

Cloud Microphysics

Take Home Messages

Chapter

3	Molecular structure of water substance <ul style="list-style-type: none"> water as the only liquid that has higher density than its solid form for the vapor phase we have the ideal gas model for the solid phase the ideal crystal model (although several deviations for both exist) but for the liquid phase no such model exists since it has structural properties between the former two: short-range order but no long-range order seems to imply that H₂O molecules are ordered like ice in short distance but randomly distributed over a long distance $pV = nRT \text{ or } p = \rho RT$ the Quasi-Liquid Layer (QLL with two phases α-QLL which appears first and β-QLL always at higher temperatures) as the boundary between ice and other phases exists at temperatures as low as -30°C, may enhance chemical reactions between the ice surface and its environment, increase charge accumulation of graupel as well as increase ice crystal growth and multiplication 	<table border="1"> <thead> <tr> <th colspan="3">molecular structures of ice:</th> </tr> <tr> <th>-100°C</th> <th>-80°C</th> <th>0°C</th> </tr> </thead> <tbody> <tr> <td>Ice-I_h hexagonal</td> <td></td> <td>Ice-I_c cubic</td> </tr> </tbody> </table>	molecular structures of ice:			-100°C	-80°C	0°C	Ice-I _h hexagonal		Ice-I _c cubic
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4	Bulk thermodynamic equilibrium among water vapor, liquid water and ice <ul style="list-style-type: none"> if an air parcel in the atmosphere changes its equilibrium condition and the total energy is constant ($\Delta Q = 0$), we have adiabatic conditions ($dQ = C_v dT + p dV = 0$) and either ↑heat & ↓expansion or vice versa due to the 1st law of thermodynamics when considering a closed system or an air parcel the Clausius-Clapeyron equation describes the thermodynamic equilibrium conditions of the three phases (assuming water vapor is an ideal gas) where the separation line between ice and liquid is slightly bent to the left inferring that increase in pressure during isothermal conditions leads to a phase change from solid to liquid form $\frac{d \ln e_{sat,w}(T)}{dT} = \frac{L_e(T)}{RT^2}, \quad \frac{d \ln e_{sat,i}(T)}{dT} = \frac{L_s(T)}{RT^2}$ the Bergeron-Findeisen process describes the transition of supercooled water into ice due to the environment being subsaturated with respect to supercooled water and simultaneously supersaturated with respect to ice and therefore ice crystals grow at the expense of supercooled liquid water $e_{sat,w} > e_{sat,i}$ two failures and one assumption of the phase-diagram: condensation does not start as soon as supersaturation sets in, it is not possible to move in opposite direction of the BF-process, i.e. from ice crystal to supercooled water and it is assumed that materials exist in bulk quantities with no QLL 										
5	Surface thermodynamics of water substance <ul style="list-style-type: none"> the contact angle θ usually between 0° and 180° is a function of the liquid's properties, the substrate and the gas and indicates wettability and hydrophilicity of the substrate (e.g. low $\theta \rightarrow$ perfectly wettable, hydrophilic and many substances also hygroscopic such as sea salt) Raoult's law describes that the saturation vapor pressure over an aqueous solution droplet is decreased proportional to the amount of solute (in its mole fraction x_w) present due to molecular attraction by it (this is the solute effect) and thus a cloud droplet can survive in a subsaturated environment $e_{sat,w} = x_w e_{sat,w,0}$ the Kelvin equation describes that the saturation vapor pressure over a cloud droplet is increased and is greater the smaller the radius of the curvature ($\downarrow a \triangleq \uparrow e_{sat,a}$) since molecules on a convex curved surface are more likely to leave it (this is the curvature effect) $e_{sat,a} = e_{sat,\infty} \exp\left(\frac{2v_w \sigma}{RTa}\right) \rightarrow e_{sat,a} > e_{sat,\infty}$ the Köhler equation here in its simplified form (with assumptions $Na^+Cl^- \rightarrow v = 2$ as well as $e_{sat,a}/e_{sat,\infty} \approx 1$) and associated curves describe the equilibrium condition between an aqueous solution droplet and humid air and consists of both the Kelvin (i.e. curvature, $+A/a$) and Raoult (i.e. solute, $1 - B/a^3$) terms with the critical radius a_c and the activation supersaturation S_{act} describing the condition when the drop becomes activated (less supersaturation needed for bigger particles with more mass which act as better CCN) $S_{v,w} = \frac{e_{sat,a}}{e_{sat,\infty}} = 1 + \frac{A}{a} - \frac{B}{a^3}, \quad a_c = \sqrt{\frac{3B}{A}}, \quad S_{act} = 1 + \sqrt{\frac{4A^3}{27B}}$ the Köhler curves can be separated into stable and unstable regimes whereas the stable regime describes the droplet growth or evaporation to a new equilibrium and the unstable part states that as soon as the environment is minimally supersaturated with respect to the droplet it will grow; will still be in supersaturated conditions and thus continue its growth path to theoretical infinity $S_{v,w}$ is lower for NaCl than for (NH₄)₂SO₄ when both particles have same mass (i.e. sea salt requires less supersaturation for it to become activated), and S_{act} is lower for bigger particle masses 										

