

Chapter 2

Nanoparticles Acting as Condensation Nuclei – Water Droplet Formation and Incorporation

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Obviously the situation is more complex than expressed by the statement “without particles no precipitation”, but through assessment of the water cycle and identification of its bottlenecks we will see that nanoparticles definitely play a major role.

Accepting the fact that water can only be recycled and not newly synthesized by nature, one has to deal with the water cycle in more detail. Figure 2.1 depicts a simple scenario for this.

To begin the discussion one should note that water vapour is already present in the atmosphere to a large extent. Depending on variables such as ambient temperature, the area of free water surfaces, wetted soil surfaces, and plant exhalation, billions of tons of water in the gaseous state is translocated and dispersed globally by meteorological factors. This water vapour can be inferred to be the real source of fresh water through various mechanisms which act to change the water vapour from the gaseous state to a condensed one; the link being air-dispersed particles, i.e., aerosols.

Cloud or fog formation is not possible without the existence of submicron-sized particles. This had already been recognized in previous centuries, and Paul-Jean Coulier (1875) was the first to develop an experimental setup to visualize aerosol particles by condensing water on them. Many obscure ancient technologies including the use of large cannons in Styria (Austria) or the still-present technology of cloud seeding (to prevent hailstorm formation) by spreading artificially generated silver iodide aerosols into the cloud base, had the aim of modifying the weather, namely precipitation events.

In order to understand the role of nano-engineered particles within the natural water cycle we need to have greater knowledge of the transition of water vapour to the condensed state.

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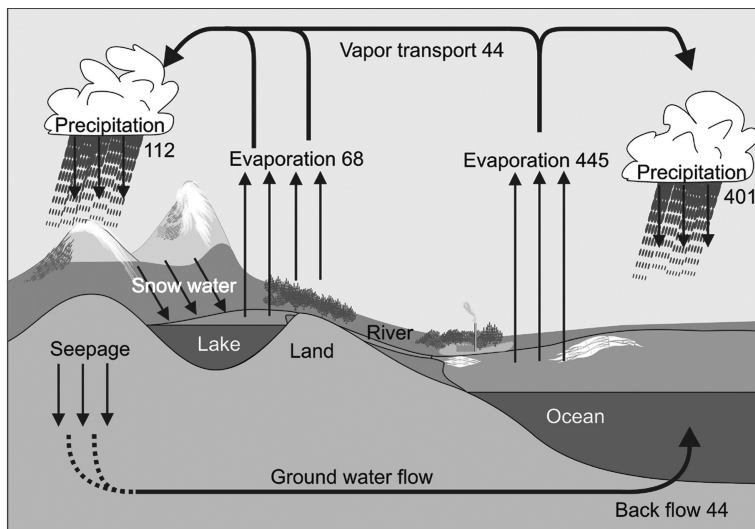


Fig. 2.1 The total water cycle and its bottlenecks. The numbers show the transported water volumes for $1,000 \text{ km}^3$ per year

2.1 Condensation of Water Vapour onto Aerosol Particles

Many reviews are available giving some insight into the different peculiarities of the condensation process within a cloud (or fog). The most comprehensive standard textbook on this was written by Pruppacher and Klett (1997).

For the evaluation of the role and impact of nano-engineered particles some requirements have to be fulfilled:

The ambient atmosphere often becomes slightly water supersaturated. This typically occurs as air masses become elevated when crossing higher orographic obstacles, for example accessing a mountain from the direction of the sea. Other mechanisms include convective cooling during changes in daylight. A supersaturated air mass exceeding 100% relative humidity will hold a few percent more water in the gaseous state for a period of time than expected in the equilibrium state.

Usually there are two main routes for the return to equilibrium conditions. The first is dilution by dry air masses – in this case no condensation of water will be observed. The second mechanism is condensation on ultrafine water-soluble particles. Simply put, water vapour forms a brine at the particle surface (e.g. NaCl). Because of solvolysis the water vapour pressure above such droplet surfaces becomes depleted (according to Raoult's law). As described by Fick's law water diffusion remains active in the direction of the "sink" (the brine), as long as there is a vapour pressure gradient between the particle acting as the condensation nuclei and the surrounding supersaturated air mass. This process comes to a halt after some time because of increasing dilution of the brine at the particle surface.

