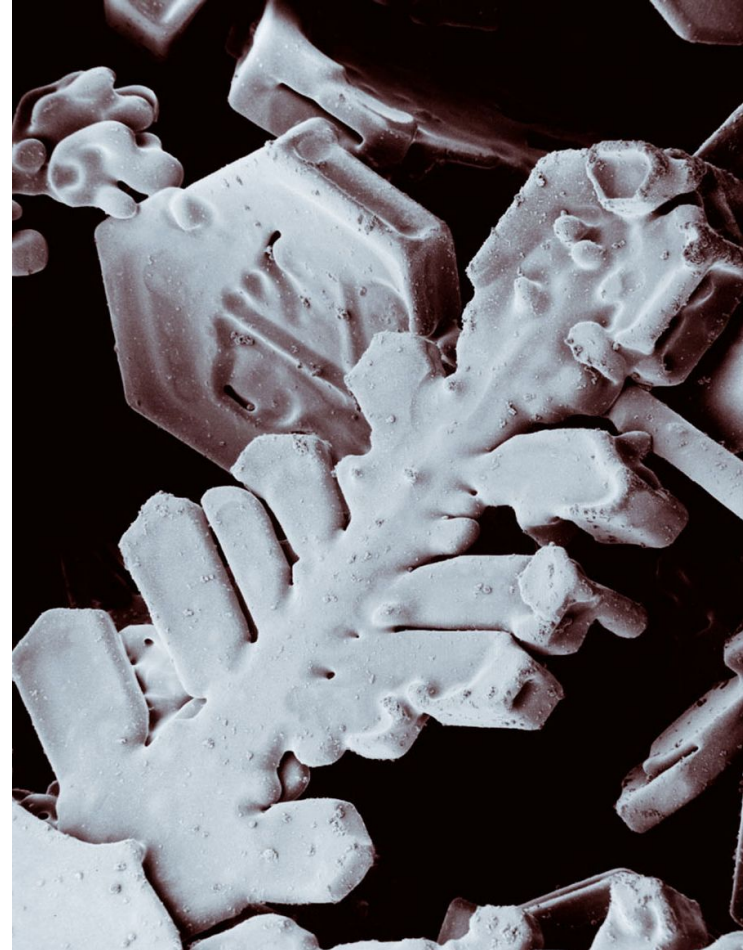
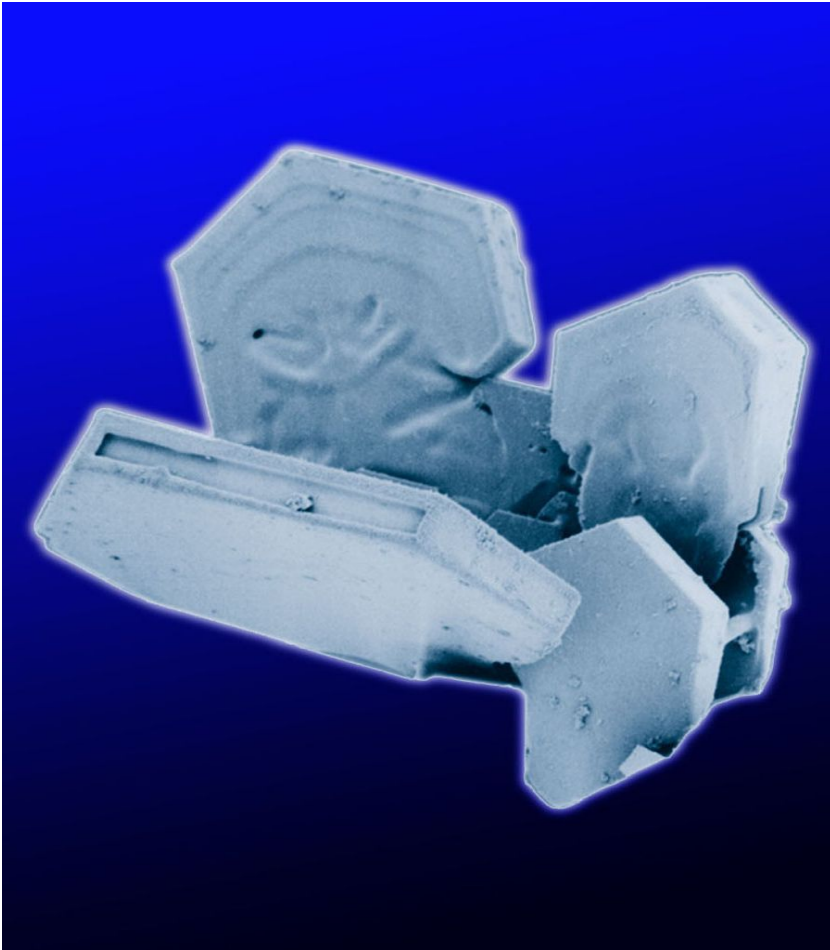