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Nucleation

- ΔF_i , the **free energy of formation of an i-mer**, must be overcome to form a homogeneous germ and as supersaturation increases, both the germ size and the free energy required decreases

$$\uparrow S_{v,w} \triangleq \downarrow a_g \triangleq \downarrow \Delta F_g$$
- the **population of embryos** N_i follows the Boltzmann distribution with the number concentration of droplets, i.e. the population, decreasing with increasing ΔF_i , i.e. **the higher** the required free **energy** to form an i-mer, **the smaller** the i-mer **concentration**

$$\downarrow N_i \triangleq \uparrow \Delta F_i$$
- at **supersaturation** $S_{v,w} = 1.0$ the curve does **not** have a **maximum** which indicates that there can never be a stable size and that ΔF_i is infinite, i.e. **homogeneous nucleation** at $RH_w = 100\%$ is **impossible**
- **homogeneous nucleation** of water droplets requires a supersaturation $RH_w \sim 400\%$ and is not possible in our atmosphere and therefore heterogeneous nucleation, i.e. formation of a new phase via another particle, is mostly responsible
- **homogeneous ice nucleation** (requires $T < -38^\circ\text{C}$ as well as $RH_i > 140\%$ → e.g. in high level Cirrus) starts at the subsurface when long-lasting hydrogen bonds, i.e. $\text{O}\cdots\text{H}$, are formed, due to two reasons
 - a) the freezing is accompanied by an **increase in volume** and the surface can accommodate that better than the aqueous bulk and
 - b) the presence of a **large electric field** at the air-water interface may help start nucleation by arranging molecules in preferable order
- four different molecular processes can occur during heterogeneous nucleation of a liquid water drop
 - a) **desorption** → leaving embryo (also during $IN_{\text{hom.}}$)
 - b) **deposition** → landing and becoming part of embryo (also during $IN_{\text{hom.}}$)
 - c) **adsorption** → landing on substrate (i.e. bulk liquid / solid)
 - d) **surface diffusion** → landing on substrate, diffusing randomly & some become part of embryo
- the **size** of an aerosol particle is **far more important than its chemical composition** to act as CCN as is shown by linear regression of observed vs. fixed chemical composition / fixed size distribution of CCNs
- criteria for effective ice nucleating particles (INP) include (see also 7a!)
 - water insolubility → wrong!
 - **size** → large particles ($r_p > 0.1 \mu\text{m}$) with more **ice-active surface sites** better
 - **hydrophobicity** → contrasting to CCN where opposite is true
 - chemical **bond similarity** → $\text{O}\cdots\text{H}$ bonds in surface promote IN
 - **crystallographic similarity**
 - **ice-active surface sites** → impurities on the surface can be more effective than pure crystal
- much more ice crystals than IN in the atmosphere due to the three ice multiplication processes (however we **overestimate** during measurement since some crystals get scattered and break, esp. at **device edges**)
 - i) **fragmentation of ice crystals by break-up** → **turbulence, collision and melting** with high impact
 - ii) **shattering of freezing drops** → if drop freezes fast no thermal mechanical equilibrium ($p' \neq p'' \neq \text{etc.}$)
 - iii) **Hallett-Mossop mechanism** → ejection of splinters during riming process (i.e. freezing of supercooled droplet onto crystal needs optimal temperatures ($T \sim -5^\circ\text{C}$ [-8°C , -3°C]) because if too cold: drop freezes too fast without splinters & if too warm: drop spreads over surface without splinters)

mean atm. concentration ratios (pages 168 & 179):