Once the concentration of ionizable surface material is in the trace regime a notable vapour pressure gradient no longer exists to stimulate further water vapour condensation. Because of the release of condensation heat during diffusion to and from a condensing nucleus the whole process might become very complex. Qualitatively, well dissolvable particle cores will serve as very efficient condensation nuclei. In essence, the particles will become incorporated into the water cycle and have a chance to become precipitated.

For the assessment of the role of dispersed nano-engineered particles within the water cycle, we have to identify those which can be involved in such water condensation processes. As already mentioned above, dissolvable material would fit perfectly. In contrast, hydrophobic particles as individuals can only act as condensation nuclei when a certain water supersaturation is present. The well-known Kelvin equation describes such a situation of condensing water vapour without any dissolution process. Originally set only for pure water droplets this equation at least qualitatively gives an estimate for the ruling principle:

$$X_K = \frac{4\sigma M}{\rho_l RT \ln S_{eq}}$$

X_K is the size of a water droplet, which is in equilibrium with the saturation ratio S_{eq} of condensable water vapour. Since the surface tension and density of water is constant, as is molecular weight M and temperature T , the existence of a water droplet is only dependent on the water supersaturation S_{eq} , at a first approximation. This would mean that nanoparticles would never be incorporated into condensing water, since the required water supersaturation for acting as condensation nuclei would be tremendously high, by far exceeding the available 1 or 2% within a cloud or fog situation. The only route to lowering the required supersaturation is described by Raoult's law, where dissolvable compounds increase the surface tension (as surface tension is directly proportional to the number of ionized molecules). Hence, any change of particle surfaces, either by a chemical reaction or agglomeration with ionizable material, will lead to an actively participating condensation nucleus. If there is a change of wettability of such a particle system, for example by agglomeration with other small particles during residence time in air, lower supersaturation is needed to trigger condensation. This is due to dissolution and diameter increase.

2.2 Experimental Verification I: Water Uptake

Besides the considerable theoretical framework published in the past there has also been convincing experimental work. To assess the condensation properties of particles and hence their incorporation into the water cycle a test system mimicking the cloud formation process would be necessary. Fortunately, such experiments have been known for decades. What is needed? According to the statements made above

beside surface properties mainly the particle diameter will govern the partitioning behaviour of particles within a condensing system.

Jean-Paul Coulier (1875) was the first to observe a droplet growth change, when changing the surrounding humidity.

Today, such experiments are performed by a so-called Tandem Differential Mobility Classifier experiment. The particles of interest are dispersed by an atomizing system creating a polydisperse aerosol system. This means it is an assembly of differently sized particles. This aerosol is now sorted by a first mobility classifier. The working principle of such a classifier is based on the particle's electrical mobility, which means the aerosol must be electrically charged. This is achieved by coagulation with charge carriers previous to the sorting process. Like in an electronic band pass filter, only those charged particles will pass the electric "gate" whose electric mobility (charge and size) fits the gate's dimension perfectly. In essence, the first classifier forms a monodisperse fraction of aerosol from any polydisperse fraction. This aerosol is in the next step subjected to different water humidities. Depending on its water-attracting properties it takes up water vapour and changes its size. This becomes measurable when such an aerosol is fed into a second classifier. To pass this "gate", after becoming swollen by water uptake, a wider gate dimension needs to be set. For NaCl aerosols the observed behaviour agrees well with calculations based on Köhler's theory of hygroscopic growth of water-soluble aerosol particles. Applying this experimental approach to artificially produced PbS nanoparticles of the same size leads to a different behaviour. When exposed to increased relative humidity up to 83% shrinkage was observed. In the case of NaCl recrystallization from the originally chain-like condensation nuclei via droplet-like brine solutions is the explanation, whereas in the case of PbS, insolubility prohibits this. Only a slight restructuring has been observed (Krämer et al., 2000).