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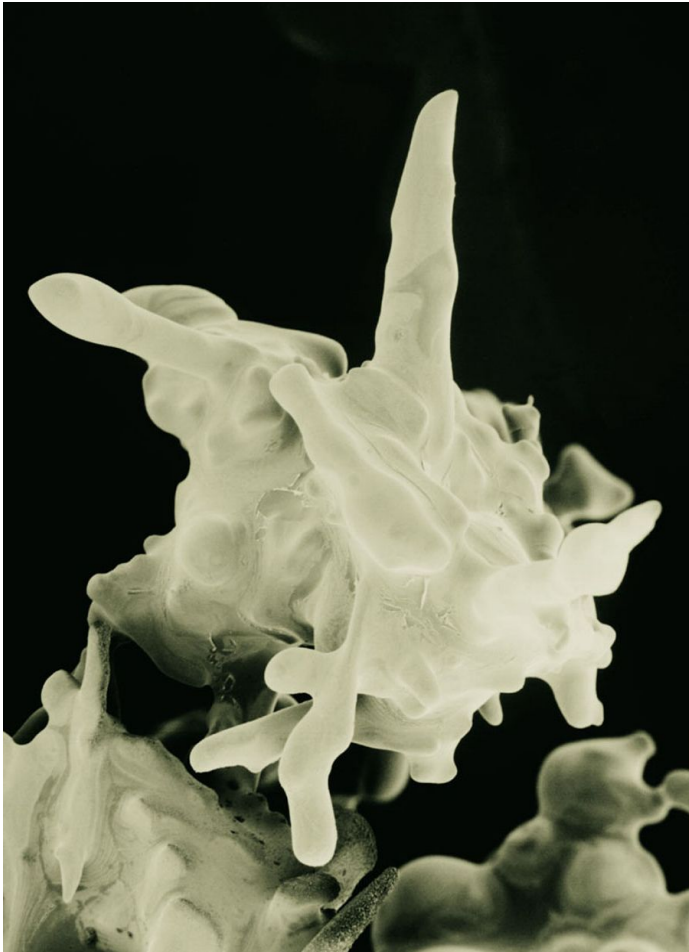


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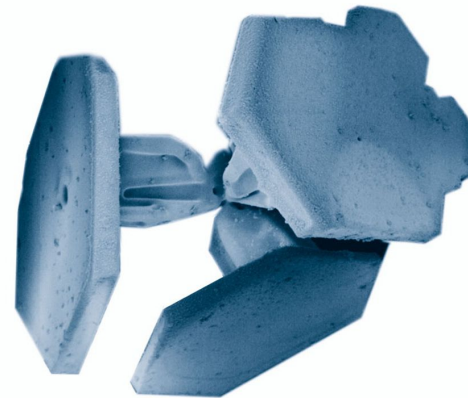
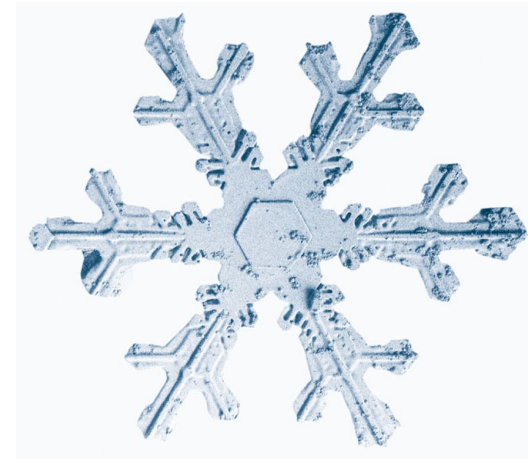
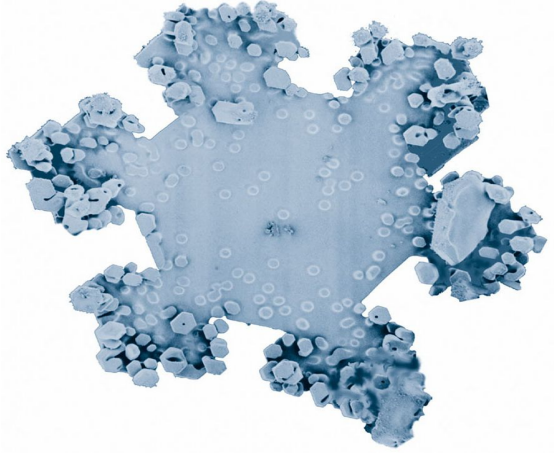
Lecture 21



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Weather Sayings

- **Mackerel sky and mares' tails make lofty ships carry low sails.**

Mackerel sky (cirrocumulus clouds) and mares' tails (cirrus clouds, кобыльи хвосты) indicate that windy, stormy weather is coming.