	1	10^1	10^2	10^3	10^4	10^5
IN						
CCN						
CRYSTALS						

→ [CCN] up to 10^2 to 10^3 higher over polluted areas on land than over ocean as well as smaller droplets over land since they have to compete over LWC

7a

Kanji et al., 2017 – Ice formation and evolution in clouds and precipitation: measurement and modelling challenges

- homogeneous freezing takes place when $T < -38^\circ\text{C}$ and $RH_i > 140\%$, otherwise we have heterogeneous nucleation aided by aerosol particles (INPs) which lower the energy barrier (ΔF_i) for germ formation and may also do so at $T < -38^\circ\text{C}$ with nucleation rates competitive enough when $RH_i \leq 140\%$
- types of atmospheric relevant INPs include
 - 1.) mineral and desert **dusts** → most important INP – particle size more important than chemical composition – large emission rates – Microcline K-feldspar, i.e. KAlSi_3O_8 , most active ice component
 - 2.) **metals** and metal oxides → efficiency varies with chemical composition – smelting, aircraft engines, etc.
 - 3.) **organics and glassy particles** → IN ability of SOA highly varied – onset of ice nucleation is a function of temperature – pure organics promote IN via deposition mode only at $T < -40^\circ\text{C}$
 - 4.) **bioaerosols** → airborne biological aerosols such as bacteria, fungal spores, virus, etc. – as $\downarrow T$, more sites on bioparticle become active – can also be attached to other particles and thus enhance IN ability
 - 5.) **soil dust** → excellent IN ability due to internal mixing with organic matter – 25% of global dust emissions
 - 6.) **biomass combustion aerosols** → i.e. soot & ash with high emission rates and high atm. concentration – the IN ability appears to be linked to fuel source & mixing state – not found in Ci clouds
 - 7.) **volcanic ash & soot particles** → act as good INPs if immersed in liquid droplets via deposition mode
 - 8.) **crystalline salts** → NaCl recognized as good CCN but also $\sim 25\%$ sea salt detected in ice particles – $(\text{NH}_4)_2\text{SO}_4$ good candidate for heterogeneous freezing in Ci
- four modes exist for heterogeneous nucleation

- a) **deposition ice nucleation** → from vapor directly to ice phase where pores help to create ice germs
- b) **contact freezing** → occurs either from 'inside-out' or from the outside when INP collides with an air-water interface
- c) **immersion freezing** → INP immersed in supercooled liquid and then freezes – however the particle **does not act as a CCN** before nucleation
- d) **condensation freezing** → the IN initially serves as CCN to form a drop at $T < 0^\circ\text{C}$ – not established yet if it is truly different from a) or c)
- known pre-requisites of ice-nucleating particles
 - for insoluble/solid particles (e.g. mineral dusts) → IN occurs at '**ice-active surface sites**' – small particles act less likely as INP – OH-bonds at surface, lattice structure, size, surface defects and nature of chemical groups play role in promoting IN
 - for soluble particles (e.g. biological ice nucleators) → may **separate from** their **carriers** – water molecules with $\text{O}\cdots\text{H}$ bonds may arrange themselves & form ice-active sites – as temperature decreases, more sites on bioparticle become active – those sites bound to host particle such as mineral dust and thus provide active sites or chemical bond necessary for stabilizing IN
 - ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ and other solid soluble salts can form ice heterogeneously (see Kanji et al., 2017 Figure 1-8 → sea salt (NaCl) detected in ~25% of Cirrus cloud ice particle residuals

primary sources of INPs include:

natural sources	anthropogenic sources
- deserts	- particles from agricultural practices
- volcanic eruptions	- deforestation
- ocean	- biomass burning
-vegetation debris	- transportation
	- industrial processes
→ materials in urban pollution may act to deactivate existing IN	

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Diffusion growth and evaporation of cloud and precipitation particles