So, for water-insoluble material used as nanoparticulate matter a different water uptake behaviour is expected.

2.3 Experimental Verification II: Inhibition of Water Condensation

When nanoparticles, like insoluble carbon nanotubes or flame-processed particles become released to the atmosphere the question arises, whether they can become initiators of water condensation, or not. If not, the residence time for such nanoparticles will become considerably prolonged as they are small and not subjected to the typical removal mechanisms of diffusion, sedimentation and interception. The only removal mechanism acting would be dry deposition, triggered by turbulent diffusion of air packages. Diffusion, deposition or sedimentation are not very effective in a size range of 300–500 nm, the size range of many nano-engineered particle systems.

The consequences connected with a prolonged residence time are numerous, including increased interaction with radiation and higher risk of inhalation.

Hence, experimental verification of the condensation properties of ultrafine particles is highly desirable. In the 1980s this question had already been raised, since airborne cloud measurements have led to the observation of the “cloud interstitial aerosol”. These aerosol particles consist of material that was not activated during cloud or fog formation during the actually existing water vapour supersaturation. They remained as small particles within the cloud or fog system. The chemical composition of these particles was thought to be similar to “fresh hydrophobic particles” (such as soot). The first experiments to understand this stem from van der Hage (1984) and Liu et al. (1984).

How does one figure out the different surface properties by means of a condensation process? Niessner et al. (1990) presented an instrumental setup, which at least provides semi-quantitative information on the influence of different surfaces of nanoparticles as condensation nuclei. They made use of a multistep condensation nuclei counter (CNC) as the detector. The features of these experiments are such that they were carried out with quasi-monodisperse aerosols and hence the only variable parameters were surface composition (wettability, dissolution properties etc.) and water vapour supersaturation. Particle number concentration and diameter were also kept constant for all experiments when comparing different nanoparticle systems. In this manner variation in the condensational behaviour of the particles can be related exclusively to differences in surface structure and surface composition.

In the following the characterization of differently coated nanoparticle systems (e.g. H_2SO_4 as an extremely hygroscopic particle core with various coating materials) is discussed briefly. From a sulphuric acid aerosol source a monodisperse fraction is selected by a differential mobility analyzer (DMA). This aerosol fraction, now monodisperse and of known size and number concentration, becomes mixed with vapours of hydrophobic coating materials, for example paraffines, terpenes etc. The coating thickness was independently measured by estimation of the diffusion coefficient of the coated and uncoated aerosol.

For a measurement the differently coated aerosols (monodisperse) are injected into the multistep condensation nuclei counter. In the CNC (Fig. 2.2) the aerosol is

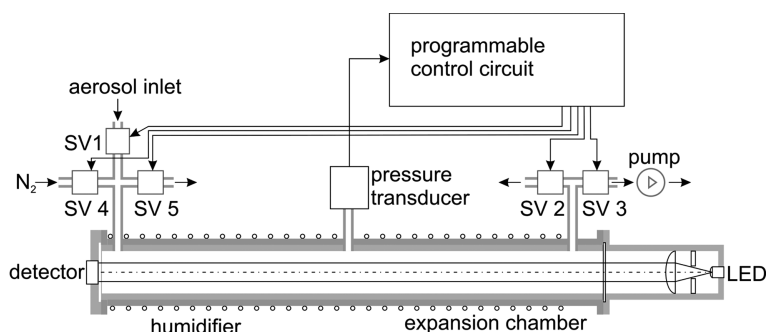


Fig. 2.2 Sectional drawing of the multistep condensation nuclei counter

fed into the expansion chamber via solenoid valve SV1. After closing SV1 and SV3, clean, particle-free nitrogen is introduced through SV4. By this means the chamber pressure, p_0 , is increased up to a preselected pressure value. After some seconds of humidification and equilibration a rapid adiabatic expansion ($t_{\text{exp}} < 15$ ms) occurs through opening of the two valves SV2 and SV5, resulting in a certain supersaturation corresponding to p/p_0 . In the case where the introduced particles acted as condensation nuclei at the employed p/p_0 ratio, they will have taken up water vapour, and the intensity of the transmitted light through the expansion chamber due to light scattering and absorption by the droplets formed. Measurement of the light absorption before and after the expansion led to a CNC-indicated particle–droplet transition. The system automatically runs through 16 stages of increasing p/p_0 to produce an activation spectrum of the nanoparticles under investigation.

Figure 2.3 depicts directly the influence of a hydrophobic surface in such activation spectra comparing H_2SO_4 droplets (diameter: 20 nm) with and without a 5-nm thick n-hexadecanol layer. Onset of droplet growth is seen at the 11th stage, in comparison to the 7th stage (for uncoated, hygroscopic H_2SO_4 droplets).

Activation spectra for various nano-engineered particles, but all of the same size (~ 20 nm) are shown in Fig. 2.4.

Water-soluble particles like H_2SO_4 or NaCl initiated droplet growth at rather low water supersaturation, much lower than calculated by the Kelvin equation theoretically. This is because of the earlier-mentioned effect of creating a salt dissociation within the growing water phase. In the case of non-soluble Al_2O_3 (pyrosynthesized from heating up AlCl_3 in the aerosol phase) and pure carbon agglomerates

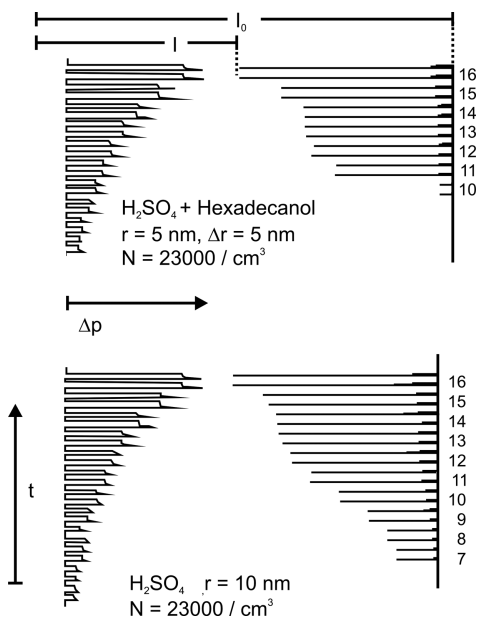


Fig. 2.3 Applied pressure difference and light intensity plots for pure and hydrophobically coated sulfuric acid droplets

Fig. 2.4 Activation spectra of sulfuric acid droplets, NaCl, Al₂O₃, carbon, and Aerosil 200 nanoparticles (diameter: 20 nm)

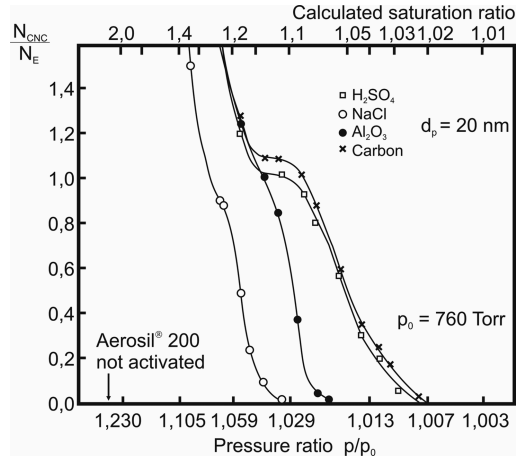


Table 2.1 Behaviour of different oxidic particles towards condensation of water vapour