- in order to have **diffusion growth** we need to have a supersaturated environment, i.e. the **water vapor density** in the **surrounding air is higher than just above the droplet surface**

$$\rho_{v,\infty} > \rho_{v,a}$$
- in the temperature range -40°C to 40°C Hall and Prusppbacher (1976) gave an empirical relation for the diffusivity of water vapor D_v around a spherical drop which states that **diffusivity increases with increasing temperature and decreasing pressure**

$$\uparrow D_v \text{ when } \uparrow T \text{ and } \downarrow p$$
- from the mass and linear growth rate equations where D_v^* is the new diffusivity which corrects for the **vapor jumping length** close to the drop surface, we know that the **mass growth rate**, i.e. dm/dt , is **greater higher up in the cloud, the larger the drop, the greater** its mass growth rate and **the smaller the drop, the greater its linear growth rate** (at $40 \mu\text{m}$ asymptotically slow linear growth rate but it may continue under favourable conditions, broaden the drop size spectrum and thus help in rain formation which is otherwise not possible without considering the effect of collision-coalescence

$$\frac{dm}{dt} = 4\pi D_v^* a (\rho_{v,\infty} - \rho_{v,a}) \quad \rightarrow \quad \frac{da}{dt} = \frac{D_v^* \rho_{v,\infty} - \rho_{v,a}}{\rho_w}$$
- diffusional growth also implies a **phase change** from the vapor to the liquid phase and incurs the **release of latent heat** which warms the drop's surface and thus it is this surface temperature that determines saturation vapor density $\rho_{v,a}$ at the surface
- ventilation** due to falling motion of droplet effect **enhances both diffusion growth & evaporation rates** which can be 10x higher than for a stationary drop and is the same if p , T & N_{Re} ($N_{Re} = Ud/v$) are the same
 - the vapor density distribution around a falling crystal is such that there is an **enhanced gradient upstream & a reduced gradient in the wake**
- for the **diffusion growth of ice crystals**, due to their many different forms, we define the **capacitance C**, a quantity regardless of the shape of the conductor and derive the diffusional growth of said conductor
- the capacitance parameter poses some problems since hollow and solid crystals (where hollow ones grow up to 10x longer after same initial conditions within a minute) have same capacitance
- each temperature / supersaturation ratio** has a **distinct** ice crystal formation **habit** and habits may change during growth with varying T & RH_i , i.e. at different conditions, growth occurs along different axes

10 Collision, coalescence, breakup and melting

- collision growth of small drops is inefficient** (the small a_2 due to low inertia follow the streamlines of the bigger droplets → small E) – becomes more efficient **with turbulence** ($\uparrow \sim 25\%$) and when the drops are large and of approx. equal sizes (higher inertia and more deflection from the streamlines of the collector droplet)
- coalescence efficiency** is low for large colliding pairs but is **higher for large drops collecting small droplets**
- both **graupel** (original crystal completely masked by rimes) and **hail** (graupel $> 5 \text{ mm}$) can go **through dry and wet growth regimes** with the **Schuman-Ludlam limit** defined as the **boundary** between the two regimes showing dry growth layers consisting of small polycrystalline grains and wet growth layers with large single crystalline patches
- the larger the crystal, the higher the collision efficiency** E_{coll} with a droplet, as long as drop is not too big and falls faster than crystal

- **riming** preferentially takes place **near the edge** of the plate and almost completely **on down-facing side**
- the **collision efficiency of ice crystals** is **higher** with **higher temperature** with the maximum close to 0°C due to near-surface melting and the influence of the QLL which increases **sintering**, i.e. sticking together
- the four breakup types, with **lower pressure increasing fragment numbers**, are as follows
 - a) **filament breakup** → small drop hits large one near equator – separation due inertia with filament
 - b) **sheet breakup** → small drop hits close to center – rips whole sheet out that gets unstable & desintegrates
 - c) **disk breakup** → small drop hits big one near center – their conglomeration forms disk which breaks up
 - d) **bag breakup** → when a disk is inflated by air – forms a bag which then desintegrates into many fragments