| Pigment type | Chemical composition | Specific surface area (m ² /g) | Manufacturer | Counting efficiency (%) |
|---------------------------------|---|---|--------------|-------------------------|
| Aerosil 200 | SiO ₂ | 206 | Degussa | 0 |
| Aerosil 380 | SiO ₂ | 375 | Degussa | 1 |
| Aerosil MOX 170 | SiO ₂ + 1% Al ₂ O ₃ | 170 | Degussa | 1.2 |
| Aerosil COK 84 | SiO ₂ + 16% Al ₂ O ₃ | 170 | Degussa | 2.5 |
| Rutil PKP 09045 | TiO ₂ | | Bayer | 4.2 |
| Titanium dioxide PKP 09040 | TiO ₂ | | Bayer | 8.3 |
| Titanium dioxide P 25 | TiO ₂ | | Degussa | 2.7 |
| Sicotrans Orange L 2515 D 80825 | Fe ₂ O ₃ | | BASF | 1.8 |
| Carbonyl iron oxide | Fe ₂ O ₃ | 80 | BASF | 1 |
| Carbonyl iron oxide | Fe ₂ O ₃ | 25 | BASF | 1.7 |
| Anatas PKP 09044 | TiO ₂ | | Bayer | 4.3 |
| Aluminium oxide C | Al ₂ O ₃ | | Degussa | 1.2 |

Counting efficiency = N_{CNC}/N_E (N_{CNC} , particle number concentration as indicated by the CNC, N_E , particle number concentration as measured with an aerosol electrometer in front of the inlet of the CNC; see Fig. 2.1).

a tremendous shift in needed water supersaturation is seen. Such supersaturation will never exist in cloud or fog formation, where supersaturations rarely exceed 1 or 2%. More than 10% would be needed to incorporate these particle systems into the vertical water cycle.

Extremely interesting behaviour can be reported for one of the currently most used nano-engineered particulates: Aerosil (Mathias and Wannemacher, 1988). Aerosil is a perfectly spherical particle consisting of SiO_2 (synthesized by high-temperature pyrolysis of SiCl_4 in hydrogen/oxygen flames). For Aerosil 200, no water vapour condensation was observed even at a saturation ratio of 230%, a value never obtained under natural conditions.

Several nano-engineered materials have been tested for their activation properties. The results are compiled in Table 2.1. All particle systems represent a considerable part of the nanomaterials widely used today. All these particle systems will not become incorporated into a water condensing system. Only after agglomeration with water-attracting or dissolvable particles may a direct incorporation into the water cycle occur.

2.4 Particle Collection During Precipitation

What remains to be discussed is the assessment of nanoparticle collection by impaction with already existing water droplets, for example during rain fall. This situation will be a common one, especially when other ambient (the majority) particles seeded cloud or fog formation. Water (rain) droplets can uptake during their fall non-activated particles.

This has been known for several decades from studies dealing with radioactive fall-out. Falling droplets may interact with particles by interception, diffusion or impaction when in the very near neighbourhood. All mechanisms together give rise to the so-called “Greenfield gap” (Kellogg, Rapp & Greenfield, 1957). Typically, around a particle size of 300–700 nm there is a minimum in the collision efficiency for such uptake. This is understandable due to the various size-dependencies of the respective mechanisms. This means that nano-engineered particles suspended in the ambient atmosphere will again have a large chance to remain as a (aero)sol in the air.

Beside this, the wettability of a contacted nanometre particle decides whether it becomes really incorporated into an existing droplet after a successful collision. Hydrophobic particles become squeezed out and do not enter a water droplet. This was shown experimentally by Mikhailov et al. (2001).

2.5 Conclusions

An attempt was made herein to describe the fate of air-dispersed nanoparticles and their incorporation route into the water cycle.

Cloud or fog formation can be seen as the origin of new water formation. This is meant physically, since only a change of state from gaseous water vapour to the condensed water phase occurs. A slight water supersaturation will serve as a water pool as long as particles are available with seeding properties. Also agglomeration of suspended dry nanoparticles with already-formed water droplets will not be a very

successful route for incorporation. Wettability properties of nanoparticles govern the attachment process.

It could be demonstrated experimentally that most of the presently used nanomaterials, because of their inherent insolubility and hydrophobicity, do not activate water condensation under natural conditions. Depending on the wettability, or agglomeration with wettable or hygroscopic nanoparticles, they will have an unknown prolonged residence time in the ambient atmosphere. The consequences will be unknown impact on the radiation balance and occupational health.

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