11 Cloud drop population dynamics in the warm rain process

- magnitude of **updraft influences cloud drop size** with **larger drop sizes** or **hydrometeors** when **updraft is bigger**
- **stochastic collection** process, i.e. unequal growth rates, **more efficient** way to produce precipitation-sized particles **than** with the **continuous growth model** since drop size **spectra broadens faster** with time and with the inclusion of diffusion growth (possible after 40 μm under right conditions) even more so
- **initial cloud drop size distribution**, i.e. how liquid water content (LWC) is distributed, **key** in determining **stability and sensitivity of rain formation** in both mean drop size and spread of spectrum
- **maritime clouds** with **fewer CCN** and therefore **larger drops** are **more** colloiddally **unstable** than continental clouds with same LWC and **more ready to rain**
- **ultragrantic nuclei** ($r > 10 \mu\text{m}$), which exist in both maritime and continental clouds, **and mixing** can **accelerate raindrop formation** by collision of giant dry particle and large drop
- rain drops get **unstable** in the range of **4.3 to 6.2 mm** due to induced circulation & collision with smaller drops

colloiddally stable cloud when:

- narrow drop size spectrum
- small drops
- small updraft velocity
- low CCN concentration
- absence of giant CCN
- low LWC

14 Cloud electricity

- electric charges in the atmosphere originate from two sources: a) **radioactive emanations** from the Earth's interior and b) **cosmic rays** which both form **small ions** with high mobility (H^+ and e^-) which attach to neutral molecules or **large ions** which are either simple or small ions attached to aerosol particles which have a lower mobility
- the **atmosphere** between surface and ionosphere (where plasma, i.e. an electric fluid that is neutral but reacts to external electric and magnetic fields and which increases its electric conductivity with higher ion concentration, is present) acts as an **electric cavity** → however, it does not insulate entirely and thus ions move from one conducting layer to the other
- the **Earth's surface** is overall **negatively charged** due to the **global fair-weather** charge and the **leakage current** tries to offset this distribution by bringing negative charges back up into the atmosphere but fails to neutralize fair-weather electric field due to **lightnings**
- the electric **charge distribution** in **thunderstorms** is usually one where **positive** charges are located at the **cloud top** and **negative charges** in **lower levels** with a **small positively charged area** at cloud base (this might be due to + charged graupel which when falling down melt, release tiny - charged mini-droplets and thus remaining graupel gets positive charge)
- lightning and thunder processes transport negative charges to the surface to replenish the fair-weather leakage via four steps and produce shock-waves at supersonic speed
 - i) **stepped leader** → with freshly ionized plasma at the tip – $\vec{v} = 10^5 \text{ m s}^{-1}$
 - ii) **streamer** → going up from the ground to meet head of leader & establish continuous channel
 - iii) **return stroke** → what we call lightning – while electric current and light go upwards, - charges transported to the surface – rapid heating of channel creates shockwaves and thunder
 - iv) **dart leader and 2nd return stroke** → return stroke can occur multiple times – impression of blinking
- **cloud electrification** (+ charges above and - below) occurs **mostly over land** due to **higher updraft** speeds than over the ocean ($\uparrow w \triangleq \uparrow \text{CAPE}$) and the **lightning frequency** in a cloud is a strong function of the **updraft speed**, but also **cloud radius** and the **ice volume** ($f = R w^6 \sqrt{V_{ice}}$) → to produce frequent lightning, large quantities of these parameters are favourable
- **charging** can either be **inductive** (i.e. occurring due to external influence of an electric field) or **non-inductive** (i.e. without an external field) and includes theories like
 - **convective charging** → + charges carried up by updraft forming a positive charge in the interior – cloud top and edges are downdraft regions & hence - drops would be carried to lower levels
 - **selective ion capture** (ind.) → underside of drop is + polarized and catches dominantly - charges and acquires overall - charge – as drop is falling, + ions have to catch up at top of droplet and therefore drop remains negatively charged (quantitatively unrealistic)
 - **charging due to rebound of particles during collision** (ind.) → transfer of charge during rebound where + charges in lower half of large particle are neutralized – after rebound large particle carries - charge & gravitational separation would result in dipole

- **charging due to collision with rimed particles** (non-ind.) → seems to be the **main mechanism** – el. charges deposit on a riming graupel when it is colliding with an ice crystal – requires supercooled droplets & is highly dependent on temperature (+ charge at $T > -10^{\circ}\text{C}$ & vice versa) – QLL also with influence

A

Cloud Microphysics – main message: mean atmospheric concentration ratios
 → she asked me what was the most interesting stuff I learned during the lecture



